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Process Optimization and Monitoring in The Printing Industry

By

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M.A.Sc Chemical Engineering (University of Ottawa)

A thesis submitted to the
Faculty of Graduate Studies and Research
in partial fulfillment of the
requirement for the degree of

Doctor of Philosophy

Department of Chemistry

Carleton University
Ottawa, Ontario
December, 1998

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acceptance of the thesis

Process Optimization and Monitoring in The Printing Industry

Submitted by

Arghavan Victoria Nawaby
M.A.Sc. Chemical Engineering

In partial fulfillment of the requirement for the degree of
Doctor of Philosophy

Chair, Department of Chemistry

Thesis Supervisor

External Examiner

Carleton University 1998

Abstract

The types of industrial wastewater are as numerous as the types of industries. As a result, it is impossible to apply a comprehensive method of treatment. Many industries are in need of process modifications in order to comply with the constant changes in regulations of aqueous waste discharge into open water and sewage systems.

The contamination of our environment by industrial waste has been known for some time; however, little or no attention has been given to the printing industry, in particular the *currency printing* industry, which uses significant quantities of surfactants and dyes as well as generating highly alkaline wastewater. The purpose of this research was to provide a thorough study of the aqueous process streams at the **British – American Banknote Inc.** (BA Banknote Inc. a local currency printing industry), to identify locations for process optimization and to develop possible improvements.

The design of the existing ultrafiltration unit at BA Banknote Inc. is not capable of performing at optimum capacity to recycle the highly alkaline wastewater. In order for the ultrafiltration unit to perform at an optimum condition, the solution passing through should be at a pH of 10. However, the subsequent flocculation step in the process will only be at an optimum condition when the solution passing through is at a pH of 12. The most common method of pH adjustment is the use of strong acids and bases, but these lead to a build-up of salts in the system. Hence, development of a temporary pH adjustment process using CO₂ gas to reduce the pH prior to the ultrafiltration unit and N₂ gas to raise the pH afterwards was attempted. This involved development of a computer model which can predict the concentration of the carbonated species, the rate constants

for the reaction $\text{CO}_2 (\text{g}) \rightleftharpoons \text{CO}_2 (\text{aq})$, and the rate of pH change (concentration of H^+ ion) as a function of temperature. The determined rate constants provided the apparent activation energy of -47 kJ/mol and -27 kJ/mol for the forward and reverse reactions respectively, of dissolution of CO_2 in water. Subsequently, mass transfer calculations were performed in order to assess the validity of the model assumed in obtaining the numerical data. Results indicate reasonable agreement between the experimental fluxes of CO_2 entering the water and those found from mass transfer calculations.

In the past few years, concern has increased about chemicals (surfactants, dyes, pesticides, etc) in the environment which have effects on the reproductive systems. Reports indicate that the majority of these industrial pollutants have a rather poor biodegradability and are capable of oestrogenic activity on various forms of life. Moreover, in certain water chlorination/disinfection steps, these chemicals can result in the formation of potentially carcinogenic compounds.

Another objective of this study was thus to develop an analytical method for fast and efficient routine analysis of the process streams for the purpose of quality control and environmental monitoring. An analytical method using Capillary Electrophoresis (CE) has been developed which is capable of fast (under 8 minutes) analysis of the surfactant Turkey Red Oil at any stage of the process; Gas chromatography-Mass Spectrometry (GC-MS) methods normally require an analysis time of 3 hours or more. However, the sensitivity of the developed method is not satisfactory enough to monitor the level of surfactants in the effluent streams entering the environment.

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Contributions Resulting from Industrially Relevant R & D

During first part of this research several reports were prepared for BA Banknote Inc.

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Nawaby, A.V.; and Kruus, P. “British American Banknote Inc., Experimental Design and Studies on the Performance Improvement of the Ultrafiltration Equipment in the Currency Printing Industry”, *Report #2*, February 1996.

Nawaby, A.V.; and Kruus, P. “British American Banknote Inc., Studies on the Environmental Monitoring and Quality Control in The Currency Printing Industry”, *Report #3*, June 1996.

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Table of Contents

Acceptance Sheet	ii
Abstract	iii
Acknowledgments	v
Academic Awards	vi
Publications and Presentations	vii
Table of Contents	ix
List of Figures	xv
List of Tables	xix
Nomenclature	xxi
Chapter 1	
1. Introduction	1
1.1 Methods of Aqueous Waste Treatment	2
1.1.1 Physical Treatments	3
1.1.2 Chemical Treatments	5
1.1.3 Biological Treatments	9
1.1.4 Membrane Processes-Reverse Osmosis	10
1.1.5 Supercritical Fluids and Environmental Cleanup	11
References	13

Part I: Identification of Locations for Process Optimization in The Currency Printing Industry

Chapter 2

2.	Canadian Currency Printing Industry	15
2.1	Aqueous Process Streams of BA Banknote Inc.	16
2.1.1	BA Banknote Inc. Liquid Waste (Wiping Solution)	19
2.1.2	BA Banknote Inc. Solid Waste (Sludge)	20
2.2	Possible Locations for Process Optimization	20
2.3	Research Objectives	22
2.3.1	pH Adjustment of the Effluent Streams with CO ₂ Gas	22
2.3.2	Temporary pH adjustment of the Process Water with Gases	23
2.3.3	Analysis of Surfactants	24
	References	25

Part II: pH Adjustment Using Gases

Chapter 3

3.	pH Adjustment of Industrial Process Water by Means of Gases	27
3.1	Carbonate Equilibrium	28
3.2	pH Adjustment Using Gases	31
3.3	Literature Review on Solution Degassing Methods	31
3.4	Research Objectives	34

3.5	Experimental Studies	38
3.5.1	Experimental Apparatus	38
3.5.2	Procedure	40
3.6	Results and Discussion	43
3.6.1	pH Adjustment of Industrial Water	43
3.6.2	pH Reversibility Studies on Distilled Water (pH $\approx$ 5.6) Using CO ₂ and N ₂ Gases	48
3.6.3	pH Reversibility Studies on Various Solutions of NaOH (pH 8, 9 and 13)	52
3.6.4	pH Studies on NaHCO ₃ and Na ₂ CO ₃ Solutions Bubbled with N ₂ Gas	54
3.6.5	Effect of Temperature on Temporary pH Adjustment Using Gases such as CO ₂ and N ₂	57
3.6.6	Temporary pH Adjustment of Solutions Using Gases such as SO ₂ and NH ₃	60
3.7	Conclusions	63
	References	65

Chapter 4

4.	Gas-Liquid Kinetics and Mass Transfer Studies	67
4.1	Gas-Liquid Equilibrium	68
4.1.1	Gas Transfer from a Bubbled to a Solution	70
4.2	Equilibrium Constants for Carbonated Systems	72
4.3	Kinetics of Hydration of Carbon Dioxide	75
4.4	Literature Review on CO ₂ -Water Systems	78
4.5	Research Objectives	81
4.6	Determination of Rate of CO ₂ (g) Dissolution	83
4.6.1	Mathematical Model	83

4.6.2.	Result and Discussion	88
4.7	CO ₂ -Water Mass Transfer Calculations	95
4.7.1.	Gas Bubble Diameter	95
4.7.2.	Bubble Terminal Velocity or Rising Velocity	97
4.7.3.	Prediction of Diffusivities in Liquids	101
4.7.4.	Mass Transfer from Gas Bubbles to Liquids	101
4.7	Conclusions	106
References		108

Part III: Development of an Analytical Method for Fast and Efficient Routine Analysis of Surfactants in the Industrial Process Streams

Chapter 5

5.	Analysis of Surfactants	111
5.1	Surfactants	112
5.1.1	Surfactant Alkleen C	113
5.1.2	Surfactant Sulphonated Castor Oil (Turkey Red Oil)	114
5.1.3	Theoretical Background on Surfactants	116
5.1.4	Surfactant Solubility in Water	119
5.1.5	Environmental Impacts of Surfactants	120
5.2	Analytical Methods for Analysis of Surfactants	121
5.2.1	Thin-Layer Chromatography (TLC)	122
5.2.2	Liquid Chromatography (HPLC)	124
5.2.3	Gas Chromatography (GC)	126
5.2.4	Gas Chromatography and Mass-Spectrometry (GC-MS)	127
5.3	Analysis of Surfactants by Capillary Electrophoresis (CE)	130
5.3.1	Applications of CE to Environmental Samples	133
5.3.2	Literature Review: Analysis of Fatty Acids and Their Surfactants using CE	134

5.4	Research Objectives	138
-----	---------------------	-----

References		141
-------------------	--	-----

Chapter 6

6.	Capillary Electrophoresis	145
-----------	----------------------------------	-----

6.1	Theoretical Background	145
-----	------------------------	-----

6.1.1	CE Apparatus	146
-------	--------------	-----

6.1.2	Electroosmotic Flow (EOF)	148
-------	---------------------------	-----

6.1.3	Factors Influencing CE Separations	149
-------	------------------------------------	-----

6.2	Experimental Studies	154
-----	----------------------	-----

6.2.1	Experimental Apparatus and Procedure	154
-------	--------------------------------------	-----

6.2.1.1	Capillary Electrophoresis (CE)	154
---------	--------------------------------	-----

6.2.1.2	Gas Chromatography - Mass Spectrometry	156
---------	--	-----

6.3	Result and Discussion	158
-----	-----------------------	-----

6.3.1	Analysis of Alklean C (Sodium alkyl Sulphonate)	158
-------	---	-----

6.3.2	Method Development, Analysis of Turkey Red Oil	159
-------	--	-----

6.3.3	Choice of Separation conditions	161
-------	---------------------------------	-----

6.3.4	Buffer Additives	165
-------	------------------	-----

6.3.4.1	Organic Solvents	165
---------	------------------	-----

6.3.4.2	Cyclodextrins	165
---------	---------------	-----

6.3.5	Buffer Concentration	166
-------	----------------------	-----

6.3.6	Optimization of Injection Time and Voltage	170
-------	--	-----

6.3.7	Peak Identification	171
-------	---------------------	-----

6.3.8	Performance Characteristics	173
-------	-----------------------------	-----

6.3.9	Application	177
-------	-------------	-----

6.4	Conclusions	179
-----	-------------	-----

References		180
-------------------	--	-----

Chapter 7

7. Conclusions	181
7.1 Summary of Conclusions	181
7.1.1 pH Adjustment	181
7.1.2 Analysis of Surfactants	183
7.2 Future Contributions	184
7.2.1 pH Adjustment	184
7.2.2 Analysis of Surfactants	184

Appendices:

Appendix A	Calibration of the Rotameter	186
Appendix B	pH Adjustment Studies for Other Gases (SO_2 and NH_3)	190
Appendix C	Computer Program for the Determination of Rate Constants in the Carbonated Systems	192
Appendix D	CE and GC-MS Analysis of Surfactant Alkleen C	201
Appendix E	GC-MS Analysis of Surfactant Turkey Red Oil, Standard Solutions and Industrial Water	204

List of Figures

Figure (2.1): Schematic diagram of the aqueous chemical process for printing currency at BA Banknote Inc.	17
Figure (3.1): Relative amount of each CO ₂ species at different pH levels.	29
Figure (3.2): Schematic diagram of the experimental apparatus for the pH studies.	39
Figure (3.3): pH studies of Tank 201 using 5M HCl, 5M H ₂ SO ₄ and CO ₂ gas at 1.2 atm and 298 K (25 ± 2 °C).	44
Figure (3.4): pH reversibility studies on distilled water (pH ≈ 5.6) using CO ₂ and N ₂ gases at a pressure of 1.2 atm and 298 K (25 ± 2 °C).	49
Figure (3.5): A visual description of the chemical reaction occurring in the process of temporary pH adjustment using CO ₂ and N ₂ gases.	51
Figure (3.6): pH reversibility studies on NaOH solution (a) pH ≈ 8 and (b) pH ≈ 9 using CO ₂ and N ₂ gases at a pressure of 1.2 atm and 298 K (25 ± 2 °C).	53
Figure (3.7): pH changes of the NaHCO ₃ solution when bubbled with N ₂ gases at a pressure of 1.2 atm and 298 K (25 ± 2 °C).	55
Figure (3.8): pH changes of the Na ₂ CO ₃ solution when bubbled with N ₂ gases at a pressure of 1.2 atm and 298 K (25 ± 2 °C).	56
Figure (3.9): pH reversibility studies on a 100 ± 1 mL of distilled water at different temperatures using CO ₂ or N ₂ gas.	58
Figure (4.1): Four steps of gas transfer from vapour phase to solution phase.	68
Figure (4.2): Transfer of a gas from a bubble to the solution phase.	71
Figure (4.3): Arrhenius and van't Hoff equilibrium constant plots for available rate and equilibrium constants.	86

Figure (4.4): A comparison of the numerically obtained data with the experimental data for distilled water at 298 K (25 ± 2 °C) when bubbled with CO ₂ gas.	91
Figure (4.5): A comparison of the numerically obtained data with the experimental data for distilled water at 298 K (25 ± 2 °C) when bubbled with N ₂ gas.	92
Figure (4.6): Determination of activation energy for the hydration and dehydration reaction of CO ₂ (g) $\leftrightarrow$ CO ₂ (aq).	94
Figure (5.1): Molecular formula and structure of surfactants in Alkleen C.	113
Figure (5.2): (a) Molecular structure of ricinoleic acid, and (b) sulphonated castor oil.	115
Figure (5.3): Basic structure of a surfactant molecule.	116
Figure (5.4): Effect of surfactant concentration on adsorption.	118
Figure (5.5): Solubility of surfactants in water as a function of temperature.	119
Figure (5.6): The Fischer esterification reaction of carboxylic acids to yield an ester.	129
Figure (5.7): Applications of CE to environmental samples.	133
Figure (6.1): Instrument set up of a capillary electrophoresis system, Beckman 2100, Beckman Instruments, Inc., California USA.	147
Figure (6.2): Electroosmotic flow (EOF, μ_{eo}) and electrophoretic mobility (μ^- , μ^+) using normal polarity configuration.	147
Figure (6.3): Chemical structure of (a) α -cyclodextrin, (b) β -cyclodextrin and (c) γ -cyclodextrin.	152
Figure (6.4): CE method development flow chart.	160
Figure (6.5): CE analysis of sulphonated castor oil. Capillary of 57 cm $\times$ 75 μ m i.d. (50 cm to detector). Buffer: 20 mM Tris, pH 8, 20 kV, 35 °C, 10 second injection, 200 nm direct UV detection.	162

Figure (6.6): Effect of temperature on plate efficiency (N). 20 mM Tris buffer pH 8, 20 kV, 35 °C, 10 second injection, 200 nm direct UV detection.	164
Figure (6.7): Effect of temperature on mobilities. 20 mM Tris buffer pH 8, 20 kV, 35 °C, 10 second injection, 200 nm direct UV detection.	164
Figure (6.8): Effect of various cyclodextrins at a concentration of 5 mM on (a) The electrophoretic mobility of Turkey Red Oil components, (b) The number of theoretical plates per meter of peak 4 (presumably ricinoleic acid).	168
Figure (6.9): Effect of HP- β -CD concentration on plate efficiency. 20 mM Tris buffer pH 8, 20 kV, 35 °C, 10 second injection, 200 nm direct UV detection.	169
Figure (6.10): Effect of HP- β -CD concentrations on the peak mobilities. 20 mM Tris buffer pH 8, 20 kV, 35 °C, 10 second injection, 200 nm direct UV detection.	169
Figure (6.11): Optimized chromatogram of sulphonated castor oil. Buffer: 30 mM Tris pH 8, 7.5 mM HP- β -CD, 35 °C, 20 kV and 10 second injection in the pressure mode.	172
Figure (6.12): CE chromatogram for standard solution of castor oil. Buffer: 30 mM Tris pH 8, 7.5 mM HP- β -CD, 35 °C, 20 kV and 10 second injection in the pressure mode.	172
Figure (6.13): Reproducibility of (a) Migration time and (b) Corrected peak area of 27 replicate injections of 0.5 g/L Turkey Red Oil obtained during two successive days (18 Injection for day 1 and 9 injections for day 2).	176
Figure (6.14): Electropherogram of twenty five-fold dilution of an industrial water sample from BA Banknote Inc. (Tank 701) Sample, (a) Unspiked and (b) Spiked with 0.5 g/L standard Turkey Red Oil.	178
Figure (A.1): Calibration curves for the rotameter using CO ₂ gas at 298 K (25 $\pm$ 2 °C).	189
Figure (A.2): Calibration curves for the rotameter using N ₂ gas at 298 K (25 $\pm$ 2 °C).	189
Figure (B.1): A comparison of pH adjustment using different gases.	191

Figure (D.1): CE chromatogram of surfactant Alkleen C.	202
Figure (D.1): GC-MS chromatogram of Alkleen C.	203
Figure (E.1): GC-MS analysis of standard solution Turkey Red Oil.	205
Figure (E.1): GC-MS analysis of Tank 701.	206

List of Tables

Table (3.1):	pH studies on a 100 ± 1 mL sample of NaOH solution.	47
Table (3.2):	Henry's law constant for various gases.	61
Table (4.1):	Equilibrium constants for carbonated systems.	73
Table (4.2):	Rate constants for the hydration reactions of CO ₂ .	77
Table (4.3):	Rate constants for the dehydration reactions of carbonated systems.	77
Table (4.4):	Magnitude and temperature dependence of equilibrium and rate constants for the forward and reverse reactions in carbonated systems using $B = A e^{-E_a/RT}$.	85
Table (4.5):	Rate and equilibrium constants for the carbonated system at various temperatures.	89
Table (4.6):	Determined rate constants for the carbonated system at various temperatures.	93
Table (4.7):	Calculated bubble diameter, bubble terminal velocity, total number bubbles in solution, and the total area between CO ₂ (g) and water at different temperatures.	100
Table (4.8):	A comparison between the calculated values of A, C _{A2} and k_L with determined k'_d at various temperatures.	103
Table (4.9):	Comparison of the calculated value of flux of CO ₂ entering water with those obtained experimentally at various temperatures.	104
Table (5.1):	Comparison of castor oil and sulphonated castor oil.	115
Table (5.2):	Methods for TLC analysis of anionic surfactants.	123
Table (5.3):	HPLC analysis of anionic surfactants.	125
Table (5.4):	Derivatized GC methods for analysis of anionic surfactants.	126
Table (6.1):	Investigated buffers.	163

Table (6.2):	Regression data for calibration curves.	174
Table (6.3):	Precision of the CE migration time and corrected peak area (CPA).	175
Table (A.1):	Calibration data for the rotameter using CO ₂ gas at 298 K (25 ± 2 °C).	187
Table (A.2):	Calibration data for the rotameter using N ₂ gas at 298 K (25 ± 2 °C).	188

Nomenclature

Abbreviations

ACN = Acetonitrile

BA Banknote Inc. = British American Banknote Inc.

CD = Cyclodextrin

CE = Capillary Electrophoresis

CMC = Critical Micelle Concentration

CPA = Corrected Peak Area

DC = Direct Current

EOF = Electroosmotic Flow

HPLC = High Performance Liquid Chromatography

GC = Gas Chromatography

GC-MS = Gas Chromatography-Mass Spectrometry

MeOH = Methanol

OMEE = Ontario Ministry of Environment and Energy

SF = Supercritical Fluids

SFE = Supercritical Fluid Extraction

THF = Tetrahydrofuran

TLC = Thin-Layer Chromatography

Symbols

A_b = Area of a bubble (m^2)

C = Drag Coefficient

C_{A1} = Solubility of CO_2 (g) in Water ($mol\ L^{-1}$)

C_{A2} = Initial solubility of CO_2 (g) in water ($mol\ L^{-1}$)

d_b = Diameter of a bubble (m)

d_0 = Diameter of the orifice (m)

$D_{AB} = D_{CO_2/H_2O}$ = Diffusion coefficient of gas (A) in liquid (B) ($m^2\ s^{-1}$)

$D^{\circ}_{H^+}$ = Diffusion coefficient of hydrogen ion ($m^2\ s^{-1}$)

$D^{\circ}_{HCO_3^-}$ = Diffusion coefficient of bicarbonate ion ($m^2\ s^{-1}$)

E = Electric field strength ($V\ cm^{-1}$)

e = Proton charge (C)

f = Frequency of bubble formation (s^{-1})

F = Faraday constant ($C\ mol^{-1}$)

g = Acceleration due to gravity ($m\ s^{-2}$)

K = Equilibrium constant

k_1 = Rate constant for the reaction of $H_2CO_3 \rightarrow H^+ + HCO_3^-$ (s^{-1})

k_{-1} = Rate constant for the reaction of $H^+ + HCO_3^- \rightarrow H_2CO_3$ ($L\ mol^{-1}\ s^{-1}$)

k_{CO_2} = First order rate constant for the hydration reaction of $CO_2(aq)$ (s^{-1})
 k_{OH} = Rate constant for the reaction of $CO_2(aq)$ and OH^- ($s^{-1} mol^{-1} L$)
 k_d = Rate constant for reaction of $CO_2(g) \rightarrow CO_2(aq)$ ($mol L^{-1} Pa^{-1} s^{-1}$)
 k_{-d} = Rate constant for reaction of $CO_2(aq) \rightarrow CO_2(g)$ (s^{-1})
 k_h = Hydration rate constant (s^{-1})
 k_{-h} = Dehydration rate constant (s^{-1})
 k' = Boltzman constant
 K_2 = Second dissociation constant of HCO_3^-
 K_H = Henry's law constant ($M atm^{-1}$)
 $K_r = K_1$ = First acid dissociation constant of H_2CO_3
 L = Distance from injection to detection (cm)
 L_T = Total capillary length (cm)
 k_L = Over all mass transfer coefficient ($m s^{-1}$)
 M_{H_2O} = Molecular weight of water ($g.mol^{-1}$)
 N = Number of theoretical plates
 N_A = Avogadro's number (mol^{-1})
 N_{CO_2} = Flux of a CO_2 gas ($mol m^{-2} s^{-1}$)
 N_{Re} = Reynolds number
 N_{Sc} = Schmidt number
 N_x = Flux of a gas ($mol m^{-2} s^{-1}$)
 P_{CO_2} = Pressure of CO_2 gas (atm)
 Q = Gas volumetric flow rate ($mL s^{-1}$)
 R = Gas constant ($J mol^{-1} K^{-1}$)
 r_H and $r_{HCO_3^-}$ = Radii of H^+ and HCO_3^-
 T = Absolute temperature (K)
 t_{eo} = Migration time of solvent (s)
 t_R = Bubble residence time (s)
 t'_R = Migration time of solute (s)
 V = Applied voltage (V)
 V_{CO_2} = Molar volume of $CO_2(g)$ ($cm^3 mol^{-1}$)
 v_{eo} = Electroosmotic velocity ($cm s^{-1}$)
 v_t = Bubble terminal or rise velocity ($m s^{-1}$)
 w = Constant
 $W_{1/2}$ = Peak width at half height (cm)
 z_i = Charge number on ions

Greek Symbols

ΔC = Concentration gradient ($mol L^{-1}$)
 ε = Dielectric constants
 ε_0 = Permittivity of vacuum
 λ_i^0 = Limiting equivalent conductivities ($m^2 equiv^{-1} \Omega^{-1}$)

ζ = Zeta potential

η = Viscosity of the buffer in electrolyte (*cp*)

μ_{H_2O} = Viscosity of water (*cp*)

μ_{eo} = Magnitude of the electroosmotic flow ($cm^2 s^{-1} V^{-1}$)

μ_{ep} = Electrophoretic mobility of solute ($cm^2 s^{-1} V^{-1}$)

ρ_{H_2O} = Density of water ($kg m^{-3}$)

ρ_{gas} = Density of gas ($kg m^{-3}$)

$\Delta\rho = \rho_{H_2O} - \rho_{gas}$ ($kg m^{-3}$)

σ = Surface tension of water with respect to air ($N m^{-1}$)

Chapter 1

1. Introduction

The contamination of our environment by industrial waste has been recognized for some time. Many industries and governments are concerned with strategies to minimize waste and to reduce environmental hazards by means of effective and economic technologies. Due to an increase in wet process industries which produce liquid waste, the potential of hazardous man-made pollutants entering our fresh water systems is also increasing. These liquid wastes are generally different in amount, strength and hazards to health and environment. The nature of *industrial aqueous waste* varies among industries and all the waste can not be treated in the same manner.

Many methods of waste treatment are currently available to industry. However, with the growth in the manufacturing sector new problems have appeared which require innovative methods of treatment, or in some cases the optimization of the existing process to reduce or eliminate waste. The most common methods of waste treatment used by industry are; sedimentation, filtration, pH adjustment, oxidation and reduction, coagulation, adsorption, ion exchange, etc (Weber, 1972 [1] and Henze *et al.*, 1995 [2],

References on page 13). Due to the impacts of pollutants on our health and ecosystems, tougher legislation and closer monitoring of pollutant effluent stream are likely to be implemented. Industry will likely be forced to look for innovative methods to treat their effluent streams prior to discharge, economize the amount of water used, and to monitor the amounts of contaminants released to the environment.

The search for new methods of waste treatment and process optimization has led researchers to use gases at atmospheric pressures for stream pH adjustment (Liquid Carbonic, 1994 [3]), and at higher pressures for extraction of contaminants (McNally, 1995 [4] and Lee *et al.*, 1997 [5]). Scientists are also working towards the development of novel, and feasible analytical methods for the routine and efficient analysis of industrial process streams for the purpose of quality control and environmental monitoring. An analytical method such as *Capillary Electrophoresis* (Kuhn and Hoffstetter-Kuhn 1993 [6]), has been developed and is capable of such analysis.

1.1 Methods of Aqueous Waste Treatment

Industry is interested in process changes for the purpose of reducing waste or changing the nature of the waste, resulting in an effluent stream that is more environmentally acceptable. Unavoidable wastes produced by industrial plants must be treated by an appropriate process before discharge. The waste treatment techniques used are generally classified into three groups: *physical*, *chemical* and *biological* operations.

The physical (also called mechanical) operations are the least expensive since no reagents are required and much of the equipment is simple. The two physical operations most commonly used in waste treatment are sedimentation and filtration. Another type

of physical treatment which has been found to have several types of applications in waste treatment is heat transfer.

Chemical operations mainly involve the chemical reactions of polluting wastes. Among these types of waste treatment are processes such as pH adjustment, oxidation and reduction, coagulation, adsorption and ion exchange.

The third class of waste treatment is biological operations. These are found to be the most effective methods of treating sewage and organic industrial wastes, i.e. aerobic and anaerobic biological waste treatments.

Recently, processes such as membrane separations as well as gases at high pressure (supercritical fluids), are being employed for the purpose of waste treatment and extraction.

1.1.1 Physical Treatments

Sedimentation. This method is one of the most commonly used and the least costly treatment operation in sewage and waste disposal. Sedimentation serves to remove settled particles and has no effect on dissolved or colloidal material. The suspended solids in a liquid settle by gravity to the bottom of a tank, from which they can be removed as sludge. The goal of a sedimentation process is to separate solids from the liquid phase of the waste, producing an effluent as free as possible from solids (Weber, 1972 [1]).

Particulates settle from suspension in different ways, depending upon the concentration of the suspension and the characteristics of the particles. There are four

distinct types of sedimentation, *class-1* clarification, *class-2* clarification, *zone* settling, and *compression zone*.

Class-1 clarification is the settling of a dilute suspension of particles which have little or no tendency to flocculate, i.e. to form a large mass. *Class-2* clarification is the removal of dilute suspension of flocculant particles. The third type of clarification is called *zone* settling. In this type, particles are sufficiently close, and as a result the interparticle forces are able to hold them in fixed positions relative to each other. The particles subside as a larger mass rather than as discrete particles. The fourth type of sedimentation is called the *compression zone*. In this type the particles actually contact each other and the resulting structure of the compacting mass restricts further consolidation.

Filtration. This is defined as the mechanical separation of suspended solids from a liquid by passing the liquid through a porous medium which retains the solids on its upstream. The filtration process serves the same purpose as sedimentation, although the technique is different. This operation is usually more expensive than settling; however, the equipment requires less space, operation is more rapid, and the solids recovered are nearly dry. The filtration processes are often employed in water treatment, with or without pretreatment by coagulation and sedimentation (Weber 1972, [1]).

Ultrafiltration is also a physical process requiring elevated pressures to achieve passage of fluid through the filter (Patterson, 1985 [7]). This is a filtration process which uses porous membranes and is effective down to molecular dimensions of 1 – 10 nanometer (nm). Essentially, in this separation technique the water molecules and other

low molecular weight solutes pass through the membrane pores while larger ones such as oils for example are rejected. The actual performance of the ultrafiltration unit is dependent on the structure and thickness of the membrane, the membrane composition, applied pressure, temperature, concentration of wastewater and the pH.

Heat Transfer Operations. The treatment of industrial waste by heating and cooling is not economical. Large amounts of fuel and energy are required to obtain a temperature change. Heat transfer operations may however be carried out on the treatment of concentrated waste or concentrate recovered from waste. This technique involves evaporation of liquids, drying of solids and incineration.

Heat transfer operations can be used to coagulate proteins and other colloidal materials, increasing their rate of removal from wastes. In addition it could also be used to drive off volatile gases from a waste; concentrate liquours; and to dry sludge or concentrates from primary treatment processes (Weber 1972, [1]).

1.1.2 Chemical Treatments

This kind of treatment generally involves the chemical reaction of polluting constituents of wastes, with added chemicals. The end product of such reactions is either less environmentally harmful or easier to remove through mechanical means, such as precipitates. pH adjustment is a common method of chemical treatment of industrial waste.

pH Adjustment. The acidity and alkalinity of wastes entering the natural streams and municipal sewers are monitored closely due to government regulations. Wastes excessively acidic would have a pH value under 4. The highly basic (alkaline) wastes

normally tend to have a pH value over 9. These types of wastes must be treated prior to discharge. The removal of excess acidity and alkalinity by treatment with chemicals of opposite nature is called "*neutralization*". For this purpose, many chemicals and reagents are available; the choice therefore depends on economics and chemical compatibility for the particular waste and conditions. Another application of pH adjustment is the acidification of emulsified wastes for the purpose of separating oily constituents. In this particular process a subsequent neutralization is usually required.

Today many pH adjustments of alkaline streams are carried out using carbon dioxide gas (Liquid Carbonic Co., 1995 [8]). Carbon dioxide gas is not only a safe and effective chemical for lowering the pH of highly basic industrial streams, but also economic and easy to control.

Oxidation and Reduction. Oxidation and reduction processes are useful in treating almost all types of industrial waste. Chemical oxidation is the process in which the oxidation state of a substance is increased. Conversely, chemical reduction is the process in which the oxidation state of a substance is reduced.

By oxidizing the waste constituents that would consume oxygen, the lowering of the biochemical and chemical oxygen demand can be achieved. An example of such oxidation includes the destruction of compounds such as phenols and cyanides. The complete oxidation of these organic pollutants leads to formation of carbon dioxide, water, nitrogen gas, nitrite, nitrate, and sulfate ions. The reduction process, the reverse of oxidation, has fewer applications in waste treatment, but it is a necessary step in the

processing of certain wastes which contain chromium (reduction of chromium from a valence of +6 to +3).

In the chemical oxidation of industrial waste, atmospheric oxygen or dissolved oxygen is widely used. Other common oxidizing agents include chlorine and related chlorine compounds, ozone, and finally substances such as permanganates, chromates, and nitrates. Oxidation-reduction reactions can also be carried out electrolytically (Weber 1972, [1]).

Coagulation and Chemical Reaction. The product of coagulation and chemical reaction processes with the addition of a chemical reagent are precipitates, but occasionally a gas. The impurities in an aqueous waste stream may vary in size by about six orders of magnitude, from a few nanometers (nm) for soluble substances, to a few microns (micrometer, μm), for suspended materials. The removal of a large portion of the impurities in the water and wastewater treatment is mainly accomplished by means of sedimentation. However, many impurities are too small for gravitational settling to be effective. As a result, the transformation of these particles into larger ones that settle readily is essential for successful separation. This process of aggregation is normally called “coagulation”.

In cases where the suspended pollutants are of organic nature, they may often be oxidized by biological means before coagulation. In the process of chemical coagulation the polluting substances themselves enter into the chemical reactions with the reagent, instead of being mechanically adsorbed or entrained on the reagent floc. Chemical

coagulation is mainly used with inorganic or ionic pollutants as well as the heavy-metal ions (Weber 1972, [1]).

Adsorption and Ion Exchange. Liquid waste may be treated by the unit operations of adsorption and ion exchange. In both processes, liquid waste is brought into contact with solid reagents that have the properties of concentrating and holding certain constituents of the waste on their surface.

There are three fundamental steps involved in all adsorption and ion exchange processes. The first step is the contact of the liquid with the solid adsorbent. During this time, unwanted ions or molecules are selectively adsorbed on the solid surface. Following the solid adsorption, the second step involves the separation of treated liquid from the solid by draining or settling. In the final or third step, the adsorbent is regenerated either by removing the adsorbate, or by discarding the entire solid mixture and replacing it with a fresh sample.

Adsorption may be accomplished by a variety of methods which are: percolating the fluid through a stationary bed of adsorbent, mixing adsorbent particles into the fluid and then separating them by settling or filtering, and through continuous movement of both solid and liquid phases in a counter-current flow manner. An example of applications of adsorption in waste treatment is the treatment of phenolic wastes. Activated carbon adsorption beds are used for removal and recovery of these wastes (Weber 1972, [1]).

Ion exchange processes are mainly used for water and wastewater treatment. Their primary use is for the removal of “hardness” ions (Ca^{2+} and Mg^{2+}) as well as the removal of iron. The unwanted ions are exchanged for the Na^+ ions which are present on a resin.

They are also used for the treatment of a variety of industrial wastes to allow for recovery of valuable materials or by-products. This process is particularly important in the recovery of ionic forms of precious metals such as silver, gold and uranium.

1.1.3 Biological Treatments

Aerobic and Anaerobic Biological Waste Treatment. Industrial wastewater containing toxic substances that have an adverse effect on biological systems can be treated using *aerobic* and/or *anaerobic* biological treatments.

The aerobic treatment is a process in which a mixture of primary sludge (result of the sedimentation process) is aerated for an extended period of time. This process results in cellular destruction with a decrease in volatile components. The purpose of this process is to reduce the amount of sludge to be disposed. The limiting factor for most aerobic processes is the large contact area required during the aeration process. The most important advantage is that the products are relatively odorless and are fully oxidized.

The *anaerobic* treatments are carried out in the absence of gaseous or dissolved elemental oxygen. This process is usually accompanied or followed by an oxidation-reduction reaction of soluble constituents in the living cells. The products of anaerobic decomposition are less oxygenated than the products obtained under aerobic conditions. Anaerobic fermentation and digestion are carried out by bacteria and microorganisms and are usually characterized by malodorous noxious gases such as ammonia and hydrogen sulfide, and combustible gases such as methane and hydrogen. If this process is to be used on a large scale, one should consider the factors of odor to avoid nuisance and toxicity of the gases to avoid health hazards. A major advantage of anaerobic

processes is that there is no need for large surfaces and interfacial areas; reactions may be carried out at great depth; such processes are carried out in closed tanks (Sawyer *et al.*, 1994 [9]).

1.1.4 Membrane Processes – Reverse Osmosis

Membrane separations are becoming more and more important in water and wastewater treatment processes. Reverse osmosis and membrane processes can selectively reject molecules and ions of the same size order as water molecules. A membrane may be defined as a phase which acts as a barrier to flow of molecules or ionic species between the phases that it separates. The membrane phase is usually heterogeneous. It can be a dry solid, a solvent swollen gel, or a liquid that is immobilized. A membrane transports some molecules faster than others, i.e. it has high permeability for some species and lower for others.

Membrane separation processes can treat sea water and waste streams having high organic loading. Such processes have applications in food, pharmaceutical and printing industries. This treatment process has also found applications in wastewater treatment as a substitute to thickeners, clarifiers and flocculation. This technique can also be used to remove a number of constituents from water, clays, vegetable matter, microorganisms, and in some processes, inks.

The process of osmosis is the movement of a solvent through a membrane that is impermeable to a solute. This process is somewhat similar to filtration, in that they both involve removing of a liquid from a mixture by passing it through a device which retains the other components. In order to clean the solvent, i.e. to concentrate the solution on the

other side of the membrane, it is necessary to overcome the osmotic pressure of the solution. Solvent water thus flows through a semipermeable membrane as pressure is applied. This membrane acts like a filter to retain the particles and the ions.

Reverse osmosis processes can produce desalted effluent by forcing water through semipermeable membranes at high pressure. Other applications of osmotic pressure in environmental engineering is the removal of contaminants such as nitrate and radium from water (Sawyer *et al.*, 1994 [9]).

1.1.5 Supercritical Fluids and Environmental Cleanup

In recent years the use of Supercritical Fluid Extraction (SFE) has become accepted as a possible method. For waste treatment, the higher diffusion rates and the possibility of solvent selectivity are among the most important advantages of the SFE over traditional methods of extraction such as liquid-liquid and liquid-solid.

The special and unique properties of the supercritical fluids (SF) have made them attractive solvents for separation processes and extraction purposes. The solvating power of this solvent may be varied by changing the temperature, the pressure and/or by the addition of a small amount of a “*modifier*” such as methanol. SFs have now been evaluated as a solvent for use in many areas (McHugh and Krukonis, 1986 [10]).

An attractive and promising application of SFE is in the area of aqueous industrial waste treatment. SFEs have been found to be capable of removing contamination and toxic chemicals from various environmental samples (Sengupta *et al.*, 1994 [11]). Many researchers believe that SFE could be used as a treatment method for the most

challenging environmental and polluting problems of the next century. Special care must however be taken while working at the high pressures required (typically 300 atm.).

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**Part I: Identification of Locations for Process Optimization in
The Currency Printing Industry**

Chapter 2

2. Canadian Currency Printing Industry

Quebecor Printing Inc. is a global printing company with a wide range of printed products. It also has services in several countries: Canada, United States, United Kingdom, France, Spain, Chile, Argentina, Mexico and India. Quebecor Printing Inc. is a leader in the production of chip cards, CD-ROMs, magazines, catalogs, books, directories, checks, bonds and banknotes (References on page 25).

British – American Banknote Inc. (BA Banknote Inc., Ottawa – Canada) is a division of Quebecor Printing Canada. It is an international leader in security printing of banknotes, passports, gift vouchers, bonds, certificates and similar products. BA Banknote Inc. has had contracts from over 35 central banks and governments in the past ten years. This company, operating under absolute security, also supplies the Canadian government with currency and security printed documents. BA Banknote Inc., is a part of the Canadian manufacturing sector and is monitored on a regular basis for compliance with the environmental regulations set by all levels of government.

Due to changing environmental standards, the printing industry, in particular the currency printing industry, is now being monitored very closely. Production of currency requires the use of significant quantities of surfactants and inks, as well as the generation of large amounts of wastewater. Reports indicate that these wastes could have a significant effect on the aquatic environment.

2.1 Aqueous Process Streams of BA Banknote Inc.

BA Banknote Inc. has 130 years of experience in printing international and national currency. The process used to print banknotes is described in this section and a schematic diagram is given in Figure (2.1).

In order to become familiar with this operation, a great deal of time was spent on site at BA Banknote Inc. This was required for the identification of process equipment, tanks and pumps. A flowchart was not available from BA Banknote Inc.; thus the information obtained was used to prepare the schematic diagram presented in Figure (2.1).

Printing of the currency begins at the two printing presses. Depending on the currency being printed, an appropriate ink solution is applied to the engraved printing plates. The currency is then printed by contacting the plates with the supplied paper (Domtar Canada, Cornwall Plant). Once the currency is printed, the printing press must be cleaned prior to the application of the ink solution for the next print process. For quality control purposes, this step is carried out after each sheet of currency is printed. This cleaning process is carried out using the wiping solution from Tank 500. The solution is prepared by mixing sodium hydroxide (NaOH) with surfactant and softened water.

Figure (2.1): Schematic diagram of the aqueous chemical process for printing currency at BA Banknote Inc (Progress Report 1, 1995 [1]).

The wastewater is transferred to Tanks 101 and 201 prior to entering the ultrafiltration units. There are two ultrafiltration units; the main unit contains 80 filters, and a backup unit contains 40 filters. With the main ultrafiltration unit operating at optimum conditions, approximately 80% of the wiping solution can be recycled to Tank 701. The concentrations of surfactant and caustic soda are estimated and are then added to obtain the required levels in Tank 500. The optimum temperature for this filtration process is reported by BA Banknote Inc. to be 305 K (32 ± 2 °C).

The remaining 20% (sludge) is transferred from the ultrafiltration to Tank 301 for further treatment. In cases where Tank 201 is full, the wastewater is transferred directly to Tank 301 for treatment. There are times when the ultrafiltration units are not operating at an optimum condition, or both are being cleaned, or filters are being changed. In this case, all the wastewater from the cleaning process is transferred to the underground pit and is kept for later treatment.

When the ultrafiltration units are operating at optimum conditions, the resulting sludge is flocculated in Tanks 437 and 403 using ferric chloride (FeCl_3) and calcium chloride (CaCl_2) solutions. The sludge is then transferred to the rotary vacuum system by gravity. The de-watered sludge from the rotary vacuum system is bagged and transferred to landfill. The water collected in Tank 601 is then neutralized using 50% sulphuric acid (H_2SO_4), and passed through a sand and charcoal filter for discharged into the storm sewers.

2.1.1 BA Banknote Inc. Liquid Waste (Wiping Solution)

For many years water has been the receiving medium for rejected chemicals and materials. The printing currency process is indeed one that generates high amounts of water pollution if not regulated properly. Today this industry and others are well on their way to reducing, recycling and reusing water whenever possible. As a result, there must be a good knowledge of the generated wastewater in order to have a highly efficient treatment process.

The wastewater generated by the currency printing industry in Canada is due to the printing presses being washed with the wiping solution after each sheet of currency is printed. Over the years, the wiping solution formulation has been modified to suit the new types of inks developed to improve productivity, quality and safety in intaglio printing (technology of printing plates).

It has been reported that the most suitable wiping solution consists of NaOH (0.7 - 1% w/v), a surfactant (1 - 1.2% v/v) in a solution of softened water (Note, Printing Works Bank of Thailand (for Bank of Mexico Printing works), 1981 and 1989 [2], [3]). There have been several surface active agents used at BA Banknote Inc. for the formulation of the wiping solution; however, the two most effective for purpose of quality control are sulphonated castor oil (Turkey Red Oil) and Alkleen C (see Chapter 5 for further description).

The liquid waste from this industry is highly alkaline in nature and consists of inks and surfactants. The main function of NaOH is to neutralize the varnish in the inks, which is inherently acidic, thereby rendering it soluble or emulsifiable in water. The

surfactant functions as a surface active agent which assists in dispersing the oil varnish and other ink components, producing a stable emulsion or suspension of wiped ink in water.

2.1.2 BA Banknote Inc. Solid Waste (Sludge)

Various types of inks are used for intaglio printing; some of them contain heavy metals. During the ultrafiltration process it is presumed that most of the inks and surfactants are removed from the wastewater and transferred to the flocculation process and finally into the dewatered sludge which is transferred to the landfill.

A preliminary study was performed on the dewatered sludge from the rotary vacuum system (Figure (2.1)) to test for the metal content. A sample of this sludge was collected and dried in the oven for two hours at a temperature of 473 K (200 ± 1 °C). The elemental analysis of the sludge was performed using a CM-20 transmission electron microscope (20 ± 1 kV) at National Research Council of Canada (NRC). The results indicate large amounts of Ca and Cl, as well as traces of Cu, Fe and Ti. The large amounts of Ca, Cl, and Fe are due to the flocculation process and the addition of ferric chloride (FeCl_3) and calcium chloride (CaCl_2). The traces of copper and titanium are thought to be from the piping. There was no evidence of the presence of heavy metals.

2.2 Possible Locations for Process Optimization

Industry is constantly searching for simpler (cheaper) processes, which would have small or no environmental impact. As a result gases have become an alternative to aqueous acids for the purpose of pH adjustment and an alternative to solvents for

extraction purposes. Carbon dioxide gas has been known for some time to effectively lower the pH of aqueous solutions. There are two possible location in the currency printing process at BA Banknote Inc. that could be optimized using gases for pH adjustment.

The first location for process optimization is the pH adjustment of tank 601 (Figure (2.1)). Carbon dioxide gas could be used to lower the pH of this effluent stream prior to discharge. This therefore eliminates the use of a hazardous and highly corrosive acid such as sulphuric acid (H_2SO_4).

The second location for pH adjustment would be prior to and after the ultrafiltration units. The filter membranes are highly pH sensitive and require replacement quite frequently (typically 2 times a year). The frequent replacement is due in part to using the filters at a pH (usually 12) that is considerably higher than the optimal condition (around 10). A temporary pH adjustment of the streams for the filtration process could thus result in a great deal of cost savings (up to \$80,000/year). The ultrafiltration unit would also run at an optimum condition for a longer period of time.

Quantification of surfactants entering our environment by industrial activity is very important since these chemicals could pose a hazard to our fresh water systems. A fast and efficient analytical method that would provide process stream analysis for the purpose of environmental monitoring and quality control would thus be advantageous. In cases where significant quantities of surfactants are being discharged, it would also be worthwhile to develop an extraction process for the purpose of removal of these

contaminants from the discharge stream. This may make greater recycling of surfactants possible.

2.3 Research Objectives

Water-borne wastes present a potential hazard to natural water systems. These wastes may contain certain organic matter, which cause deoxygenation by promotion of microbiological activity. They may also contain materials which are toxic to various life forms in the water systems. As a result, the treatment of such wastes is of paramount importance.

Water is vital to sustain life, and as populations increase, the demand for water grows accordingly. In most countries the public demands water that is free of color, turbidity, taste, odor, harmful metal ions, and a wide variety of organic chemicals and chlorinated solvents. Some of the possible health hazards associated with these compounds include cancer, birth defects, and heart disease.

The purpose of this study is to develop a system which optimizes the use of water in aqueous process streams of BA Banknote Inc. This involves the monitoring, removal and recovery of materials used. The major components of such aqueous processes contain surfactants, inks, and caustic soda.

2.3.1 pH Adjustment of the Effluent Stream with CO₂ Gas

The recovered water from the rotary vacuum system filter (tank 601, Figure (2.1)) is highly basic in nature; as a result, prior to discharge, concentrated sulfuric acid (H₂SO₄) is used for neutralization. A new method of pH adjustment is desirable as accidental or

long-term exposure of workers to sulfuric acid constitutes an occupational and environmental hazard.

2.3.2 Temporary pH Adjustment of the Process Water with Gases

Large volumes of water are used in order to prepare the wiping solution for the purpose of cleaning the printing plates. The design of the existing process is such that in some cases the ultrafiltration units are not capable of performing at an optimum condition to recycle the water. This results at times in a complete discharge of the water to the storm sewers. Moreover, this has resulted in large costs for water.

One primary goal of this research project is thus to develop a method for temporary pH adjustment which does not involve the addition of strong acids and bases; which results in a buildup of salts in the system as the water is recycled.

In order for the ultrafiltration units (Figure (2.1)) to perform at optimum conditions, the solution passing through must be at a pH of 10. Unfortunately, the flocculation process will be at an optimum condition when the solution is at a pH of 12. Hence, an investigation is carried out in the use of gases such as carbon dioxide (CO_2) to lower the pH prior to the ultrafiltration process, and with subsequent flushing of CO_2 with another gas such as with nitrogen (N_2) to raise the pH after this unit. The advantage of this method of pH adjustment is that no salt buildup will result in the system, and hence the water could be recycled. A considerable portion of the gases could also be recovered, recycled and reused.

A computer model for the carbonated system is developed which predicts the rate of pH change as a function of temperature and time. This numerical model not only

provides the concentration of carbonated species at each time interval, but also the estimated rate constants (k_d and k_{-d}) for the dissolution of $\text{CO}_2(\text{g})$. Analysis of these rate constants yields activation energies for both the forward and reverse reactions.

2.3.3 Analysis of Surfactants

Another objective of this study is development of an analytical method for fast and routine analysis of the process streams for the purpose of quality control and environmental monitoring. Since no analytical method is currently used, it is not known if the process is operating at optimum conditions (Figure (2.1)). The amount of surfactants discharged into the environment is also unknown. A benefit of this analysis is the information gained on determining the exact amounts of surfactants and caustic soda required to be added to Tank 701. This will minimize the amount of chemicals used in the process, consequently lowering the amounts treated and discharged into the environment.

Development of an analytical method is carried out using capillary electrophoresis (CE) for the routine analysis of the process streams and for determination of the amounts of contaminants in the discharge. The results obtained can then be compared to the accepted limits of the Ontario Ministry of Environment and Energy (OMEE) for aqueous waste discharge.

In the event that the contamination level is higher than the discharge limit, yet another goal of this project could be to develop an extraction process that removes the contaminants to a level, which is acceptable by OMEE standards. This part of the project was however not carried out in this thesis research.

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Part II: pH Adjustment Using Gases

Chapter 3

3. pH Adjustment of Industrial Process Water by Means of Gases

Printing industries are known to generate highly alkaline wastewater due to the solubility of inks at higher pH ranges. If not treated, such wastewater could result in the formation of calcium carbonate deposits in the sewer pipes, which could build up to a point where there is restriction of flow. Furthermore, any biological treatment of this wastewater would not be possible since the microorganisms are only effective in a narrow, lower pH range (References on page 65).

Most pH adjustment of process streams is carried out through addition of acids or bases. This method is effective, but it introduces new problems: corrosion, a high degree of equipment maintenance, frequent replacement of system components, and work place hazards of strong acids and bases. A further disadvantage of this method of pH adjustment is the build-up of salt, which limits the recycling of the process water within the industry. Today, gases are becoming an attractive alternative to these chemicals. This chapter focuses on the use of CO_2 and N_2 gases in order to temporarily or

permanently adjust the pH of industrial process streams, especially those of BA Banknote Inc.

3.1 Carbonate Equilibrium

The amount of gas dissolved in a liquid will depend on the nature of the solvent, the pressure and the temperature. For example, at 0°C and 1 atm, 0.0489 L of oxygen will dissolve in 1 L of water as compared to 1.713 L of carbon dioxide (Holtzclaw *et al.*, 1984 [1]).

When carbon dioxide (CO₂) dissolves in water it forms a weak acid. There are four forms of carbon dioxide in solution: dissolved CO₂ (CO₂(aq)), carbonic acid (H₂CO₃), bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) ions. The sum of these concentrations in solution is the total carbonate species concentration (Loewenthal and Marais, 1976 [2]). The carbonic species together with the OH⁻ and H⁺ ions of the water exist in a state of dynamic equilibrium described by the following reactions:

The interaction of the carbonated species with water will result in a displacement of equilibrium between H⁺ and OH⁻ ions. This will manifest itself by the establishment of a specific pH. At this pH the relative concentrations of H₂CO₃, HCO₃⁻ and CO₃²⁻ are

fixed according to the equilibrium relations. It is thus convenient to relate these relative concentrations to pH; as a result, the pH is a significant independent variable. Figure (3.1) is a representation of the CO_2 chemical equilibrium as given by equations (3.1) to (3.3). The curves in this figure show the relative amounts of the CO_2 species that exist at different pH levels.

Figure (3.1): Relative amount of each CO_2 species at different pH levels
(Stumm and Morgan, 1996 [3])

Literature studies indicate that there is a parallel relationship between dissolved CO_2 ($\text{CO}_2(\text{aq})$) and H_2CO_3 (Loewenthal and Marais, 1976 [2]). It has been reported that normally a fixed proportion, about 0.3%, of $\text{CO}_2(\text{aq})$ forms H_2CO_3 . If CO_2 is added or removed from water, the result will be a change in the concentration of the H_2CO_3 , and hence changes in H^+ , OH^- , HCO_3^- , and CO_3^{2-} concentrations; hence also changes in the pH of the solutions.

The pH in such systems depends on the concentration of CO₂ in water. This can be increased or decreased by changing the pressure of the gas. This relationship is quantitatively expressed by *Henry's Law*, which states that the mass of gas that dissolves in a definite volume of a liquid is directly proportional to the pressure of the gas. This is represented by equation (3.5):

$$K_H = \frac{[CO_2(aq)] (mol * L^{-1})}{P_{CO_2} (atm.)} \quad (3.5)$$

This relationship is valid under dilute solution conditions and for low pressures. The effect of pressure is evident in the carbonated beverages. Pressure forces CO₂ into the solution; bottles are capped to maintain this pressure. Upon opening the bottle the pressure decreases and some of the gas will escape from the solution. The escape of the bubbles of a gas from a solution is known as *effervescence*.

Finally, gas solubility in liquids decreases with increasing temperature. This phenomenon is an important factor in thermal pollution. Most gases can be released from solutions through a boiling process. The fact that a gas is expelled from a solution during boiling is due not only to the rise in the temperature, but also the escape of the vapours of the solvent carrying with it some of the gas above the solution. This lowers the partial pressure of the gas in contact with the solution, and according to Henry's law more gas escapes from solution.

3.2 pH Adjustment Using Gases

Upon the addition of CO₂ gas to an aqueous solution, the pH will decrease due to the formation of carbonic acid and its subsequent dissolution into bicarbonate, carbonate and hydrogen ions in the solution. Liquid Carbonic Inc. (Liquid Carbonic, 1994 [4]) has successfully used this phenomenon to lower the pH of aqueous industrial streams. There are many advantages in using CO₂ gas as a mean of lowering the pH alkaline waters. Among the most important advantages are: up to 48% cost savings when neutralizing at high pH levels, greater control (eliminates over-treatment), greater safety (CO₂ is a natural chemical) and reduced maintenance costs (requires less equipment and monitoring devices).

Although the addition of CO₂ gas to wastewater for pH adjustment (lowering the pH) has been used, the reverse of this process, removal of this gas (to increase the pH) has not been studied to any extent. If the CO₂ is removed from the solution, the concentration of the hydrogen ion must decrease in solution and hence the pH of the solution will increase. There are several methods reported in literature for the removal of dissolved gases from solutions: membrane processes, packed towers, ultrasound, and vacuum technology.

3.3 Literature Review on Solution Degassing Methods

The separation of gases from solutions is dependent on different physical and/or chemical properties of the materials. For example, this separation is dependent on the

boiling points of the components, special adsorption or absorption properties, different diffusion behavior, and different equilibria.

Removal of gases from solutions using membranes has been under investigation for some time (Royal Society of Chemistry, 1989 [5] and Huang, 1991 [6]). There are a number of publications on the use of membranes for the removal of dissolved gases from water. A water gas shift membrane has been developed in the Netherlands for the removal of CO₂ from water (Bracht *et al.*, 1997 [7]). The efficiency of this system for CO₂ removal has been reported to be 80%. This has been achieved using a catalytic membrane reactor in conjunction with a ceramic membrane selectively permeable to the gas.

The removal of dissolved O₂ from water has been studied using a silicone rubber hollow-fiber membrane module (Ito *et al.*, 1998 [8]). The concentration of dissolved O₂ in water was effectively reduced. This was achieved using the vacuum degassing (pervaporation) process through a non-porous membrane. In this process the permeabilities of oxygen, nitrogen and water vapour were independently measured. The experimental apparatus in this study consisted of silicone rubber micro-tube membrane module (effective length of 14 cm, 6000 tubes and 4950 cm² of effective area) and a vacuum pump. Ultra pure water with an adjusted oxygen concentration was fed into one side of the membrane module. The shell side of the membrane was evacuated by a vacuum pump. The gas permeability through the membrane was measured which is the controlling transport property.

Packed towers are another method used in industry to either enrich a liquid phase with a gas or to remove dissolved gases (Treybal, 1980 [9]). Packed towers are used for continuous contact of liquid and gas in both counter-current and co-current flow. The tower is filled with packing or devices with large surfaces. Liquids containing bubbles or dissolved gases are trickled down through the packed bed where they are exposed to large surfaces in order to contact another gas flowing in the opposite direction. This will result in the lowering of the concentration of the bubbled or dissolved gas in solution and subsequent removal through the exit gas stream from the packed tower.

In recent years ultrasonics has been used for the purpose of liquid degassing (Kuttruff, 1991 [10], and Suslick, 1988 [11]). Degassing of liquids by this method (rectified diffusion) is quite effective, particularly in cases where release of gas from liquid by vacuum techniques has been exhausted.

Degassing of liquids by ultrasound is by diffusion into the oscillating cavitation bubbles. Cavitation is a phenomenon typical of ultrasonic fields in liquids. Cavitation means the formation of voids or cavities in liquids under the influence of a negative pressure. These cavities or bubbles are filled with the same gas that is dissolved in the liquid. At rest the bubbles are spherically shaped and the gas pressure inside the bubble is equal to the ambient pressure in the liquid plus the pressure caused by the surface tension. In a stationary sound field, these bubbles (cavities) will undergo a radial oscillation. As the bubble oscillates it grows, with more gas entering the bubble. As the bubbles get larger, its resonance frequency decreases. If the bubble resonance frequency is below the sound frequency, the oscillating bubble is propelled out of the sound field.

As a result, the irradiation of a liquid with dissolved gas leads to degassing of the liquid. This phenomenon is known as the rectified diffusion method.

Degassing using vacuum technology is the liberation of gases and vapours taken up by a material such as a liquid or an absorber (Harris, 1989 [12] and Hablanian, 1990 [13]). Degassing or outgassing is dependent on the characteristics of the gas itself, the surface temperature, and time of exposure to vacuum (Hucknall, 1991 [14]). Absorbed gases must first diffuse from the substance to the surface, from where they are discharged to the gas phase. The release of absorbed gas is usually very rapid, and with rising temperature the desorption process accelerates. In the presence of vacuum, the gas from the desorbed bubble can be continually removed from the surface and more gas escapes from the solution.

3.4 Research Objectives

As described in Chapter 2, there are two locations in the chemical process streams of BA Banknote Inc. (Figure (2.1)) which could be optimized with regard to pH alterations. The locations for improvement are: the permanent pH adjustment of the effluent stream (Tank 601) using CO₂, and the temporary pH adjustment of the streams prior to and after the ultrafiltration units.

The permanent pH adjustment using CO₂ gas can be achieved by the addition of this gas to the solution and monitoring the changes of the pH over a time period. This will give an indication of the stability of the pH of the solution even after the discharge of the effluent stream. The temporary pH adjustment of this process can be done by the

addition of CO₂ gas to lower the pH and the subsequent removal of this gas to raise the pH.

As described in the literature review, there are several methods for solution degassing. One simple method of solution degassing is the sweeping of the surface of the solution using other gases, heating the solution or a combination of two. In this case both methods contribute to a decrease in the vapour pressure of CO₂ above the solution and shifting the equilibrium to the recombination of the ions and the release of CO₂ gas. Compressed air could be used as one of the gases to sweep away the CO₂ from the surface. However, compressed air itself contains low concentrations of CO₂ gas, which might limit the reversibility process. As a result, for industrial applications one requires a CO₂ trap (e.g. a Ca(OH)₂ solution) in order to reduce the concentrations of this gas in compressed air.

For convenience in the preliminary investigations, N₂ gas can instead be used to sweep away the CO₂ dissolved in the solution. The equilibrium reactions when the solution is bubbled with N₂ gas can be represented as follows,

This method can be used, at least in principle, to temporarily decrease and increase the pH of industrial streams. The advantage of this method of pH adjustment lies in the fact that there are no chemicals added (acids or bases) to the process streams, and hence

there is no salt build-up within the process lines. Further applications of this method require a detailed study of the literature to obtain the necessary equilibrium and kinetic data.

In this research study, several cases will be studied for the purpose of using gases as a means of pH adjustment:

1. Permanent pH adjustment of Tank 601 using CO₂ gas.
2. Temporary pH adjustment of Tank 201 using CO₂ and compressed air. This will provide information on the feasibility of this method for industrial applications.
3. Temporary pH adjustment of fresh wiping solution using CO₂ and compressed air. This will give information on the effect of inks and dyes on using gases as a means of pH adjustment and their effect on the reversibility process.
4. pH Studies on NaOH and Ca(OH)₂ solutions. This experimental step is carried out in order to gain an insight on the effect of different bases when pH adjustments are done using gases.
5. Temporary pH adjustment of distilled water (pH $\approx$ 5.6) using CO₂ and N₂ gas. This will provide information on the effect of surfactants on temporary pH adjustment using gases. In this case the effect of gas flow rate and solution surface coverage will also be examined.
6. pH reversibility studies on solution of NaOH (pH of 8, 9 and 13). The pH adjustment of solutions using gases may have some kinetic limitations at various pH ranges. These experiments will provide a better understanding on these limitations and pH ranges for the temporary pH adjustment using CO₂ and N₂ gases.
7. pH studies on NaHCO₃ and Na₂CO₃ solutions bubbled with N₂ gas. The carbonate salts will form in the solution when bubbled with CO₂ gas. This step

will give knowledge of the reversibility of the formation of these salts. This becomes important in the cases when N_2 gas is used to increase the pH.

8. Effect of temperature on temporary pH adjustment using CO_2 and N_2 gases. This provides information on the rates of gas dissolution and solution degassing. It will also provide information for kinetics (determination of rate constants), as well as mass transfer studies.
9. Effect of other gases such as SO_2 and NH_3 on pH adjustment of solutions. These gases are chosen to compare their rate of pH adjustment with the ones obtained from CO_2 and N_2 .

3.5 Experimental Studies

3.5.1 Experimental Apparatus

Reagents and Chemicals

Solid samples of NaOH, NaHCO₃ and Na₂CO₃ were all purchased from Sigma Chemicals (Toronto, Canada). Acids such as HCl and H₂SO₄ were obtained from Aldrich Chemicals (Toronto, Canada). Gases such as CO₂ 99% purity, compressed air, and N₂ 99% purity were supplied by Air Products Canada (Ottawa, Canada). The SO₂ and NH₃ 99.98% purity gases were supplied by Matheson Gas Products (Ottawa, Canada). Buffer solutions of pH 2.00 ± 0.02 (298 K) and 10.00 ± 0.02 (298 K) were used for the calibration of the pH meter. These buffers were low ionic strength and were purchased from Anachemica (Toronto, Canada). The surfactants Alkleen C and Turkey Red Oil were purchased from Hoechst (Montreal, Canada) and Produits Chimiques ADRO Inc. (Montreal, Canada) respectively.

Apparatus

Figure (3.2) is the representation of the apparatus used for pH adjustment studies using gases. This apparatus consisted of two supply gas cylinders (CO₂ and N₂ or compressed air) which are connected to a rotameter or flow meter (Matheson Gas Products, Model 7630T-602). The cylinders deliver the gas at a pressure of 1.2 atm (16 psi or 121.6 KPa) at room temperature 298 K (25 ± 2 °C). The gas is introduced to a reaction vessel (flask) resting on a magnetic stirrer, which holds the sample. The changes in pH are monitored using a pH meter (Fisher Accumet, Model 950 with RC-323

serial port). The pH meter is connected to a computer (IBM Compatible, Windows 95) where pH changes are recorded and data is collected continuously. The rate of data collection was every 0.5 seconds when the solution was bubbled with CO₂ gas and every 60 seconds when bubbled with N₂ gas. The pH meter was calibrated every day before and after the experiment in order to ensure little or no drift in the electrode during measurements.

Figure (3.2): Schematic diagram of the experimental apparatus for the pH studies.

3.5.2 Procedure

In this study two types of solutions have been examined for pH adjustment using gases. Real industrial water samples from BA Banknote Inc. and prepared model solutions are the two aqueous samples studied.

pH Studies on Industrial Water Samples. A sample of 100 ± 1 mL of industrial water (Tank 601 or Tank 201, Figure (2.1)) was placed in the flask and the initial pH was recorded. The solution was then bubbled with CO_2 gas and the changes in the pH of the solution were recorded as a function of time.

As soon as the pH of 7 (neutral) was reached, the flow of CO_2 gas was stopped. At this time the solution was sparged with compressed air in order to investigate the reversibility and stability of the pH of the solution after adjustment by means of gases. All experimental data were collected on the computer.

A separate study was also conducted in using strong acids and bases for the purpose of pH adjustment of industrial water samples. Water samples (Tank 201) were tested for pH changes when solutions of 5M HCl and 5M H_2SO_4 were added. The acids were added by means of a buret and the total volume of acid needed to neutralize each solution was recorded. The changes in pH were recorded as a function of acid volume added and the results were compared to those when the pH adjustment is performed using gases such as CO_2 .

pH Reversibility Studies on Model Solutions. A 100 ± 1 mL sample of water was placed in the flask and the original pH was recorded. The pH of this water sample was then varied through three cycles of bubbling with N_2 and CO_2 gas.

This solution was first bubbled with N₂ gas and the pH changes were recorded at 60 seconds intervals using the computer. When the pH of solution was stable at 7.0 for water (a change from 5.6 to 7), the flow of the nitrogen gas was stopped. The process of bubbling with N₂ ensured that there were no carbonates in the system. This cycle took approximately 30 to 40 minutes.

Bubbling with CO₂ gas was then started. As CO₂ gas was bubbled into the solution, the pH changes were again monitored and recorded on the computer. Once a pH of 3.9 (decrease from pH 7.0 to 3.9) was reached, the flow of CO₂ gas was stopped. The data was collected in time intervals of 0.5 seconds, for a total of 8 minutes. However, the maximum change was observed in the first 2 minutes of the experiments.

Finally, the third cycle was tests for the reversibility of this pH adjustment process. The solution was again bubbled with N₂ gas, removing the dissolved CO₂ and hence increasing the pH to its original point (change from 3.9 to 7). The changes in pH were again recorded on the computer. All experimental data were recorded and saved in a separate data file for further analysis.

The studies of temporary pH adjustment using gases were also carried out at different temperatures using a water bath. This experimental study provides data for kinetic studies. The investigated temperatures ranged from 275 - 315 K (2 - 42 °C) with increments of 10 degrees.

Other solutions were also studied for this method of temporary pH adjustment. These solutions were 100 ± 1 mL of distilled water when its pH was adjusted to 8, 9 and

13 by means of NaOH solution. All three gas bubbling cycles were performed in the same manners as described in the above procedure.

Finally solutions of NaHCO_3 and Na_2CO_3 were also studied for pH changes when only bubbled with N_2 gas. All these studies were carried out at room temperature, with the data collected on the computer.

The gas flow rates for all the experimental studies was chosen to be 6.2 mL/sec. A further study on the effect of flow rate on pH adjustment had been carried out to determine the best gas flow rate has been determined (Appendix A).

3.6 Results and Discussion

3.6.1 pH Adjustment of Industrial Water

Tank (601). The current process of stream neutralization prior to effluent stream discharge to the sewers is with the addition of 50% H_2SO_4 solution (Figure (2.1)). A study on the replacement of this chemical by CO_2 gas was performed. Carbon dioxide gas at a pressure of 1.2 ± 0.1 atm and 298 K (25 ± 2 °C) was bubbled through a 100 ± 1 mL sample from this tank. The pH of the solution was lowered to 5.7 from its original value of 11.2 within one minute. Subsequent to this, the solution was sparged with compressed air and the pH was increased to 7.0. The solution was transferred to a beaker and was left in the room uncovered and the changes in pH were monitored periodically. The pH of the solution remained reasonably neutral at 7.9 after 13 days; hence, CO_2 gas can be used as a means of pH adjustment in replacement of concentrated H_2SO_4 .

Tank (201). pH studies of the process streams of BA Banknote Inc. (Figure (2.1)) has indicated highly basic streams ($\text{pH} \approx 13$). The ultrafiltration units in this chemical process are a combination of membranes which are highly sensitive to basic solutions. As a result, the same experimental procedure for pH adjustment (CO_2 and compressed air) has been applied for temporary pH adjustment. This method of pH adjustment would allow greater amount of water recirculated within the system without a buildup of salts. In the study of pH adjustment of this tank using gases, the results are also compared to those of using two common strong acids such as H_2SO_4 and HCl . Figure (3.3) is the representation of the pH studies performed on a 100 ± 1 mL sample from Tank 201.

A 100 ± 1 mL of Tank (201) was pH adjusted ($\text{pH} \approx 1.7$) using 5M HCl. Upon the addition of this acid, the formation of solids was noticed at pH 5.5. The total amount of solids collected was 3.1 ± 0.03 g after passing the solution through a pre-weighted filter paper. pH changes using 5M H_2SO_4 indicated that with the addition of this acid the solution turned into a solid at pH 7.86. Due to this effect the pH was not lowered any further, the total amount of solids collected were 32.0 ± 0.03 g.

Figure (3.3): pH studies of Tank 201 using 5M HCl, 5M H_2SO_4 and CO_2 gas at 1.2 atm and 298 K (25 ± 2 °C).

Finally the same studies were carried out using 99% pure CO₂ (Figure (3.3)) gas at a pressure of 1.2 atm and 298 K (25 ± 2 °C). The changes of pH using this gas were recorded with respect to time; the pH of the sample from Tank 201 was lowered to 6.97 in 7.3 minutes. Using this gas, the formation of a slight emulsion was noticed at pH 7.5. After reaching pH 6.97, the flow of CO₂ gas was stopped and the solution was sparged with compressed gas at the same pressure and temperature. This resulted in a slight increase in the pH from 6.97 to 8.3 in 4.4 minutes; the final solution was still in the form of an emulsion.

Results of this study suggest that the ink resins and surfactants precipitate more easily with H₂SO₄ as compared with HCl. Using CO₂ gas, a slight complexation is observed due to the formation of the emulsion. However the pH reversibility studies (temporary pH adjustment) seem to be more feasible using gases for this process than conventional ways of added acids and bases.

The filters in the ultrafiltration units will have an extended lifetime when the solution passing through is at a pH of about 10. Therefore, the pH of Tank 201 in a separate study was lowered to 9.05 with CO₂ gas, and the solution was then sparged with compressed air. After two hours the pH of the solution was increased to 9.23. The solution was left in the open air for 13 days and the final pH recorded was 9.57.

Experimental results suggest that the pH of this tank can be successfully lowered with CO₂ gas in a short time. Further, there is an evidence of some reversibility in this process. Some components in the solution, or formed in the solution with the addition of CO₂ gas may be the cause of this incomplete reversibility. As a result, the temporary pH

adjustment of a sample of freshly prepared wiping solution was carried out using CO₂ gas and compressed air.

Fresh Wiping Solution. It is of interest to investigate whether the inks or dyes within the solution limit the reversibility of this process. A batch of fresh wiping solution free of any dyes or inks was prepared in the laboratory. This solution was made from 0.42% v/v of surfactant, 0.7 % w/v of NaOH dissolved in 1000 ± 2 mL of softened water supplied by BA Banknote Inc. A series of two tests were performed on this solution. Using CO₂ gas, the pH of this solution (100 ± 1 mL) was lowered to 6.83 from its original value of 12.93 within 7.5 minutes. During this process no formation of solids or emulsion was observed. Subsequent to this pH decrease, the solution was sparged with compressed air and the pH rose to 8.7 in 16 minutes. This process was thus not completely reversible; a second experimental investigation was therefore conducted.

A second 100 ± 1 mL sample this wiping solution was also bubbled with CO₂ gas and the pH of the solution only lowered to 9.13. The solution was then sparged with compressed air for 6 minutes and the pH rose to 9.14. The beaker was left uncovered in the open air, and the pH changes were recorded regularly. After 13 days the pH of the solution was found to be 9.82.

The results of this study indicate that the incomplete reversibility of this process (when sparged with compressed air) could be dependent on the type of the surfactant, or the cations present in the basic solution. A study on the pH changes of NaOH and Ca(OH)₂ solutions bubbled with CO₂ was therefore carried out.

pH Studies on NaOH and Ca(OH)₂ Solutions. This set of experiments was carried out in order to find out whether the base has an effect on the reversibility process. Two types of hydroxides were used: NaOH was chosen since it is one of the components used for the formulation of the wiping solution, and Ca(OH)₂ was chosen so that a comparison between the two bases could be done.

A fresh solution of NaOH of pH 12.77 was prepared using the softened water provided by BA Banknote Inc. A 100 ± 1 mL sample was bubbled with CO₂ gas and the pH was lowered to 6.56. This solution was then sparged with compressed air (pH 7.41) and then left in the open air without any coverage and the pH was monitored regularly. After 14 days the pH of the solution was recorded to be 9.84 (Table (3.1)).

These results indicate that a more complex process is involved when CO₂ gas is added to such solutions. With the addition of this gas to the sodium hydroxide solution, several carbonated species will form. In essence, a solution of NaHCO₃ is formed.

Table (3.1): pH studies on a 100 ± 1 mL sample of a NaOH solution.

Function	PH of the Solution	Time
Original pH	12.77	0
Sparged with CO ₂ gas	6.57	22 minutes
Sparged with Compressed Air	7.41	12 hours
Solution Left in Open Air	9.05	Day 1
	9.72	Day 6
	9.84	Day 14

Experimental studies using $\text{Ca}(\text{OH})_2$ further validate this finding. A solution of $\text{Ca}(\text{OH})_2$ in the softened water was prepared. This solution was milky, indicating incomplete dissolution; the original pH was 12.58. A sample of 100 ± 1 mL was then sparged with CO_2 gas and the pH was lowered to 6.13. The solution was then sparged with compressed air and subsequently left in the open air (pH 7.17). The changes in pH were regularly recorded and after 14 days this solution was still milky with pH at 9.61.

These results have led to designing experiments where pH studies are performed using CO_2 and N_2 gas. When a sample of distilled water having an original pH of 5.6 is sparged with compressed air the pH of this solution decreases to 5.0. This is due to that fact that compressed air itself contains some CO_2 . Therefore, in the experiments of temporary pH adjustment using gases the sparging was subsequently done with N_2 gas rather than compressed air. This will provide a better understanding on the reversibility of pH adjustment process using gases.

3.6.2 pH reversibility Studies on Distilled Water (pH $\approx$ 5.6) Using CO_2 and N_2 Gases

For many years it has been known that water in equilibrium with air is not at pH 7 (Bunce, 1996 [15]). This water is slightly acidic with a pH $\approx$ 5.6 due to presence of dissolved CO_2 from air. This phenomenon can easily be explained using Henry's law: when any gas equilibrates with a solvent, the amount of gas that dissolves is proportional to the partial pressure of the gas. Therefore, if the partial pressure of the gas (CO_2) above the solvent is kept at zero, the pH should rise to 7.0.

Figure (3.4): pH reversibility studies on distilled water ($pH \approx 5.6$) using CO_2 and N_2 gases at a pressure of 1.2 atm and 298 K. ($25 \pm 2^\circ C$). (a) Solution bubbled with N_2 gas to change the pH from 5.6 to 7. (b) Solution bubbled with CO_2 gas to change the pH from 7 to 3.8. (c) Solution bubbled with N_2 gas to study the reversibility of this process, ie. change of pH from 3.8 to 6.8.

A sample of distilled water (100 ± 1 mL) was placed in the sample holder of Figure (3.2). The pH of the water was tested and found to be 5.6 at 298 K (25 ± 2 °C). The pH studies on distilled water were carried out through three gas bubbling cycles. Figure (3.4) represents the experimental results.

Nitrogen gas (N_2) was first bubbled into the sample of pH 5.6 and the changes in the pH were recorded at 60 second time intervals using the computer. It was observed that by keeping the partial pressure of CO_2 gas above the surface of water equal to zero, the equilibrium conditions presented by equations (3.1-3.4) were shifted. This resulted in an increase in the pH from 5.6 to 7 in 30 minutes.

The first cycle of bubbling the solution with N_2 gas provided a carbonate free solution. At this point the flow of N_2 gas was stopped and the sample was bubbled with CO_2 gas. Throughout these studies the pressure of both gases at all three cycles were kept constant at 1.2 atm to ensure a constant internal gas pressure. The flow rate of the gases was set at an arbitrary value of 6.2 mL/sec. Introduction of CO_2 into water resulted in a decrease in the pH from 7 to 3.8 in a total time of 4.5 minutes.

To test the reversibility of this pH adjustment process, N_2 gas was again bubbled to remove the dissolved CO_2 ; there was an increase of pH from 3.8 to 6.8 in 375 minutes. Figure (3.5) provides a detailed description of the chemical reactions that occur in the reaction vessel.

Studies on the effect of gas flow rate on the pH adjustment were also carried out. These studies were performed in order to determine the best flow for subsequent experimental studies.

Figure (3.5): A visual description of the chemical reaction occurring in the process of temporary pH adjustment using CO₂ and N₂ gases.

The best flow rate was found to be at a rotameter reading of 50, which corresponds to a gas flow rate of 6.3 (mL/s) for CO₂, and 6.7 (mL/s) for N₂ (see Appendix A).

Higher flow rates resulted in excessive solution agitation, and prevented obtaining reliable results from the pH meter. Therefore, for all the pH adjustment experimental studies rotameter reading of 50 was used.

Finally a study was carried out on the effect of surface coverage on the rates of gas dissolution and solution degassing. It was noticed that when one half of the surface of the sample holder was covered, the rates decreased by one half. The surface of the sample holder was covered using a thin layer of polymeric material fitting the geometry of the sample holder of Figure (3.2).

3.6.3 pH Reversibility Studies on Various Solutions of NaOH (pH 8, 9, and 13)

The pH reversibility studies were also performed on other samples. In these studies 100 ± 1 mL of distilled water sample was taken and the original pH was recorded. The water sample was then bubbled with N₂ gas and the pH was raised from 5.7 to 7 in a total time of 30 minutes. At this time the flow rate of N₂ gas was stopped and a small amount of concentrated NaOH solution was added to the water sample to increase the pH from 7 to 8. This solution was then bubbled with CO₂ gas to lower the pH to 4.1 in 4.5 minutes. To test the reversibility process, the flow of CO₂ was stopped and the solution was sparged with N₂ gas. This process was found to be reversible and the pH of the solution was raised from 4.1 to its original value of 8 in 16.5 hours. Figure (3.6a) is the representation of the experimental findings.

Figure (3.6): pH reversibility studies on NaOH solution (a) pH ≈ 8 and (b) pH ≈ 9 using CO_2 and N_2 gases at a pressure of 1.2 atm and 298 K (25 ± 2 °C).

A second water sample of 100 ± 1 mL was placed in the sample holder, original pH recorded and its pH raised to 7 by means of bubbling with N_2 gas. With the addition of small amount of concentrated NaOH solution the pH was then adjusted to 9. Studies showed that in 4.5 minutes the pH of this solution was lowered to 4.1 by bubbling CO_2 gas through. This process was also found to be reversible, and the original pH of 9 from 4.1 was reached in 16.7 hours by sparging with N_2 gas. The experimental results for this solution is presented in Figure (3.6b).

Finally a third sample of water was studied for reversibility when the pH was adjusted to 13 using the concentrated NaOH solution. The pH of this solution was only lowered to 10 using CO_2 gas in order to be closer to the operating conditions of the streams prior to the ultrafiltration unit in Figure (2.1). It was noted that using the CO_2 gas to lower the pH from 13 to 10 only took 4.5 minutes; however, the process of raising the pH to its original value of 13 using N_2 gas was not possible, at least not in a reasonable time period. These findings therefore indicate kinetic limitations for the temporary pH adjustment in the range of 10 – 13.

3.6.4 pH Studies of $NaHCO_3$ and Na_2CO_3 Solutions Bubbled with N_2 Gas

The previous experimental results and studies confirm that carbon dioxide gas reacts with water slowly enough to be observed using a pH meter. When a solution of sodium hydroxide is saturated with CO_2 , sodium hydrogen carbonate ($NaHCO_3$) is formed:

The solution of NaHCO_3 , i.e. of sodium bicarbonate or baking soda, is weakly alkaline. This set of experimental studies was carried out in order to determine whether the reverse of the reaction (equation 3.6) is valid (i.e. if NaOH solution could be formed from NaHCO_3 solution). Solutions of various molarities (10^{-4} , 10^{-3} , 10^{-2} M) of sodium bicarbonate were prepared and the pH of each solution recorded. Each solution was then placed in the sample holder (Figure (3.2)) and bubbled with N_2 gas. The changes of the pH were recorded as a function of time and the results are presented in Figure (3.7). The final pH values should be 10.0, 11.0 and 12.0, respectively upon the removal of all of the CO_2 from the solution.

Figure (3.7): pH changes of the NaHCO_3 solution when bubbled with N_2 gases at a pressure of 1.2 atm and 298 K (25 ± 2 °C).

Upon the removal of the CO_2 from equation (3.6) with bubbling N_2 , one is essentially first forming a solution of sodium carbonate Na_2CO_3 . If this solution is further bubbled with N_2 gas, the removal of more CO_2 will result in the formation of NaOH . As a result, solutions of Na_2CO_3 with different molarities (10^{-4} , 10^{-3} , 10^{-2} M) were prepared and the original pH recorded. The solutions were then bubbled with N_2 gas and the changes in the pH were noted. The experimental findings are presented in Figure (3.8). If all the CO_2 were removed from the solution, the 10^{-4} M solution of Na_2CO_3 should have a pH of 10.3, 10^{-3} M a pH of 11.3, and the 10^{-2} M a pH of 12.3.

Figure (3.8): pH changes of the Na_2CO_3 solution when bubbled with N_2 gases at a pressure of 1.2 atm and 298 K (25 ± 2 °C).

Sodium carbonate is industrially called soda ash and the solutions of this compound are strongly basic due to extensive hydrolysis of the carbonate ions by the following chemical equation:

The experimental results indicate that at lower molarities the pH can be changed using N₂ gas. As the concentration of Na₂CO₃ in the solution increases, the rate of pH changes decreases until there is no change observed (eg. 10⁻²M solution). At higher concentrations the solution is more basic and the reversibility process becomes more difficult. This is due to a decrease in the rate of formation of H₂CO₃ when sparging with N₂ gas, since the concentrations of H⁺ in the solution are very low.

3.6.5 Effect of Temperature on Temporary pH Adjustment Using Gases such as CO₂ and N₂

It is known that the solubility of gases in solutions is affected by temperature. As temperature increases, the solubility of gases in solution decreases. The dissolution of CO₂ gas in water is a relatively rapid process and the lowering of the equilibrium pH is reached in no more than few minutes (less than 2 minutes for 100 ± 1 mL sample). However, the degassing (removal of CO₂ from solution) is found to be a slow process. Studies on the rates of lowering of pH using CO₂ gas and the subsequent increasing of pH using N₂ gas has been carried out at various temperatures in order to observe the temperature dependence.

Figure (3.9a) represents the experimental results for the sample of distilled water when bubbled with CO₂ gas at five different temperatures. During these studies the pressure of the gas was kept constant at 1.2 atm.

Figure (3.9): pH reversibility studies on a 100 ± 1 mL of distilled water at different temperatures using CO₂ or N₂ gas.

Results indicate that the pH of water was changed from 7 to 3.9 in less than 2 minutes. As the temperature increases, there is a decrease in the rate at which the pH decreases or H^+ ion concentration increases. The reaction that takes place in the reaction vessel of Figure (3.2) is as follows:

As seen in Figure (3.9a), for the first 0.025 minutes the reaction of CO_2 with water is not instantaneous, as expected. This could be explained by the fact that there are three gas cycles used for adjusting the pH of the solution. As mentioned, the first gas cycle in these studies was bubbling the solution with N_2 gas in order to have a solution that is free of any carbonated species. As a result, when the solution is bubbled with the second gas cycle (CO_2 gas), there is a lag time at the beginning which is the time required for the vessel to be cleared of the N_2 gas used in the previous cycle and the gas bubbles contain only CO_2 .

It is well known that gases are more soluble in liquids at lower temperatures. This phenomenon is also observed when CO_2 gas is bubbled in water. At lower temperatures the rate of pH change is faster than at higher temperatures, and the final pH which is approached is lower.

In the case where N_2 gas is used to raise the pH of the solution, results are represented by Figure (3.9b). In this step the original pH of the solution is reached in 40 minutes (pH change from 3.9 to 7). As the temperature increases the rate of rise of the

pH also increases. The reactions taking place in the reaction vessel of Figure (3.2) are as follows:

As the CO₂ gas is removed from the vessel, H⁺ and HCO₃⁻ ions are recombined giving H₂CO₃ and finally CO₂ in the aqueous form. The rate of this reaction increases with temperature. The rate of pH change is thus greater at higher temperatures, in contrast to the case when the CO₂ is bubbled.

The data shown in Figure (3.9a and 3.9b) describing the rate of pH changes with respect to temperature will be further analyzed in terms of fundamental mechanisms which occur in these systems (Chapter 4).

3.6.6 Temporary pH Adjustment of Solutions Using Gases Such as SO₂ and NH₃

Studies on the use of CO₂ and N₂ gases for the purpose of pH adjustment has been briefly compared with studies using other gases. In this investigation the experimental conditions were kept the same, including the three cycles of gas bubbling. The only conditions that are different is the gases used to adjust the pH of the solutions.

SO₂ Case. A sample of distilled water (100 ± 1 mL) was placed in the reaction vessel (Figure (3.2)). In the first cycle of gas bubbling, the pH of water was raised from 5.6 to 7 by bubbling with N₂ gas to clear the solution from the carbonated species. In the second cycle, the SO₂ gas was bubbled to lower the pH of the sample from 7 to 1.8 in a total time of 0.12 minutes. In the third and final cycle the solution was once again

bubbled with N_2 gas, the pH of the solution increased only to 2.2 in 80 minutes. The results of this experiment are summarized in Figure B.1 (Appendix B).

As expected, with the use of SO_2 gas the pH of the solution decreases due to the formation of H_2SO_3 . However, the reverse process, removal of this gas from the solution by sparging with N_2 gas was extremely slow. This could be explained by the Henry's law constant presented for each gas in Table (3.2).

Table (3.2): Henry's law constants for various gases
(Stumm and Morgan, 1996 [3])

Reaction	Product	$K_H (M atm^{-1})$
$CO_2 (g) + H_2O \rightleftharpoons$	$H_2CO_3 (aq)$	3.39×10^{-2}
$N_2 (g) \rightleftharpoons$	$N_2 (aq)$	6.61×10^{-4}
$SO_2 (g) + H_2O \rightleftharpoons$	$SO_2 \cdot H_2O (aq)$	1.25
$NH_3 (g) \rightleftharpoons$	$NH_3 (aq)$	57

By comparing the Henry's law constants, one can see that CO_2 is 50 times more soluble than N_2 , but it has a much lower solubility than SO_2 . The degassing of a solution having dissolved CO_2 would therefore be easier than one with dissolved SO_2 .

NH_3 Case. A sample of distilled water (100 ± 1 mL) was placed in the reaction vessel of Figure (3.2). The first cycle of bubbling with N_2 gas was carried out and the pH

was raised to 7. The solution was then bubbled with NH_3 (second gas cycle) and the pH of the solution increased from 7 to 11.25 in 0.2 minutes. The third gas cycle of bubbling with N_2 gas resulted in a further increase in the pH of the solution to 11.35 after 200 minutes. The experimental results for this case are presented in Figure (B.1) of Appendix B.

As expected, when a solution is bubbled with NH_3 gas, the pH increases due to the formation of NH_4^+ and OH^- ions. The largest value of K_H belongs to NH_3 gas; hence the very rapid change in pH. The process of degassing would be expected to be very slow, but a decrease in the pH of the solution from 11.2 to the original value of 7 would be expected to occur eventually when N_2 gas is bubbled into the solution. The experimental results are however the opposite of this; the explanation for this is unknown at this time.

One possible explanation may be that some of the NH_3 is present in the water in the form of hydrates. The gas from these hydrates maybe released by the N_2 sparging, resulting in an increase in the pH (formation of more OH^-). A similar effect can be seen in the case of SO_2 (Figure (B.1), Appendix B). In the third cycle (N_2 sparging), the pH initially drops (H^+ increases); before starting to increase towards the value of 7, as expected.

3.7 Conclusions

Simple experimental studies using CO_2 gas and compressed air for the purpose of temporary pH adjustment of the supplied industrial water were carried out. The results indicate that CO_2 gas can be used successfully to lower the pH of industrial process water. This gas can replace the use of highly corrosive acids such as H_2SO_4 . However, in the cases where a temporary pH adjustment was required, there were serious limitations to the use of compressed air to remove carbon dioxide from the solution and hence to raise the pH.

The effect of dyes on the process of temporary pH adjustment was also examined. Fresh wiping solutions without any dissolved dyes or printing inks prepared and tested for the temporary pH adjustment using CO_2 gas and compressed air. It was found that the dyes did not affect the pH reversibility process. Since compressed air contains a small concentration of CO_2 gas, it was thought that this could have affected the reversibility process.

As a result model solutions were prepared and the temporary pH variation studies were carried out using CO_2 and N_2 gas. Results indicate the temporary pH adjustment using these gases is possible, but only in a reasonable time only for solutions with a pH lower than 8. This type of pH adjustment is possible for solutions with pH 9; however, the degassing process is very slow. For solutions above pH 9, there is a serious kinetic limitation for the degassing process. It may be possible to increase the rate of degassing of CO_2 . The options for this were however not tested out in this project.

Studies on the effect of temperature on solution degassing indicated that this rate increased with an increase in the solution temperature. As expected, gases are less soluble in aqueous solutions at higher temperatures, and there is an increase in the rate of CO₂ removal from the solution. On the other hand, gases are more soluble in solutions at lower temperatures; therefore, lowering the pH of solutions is faster at lower temperatures.

Finally, the use of CO₂ gas for pH adjustment seems to be preferable to the use of other gases such as SO₂ or NH₃. The variation of the pH of the solution with these gases is more rapid due to their higher solubilities in aqueous solutions. They are however toxic, and their pH effects are difficult to reverse. The CO₂ is not only environmentally friendly but also readily available and economically feasible.

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Chapter 4

4. Gas-Liquid Kinetics and Mass Transfer Studies

Gas transfer processes are operative in a number of water and wastewater systems. Gas-liquid reactions are used widely in industry for various purposes such as removal of unwanted components; in our case these reactions will be used for temporary or permanent pH adjustments (Thomas and Chua, 1988 [1], References on page 108). The reaction of a gas with a liquid is dependent on several factors, namely the solubility of the gas in the liquid, the contacting scheme and the mass transfer of the gas in the liquid phase (Levenspiel, 1976 [2]).

The hydration reaction of CO_2 is dependent on diffusion as the gas transfer to the liquid phase must take place before a reaction occurs. The degree of solubility of a gas in water is also a critical determinant of the rate of transfer of that gas from vapour phase to solution phase.

4.1 Gas-Liquid Solution Equilibrium

When a gas is dissolved in water, the process is generally treated as approximating a mass transfer over four distinctive steps (Treybal, 1980 [3]). Figure (4.1) is a representation of these steps.

Figure (4.1): Four steps of gas transfer from vapour phase to solution phase (Treybal, 1980 [3]).

The first step is the passage of the gas to the gas-liquid interface. In the second step of the transfer, the gas will pass through a “gas film” on the vapour side of the interface. The third step of the transfer is through the “liquid film” on the liquid side of the interface. Finally the gas gets dispersed throughout the bulk of the liquid.

Each transfer step involves a finite increment of time. However, in some cases one step may take more time relative to the others; consideration of the rate of the remaining

steps will thus not be significant to the overall process. The step taking the longest time under a given set of conditions is termed as the “rate-limiting step”, and the overall gas transfer calculation may be based on this step alone.

Very rarely is the passage of a gas to the gas liquid interface (I) rate-limiting. Under perfectly stagnant conditions, diffusion of a gas throughout the bulk of a solution (IV) is the slowest step. Under these conditions molecular diffusion expressions may be used to predict the rate of transfer of gas into the liquid.

If the solution is sufficiently agitated by natural turbulence or by induced mechanical mixing, bulk solution diffusion ceases to be rate limiting and the rate of transfer through the gas-liquid interface (II and III) becomes the controlling factor. In this case the solubility of the particular gas in the solution phase will determine which of the two interfacial “films” limits the rate of transfer across the interface.

The respective solubility of these gases in water as described in equation (3.5) of Chapter 3 is defined in terms of Henry’s law. At equilibrium, the concentration of a dissolved gas in a liquid is directly proportional to the partial pressure of that gas in the vapour phase with which that solution is in contact. Rates of dissolution of gases of high solubility in water, such as ammonia, are controlled by the rate of transfer across the gas film (II) due to the large K_H values. In this case, the rate can be increased by stirring the gas phase so as to reduce the thickness of the “gas film”.

The transfer of gases with low solubility such as oxygen (O_2), nitrogen (N_2), and carbon dioxide is usually controlled by the rate of transfer on the liquid side of the interface (III) since these systems have a small K_H . The transfer of gases with

intermediate solubility in water, such as hydrogen sulfide (H_2S), will be controlled by a combination of gas and liquid interfacial resistance. In such cases the agitation and mixing of the system is necessary to promote more rapid gas transfer.

The degree of solubility of a particular gas in water is a significant determinant of the rate of transfer of that particular gas from vapour phase to solution phase. Solubility is a function of the partial pressure of the particular gas in the atmosphere with which the water is in contact. The solubility of a gas in water is adversely affected by increasing temperature and by increasing concentrations of ionic solutes.

4.1.1 Gas Transfer from a Bubble to a Solution

When the bulk of the solution in which the gas is being dissolved is agitated, the rate-limiting step for the overall transfer process will likely be the passage of the gas through the gas-liquid interface. Passage of the gas through the liquid side of the two-layer interface will limit the rate of transfer of gases, as the transfer of the gas is through the gas film at the interface is rapid as compared to transfer through the liquid film. The overall process can then be expressed in terms of the diffusion of the gas across the liquid film only (III); the equation for this type of mass transfer can be expressed as:

$$N_x = k_L \Delta C \quad (4.1)$$

Where, N_x is the flux of the gas in the x direction, k_L is the overall mass transfer coefficient, and ΔC is the concentration difference between the gas-liquid concentration at the liquid surface and the average concentration within the bulk liquid phase (Treybal,

1980 [3]). The mass transfer occurs in the direction of decreasing concentration. Since the liquid film is the controlling resistance to mass transfer in this case, the coefficient k_L is referred to as “film coefficient “.

The film theory is based on the concept that the entire resistance to diffusion of a gas through the liquid surface to the bulk liquid phase is comprised of a hypothetical film. The thickness of this hypothetical film is δ . Figure (4.2) represents the transfer of a gas from a bubble to a solution phase.

Figure (4.2): Transfer of a gas from a bubble to the solution phase ((Levenspiel, 1976 [2])

Thus δ represents the thickness of the stagnant layer offering resistance to molecular diffusion. As described in Chapter 3, once diffused into the bulk of the liquid, CO_2 gas will chemically react with water to produce carbonic acid, which results in the lowering of the pH of the solution. In the next sections these reactions are described in more detail. Some kinetic data available in the literature for these systems are also presented.

4.2 Equilibrium Constants for Carbonated Systems

As represented in section 3.1, upon bubbling an aqueous solution with CO₂ gas, there will be reactions which are represented by equation (3.1) to (3.4). The hydration equilibrium of CO₂ can be represented with the dissociation constants for the carbonic acid in the reaction given by equation (3.2). This dissociation constant is usually referred to as the "real first dissociation constant, K_r " (Stumm and Morgan, 1996 [4]),

$$K_r = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \quad (4.2)$$

where,

$$K_r = 1.72 \times 10^{-4} \text{ at } 298 \text{ K } (25 \pm 2 \text{ } ^\circ\text{C}).$$

The square brackets refer strictly to activities; however, in dilute solutions or rough calculations, they can be taken as concentrations, i.e. mol/L.

The second dissociation constant is for the equilibrium reaction given by equation (3.3). The constant K_2 is for the dissociation of HCO₃⁻ and is given by the following equation,

$$K_2 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} \quad (4.3)$$

The values of these first and second dissociation constants are temperature dependent. Stumm and Morgan, 1996 [4], have provided a table which summarizes the

equilibrium constants for carbonated systems. Table (4.1) provides values for the equilibrium constants for dissolution of carbon dioxide and subsequent dissociations at different temperatures.

Table (4.1): Equilibrium constants for carbonated systems
(Stumm and Morgan, 1996 [4]).

<i>Reaction</i>	<i>-log K</i>						
	<i>5°C</i>	<i>10°C</i>	<i>15°C</i>	<i>20°C</i>	<i>25°C</i>	<i>40°C</i>	<i>100°C</i>
$CO_2(g) + H_2O \rightleftharpoons H_2CO_3^*$	1.20	1.27	1.34	1.41	1.47	1.64	1.99
$H_2CO_3^* \rightleftharpoons H^+ + HCO_3^-$	6.52	6.46	6.42	6.38	6.35	6.35	6.45
$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	10.56	10.49	10.43	10.38	10.33	10.22	10.16
$H_2O \rightleftharpoons H^+ + OH^-$	14.73	14.53	14.34	14.16	14.0	13.53	11.27

The $H_2CO_3^*$ notation is used because of the difficulty of specifically measuring the species H_2CO_3 . The apparent first dissociation constant for this equilibrium system is thus traditionally written as the sum of the concentrations of molecularly dissolved CO_2 and H_2CO_3 . Only a small fraction of CO_2 dissolved in water is actually in the form of H_2CO_3 , most is present as dissolved molecular CO_2 ($CO_2(aq)$) (Loewenthal and Marais, 1976 [5]).

In this study we let $[H_2CO_3^*]$ represent the sum of $[H_2CO_3]$ and the $[CO_2(aq)]$; equation (4.2) will then become;

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]} \quad (4.4)$$

$$K_1 = \frac{[H^+][HCO_3^-]}{([CO_2(aq)] + [H_2CO_3])} \quad (4.5)$$

The literature value for K_1 from Table (4.1) is given to be 4.45×10^{-7} at 298 K ($25 \pm 2^\circ\text{C}$). Therefore, from the given information it is possible to determine the fraction of $H_2CO_3^*$ existing as H_2CO_3 . Dividing equation (4.5) by (4.2) yields:

$$\frac{[H_2CO_3^*]}{[H_2CO_3]} = \frac{K_1}{K_r} = \frac{4.45 \times 10^{-7}}{1.72 \times 10^{-4}} = 0.0026$$

at 298 K ($25 \pm 2^\circ\text{C}$)

Then at 25°C only 0.26% of $H_2CO_3^*$ exists as H_2CO_3 and 99.4% as $CO_2(aq)$. The same kind of calculation may be used to determine the concentrations of H_2CO_3 and CO_2 at different temperatures

The equilibrium between gas phase and liquid phase is interrelated through Henry's law constant and is best represented by the following equation:

$$[H_2CO_3^*] \approx [CO_2(aq)] = K_H P_{CO_2} \quad (4.6)$$

Here K_H is the Henry's law constant; the values at different temperatures are given in the first line of Table (4.1).

4.3 Kinetics of Hydration of Carbon Dioxide

The kinetics of hydration of CO_2 (aq) has been under study for some time. However, there are surprisingly a few studies in this area considering its importance in nature and human health. Early studies started with Kern in 1960 [6], who reported the rate constants for the hydration reaction. In his study, Kern reports that the hydration reaction occurs in two pathways. At $\text{pH} < 8$ the predominant mechanism is via direct hydration:

This reaction is reported to be of first order with k_{CO_2} as the forward rate constant, and the corresponding rate law is formulated as follows:

$$\frac{-d[\text{CO}_2(\text{aq})]}{dt} = k_{\text{CO}_2}[\text{CO}_2(\text{aq})] \quad (4.7)$$

At $\text{pH} > 10$ the reaction is believed to be predominately through direct reaction of CO_2 with OH^- given by:

The corresponding rate law for equation (4.8) has been given as follows, where k_{OH} is the rate constant for the forward reaction:

$$\frac{-d[CO_2(aq)]}{dt} = k_{OH} [CO_2(aq)] [OH^-] \quad (4.9)$$

For studies where the pH is between 8 and 10, both mechanisms must be taken into account. Rate constants for the reverse reactions, corresponding to the release of CO_2 to the atmosphere, have also been provided by Kern [6].

Table (4.2) is a representation of these values and the corresponding reactions. All reported values are for a temperature of 293-298 K ($20-25 \pm 2$ °C). Both reactions (pH <8 and pH >10) in the above table require rearrangement of covalent bonds, and it is therefore not surprising that these reactions proceed with such moderate rates at room temperature (Jönsson *et al.*, 1977 [7]). The ionization into HCO_3^- and CO_3^{2-} are rapid processes as they only involve breaking of a bond.

The dehydration reactions were also considered. The reactions and the corresponding rate constants for these systems are presented in Table (4.3).

A thorough literature search has provided several reports on the formation of H_2CO_3 . However, there has never been experimental evidence of existence of this compound. In 1981, Abbott *et al.*, 1981 [8] conducted a ^{13}C nuclear magnetic resonance and Raman investigations of aqueous carbon dioxide. In this study, at different pH values the chemical shifts for species CO_2 (g), CO_2 (aq), HCO_3^- (aq), and CO_3^{2-} (aq) were determined.

Table (4.2): Rate constant for hydration and dehydration reactions of CO₂
(Kern, 1960 [6])

Reaction	Temperature	Rate Constant
pH < 8	293-298 K	
$CO_2(aq) + H_2O \xrightarrow{k_{CO_2}} H_2CO_3$ $H_2CO_3 \rightarrow HCO_3^- + H^+$		$k_{CO_2} = 0.03 \text{ s}^{-1}$ <i>(instantaneous)</i>
pH > 10	293-298 K	
$CO_2(aq) + OH^- \xrightarrow{k_{OH}} HCO_3^-$ $HCO_3^- \rightarrow H^+ + CO_3^{2-}$		$k_{OH} = 8500 \text{ s}^{-1} \text{ mol}^{-1} \text{ L}$ <i>(instantaneous)</i>

Table (4.3): Rate constants for the dehydration reactions of carbonated systems
(Kern, 1960 [6] and Patel *et al.*, 1973 [9]).

Reaction	Temperature	Rate Constant
pH < 8	293-298 K	
$H_2CO_3 \xrightarrow{k_{H_2CO_3}} CO_2(aq) + H_2O$		$k_{H_2CO_3} = 20 \text{ s}^{-1}$
	286 K	$k_{H_2CO_3} = 10 \text{ s}^{-1}$
	313 K	$k_{H_2CO_3} = 70.4 \text{ s}^{-1}$
pH > 10	293-298 K	
$HCO_3^- \xrightarrow{k_{HCO_3^-}} CO_2(aq) + OH^-$		$k_{OH} = 2 \times 10^{-4} \text{ s}^{-1}$

Investigations using this method indicated no direct evidence of H_2CO_3 species. It was concluded that if H_2CO_3 was present as an equilibrium species, it was present in small quantities relative to the CO_2 (aq).

Stumm and Morgan (1996) [4] have reported the activation energies for the overall hydration and dehydration reactions. The forward reaction (hydration of CO_2) given by equation (3.1) is believed to be a first order reaction with an activation energy of 63 kJ/mol. The activation energy for the backward reaction (dehydration) is reported to be 67 kJ/mol. The proportion of H_2CO_3^* which is H_2CO_3 therefore varies very little with temperature from 0.3 %. At equilibrium, the net velocity of the reaction in both directions has been reported to be $2.4 \times 10^{-4} \text{ mol m}^{-3}\text{s}^{-1}$. There is no data on the activation energies of the ionization of H_2CO_3 into H^+ , HCO_3^- and CO_3^{2-} ions.

4.4 Literature Review on CO_2 - Water Systems

The reaction of CO_2 with water has been under investigation for some time. These studies provide further information on the kinetics and mass transfer of this system.

The hydration reaction and transfer of carbon dioxide across air/water interface indicates that this process depends on many factors (House and Howard, 1984 [10]). The factors considered important for determining the transport rate were solution composition, temperature, pH, solution flow rate and the gas-phase composition. The gas transfer velocities were predicted using a numerical model which solved second-order-nonlinear differential equations with the appropriate boundary conditions. The model made use of the collected data on changes of the pH with respect to time as the

gas came into contact with water. This investigation concentrated particularly on the transfer of CO₂ from the gas phase to bicarbonate solutions.

The kinetic study on the dissolution of CO₂ into water from the surface of CO₂ hydrate at high pressures was conducted by Shindo *et al.*, 1995 [11] and a mechanism of the decay of CO₂ hydrate was proposed. This model was applied to experimental data, which showed that the radius of liquid CO₂ droplets in water reduced linearly with time. It has been shown that the dissolution rate of CO₂ into water is dominated by the decay of CO₂ hydrate on the surface of the droplet. The CO₂ hydrate is formed at the interface between the seawater and liquid CO₂, and this hydrate membrane controls the CO₂ dissolution into the seawater. It has also been reported that the diffusion of the water molecules through the CO₂ hydrate is very slow because of the crystalline state of the hydrate, and the diffusion rate is inversely proportional to the thickness of the hydrate.

The CO₂ hydrate on the outside surface of the membrane slowly dissolves into water, which means a decay of the hydrate membrane. The decay of this hydrate membrane promotes the diffusion of water molecules through the hydrate membrane. Upon this diffusion process, water immediately reacts with CO₂ to form a new hydrate at the inside surface of the membrane. At this point the new CO₂ hydrate formed at the inside surface of the old hydrate controls the diffusion of the water molecules. Thus the diameter of the liquid CO₂ droplet gradually decreases. The rate constant of the decay of CO₂ hydrate was estimated to be $1.25 \times 10^{-6} \text{ m s}^{-1}$; however, no information on the effect of pH on this rate constant has been reported.

Dissolved CO_2 is an important component in the chemistry of fresh waters. A method of measuring free CO_2 in upland stream-water using headspace analyses was therefore developed by Hope et al, 1995 [12]. A closed vessel was used for the experimental study, which has been reported to minimize the loss of free CO_2 in solution prior to measurement. The headspace technique provided analysis of free CO_2 in low-ionic strength, organic-rich stream-water. In this study, a sample of the stream-water was collected in a sealed flask; a headspace was then created by pumping out known volume of sample and replacing it with CO_2 scrubbed air. After equilibration of CO_2 between the remaining water and headspace, the concentration of CO_2 in the headspace was measured using an Infra Red Gas Analyser. The concentration of free CO_2 in the original sample was then calculated using Henry's law. There were no reports on kinetic and mass transfer studies using this experimental technique.

In a study in 1995 by Dudley [13], a comparison of the correlation for mass transfer from bubbles into solutions was performed, and suggestions were made for using specific correlations for specific cases. Most of these correlations require the calculation of the gas bubble diameter. These studies were further tested for solutions with surfactants, and it was found that the detergents would depress the mass transfer coefficients. However, no method to correlate the surfactant concentration to the expected decrease was found. In this particular case, all studies were for bubbling oxygen in aqueous solutions with particular applications for wastewater aeration systems.

4.5 Research Objectives

Upon a thorough examination of the literature on the CO₂-water systems it has been noted that some work on the kinetics of this systems has been performed. Some studies have even determined and reported values for the rate constant of these systems. However, to date there has been no study reporting rate constants for the reaction;

The only values available for this system are the equilibrium constants (Henry's law constants) at different temperatures.

Reaction of CO₂ gas with water is described by equation (3.1) to (3.3) of section 3.1 (chapter 3). The concentration of the carbonated species at certain pH ranges becomes important and is best described in the following manner;

In the study of using gases (CO₂ and N₂) for the purpose of temporary pH adjustment (Chapter 3) it was found that this process is kinetically limited for solutions having a pH over 10. However, this process was reversible for solutions with a pH lower than 8.

As a result, further reversibility studies were carried out as described in chapter 3 for cases with pH below 8. A mathematical model was developed using the information available in literature in order to predict the range of pH changes in aqueous solutions as

a function of temperature, and time. This mathematical model will aid in numerically determining the concentrations of the carbonated species in the aqueous solution. It can also predict the rate constants for the forward and reverse reactions of CO_2 dissolution in water ($\text{CO}_2 (\text{g}) \rightleftharpoons \text{CO}_2 (\text{aq})$) at various temperatures.

The numerically determined concentrations of $[\text{H}^+]$ were then compared to those found experimentally at different temperatures (section 3.6.5) and the rate constants were compared to those found using the mass transfer calculation for CO_2 transfer in an aqueous solution. The developed mathematical model is a valuable tool for industries that wish to use temporary pH adjustment. This model will aid them in determining the experimental conditions, the amount of gas, and the total time required to obtain the desired pH.

The determined rate constants will also aid in the finding of activation energy for the forward and reverse reaction $\text{CO}_2 (\text{g}) \rightleftharpoons \text{CO}_2 (\text{aq})$. This has not been found in the literature.

4.6 Determination of Rate of CO₂ (g) Dissolution

4.6.1 Mathematical Model

The reaction of CO₂ gas with water can occur by two paths that are highly dependent on the pH of the solution. These pathways are represented by reactions (3.1)-(3.4) (see also section 4.3). In our study, only reaction (3.1) - (3.3) will be considered (for pH values below 8.3):

The rate constants k_d and k_{-d} for dissolution of CO₂ (g) into water are dependent on several aspects, as discussed in section 4.1. Their ratio (k_d/k_{-d}) is however related to the Henry's law constant (equation 4.6 and Table (4.1)). The term $[\text{H}_2\text{CO}_3^*]$ in the Henry's law constant is also the sum of the carbonated species $[\text{CO}_2(\text{aq})]$ and $[\text{H}_2\text{CO}_3]$. After proper corrections for this term are made, k_d and k_{-d} are related by equation (4.11):

$$K_H = \frac{k_d}{k_{-d}} \left[1 + \frac{k_h}{k_{-h}} \right] \quad (4.11)$$

Literature studies report values for the hydration and dehydration rate constants k_h and k_{-h} at various temperatures using the activation energies reported by Stumm and Morgan, 1996 [4]. The activation energy for the forward reaction (k_h) is approximately 63

kJ/mole at 298 K (25 °C). Similarly the activation energy for the dehydration process (k_h) is reported to be 67 kJ/mole at 298 K (25 °C).

The formation of H_2CO_3 is followed by ionization into H^+ and HCO_3^- ions. The forward and reverse rate constants for these are k_f and k_{-f} . The recombination is thought to be a very rapid process and reported to be close to diffusion controlled (Jönsson *et al.*, 1977 and Goldman and Dennett, 1983 [7][14]). Hence, the rate constant k_{-f} can be calculated assuming diffusion controlled rate theory as described by equation (4.12a) (Green *et al.*, 1976 and Levine, 1988 [15][16]).

$$k_{-f} = 4\pi N_A (D_{H^+}^0 + D_{HCO_3^-}^0) (r_{H^+} + r_{HCO_3^-}) \left(\frac{w}{e^w - 1} \right) \quad (4.12a)$$

Where w is;

$$w = \frac{z_{H^+} z_{HCO_3^-} e^2}{4\pi\epsilon_0 \epsilon k' T (r_{H^+} + r_{HCO_3^-})} \quad (4.12b)$$

The determination of this k_{-f} using the above equations require the diffusion coefficients for H^+ and HCO_3^- ions, the charge number of ions (z_i), the dielectric constant (ϵ), the permittivity of vacuum (ϵ_0), Boltzman constant, and the radii of the ions. These can be obtained from the electrical conductivity data (Robinson and Stokes, 1970, and House and Howard, 1984 [17] [10]). The rate constant k_f is then determined using the values for the first acid dissociation constant K_1 , keeping in mind that the concentration of the $[H_2CO_3^*]$ in the first acid dissociation constant is the sum of $[CO_2(aq)]$ and $[H_2CO_3]$ species (see equation (4.5)). Proper corrections in the relationship of K_1 must

be made; the rate constant k_l is thus determined through equation (4.13), which is as follows:

$$k_l = K_1 k_{-1} \left[\frac{k_{-h}}{k_h} + 1 \right] \quad (4.13)$$

Stumm and Morgan (1996) [4] provides values for both the first acid dissociation constant K_1 , and the Henry's law constant K_H at different temperatures. Hence, Table (4.4) is a representation of the activation energies for the forward and reverse reactions using the available rate constants and Arrhenius or van't Hoff plots (Figure 4.3).

Table (4.4): Magnitude and temperature dependence of equilibrium and rate constants for the forward and reverse reactions in carbonated systems using $B = Ae^{-E_a/RT}$

B (Units)	A (298 K values)	ΔH or E_a (kJ/mol)	Reference
k_h (s^{-1})	3.22×10^9	62.8	Stumm and Morgan, (1996) [4]
k_{-h} (s^{-1})	8.03×10^{12}	66.9	"
$D_H^{\circ+}$ ($m^2 s^{-1}$)	2.33×10^{-6}	13.6	Robinson and Stokes, (1970) [17]
$D_{HCO_3^-}^{\circ}$ ($m^2 s^{-1}$)	5.03×10^{-6}	18.9	"
K_1 ($mol L^{-1}$)	2.63×10^{-6}	4.5	Stumm and Morgan, (1996) [4]
K_H ($mol L^{-1} Pa^{-1}$)	7.05×10^{-6}	-21.0	Stumm and Morgan, (1996) [4]
k_l ($L mol^{-1} s^{-1}$)	2.39×10^{13}	14.2	Levine, (1988) [16]

Figure (4.3): Arrhenius and van't Hoff equilibrium constant plots for available rate constants.

This information (Table (4.4)) can then be used to get the rate constants for the differential rate equations found from reaction (4.10). The rate of change of $\text{CO}_2(\text{aq})$, H_2CO_3 , H^+ and HCO_3^- are thus given by equations (4.14)-(4.16).

$$\frac{d[\text{CO}_2(\text{aq})]}{dt} = k_d[\text{CO}_2(\text{g})] + k_{-h}[\text{H}_2\text{CO}_3] - (k_h + k_{-d})[\text{CO}_2(\text{aq})] \quad (4.14)$$

$$\frac{d[\text{H}_2\text{CO}_3]}{dt} = k_h[\text{CO}_2(\text{aq})] + k_{-1}[\text{H}^+][\text{HCO}_3^-] - (k_{-h} + k_1)[\text{H}_2\text{CO}_3] \quad (4.15)$$

$$\frac{d[\text{HCO}_3^-]}{dt} = k_1[\text{H}_2\text{CO}_3] - k_{-1}[\text{H}^+][\text{HCO}_3^-] \quad (4.16)$$

Applying the conditions for self-dissociation of water (4.17), the electrical neutrality, equation (4.18) and assuming that the concentration of $[\text{CO}_3^{2-}]$ is zero at $\text{pH} < 8.3$ (Stumm and Morgan, 1996 [4]), the concentration of $[\text{H}^+]$ is found from equation (4.19).

$$K_w = [\text{H}^+][\text{OH}^-] \quad (4.17)$$

$$[\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] \quad (4.18)$$

$$[\text{H}^+] = [\text{HCO}_3^-] + \frac{K_w}{[\text{H}^+]} \quad (4.19)$$

The above differential equations ((4.14) - (4.16)) may be solved numerically (Gerald and Wheatley, 1989 [18]) resulting in $[\text{H}^+]$ as a function of time with an initial guess for k_d . Appendix C provides the computer program developed to predict the rate constants as well as the concentrations of the species $\text{CO}_2(\text{aq})$, H_2CO_3 , H^+ and HCO_3^- . The

numerically obtained H^+ ion concentrations can then be compared to those obtained experimentally. These results are provided in the next section.

4.6.2 Results and Discussion

The experimental data obtained for pH changes of solutions at various temperatures (Figure (3.9)) were used as a comparison with the concentrations obtained numerically from the developed program (Appendix C).

The program was able to predict the concentrations of the carbonated species using an initial guess for the rate constant k_d . The rate constant k_d was then determined using equation (4.13). Table (4.5) represents the values determined for the rate and equilibrium constants at various temperatures from data available in the literature (see Table (4.4) summary). The temperatures are those for which experimental data had been obtained (Figure (3.9)).

As it can be seen in Figure (3.9) of Chapter 3, all curves obtained for both cases (bubbling with CO_2 and N_2 gases) have an initial delay. For the CO_2 case, this initial delay lasts for the first 0.25 seconds and for N_2 case the first 5 minutes. This could be explained by the fact there were three gas cycles used for the temporary pH adjustment.

The first cycle, as explained earlier was to bubble the solution with N_2 gas in order to have a solution free of any dissolved carbonates and therefore having a starting pH of 7. As a result, in the second cycle when the CO_2 gas is bubbled in the reaction vessel of Figure (3.2), for the first 0.25 seconds this gas is diluted with the existing N_2 gas from the first cycle in the system and the headspace. Hence this contributes to a slow change in the pH for the first 0.25 seconds. When all the system is cleared of the N_2 gas, the

reaction proceeds faster; only then it is valid to have assumed condition of $P_{CO_2} = 1.2$ atm.

Table (4.5): Rate and equilibrium constants for the carbonic system at various temperatures.

Constant	Temperature (°K)				
	275 ± 2	286 ± 2	294 ± 2	304 ± 2	314 ± 2
$k_h (s^{-1})$	3.8×10^{-3}	1.1×10^{-2}	2.2×10^{-2}	5.2×10^{-2}	1.1×10^{-1}
$k_{-h} (s^{-1})$	1.6	4.9	10.4	25.6	59.6
$D_{H^+}^0 (m^2/s)^a$	6.0×10^{-9}	7.0×10^{-9}	8.0×10^{-9}	10.0×10^{-9}	12.0×10^{-9}
$D_{HCO_3^-}^0 (m^2/s)^a$	1.0×10^{-9}	1.0×10^{-9}	2.0×10^{-9}	2.0×10^{-9}	3.0×10^{-9}
$K_1 (molL^{-1})$	3.6×10^{-7}	3.9×10^{-7}	4.14×10^{-7}	4.4×10^{-7}	4.7×10^{-7}
$K_H (molL^{-1} Pa^{-1})$	6.8×10^{-7}	4.8×10^{-7}	3.8×10^{-7}	2.9×10^{-7}	2.2×10^{-7}
$k_{-1} (Lmol^{-1} s^{-1})^b$	4.8×10^{10}	6.0×10^{10}	7.1×10^{10}	8.6×10^{10}	10.3×10^{10}
$k_1 (s^{-1})^c$	1.7×10^4	2.4×10^4	2.9×10^4	3.8×10^4	4.8×10^4

^a $D_i^0 = \lambda_i RT/F^2 z_i$ (Robinson and Stokes, 1970 [17])

^b $k_{-1} = 4\pi N_A (D_{H^+}^0 + D_{HCO_3^-}^0) (r_{H^+} + r_{HCO_3^-}) (w/e^w - 1)$ (Levine, 1988 [16])

$$^c K_1 = \frac{k_1}{k_{-1} \left[\frac{k_{-h}}{k_h} + 1 \right]}$$

$$1 \text{ atm} = 101.325 \times 10^3 \text{ Pa}$$

In the third cycle, when the N_2 gas is bubbled to increase the pH from 3.9 to 7, the entire reaction vessel is filled with CO_2 gas. The time delay of 5 minutes before observing any changes in the pH of the solution is thought to be the time required

clearing the headspace from CO₂. The solubility of CO₂ is 50 times that of N₂; hence the longer time needed for eliminating the CO₂. Due to these effects, all of the experimental data for bubbling CO₂ and N₂ were re-zeroed at 0.25 seconds and 5 minutes respectively when comparing to the results obtained from the solutions of the differential equations.

Figure (4.4a) is an example of the predicted changes in the H⁺ ion concentrations with time and of the experimentally determined changes in [H⁺] when the solution was purged with CO₂ gas. The experimental data used for comparison are the ones obtained at 285 K (Figure (3.9)). As it can be seen in Figure (4.4a), the determined concentrations of H⁺ ions are very close to the one obtained experimentally using the predicted k_d values. Figures (4.4b and 4.4c) are the representation of the numerically obtained concentrations of species CO₂ (aq), H₂CO₃, H⁺ and HCO₃⁻.

Figure (4.5a) is the representation of the calculated H⁺ ion concentrations found with experimental ones when the solution was bubbled with N₂ gas. The numerical concentrations of H⁺ were determined using the same k_d and k_{-d} found from the CO₂ case. The only difference in this case is that the term for the pressure of CO₂ gas in equation (4.14) was set equal to zero in the computer program (Appendix C), since the solution is being bubbled with N₂.

The results obtained for the numerically obtained H⁺ ion concentrations as compared to the experimental values for this ion are slightly different. This could be explained by the fact that the assumption that the pressure of CO₂ in equation (4.14) is equal to zero is not entirely correct; some CO₂ enters the bubble right away.

Figure (4.4): A comparison of the numerically obtained data with the experimental data for distilled water at 285 K (12 ± 2 °C) when bubbled with CO_2 gas. (a) Comparison of the numerically obtained H^+ ion concentrations and the experimental values. (b) and (c) numerically obtained concentrations of species $\text{CO}_2(\text{aq})$, and H_2CO_3 , HCO_3^- .

Figure (4.5): A comparison of the numerically obtained data with the experimental data for distilled water at 285 K (12 ± 2 °C) when bubbled with N_2 gas. (a) Comparison of the numerically obtained H^+ ion concentrations and the experimental values. (b) and (c) Numerically obtained concentrations of species $CO_2(aq)$, and H_2CO_3 , HCO_3^- .

Figures (4.5b and 4.5c) are the representation of the numerically obtained concentrations of species $\text{CO}_2(\text{aq})$, H_2CO_3 , H^+ and HCO_3^- when the solution is bubbled with N_2 gas.

The rate constants k_d and k_{-d} for the CO_2 –water system were determined for five different temperatures as provided by Table (4.6). The error on the rate constants for all cases studied (275 – 314) was found to be $\pm 15\%$. This error estimation was obtained by varying the value of the k_d and noting the changes in the fit of the calculated and experimental curves such as Figure (4.4a).

Table (4.6): Determined rate constants for the carbonic system at various Temperatures.

Constant	Temperature (°K)				
	275 ± 2	286 ± 2	294 ± 2	304 ± 2	314 ± 2
K_H ($\text{mol L}^{-1} \text{Pa}^{-1}$)	6.8×10^{-7}	4.8×10^{-7}	3.8×10^{-7}	2.9×10^{-7}	2.2×10^{-7}
k_d ($\text{mol L}^{-1} \text{Pa}^{-1} \text{s}^{-1}$)	6.0×10^{-9}	3.0×10^{-9}	9.6×10^{-10}	9.1×10^{-10}	5.3×10^{-10}
k_{-d} (s^{-1})	3.5×10^{-3}	4.5×10^{-3}	5.5×10^{-3}	6.4×10^{-3}	6.9×10^{-3}
$k'_d = k_d/K_H$ (s^{-1})	8.8×10^{-3}	6.3×10^{-3}	2.5×10^{-3}	3.1×10^{-3}	2.4×10^{-3}

$$k_{-d} = \frac{k_d}{K_H} \left[1 + \frac{k_h}{k_{-h}} \right]$$

Using the obtained rate constants, an Arrhenius plot was prepared and the apparent activation energy for the forward and reverse reaction of $\text{CO}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{aq})$ was determined as represented by Figure (4.6). The activation energy for the forward reaction

was found to be -47 kJ/mol and for the reverse was found to be -27 kJ/mol. In section 4.7, there is a comparison of the obtained rate constants with theoretical values found from mass transfer calculations.

Figure (4.6): Determination of activation energy for the hydration and dehydration reaction of CO_2 (g) $\rightleftharpoons$ CO_2 (aq).

The results of the activation energy can be used to estimate the activation energy for the rate constant k'_d , which can more directly be compared to the over all mass transfer coefficient k_L (equation (4.1)). The rate constant k_d should be proportional to the solubility of CO₂ if the rate limiting step is as described in section 4.1.1. As temperature increases the solubility of the gas in solution decreases resulting in negative activation energy. The activation energy for this rate constant k'_d , can simply be found by subtracting the activation energy found for k_d from the ΔH for Henry's law constant (Table (4.4)). The results give an apparent activation energy (-26 kJ/mol) for the rate constant k'_d .

4.7 CO₂-Water Mass Transfer Calculations

In order to determine whether the numerically obtained rate constants were correct or close to reality, mass transfer calculations were performed for the CO₂-water system. These mass transfer calculations required the calculation of the bubble diameter, the terminal rise velocity and the diffusion coefficient. The calculations were only performed on the case of CO₂ transfer to water (k_d). All of the sample calculations presented in this section are for the CO₂-water system at 285 K (12 ± 2 °C).

4.7.1 Gas Bubble Diameter.

The gas flow rate through the orifice, the orifice diameter, the fluid properties, and the non-laminar motion in the liquid are some of the factors that determine the size of the gas bubbles (Treybal, 1980 [3]). For very slow gas flow rates and for water-like liquids, the diameter of the bubble can be calculated from the following equation:

$$d_b = \left(\frac{6 d_0 \sigma}{g \Delta \rho} \right)^{\frac{1}{3}} = 4.15 \times 10^{-3} (m) \quad (4.20)$$

This equation is obtained by equating the bouyant force on the immersed bubble, which tends to lift the bubble away from the orifice, to the force due to surface tension, which tends to retain it at the orifice. In this equation (4.20) the following terms are:

d_0 = Diameter of the orifice, $1.58 \times 10^{-3} \pm 0.01$ (m) as measured with a micrometer at Science and Technological Center, Carleton University.

σ = Surface tension of water with respect to air (Handbook of Physics and Chemistry, 1972, [19]), 73.93×10^{-3} (N/m)

g = Acceleration due to Gravity, 9.8 (m/s²)

$\Delta \rho = \rho_{H_2O} - \rho_{gas} = 997.23$ (kg/m³)

ρ_{H_2O} , (Handbook of Physics and Chemistry, 1972 [19]), 999.49 (kg/m³)

ρ_{gas} , Calculated from ideal gas law ($PV=nRT$), $P = 1.2$ atm, $T = 285.15$ K and $R = 0.08206$ (L.atm/mol.K), 2.26 (kg/m³)

Using the calculated bubble diameter and assuming that the bubble is spherical in shape, the total area of the bubble was calculated using the following equation;

$$A_b = \pi (d_b)^2 = \pi \times (4.15 \times 10^{-3})^2 = 5.4 \times 10^{-5} (m^2) \quad (4.21)$$

The calculated diameter is consistent the size of observed bubbles. It is obvious that equation (4.20) is for an ideal situation, thus the actual diameter of bubbles may vary considerably from the calculated ones.

4.7.2 Bubble Terminal Velocity or Rising Velocity

Generally the bubble rising velocity varies with bubble diameter. The rising of the bubble occurs when the buoyant force equals the drag force on the bubbles. For bubbles with $d_b < 0.7 \times 10^{-3}$ (m), that are spherical and behave like rigid spheres (Treybal, 1980 [3]), the terminal velocity can be calculated from Stokes' law (equation (4.22)).

$$v_t = \frac{gd_b^2 \Delta \rho}{18\mu_{H_2O}} = 7.57 \quad (m/s) \quad (4.22)$$

Here μ_{H_2O} is the viscosity of the water. The calculation of the Reynolds number (N_{Re}) with the velocity (v_t) is given by equation (4.23);

$$N_{Re} = \frac{d_b v_t \rho_{H_2O}}{\mu_{H_2O}} = 25424 \quad (4.23)$$

Results of this calculation give a value of 25400 for N_{Re} . This indicates non-laminar flow, so that the use of equation (4.22) for calculation of v_t is inappropriate.

It has been reported by Treybal, 1980 [3] that when $1.44 \times 10^{-3} < d_b < 6 \times 10^{-3}$ (m), equation (4.24) can be used to calculate the bubble terminal velocity for liquids of low viscosity. It is noteworthy that the viscosity of the liquid is not involved in this equation (4.24).

$$v_t = \left[\frac{2\sigma}{d_b \rho_{H2O}} + \frac{gd_b}{2} \right] = 2.36 \times 10^{-1} (m/s) \quad (4.24)$$

As a result, due to the high value of the Reynolds number and the calculated diameter of the bubble, equation (4.24) was used for the determination of the terminal velocity of the bubbles at different temperatures. As expected, the terminal velocity for the case of non-laminar conditions (equation (4.24)) is significantly smaller than that calculated from Stokes' law (equation (4.22)).

The Perry's Chemical Engineering Handbook (section 5-63), 1982 [20] provides an alternative method of calculation of bubble terminal velocity. This method of calculation is based on an iterative method using the Reynolds number and the drag coefficient, C . The Reynolds number of 25424 corresponds to a drag coefficient of 0.4 given by the handbook (page 5-64). The terminal bubble rise velocity is then calculated from the equation (4.25),

$$v_t = \left[\frac{4gd_b \Delta \rho}{3\rho_{H2O} C} \right]^{\frac{1}{2}} = 3.67 \times 10^{-1} \frac{m}{s} \quad (4.25)$$

The Reynolds number for the corresponding velocity is then calculated from equation (4.23) and found to be 1234. The drag coefficient for this Reynolds number was found to be 0.46 from Perry's Handbook, page 5.64. The bubble rise velocity was once more calculated from equation (4.25) with the new drag coefficient and found to be 0.35 m/s. This velocity is about 30% greater than the one found from equation (4.24).

The calculated terminal velocities from both Treybal, 1980 [3] and Perry's Handbook, 1982 [20] are independent (to within 5%) of changes in the temperature.

The formation of a bubble at an orifice or capillary immersed in water has been the subject of much study. There are two equations by which the frequency of formation of a bubble can be calculated. Perry's Chemical Engineering Handbook, 1982 [20] suggests that the frequency of bubble formation can be calculated from equation (4.26):

$$f = \frac{Qg\Delta\rho}{\pi d_0 \sigma} \quad (4.26)$$

$$f = 170 \text{ (s}^{-1}\text{)}$$

In this equation, Q is the gas volumetric flow rate as provided by Appendix A. The volumetric flow rate for CO_2 gas was $6.4 \times 10^{-6} \text{ (m}^3\text{/s)}$. The other method of calculation of the frequency of bubble formation is by dividing the gas flow rate by the volume of the bubbles. Assuming that the bubbles are spherical in shape, the volume of a bubble can be calculated knowing its diameter, which is calculated from equation (4.20). Equation (4.27) is a sample of this calculation:

$$f = \frac{Q}{\frac{4}{3}\pi r^3} = 172 \text{ (s}^{-1}\text{)} \quad (4.27)$$

The bubble residence time (t_R) was determined by dividing the height of the solution in the reaction vessel (Figure (3.1)) by the bubble terminal velocity (v_t). The height of

the solution in the vessel was estimated to be 0.041 ± 0.005 (m). The bubble residence time at 285 K was estimated to be 0.173 (s).

Table (4.7): Calculated bubble diameters, bubble terminal velocity, total number of bubbles in solution, and the total area between CO₂ (g) and water at different temperatures.

Temperature (± 2 K)	d_b (m)	v_t (m/s)	Total # of Bubbles	Total Area (m ²)
275	4.18×10^{-3}	2.38×10^{-1}	28.7	1.58×10^{-3}
285	4.15×10^{-3}	2.36×10^{-1}	29.5	1.59×10^{-3}
295	4.13×10^{-3}	2.35×10^{-1}	30.2	1.62×10^{-3}
305	4.10×10^{-3}	2.34×10^{-1}	30.9	1.63×10^{-3}
315	4.07×10^{-3}	2.32×10^{-1}	31.8	1.65×10^{-3}

The total number of bubbles present at any time was found by multiplying the bubble residence time with the frequency of bubble formation. Finally, the total area of the gas-water interface was calculated by multiplying the area of a bubble by the total number of bubbles present. Table (4.7) provides a summary of the calculated bubble diameter, bubble terminal velocity, the total number of bubbles in the 100 mL of solution at any time, and the total area between CO₂ (g) and water at different temperatures. The variation of total area with temperature is surprisingly small. This finding is also supported by the calculation of the total area of the bubble using the bubble rise velocity found from equation (4.25). The total area of the bubble using this velocity for the

temperature of 285 K was found to be $1.1 \times 10^{-3} \text{ (m}^2\text{)}$ a small variation of the total bubble area with temperature was observed in this case as well.

4.7.3 Prediction of Diffusivities in Liquids

The next parameter to calculate was the diffusivities in liquids D_{AB} . The Wilke-Chang correlation (Geankoplis, 1978, [21]) can be used for cases where the solute A is dilute in Solvent B. This correlation is represented by equation (4.28) and is applicable in the temperature range of 275 to 315.

$$D_{AB} = 7.4 \times 10^{-12} (\phi M_{H_2O})^{\frac{1}{2}} \frac{T}{\mu_{H_2O} V_{CO_2}^{0.6}} \quad (4.28)$$

In equation (4.28), M_{H_2O} is the molecular weight of the solvent (18 g/mole), μ_{H_2O} is viscosity of solvent (1.235 cp) at 285 K (Handbook of Physics and Chemistry, 1972 [19]). The term V_{CO_2} is the solute (CO_2) molar volume and ϕ is an association parameter for the solvent water, these are reported by Geankoplis, 1978 [21] to be $34.0 \text{ (cm}^3\text{/mol)}$ and 2.6 respectively. Finally T is temperature in Kelvin (285 K). The calculation of D_{AB} using the given data will result in a value of;

$$D_{AB} = D_{CO_2/H_2O} = 1.41 \times 10^{-9} \text{ (m}^2\text{/s)}$$

4.7.4 Mass Transfer from Gas Bubbles to Liquids

Equation (4.29) has been reported to give values of the mass transfer coefficient (k_L) from the gas bubbles to the liquid phase (Geankoplis, 1978 [21]):

$$k_L = \frac{2D_{AB}}{d_b} + 0.31N_{Sc}^{-2/3} \left(\frac{\Delta\rho\mu_{H_2O}g}{\rho_{H_2O}^2} \right)^{\frac{1}{3}} \quad (4.29)$$

Most of the parameters in the above equation have already been identified and the corresponding values have been reported. The term N_{Sc} is the Schmidt number, which is defined as follows;

$$N_{Sc} = \frac{\mu_{H_2O}}{\rho_{H_2O}D_{AB}} \quad (4.30)$$

Using the available data and the above equations (4.29) and (4.30) the values for the Schmidt number and the mass transfer coefficient have been found to be,

$$N_{Sc} = 876$$

$$k_L = 7.84 \times 10^{-5} \text{ (m/s)}$$

Therefore, using the obtained value for the mass transfer coefficient, the flux of CO_2 can now be determined using equation (4.31) (see equation (4.1)):

$$N_{CO_2} = k_L (C_{A2} - C_{A1}) \quad (4.31)$$

In this equation N_{CO_2} is the flux of CO_2 gas in to water ($\text{mol/m}^2.\text{s}$), k_L is the mass transfer coefficient (m/s), C_{A2} is the solubility of CO_2 in water and C_{A1} is the initial concentration of CO_2 in bulk water (mol/L). The solubility of CO_2 in water was obtained from Table (4.5), and the reported value at 285 K is $4.81 \times 10^{-2} \text{ mol/L}$. The initial concentration of CO_2 in bulk water has been taken as zero. The flux was then calculated and found to be $3.77 \times 10^{-3} (\text{mol/m}^2.\text{s})$.

Table (4.8) reports the mass transfer coefficients (k_L) obtained, the total area between CO₂ (g) and water (from Table (4.7)), the solubility of CO₂ (g) in water from Table (4.5), and the values obtained for k'_d at various temperatures (from Table (4.6)).

Table (4.8): A comparison between the calculated values of A , C_{A2} and k_L with determined k'_d at various temperatures.

Temperature (± 2 K)	Total Area (m ²)	C_{A2} (mol/L)	k_L (m/s)	k'_d (s ⁻¹)
275	1.58×10^{-3}	7.1×10^{-2}	5.6×10^{-5}	8.8×10^{-3}
285	1.59×10^{-3}	4.8×10^{-2}	7.8×10^{-5}	6.3×10^{-3}
295	1.62×10^{-3}	3.6×10^{-2}	1.0×10^{-4}	2.5×10^{-3}
305	1.63×10^{-3}	2.5×10^{-2}	1.3×10^{-4}	3.1×10^{-3}
315	1.65×10^{-3}	1.9×10^{-2}	1.6×10^{-4}	2.4×10^{-3}

The comparison between k_L and k'_d can not be done on an absolute basis, but a relative comparison is meaningful. It is significant to note that the calculated mass transfer coefficient k_L increases slightly with temperature (positive apparent activation energy). However, the experimentally determined rate constant k'_d decreases slightly with temperature (negative apparent activation energy of -26 kJ/mol, section 4.6.2). The temperature variation in both cases is small, but the difference in the trends nevertheless suggest that further modification may be needed in the model (section 4.6.1) and or the mass transfer scheme suggested here.

An absolute comparison between k_d and the flux was performed by changing the units of both parameters to (mol/s). The flux was multiplied by the total area of the bubbles and k_d was multiplied by the volume of the solution (100 ± 1 mL) and the pressure of the CO₂ gas at 1.2 atm (122 kPa). The calculations were as follows:

$$\begin{aligned} k_d &= 3.0 \times 10^{-9} \text{ (mol/L.s.Pa)} & N_{CO_2} &= 3.77 \times 10^{-3} \text{ (mol/m}^2\text{.s)}. \\ k_d &= 3.54 \times 10^{-5} \text{ (mol/s)} & N_{CO_2} &= 6.0 \times 10^{-6} \text{ (mol/s) (Treybal, 1980 [3])} \\ & & N_{CO_2} &= 4.1 \times 10^{-6} \text{ (mol/s) (Perry's, 1982 [20])} \end{aligned}$$

Table (4.9) provides a comparison between the calculated flux (N_{CO_2}) and the numerically obtained k_d .

Table (4.9): Comparison of the calculated value of flux of CO₂ entering water with those obtained experimentally at various temperatures.

Temperature (± 2 K)	N_{CO_2} (mol/s) ($\pm 30\%$) (Treybal, 1980 [3])	N_{CO_2} (mol/s) ($\pm 30\%$) (Perry's, 1982 [20])	k_d (mol/s) ($\pm 15\%$)
275	6.3×10^{-6}	4.4×10^{-6}	7.1×10^{-5}
285	6.0×10^{-6}	4.1×10^{-6}	3.5×10^{-5}
295	5.7×10^{-6}	3.9×10^{-6}	9.7×10^{-6}
305	5.5×10^{-6}	3.7×10^{-6}	9.2×10^{-6}
315	5.2×10^{-6}	3.5×10^{-6}	5.4×10^{-6}

The data obtained by curve fitting the $[H^+]$ vs time curves show reasonable absolute agreement with the data obtained using mass transfer calculations. Both estimations of

the flux decrease as temperature increases; however the flux calculated from mass transfer decreased considerably less.

The uncertainty estimate of $\pm 15\%$ for k_d was made on the basis of sensitivity analysis of the fit of calculated curves with experimental curves on altering k_d (Figure (4.4.a)). An uncertainty of $\pm 30\%$ for N_{CO_2} was made on the basis of the uncertainties in input data (e.g. over 10% the height of solution in the vessel), as well as uncertainties in the validity of the empirical relations used. These uncertainties could be much greater, however the absolute magnitude of k_d and N_{CO_2} is the same.

Table (4.7) indicate that the terminal velocity as determined by equation (4.24) is essentially constant with temperature; this is because it is independent of viscosity. The condition of low viscosity may however not be valid for water at 275 K. If viscosity enters into the determination of terminal velocity, then it will favour an increase in k_L at lower temperatures, since the rise time (and hence the contact area) would be greater. This would make the mass transfer calculation results in better agreement with the k_d results from the curve fitting.

4.8 Conclusions

An attempt was made to numerically predict the time variation of the concentrations of H^+ ion, which had been found experimentally at different temperatures. The predictions of this concentration and the other carbonated species in the solution required some information regarding the rate constants (k_d and k_{-d}) for the dissolution of CO_2 (g) in an aqueous solution. Since these rate constants had not been determined previously, the prediction of the H^+ ion concentrations by the computer program were done with initial guesses for k_d . The value of k_{-d} was also found from this initial guess since these two rate constants are related through Henry's law constant.

The developed computer program predicts the time dependence of the H^+ ion concentration well for systems when bubbled with CO_2 gas. The rate constant k_d could be determined with an error approximately of $\pm 15\%$. However in the cases where the system is bubbled with N_2 gas, the predictions are not as close. This is thought to be due to the pressure assumed in equation (4.14). In this term $[\text{CO}_2$ (g)] has been set to zero for the cases when the solution is bubbled with N_2 gas. This is not entirely correct since a small amount of CO_2 will always be in the system.

The apparent activation energies for the forward and reverse reaction of CO_2 (g) $\rightleftharpoons$ CO_2 (aq) was calculated through Arrhenius plot to be -47 kJ/mol and -27 kJ/mol, respectively. Results of mass transfer calculations give reasonable absolute agreement between the flux of CO_2 entering the water as compared to that obtained from curve-fitting the $[\text{H}^+]$ vs time curves. There is a difference in the temperature dependence

obtained between the two approaches. This may be due to the use of inappropriate empirical relations.

There is evidence from the time variation of pH that there is a slow hydration step in the reaction of CO_2 (g) with water. Therefore, it may be possible refine this method for the determination of rate constants for fundamental reactions.

In the study of solution degassing, the rates of degassing were not optimized since the aim was to only obtain the mechanism by which the transfer occurs. The process of CO_2 degassing by sparging with N_2 was relatively slow. It could however be optimized by using one of the solution degassing methods described in section 3.3 of Chapter 3.

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**Part III: Development of an Analytical Method for Fast and Efficient
Routine Analysis of Surfactant in the Industrial Process Streams**

Chapter 5

5. Analysis of Surfactants

Environmental contamination resulting from surfactants from both point and non-point sources has become a major public and scientific concern in recent years. The production of synthetic surfactants in 1993 was estimated to be 7.2 million tons. The largest fraction (55%) of this production was anionic surfactants (Di Corcia, 1998 [1]). After household and industrial usage of these compounds, they are disposed to the sewage treatment facilities, which are capable of removing up to 85-95% of the surfactants. Small amounts of surfactants enter the surface waters as a part of treated effluent, and soil as a part of the sludge when applied as fertilizers. Recent studies have shown that the presence of surfactants in the environment causes disturbances of the ecological equilibrium. An example is the toxic impact on aquatic organisms due to interactions with their biomembranes (Vogt *et al.*, 1995 [2], References on page 141).

Due to these environmental impacts, the detection of these compounds in wastewater and environmental samples is of paramount importance. The simplest test is the visual examination of the samples for foam generation upon shaking. Measurements of the

surface tension either directly or electrochemically is an alternative method for surfactant detection.

For samples with small or trace levels of these chemicals, a more sensitive, efficient analytical method is needed. Today, the following analytical methods are available: High Performance Liquid Chromatography (HPLC), Thin-Layer Chromatography (TLC), Gas Chromatography (GC), and Gas Chromatography-Mass Spectrometry (GC-MS). Although almost all of these methods are capable of identifying and quantifying the surfactants in samples, they are most efficient for certain classes of surfactants. In addition they may require sample pre-treatment such as derivatization or separation prior to analysis.

For industrial applications analytical methods must be selective, fast, efficient, and economically feasible. In recent years *Capillary Electrophoresis* (CE) has been developed and applied for the analysis of surfactants and found to be very promising. It is therefore our objective to develop an analytical method using CE instrumentation for the analysis of anionic surfactants, particularly the fatty acid base surfactants. The developed method is then used for the analysis of industrial process and wastewater samples (e.g. BA Banknote Inc.), for quality control and for environmental monitoring.

5.1 Surfactants

Surfactants are generally described as anionic, nonionic, and cationic depending on their particular chemical structure. The term “surfactant” is an abbreviation for surface active agent, which literally means active at a surface. This surface can be between a solid and liquid, air and liquid, or between a liquid and a different immiscible liquid.

The primary property of a surfactant manifests itself in a solution. The concentration of the surfactant is higher at the surface than in the bulk of the liquid (Porter, 1994 [4]).

The surfactants used in the preparation of the wiping solution in this industry are either a formulated product by the name of Alkleen C or sulphonated castor oil (Turkey Red Oil). These two types of commercially available surfactants are used due to their low cost. Depending on the type of banknotes being printed, the surfactant in the wiping solution will differ due to the types of inks used.

5.1.1 Surfactant Alkleen C

Alkleen C is a mixture of anionic (3-7 wt%) and nonionic (5-10 wt%) surfactants in aqueous solution (Hoechst Canada Inc., 1997). The pH of this surfactant is in the range of 5.5-6.5. The anionic portion of Alkleen C is sodium alkyl sulphonate (SAS). Figure (5.1a) represents the molecular formula of the SAS. The alkyl group on this surfactant has been reported to have with 7 to 13 carbons.

The nonionic portion of Alkleen C, is nonylphenol polyglycol ether (NPPE). This is represented by Figure (5.1b). In this structure, C_9H_{19} represents the nonyl group.

(a)

(b)

Figure (5.1): Molecular formula and structure of surfactants in Alkleen C (Porter, 1994 [4]).

Among the most important characteristics of the Alkleen C surfactant are that they are chemically stable, have high salinity tolerance, and have high surface active properties. Further, they provide good detergency power as well as lubrication.

5.1.2 Surfactant Sulphonated Castor Oil (Turkey Red Oil)

The second type of surfactant used is sulphonated castor oil. This is an anionic surfactant commercially known as “Turkey Red Oil”, and is one of the most widely used industrial surfactants, especially in the printing and textile industries. The popularity of this surfactant is due to its ease and low cost of production, as well as widespread availability of raw material. Castor oil or ricinus oil is obtained by cold pressing of the seeds of the ricinus plant (Budavari *et al.*, 1992 [3]). Turkey Red Oil has been classed as an excellent detergent with good wetting and emulsifying properties (Porter, 1994 [4]).

This surfactant is prepared by reaction of concentrated sulphuric acid (H_2SO_4) with castor oil at 32 °C for 2 hours. This process results in ~75% sulphonated castor oil. Table (5.1) is a representation of the composition of castor oil and sulphonated castor oil. As seen in this table the major component in castor oil is ricinoleic acid, with oleic and linoleic acids as the second and third major components. Finally, samples of this surfactant will contain ~25% of the raw material (castor oil) which should be taken into account when an analytical method is being developed.

Ricinoleic acid (90% of castor oil) is an 18-carbon acid having a double bond on the 9-10 position and a hydroxyl group on the 12th carbon. This combination of hydroxyl group and unsaturation exists only in castor oil. Figure (5.2a) is a representation of this acid.

Table (5.1): Composition of castor oil and sulphonated castor oil
(McMurry, 1986 [5]).

Castor Oil	Sulphonated Castor oil
<ul style="list-style-type: none"> Ricinoleic Acid (87%) $C_6H_{13}CH(OH)CH_2CH=CH(CH_2)_7COOH$ Oleic Acid (7%) $C_8H_{17}CH=CH(CH_2)_7COOH$ Linoleic Acid (3%) $C_5H_{15}CH=CHCH_2CH=CH(CH_2)_7COOH$ Palmitic Acid (2%) $CH_3(CH_2)_{14}COOH$ Stearic Acid (1%) $CH_3(CH_2)_{16}COOH$ 	<p><i>Product of Sulphonation</i></p> <ul style="list-style-type: none"> Reaction with the OH group of the fatty acid.

The hydroxyl group in castor oil accounts for a unique combination of physical properties; relatively high viscosity and specific gravity, and solubility in alcohol in any proportion. The uniformity and reliability of its physical properties are demonstrated by the long-term use of this oil as an absolute standard for viscosity.

(a)

(b)

Figure (5.2): (a) Molecular structure of ricinoleic acid, and (b) sulphonated castor oil (McMurry, 1986 [5]).

Upon the reaction of castor oil with sulphuric acid, the SO_3H group will react with the hydroxyl group of ricinoleic acid and it becomes sulphonated as shown in Figure (5.2b).. The temperature under which this process is carried out is 32°C . Sulphonated castor oil has excellent lubricating properties in addition to having the ability to wet and disperse dyes, pigments and fillers.

5.1.3 Theoretical Background on Surfactants

The major applications of surfactants are in aqueous media. In some cases, mixtures of surfactants have been found to be most effective for specific cleaning purposes (Progress Report 2, 1996 [6]). The principal properties that characterize any surfactant (mixture or on their own) are described as,

• Adsorption	• Micelles
• Solubility	• Solubilisation
• Microemulsions	• Wetting
• Foaming/defoaming	• Macroemulsions
• Dispersing/aggregation of solids	• Detergency
• Surfactant interaction	

The most important characteristic of any surfactant is that it is at a higher concentration on the surface than the bulk of the liquid. The capability of a surfactant to adsorb is due to the presence of two groups in the molecule; one hydrophobic (water disliking) and the other hydrophilic (water liking). Figure (5.3) a simple representation of a surfactant.

Figure (5.3): Basic structure of a surfactant molecule (Porter, 1994 [4]).

It is the relative sizes and shapes of these hydrophobic and hydrophilic groups that determine the specific properties of the particular surfactant. It is important to note that even a small variation in these groups can result in surfactants with considerably different properties.

The main difference between the majority of surfactants on the market is the difference in the hydrophilic groups. These different groups will result in anionics surfactants (sulphates and sulphonates), nonionics (ethoxylates), and cationics. Anionic surfactants have applications in formulation of detergents, and adsorption on polar surfaces. Nonionics are also used in detergents and are very stable in solutions of hard water and varying pH. Cationics are used for adsorption on surfaces.

Adsorption of a surfactant on to the surface of a solution is strongly dependent on the concentration. At very low concentrations of surfactants, the molecule lies flat on the surface. Figure (5.4) represents the effect of surfactant concentration on absorption. As the concentration increases, the number of surfactant molecules on the surface increases, resulting in molecules not having enough room to lie flat; hence depending on the nature of the hydrophilic group, they begin to orient. When the concentration of the surfactant is high enough, they form a unimolecular layer; this is known as the *critical micelle concentration (CMC)*.

At concentrations below the CMC, there is no apparent change in adsorption at hydrophobic surfaces; however, at hydrophilic surfaces more than one layer of the surfactant molecule can form ordered structures on the surface known as micelles (colloidal-size clusters).

Concentration	Water/Hydrophobic Surface	Water/Hydrophilic Surface
<i>Very Low</i>
<i>Low</i>
<i>Monolayer at CMC</i>
<i>Above CMC</i>

Figure (5.4): Effect of surfactant concentration on adsorption (Porter, 1994 [4]).

The actual size and shape of a micelle is dependent on the temperature, type and concentration of surfactants, as well as the presence of other types of ions and other soluble organics in the solution. Depending on these conditions, micelles can form spherical or rod-like shapes.

5.1.4 Surfactant Solubility in Water

One of the most important properties of a surfactant is its solubility. When solubility is low, adsorption and surface active properties are high. If the hydrophobic group in the surfactant increases in molecular weight, then the surfactant becomes less soluble in water. Similarly, the surfactant becomes more soluble as the hydrophilic groups becomes more water soluble. Figure (5.5) is a representation of the solubility of ionic and nonionic surfactants in water with respect to temperature.

Surfactants show abnormal solubility characteristics in water as compared to other organic chemical compounds. The solubility of most common compounds in water increases with temperature. As shown in Figure (5.5), the solubility of ionic surfactants increases as the temperature rises to a certain temperature (Krafft point temperature).

Figure (5.5): Solubility of surfactants in water as a function of temperature
(Porter, 1994 [4]).

After this temperature there is a very rapid rise in the solubility of the ionic surfactant with no further increase in temperature. The micelles of ionic surfactant are

formed below this temperature and the solubility is limited. Above the Krafft point temperature the solubility of these micelles is appreciably increased.

Moreover, the solubility of the nonionic surfactants decreases dramatically above the Cloud-point temperature (Figure 5.5). The solubility of the nonionic surfactant in the water is due to the hydrogen-bonding between water and the glycol groups. These surfactants are found to be very soluble in water at 0 °C. Upon heating a solution of nonionic surfactant, the hydrogen-bonding between the water and glycol group will start to break. This will result in the surfactant becomes water insoluble; hence the solution becomes cloudy. The temperature at which this occurs is known as the Cloud point temperature. The dotted line on Figure (5.5) is the representation of the solubility of the non-surfactant compounds with increasing temperature.

Hence, for each surfactant the knowledge of CMC, Krafft-Point and Cloud-Point will give practical information about the surfactant's solubility and its extraction from environmental samples for analysis.

5.1.5 Environmental Impacts of Surfactants

Recently concerns have increased about chemicals in the environment which influence the reproductive capabilities of humans and animals (Stahlschmidt-Allner *et al.*, 1997 [7]). Every year a variety of chemicals such as dyes, pesticides and surfactants find their way into the fresh water systems. The majority of these compounds have rather poor biodegradability (Janssens *et al.*, 1997 and Marcomini *et al.*, 1998 [8] [9]). As a result, the fresh water systems are becoming more and more contaminated with micro-quantities of these industrial pollutants. Moreover, some of these pollutants have the

undesirable capability of oestrogenic activity on various forms of life in the aquatic environment.

Oestrogens are the principal group of the female sex hormones in invertebrates and vertebrates, including humans. They are essential for the development of the female sex organs and the control of reproduction in females. The biological responses produced by oestrogen are extremely complex and are mediated by specific receptors (Lye *et al.*, 1997 [10]). Therefore a variety of chemicals (e.g. surfactants) can interact with the receptors inducing a response.

A large number of industrial chemicals that are used daily (surfactants), organochlorine pesticides, paints and dyes) may find their way into the environment, and there can mimic the action of oestrogen. These chemicals are highly persistent (break down very slowly) and accumulate in the fatty tissue.

As a result, sensitive and efficient analytical methods are needed for identification and quantification of such chemicals in the effluent streams of the industries. This will aid in determining the amounts of these chemicals being discharged and a comparison to the accepted limits in the effluent streams. Moreover, such an analytical method would also determine the efficiency of the removal processes involved in treatment of these effluent streams.

5.2 Analytical Methods for Analysis of Surfactants

Surfactant analyses rely mainly on the characteristics of the surfactant molecule and its end groups. Various chromatographic methods have already been developed and

applied for the analysis of this class of chemicals. Each method has advantages, but none are free of limitations. For example, some are found to be more efficient for pure surfactants; others for isomeric surfactants. In the case of alkyl sulphonates, both GC and HPLC analytical methods require derivatization steps to obtain volatility and detectability. TLC studies require a separation step for mixtures of surfactants prior to detection.

5.2.1 Thin-Layer Chromatography (TLC)

Thin-Layer chromatography (TLC) is used both for characterization of pure surfactants and for detection of surfactants in complex matrices prior to determination with instrumental techniques. This method is mainly used and found to be advantageous when mixtures of surfactants are present and need to be initially separated into classes (e.g. separation of anionics from nonionics). Separation, identification, and estimation may be performed in a single step using TLC (Milster *et al.*, 1967 [11]).

TLC analysis of alkyl sulphonates is performed with the methylisobutyl ketone/propanol/acetic acid/acetonitrile system (Yonese *et al.*, 1982 [12]). In addition, using ethyl acetate/pyridine or chloroform/methanol as the solvents and alumina plates, anionic surfactants may be separated from nonionics. The anionics will remain at the origin of the plates while nonionics will travel far up the plates.

TLC has been reported to be a rapid and inexpensive method for the analysis of anionic surfactants. Table (5.2) provides information on several normal phase systems designed to separate anionic surfactants of the alkyl sulphonate family.

Determination of fatty acids with TLC is rarely performed since HPLC and GC analysis provides more precise quantitative information. However, HPLC and GC analysis of fatty acids requires derivatization of these acids to their methyl esters. There has been at least one report in the literature of analysis of fatty acids with TLC (Bey, 1965 [15]). The reported method will give good separation of fatty acids by carbon chain length up to C₃₀ if carried out at 42 °C.

Table (5.2): Methods for TLC analysis of anionic surfactants
(Schmitt, 1992 [13]).

Surfactant	Stationary Phase	Developing System	Visualizer	Reference
Paraffin Sulfonates; detergents of alkyl sulphonates and unsulphonated material	Silica gel G with added ammonium sulphate, 0.3 mM	70:30:6 CHCl ₃ /MeOH/ 0.05M H ₂ SO ₄	Iodine Vapour, Heat at 350 °C	Mutter, 1968 [14]
Fatty Acid Soaps	Silica gel G, impregnated with 5% tetradecane	8:3:4:1.3 isopropanol/ ethanol/acetic acid/water	Rhodamine B	Bey, 1965 [15]
Alkyl Sulphonates, Alkylbenzene Sulphonates, Separation by Alkyl chain length	Polyamide Powder B-0 (Wako, Osaka, Japan) Bound with cellulose (Camag)	15:1 0.1 M NH ₃ /Pyridine	Pinacryptol Yellow	Takeshita <i>et al.</i> , 1976.[16]
Alkyl Sulphonates, Hydrophobes, Qualitative Analysis	Merck Silica gel 60	90:10 acetone/ tetrahydrofuran; develop 3 times to 10 cm	Pinacryptol Yellow, UV light	Koehler and Chalupka, 1982 [17]

5.2.2 Liquid Chromatography (HPLC)

High-Performance liquid chromatography (HPLC) has been reported to be the preferred technique to determine ionic surfactants in mixtures. This technique is able to characterize surfactants according to their molecular composition.

Analysis through this method will aid in the determination of individual surfactants in mixtures with other components. Conventional HPLC is most useful for the analysis of compounds with a phenyl ring, where direct UV detection is applicable (Gloor and Johnson, 1977 [18]).

HPLC studies can be effectively used to determine the degree of sulphonation or the alkyl chain length in anionic surfactants. However, it has been reported that the peak resolution of HPLC methods for alkyl sulphonates is inferior to that obtained with capillary GC (Schmitt, 1992 [13]).

For the analysis of alkyl sulphonates, most methods reported are reverse-phase separations on C₈ or C₁₈ packing. However, anion exchange columns are occasionally used for lower molecular weight compounds. An organic or inorganic salt is added to the mobile phase unless the detection system prevents this and some form of pH control is needed. Indirect UV absorbance is most readily used since some alkyl sulphonates can not be detected using direct UV detection due to low absorbance. The main separation mechanism in this method is by alkyl chain length, with the longer chain compounds retained more than shorter chains.

Table (5.3) provides some information on the available methods for HPLC analysis of alkyl sulphonates. More recently, an analytical method using liquid chromatography-

mass spectrometry (LC-MS) has been developed for the analysis of anionic and non-ionic surfactants (Di Corcia, 1998 [1]).

There are HPLC columns and systems designed for the analysis of fatty acids, usually with refractive index as detection. Fatty acid soaps can be analyzed with conventional reversed phase HPLC columns with the addition of an organic or inorganic acid to the mobile phase. This step is carried out to control the ionization of the fatty acid. The separation may be made at high pH in the presence of an ion-pairing agent, or at low pH without the ion pairing agent.

Table (5.3): HPLC analysis of anionic surfactants (Schmitt, 1992 [13]).

Surfactant	Stationary Phase	Developing System	Detector	Reference
Alkyl Sulphonates, Separation by chain length	Anion exchange column Whatman Partisil 10 SAX, 4.6 × 250 mm	Acetonitrile/water containing potassium biphthalate, pH 5, sulfosalicylic acid, pH 2.4, or <i>m</i> -sulfobenzoic acid, pH 3.6	Indirect UV, 297 or 320 nm	Larson, 1986 [19]
Alkyl Sulphonates; Separation by position of sulphonation	Shandon Hypersil ODS 3 columns, 4.6 × 200 mm in series, 27 °C	Gradient, water/acetonitrile 0.0003 M in <i>N</i> -methylpyridinium chloride	Indirect UV, 257 nm	Liebscher <i>et al.</i> , 1989 [20]
Fatty Acid Soaps, Characterisation by chain lengths	Waters μ Bondapak C ₁₈	Methanol/Water, 85:15, 0.2% acetic acid	Refractive Index	Thomas and Rocca 1979[21]

5.2.3 Gas Chromatography (GC)

Gas Chromatography (GC) analysis of anionic surfactants can be problematic due to the low volatility of these chemicals. As a result, GC analysis of these compounds requires a derivatization step to obtain a more volatile component for analysis. Table (5.4) provides further information on the GC analysis of anionic surfactants.

Table (5.4): Derivatization GC methods for analysis of anionic surfactants (Schmitt, 1992 [13])

Surfactant	Derivatization Technique	Column	Temperature	Detector	Reference
Alkylaryl Sulphonates	Methyl Sulphonate Derivatives	1.5% OV-1 Silicone on Chromosorb W AW-DM	50-300 °C at 4 °C/min	FID	Hon-nami and Hanya, 1978 [22]
α -Olefin-sulphonates	Hydrogenation and conversion to sulphonyl chlorides	30% SE-30 on silanized Chromosorb WAW glass, 4mm $\times$ 2.5 m	200 °C	FID	Nagai, <i>et al.</i> , 1970 [23]
Paraffin Sulphonates	Estrification with diazomethane	30% SE-30 silicone on diatoport P	130-250 °C at 1 °C/min	FID	Kupfer <i>et al.</i> , 1969 [24]

The most commonly reported derivatization method for alkyl sulphonates in GC analysis is desulphonation. This process is carried out in the presence of an acid by heating. Other attractive derivatization methods are the formation of either sulphonyl chloride or the methyl ester of the surfactants. The sulphonyl chloride of the surfactants

is prepared by reaction with thionyl chloride (Kirkland, 1960 [25]). Methyl sulphonates are normally prepared by reaction with diazomethane (Okazaki *et al.*, 1989 [26]). These reactions are reported to be more attractive than desulphonation since the excess derivatizing agent can be evaporated. Desulphonation using acids will result in oils which must be distilled and then extracted from the acid.

Analysis of fatty acids using GC requires derivatization to the methyl esters of the fatty acids. This will result in a more volatile compound, which could be analyzed using this GC method (Rezanka and Podojil, 1989 [27]).

5.2.4 Gas Chromatography - Mass Spectrometry (GC-MS)

Mass Spectrometry has been a tool in analytical chemistry for about 30 years; however, only in the past few years it has been applied to the analysis of surfactants. This method is a sensitive and specific for the analysis of compounds and mixtures. For example, the molecular weight distribution of surfactant oligomers can be directly found from the mass spectra of the parent ions. Furthermore, the location of unsaturation, side chains, degree of branching and isomer distribution can be determined using the fragmentation patterns.

Mass spectrometry analysis of surfactants is usually carried out in conjunction with GC. However, as described in the previous sections, surfactants are not sufficiently volatile and a derivatization step is needed. A study by Field *et al.* 1992 [28] reports on the GC-MS studies of sulphonated aliphatic and aromatic surfactants in sewage sludge. In this study, anionic surfactants such as secondary alkyl sulphonates (SAS) and linear alkylbenzene sulphonate (LAS) were extracted from the sewage sludge as their

tetrabutylammonium ion pairs using supercritical fluid CO₂ at 400 atm and 80 °C. The ion pairs of SAS and LAS quantitatively formed butyl esters in the injection port of the GC-MS, and analysis of these chemicals was shown to be feasible. This GC-MS method of analysis of SAS and LAS was further applied to sewage wastewater using solid-phase extraction (Field *et al.*, 1994 [29]).

Ion-pair derivatization, is a rapid, simple and robust method for the analysis of anionic surfactants of the sulphonated family. This process proceeds through the reaction of sulphonated surfactant [RSO₃⁻Na⁺] with tetrabutylammonium hydrogen sulphate [N(Bu)₄⁺HSO₄⁻] to form [RSO₃⁻N(Bu)₄⁺] according to the following scheme:

Upon introduction of the ion-paired surfactant to the GC injection port at 300 °C, an esterification process takes place. This will result in the butyl ester of the sulphonated surfactant [RSO₃Bu]:

The column for the GC-MS studies was HP-5 (20 m × 0.2 mm i.d. × 0.33 μm film thickness; Hewlett-Packard). The reported GC temperature program was an initial temperature of 110 °C, followed by 10 °C/min ramp to 220 °C, followed by a second ramp of 6 °C/min to a final temperature of 300 °C. The final temperature was held for 3 min. The conditions for the injection port were an injection temperature of 300 °C, a

split ratio of 1:7 with an injection volume of 1 μL . The detection was with a mass selective detector with electron impact ionization operated in a selected ion mode. The accuracy of this method has been reported by Field *et al.*, 1994 [29] to have a relative standard deviation (RSD) of 7%.

Analysis of fatty acids using GC-MS requires derivatization of these components to methyl esters. This is accomplished by a nucleophilic acyl substitution reaction of a carboxylic acid with an alcohol (McMurry, 1986 [5]). This reaction is known as the **Fischer esterification reaction**, which involves heating the carboxylic acid with a small amount of mineral acid catalyst in an alcohol solvent. The mechanism of this reaction is shown in Figure (5.6).

Figure (5.6): The Fischer esterification reaction of carboxylic acids to yield an ester (McMurry, 1986 [5]).

Free carboxylic acids ($\text{R}-\text{COOH}$) are not reactive enough to be attacked by most nucleophiles; however, they can be made much more reactive in the presence of a mineral acid such as HCl or H_2SO_4 . The first action of the mineral acid is the protonation of an oxygen atom on the $-\text{COOH}$ group. This gives the carboxylic acid a full positive charge, which results in it being much more reactive towards nucleophiles. The subsequent addition of an alcohol molecule to the protonated carboxylic acid will

result in loss of water and hence the ester product. The analysis of fatty acids by this method is commonly used; the conditions of analysis are well documented by Kitson *et al.*, 1996 [30].

5.3 Analysis of Surfactants by Capillary Electrophoresis (CE)

Capillary Electrophoresis (CE) has become an important separation technique for the analysis of peptides, proteins and other related compounds. In recent years this modern technique has found applications for the analysis of surfactants. Due to the quantities of surfactants used in industries and households, there is an ever-growing concern about their environmental fate. As a result, sensitive, rapid methods are needed for the trace analysis of these chemicals in water, wastewater, foods, plants and animal tissues.

The literature contains several studies (Desbène *et al.*, 1992 [31]) on the analysis of sulphonated (RSO_3^-) and sulphated (ROSO_3^-) surfactants using CE. Early studies on alkylbenzene sulphonate indicated best separation and resolution using a borate-boric acid buffer of pH 9 and acetonitrile mixture. In this study, direct UV detection at 214 nm was used.

It has been reported that the resolution and the migration time in CE for alkyl sulphonates and alkyl sulphates can be improved by using a cation in the buffer (Chen and Pietrzyk, 1993 [32]). This study suggests that divalent cations increased migration time and peak resolution to a greater extent as compared to the monovalent cations. Since the alkyl sulphonates and alkyl sulphates are nonaromatic, indirect UV detection at

230 nm was used. The buffer additive for indirect detection was salicylate anion, and a detection limit of 0.6 pmol was achieved.

Analysis of linear alkylbenzene sulphonates and the separation of its homologues using HPLC has been found to be inefficient (Chen and Pietrzyk, 1993 [32]). Hence, CE studies of these molecules indicated that the separation of these homologues and structural isomers were possible using direct UV detection at 200-214 nm with injection at the anodic end (Vogt *et al.*, 1995 [2]). The injection was in the pressure mode with a 10 second injection time. Fused silica capillaries of 57 cm length (50 cm to detection window) $\times$ 75 μ m i.d. were used and the operating voltage was set at 20 kV. For the analysis of these compounds, 100 mM of phosphate buffer at pH 6.8 was used. The buffer additives were 20% acetonitrile and 20 mM of α -cyclodextrin (α -CD). These studies were further extended to real river water samples with a pre-concentration step for the surfactants.

An example of an industrial application of CE is the analysis of sodium dodecylbenzene sulphonate (SDBS) in pharmaceutical processing equipment, including monitoring of detergent residues after cleaning (Altria *et al.*, 1995 [33]). This method was successful in validation of acceptable levels of sensitivity, recovery, precision, repeatability, and detector linearity. The method was shown to be selective with no interferences from the wash water or from cotton wool extracts in real industrial water samples.

Some of the most important anionic, cationic and nonionic surfactants used in laundry detergents and tooth pastes were analyzed using CE, and the results were

compared to those found using HPLC (Heinig *et al.*, 1996 [34]). These surfactants were analyzed in both river water and sewage sludge. Results indicate that the aliphatic anionics (alkyl sulphonates and sulphates) can be determined by HPLC with a conductivity detector and by CE with indirect and direct UV detection. The detector was set at 200 nm for direct and 214 nm for indirect detection. The operating voltage was set at 20 kV and the injection was in the pressure mode at 5 seconds. Fused silica capillaries of 57 cm $\times$ 75 μ m i.d. were used for the analysis.

Alkyl sulphates were analyzed using a buffer of 20 mM salicylate pH 6, and an organic solvent content of 30% acetonitrile (Heinig *et al.*, 1996 [34]). Analysis of branched and straight chain alkyl sulphonates were carried out using 5 mM dodecylbenzene sulphonate, 5 mM phosphate buffer pH 6.8 and 30% of acetonitrile. The cationic surfactants such as nonylphenol polyethoxylates were examined using a buffer of 10 mM phosphate pH 6.8 containing 70 mM sodium dodecylbenzene sulphonate and 20% acetonitrile. The nonionic surfactants required a buffer of 50 mM phosphate pH 6.8 and an acetonitrile content of 50%.

Results of these studies indicated that CE provides high resolution separation of a large number of compounds in a small sample volume. The most important advantages of CE are: (i) analysis of different kinds of surfactants is possible by changing only the electrolyte composition, and (ii) no sample pre-treatment is required. However, it has been reported that high efficiency separation of nonionic surfactants using CE can not be achieved; better results in this case are obtained using chromatographic methods such as HPLC.

5.3.1 Applications of CE to Environmental Samples

A major objective in environmental analytical chemistry research is to develop fast, efficient, economic and environmentally friendly methods for the analysis of environmental pollutants.

Figure (5.7): Applications of CE to environmental samples.

Most environmental monitoring and site characterizations demand analytical methodologies that are easy to carry out and that generate a small amount of laboratory waste. CE applications in environmental studies have advantages in that they are economical and use sample volumes of 1 to 10 nL. In recent years, CE has found many environmental applications; these are best represented by Figure (5.7).

The number of studies on the use of CE for determining various pollutants, after a slow start, is now growing rapidly and it is emphasized by the appearance of a number of review articles (Dabek-Zlotorzynska, 1997 [35] [36])

Many reports have now been published on the applications of this method to environmental chemicals (McLaughlin *et al.*, 1996 and Brumley, 1995 [37], [38]). Some examples of the environmental chemicals analyzed by CE are chlorophenols and phenoxy acid herbicides, organochlorines, phenolic carboxylic acids, aliphatic amines, metabipyridine complexes and flavonoids.

5.4 Literature Review: Analysis of Fatty Acids and Their Surfactants Using CE

Today CE has a wide variety of applications in analytical chemistry. However, there has been limited information on the use of this analytical method for the analysis of fatty acids, and more important, the surfactants prepared from these fatty acids.

Although there are many GC and HPLC methods available for the analysis of fatty acids and their surfactants, they most often have time-consuming steps such as sample pre-treatment or derivatization. A thorough literature study indicates that research groups have started the development of methods using CE instrumentation for the analysis of long chain fatty acids.

An early study in Germany (Gutnikov *et al.*, 1994 [39]) reported on CE methods with normal and reversed electroosmotic flows (EOF) (see section 6.1.2, Chapter 6), and indirect UV detection for the separation of fatty acids. Fatty acids up to C₁₂ were separated using cationic surfactant cetyltrimethyl ammonium bromide (CTAB), and 3,5-

dinitrobenzoic acid as the buffer electrolyte. In addition to these, the buffer (pH = 9) contained 30% acetonitrile. The fused silica capillaries used were 57 cm $\times$ 75 μ m i.d. with the detection window at 50 cm. The injection times were from 5 to 15 seconds in the pressure mode and an applied voltage of 20-30 kV. However, the temperature at which the measurements were performed was not reported.

The detection limit for this set of fatty acids was reported to be 5-10 ppm (Gutnikov *et al.*, 1994 [39]). Analysis of fatty acids up to C₁₈ chain length was possible using normal EOF with trinitrobenzene sulfonic acid (TNBSA) as buffer carrier and 60% acetonitrile as solvent. The pH of this buffer was 9. Recommendations made in this study were the amounts and types of organic solvents added to the buffer. Acetone was found to be the best solvent, but an increase in acetone concentration was found to further decrease the mobilities of the components. Moreover, there would be a danger of UV absorption of buffer with an increased amount of acetone. Analysing the UV spectrum of acetone indicated it to be a suitable buffer additive when detection wavelengths are greater than 340 nm and between 205 to 220 nm.

Other solvents such as acetonitrile (ACN), tetrahydrofuran (THF) and methanol (MeOH) are most often used in CE studies; however, acids are somewhat less soluble in ACN. The best recommended wavelength for ACN is as low as 195 nm. THF has been found to be an excellent solvent for the fatty acids and reported to be transparent to 210 nm. The one most important disadvantage of THF is that it attacks the latex caps of CE sample vials. Finally, methanol and isopropanol provide detections as low as 210 nm; however, they affect the double layer of CTAB at the capillary wall.

Analysis of free fatty acids using CE was investigated (Roland-Assad and Gareil, 1995 [40]), and the separation of C₂-C₁₄ was achieved in less than 10 minutes. Fatty acids of C₇-C₁₈ homologues were separated in under 20 minutes. The minimum detection limit reported is 0.2-0.5 ppm using indirect UV absorbance at 270 nm. Fatty acids of C₂-C₁₄ chain length were separated using a mixture of 20 mM Tris (hydroxymethyl aminomethane) and 10 mM *p*- anisic acid (pH=8.2). The peak separation was further optimized by the addition of 0.75 mM of trimethyl- β -cyclodextrin. Likewise, C₇-C₁₈ fatty acids were separated using a mixture of 20 mM Tris and 10 mM *p*- anisic acid (pH=8.2) as well as 60% methanol and 1 mM of trimethyl- β -cyclodextrin. The fused silica capillary was 72 cm $\times$ 50 μ m i.d. (50 cm to detector), applied voltage 30 kV, analysis temperature of 30 °C, and hydrodynamic injection for 1 second. Capillaries of 50 μ m i.d. were purchased from Applied Biosystem Inc. The method was further extended to the analysis of coca oil extract with results, which correspond closely to those found by GC studies.

In 1995 a study (Erim *et al.*, 1995 [41]) on the analysis of butter using CE was performed. In this study, saturated fatty acids of C₈-C₂₀ chain were also analyzed. However, these studies had a buffer of 10 mM sodium dodecylbenzenesulphonate (SDBS), 50% acetonitrile and 30 mM Brij 35 (polyoxyethylene lauryl ether) as background electrolyte. Analysis was also through indirect UV detection set at a wavelength of 198 nm. The analysis voltage was 20 kV and the sample injection time was 0.06 minutes in the pressure mode. The fused silica capillaries were 60 cm $\times$ 50 μ m

i.d. and the distance to the detection window was set to be 45 cm. The experiments were performed at room temperature (23 ± 2 °C).

One of the most recent studies (Schmitz and Gáb, 1997 [42]) on the analysis of fatty acids using CE has been the development of an analytical method for the analysis of hydroperoxides. The hydroperoxides result from the reaction of oleic, linoleic and linolenic acids with oxygen. This report indicates that due to the strong adsorbance of the fatty acids to the walls of the capillary, coating of the capillary would be beneficial. Further, this study provided a comparison between un-coated and coated fused silica capillaries for the separation of hydroperoxides and the corresponding fatty acids.

Brij 35 was used for the dynamic coating of the capillary as well as being a surfactant for micellar electrokinetic chromatography. C₁₈ coated fused silica capillaries were used indicating that these gave the best separations for these compounds. However, the retention times were longer as compared to un-coated capillaries (Schmitz and Gáb, 1997 [42]). Detection was by UV-photodiode array; all experimental studies were performed at room temperature (25 °C) with fused silica capillaries of 57 cm × 50 µm i.d. (50 cm to the detector). The samples were injected under pressure mode for 5 seconds; no information on the applied voltage was provided.

The buffer for the studies with un-coated capillaries was 70% potassium phosphate (50 mM, pH 4.86), 30% methanol and 1.1 g/L Brij 35. Results suggest that the greatest sensitivity of this method and the buffer was at 195 nm for the fatty acids and at 234 nm for the hydroperoxides with a detection limit of 90 µM (Schmitz and Gáb, 1997 [42]). The buffer used for the studies with the coated capillary consisted of 70% potassium

phosphate (60 mM, pH 6.30) and 30% methanol and 1.1 g/L Brij 35. For the case of C₁₈ coated capillary, the detection wavelength was the same as un-coated with an improved detection limit of 190 µM.

5.5 Research Objectives

As indicated in section (5.2) there are many analytical methods such as TLC, HPLC, GC, and GC-MS available for the analysis of sulphonated anionic surfactants as well as fatty acids. Nonetheless, there are some limitations associated with each method. Analysis of these compounds using TLC will not be quantitative. In addition, this method uses large amounts of hazardous solvents. The analysis of fatty acids with TLC is seldom performed since HPLC and GC provides more quantitative information.

There are many reports on the HPLC analysis of anionic surfactants; however, this method suffers from peak resolution when compared to methods such as capillary GC. Moreover, the HPLC columns must be conditioned regularly in order to have optimum performance. Analysis of fatty acids using HPLC requires an ion-pairing agent. For industrial applications this method has the disadvantage of being time consuming and using cancer causing chemicals (ion-pairing agent).

GC analysis of these surfactants has a major disadvantage over CE since it requires sample pre-treatment due to low volatility of the anionic species and the fatty acids. Anionic surfactants are derivatized using ion-pairing agents. The fatty acids are transformed into their methyl esters for GC analysis. The derivatization agents used are often harmful and in most cases carcinogenic, toxic or highly explosive (diazomethane). GC-MS studies of anionic surfactants are like GC studies, and require sample pre-

treatment steps. However, this method of analysis will provide information on the molecular weight, and degree of unsaturation. The analysis time is also in the same order as GC studies.

Electrophoretic separations performed in capillary columns can provide high efficiency analysis of complex samples as reported by Weinberger, 1993 [43]. The most attractive feature of this method of analysis is for separations in aqueous media. This will be of particular interest to industries generating wastewater with a need for routine analysis.

There has been at least one report on the applications of CE in the pharmaceutical industry for the analysis of residues of surfactants in the processing equipment (Altria *et al.*, 1995 [33]). However, there is no information on the application of this method to industrial process and wastewater for environmental monitoring and quality control.

As described in section (5.1) there are two types of surfactants (Alkleen C and sulphonated castor oil) used at the local currency printing industry. Alkleen C is a mixture of anionioic and nonionic surfactants. A sample of the anionic portion of this surfactant (sodium alkyl sulphonate) was obtained from Hoechst Canada Inc. Since this surfactant is a secondary alkyl sulphonate (SAS), the method of analysis developed by Vogt *et al.*, 1995 [2] and Heinig *et al.*, 1996 [34] will be used for the analysis of this surfactant.

A further objective of this research is to develop an analytical method using CE instrumentation for the analysis of an industrial anionic fatty acid based surfactant

(sulphonated castor oil). The surfactant of interest, sulphonated castor oil (Turkey Red Oil), contains $\approx 75\%$ sulphonated portion and $\approx 25\%$ unsulphonated fatty acids (oils).

These methods of surfactant analysis will then be used to analyze real industrial process water samples from the local currency printing industry (**BA. Banknote Inc.**). Both types of surfactants are used in the washing process of the printing plates.

The results obtained are then compared to those obtained using GC-MS analysis. This approach is chosen due to the availability of equipment. The procedures for analysis of sulphonated anionic surfactants using GC-MS will be the ones presented by Field *et al.*, 1992 and Vogel, 1978 [28] [44]. The CE studies will then be further extended to real industrial water samples (i.e. Tank 701, and Tank 601, see Figure (2.1), Chapter 2).

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Chapter 6

6. Capillary Electrophoresis

Electrophoresis and its theoretical principles have been known for almost 100 years. An integral part of the biomedical work is the two dimensional electrophoresis in slab gels (better known as gel electrophoresis); today capillary electrophoresis is the latest development in this series. Studies using capillary electrophoresis for the analysis of compounds were first reported in literature about 15 years ago. Today this analytical method is becoming a routine separation technique in many laboratories. The separation principles of this method are similar to those in chromatography. CE has found application in the analyses of small ions up to whole living cells and particles. In this chapter the development of an analytical method using this instrumentation for the analysis of surfactants is described (References on page 179).

6.1 Theoretical Background

Analytical electrophoresis is considered to be the passage of an electric current in a capillary through a mixture of substances in solution to obtain separation of components.

Separation using capillaries was first demonstrated by Everates in the mid-1960's; however, the potential of this technique for highly efficient separations was not used until 1981 by Jorgenson [1]. Today many classes of compounds are separated and analyzed using this method.

6.1.1 CE Apparatus

Capillary electrophoresis can be carried out using equipment that consists of three components: the capillary, the power supply and the detector (Kuhn and Hoffstetter-Kuhn, 1993 [2]). The basic instrument to carry out CE studies is represented by Figure (6.1), Beckman 2100, Beckman Instruments, Inc., California USA.

The capillaries are usually fused silica polyimide-coated with a very small inner diameter ranging from 20-100 μm i.d. The capillary is filled with the buffer solution and each end is immersed into buffer reservoirs. The high voltage direct-current (DC) electric field is applied by a power supply with its two electrodes also immersed into the buffer reservoirs.

A defined sample volume (typically 1 to 30 nL) is introduced into the capillary by replacing one of the buffer reservoirs by the sample vial. Sample introduction is either by hydrodynamic flow or electromigration. The components within the injected sample migrate at different rates along the capillary under the electric field. An on-column detector located at the end of the capillary opposite to the injection site will detect each component as it reaches the end of the capillary.

Today there are several detection modes available on the commercially built CE instruments, the most common of which is the UV-visible absorbance detector.

Figure (6.1): Instrumental set up of a capillary electrophoresis system, Beckman 2100, Beckman Instruments, Inc., California USA (Dabek-Zlotorzynska, 1998).

Figure (6.2): Electroosmotic flow (EOF, μ_{eo}) and electrophoretic mobility (μ^- ; μ^+) using normal polarity configuration (Rule, 1995 [3]).

Other types of detectors such as laser induced fluorescence as well as Raman scattering have also been successful. Finally, the detector response is recorded versus the migration time; a computer connected to the system allows data acquisition.

6.1.2 Electroosmotic Flow (EOF)

The basic phenomenon in electrophoretic separation is the electroosmotic flow (EOF, μ_{eo}). This is described as the relative motion of a liquid to a fixed surface charge (inside wall of the capillary) caused by an electric field (Kuhn and Hoffstetter-Kuhn, 1993 [2]). Fused silica capillaries contain ionizable silanol groups ($\text{Si-OH} \rightleftharpoons \text{Si-O}^- + \text{H}^+$) which are in contact with the buffer solution.

The pH of the buffer solution controls the degree of ionization of the capillary wall. An electrical double layer is created at the wall when the negatively charged wall attracts the positively charged ions from the buffer. When a high voltage is applied along the capillary, cations in the diffused portion of the double layer migrate in the direction of cathode (Figure (6.2)). This will result in a process called electroosmosis where the net flow of the buffer solution is in the direction of negative electrode. The electroosmotic velocity v_{eo} is therefore defined by (Kuhn and Hoffstetter-Kuhn, 1993 [2]):

$$v_{eo} = \frac{\varepsilon \zeta E}{4\pi\eta} \quad (6.1)$$

In equation (6.1) ε is the dielectric constant, ζ is the zeta potential measured at the plane shear close to the liquid-capillary wall surface, E is the electric field strength, and η is the viscosity of the buffer.

The neutrally charged analytes will therefore migrate to the detector at the same speed as the electroosmotic flow (EOF). Since the electrophoretic mobility of the positive ions is governed by the high voltage, the cations will migrate faster than the EOF. Finally the anionic species will be attracted to anode, and hence travel in the opposite direction of the EOF. In a normal polarity configuration the EOF is much stronger than the electrophoretic mobility of the negatively charged ions; as a result these species will be the last ones to migrate towards the detector. Figure (6.2) is representation of the migration of the species.

The magnitude of the electroosmotic flow (EOF) can be determined using the following equation (Kuhn and Hoffstetter-Kuhn, 1993 [2]):

$$\mu_{eo} = \frac{v_{eo}}{E} = \frac{L_T L}{t_{eo} V} \quad (6.2)$$

In this equation μ_{eo} , is the electroosmotic flow, L (m) is the distance from injection to detection, L_T (m) is the total capillary length, t_{eo} (s) is the migration time for the solvent, and V (Volts) is the applied voltage.

6.1.3 Factors Influencing CE Separation

Although CE separations are considered to be efficient, fast and economic, there are many factors which influence this technique. For example the choice of the electrolyte, pH and composition are among the most important. Parameters such as systems

temperature, applied voltage, complex formation, and organic modifiers must also be studied when developing a method using this system.

Choice of Electrolytes. The electrolyte system plays an important role in CE separations. The electrolyte pH and composition affect the efficiency of the separation. Generally, the electrolyte should be chosen considering that it should not have a negative effect on the separation, and that it should have a high buffering capacity over a broad pH range. The effect of temperature on the pH must be as low as possible and the mobility of the buffer ions should be similar to those of the analyte. In the case where UV-visible absorbance is used for detection, the buffer should show low absorbance at the selected wavelength.

The pH value of the buffer is one of the most important parameters in the separation as it is based on differing mobilities of the analytes. The mobilities of analytes also depend on their size and net charge.

The buffer composition is important, as the currents generated in the presence of the electrical field are dependent on this factor. Higher buffer concentrations will generate higher currents, which may result in poor separation for some components. In every CE method the optimum buffer concentration must be determined.

Effect of Voltage and Temperature. The migration of ions in CE is dependent on the field strength applied along the capillary. The field strength is the applied voltage divided by the total capillary length. The highest field strengths will result in the shortest analysis time since both the electroosmotic flow and electrophoretic velocity are directly related to the field strength. This indicates that working with the highest possible field

strength should give the highest efficiency in terms of analysis. According to Ohm's law, a linear relationship exists between the field strength and the resulting current for the buffer. However, in reality this relationship is only true in the lower voltage ranges. At higher field strengths there is an increased heat generation which results in deviations from linearity in Ohm's law. Hence, the optimum voltage may be determined experimentally when deviations from linearity begin in a plot of field strength versus current.

The effect of temperature on separations using chromatographic methods is a routine process to either improve speed (HPLC) or elution (GC). However in electrophoretic separations, when a current is passed through a capillary, the electrical energy is converted into Joule heating. Due to heat generation in this process the temperature increases; it is thus necessary to have efficient heat removal. Further, since the viscosity of the buffer changes with changes in temperature, an increase in temperature will increase both the electroosmotic and electrophoretic mobilities. As a result, the major effect of increasing temperature is to decrease the time of analysis. Working at higher temperatures may however result in poor peak resolution, in addition to not having the effective temperature control required for the system.

Effect of Cyclodextrins (CD) on CE Separation. In many CE studies, to enhance selectivity, efficiency, and peak resolution, host-guest complexation or inclusion complexation using cyclodextrins (CD's) are often used. CD's are cyclic oligosaccharides which consists of several glucose units. Corresponding to their names

α -, β -, γ -cyclodextrin they will contain six, seven or eight glucose units respectively.

Figure (6.3) provides the chemical structure of these cyclodextrins.

Figure (6.3): Chemical structure of (a) α -cyclodextrin, (b) β -cyclodextrin and (c) γ -cyclodextrin (Kuhn and Hoffstetter-Kuhn, 1993 [2]).

CD's form a cone shape configuration with secondary hydroxy groups at the rim of the larger diameter. The internal cavity of CD's is hydrophobic since it does not contain hydroxy groups. Due to the hydrophobicity of their cavities, they are able to form inclusion complexes with aromatic as well as alkyl groups. The electrophoretic mobility is influenced by this complex formation in CE even though CD's are basically neutral compounds (Vogt *et al.*, 1996 [4]). However, they can alter the electrophoretic mobility of analytes based on differing molecular masses of the complex and free species. In

some cases the complexation by CD's decrease the charge density and the electrophoretic mobility of the analyte and result in faster elutions.

Effect of Organic Modifiers on CE Separation. In order to change the physico-chemical nature of the separations system and to alter the polarity and viscosity of the mobile phase in CE, a number of organic modifiers are used. The addition of the organic modifiers will affect both the electroosmotic flow and the electrophoretic mobility of the analyte. In some cases analytes may not be soluble in an aqueous solution and organic solvents are added to enhance solubility. Among the solvents used are acetonitrile and methanol, as they have been shown to have large influences on the electrophoretic mobility. Other organic solvents such as ethanol, n-propanol and even diols and polyols are used to adjust the viscosity of the mobile phase.

6.2 Experimental Studies

6.2.1 Experimental Apparatus and Procedure

Reagents and Chemicals

Turkey Red Oil was supplied by Produits Chimiques ADRO Inc. (Montreal, QC, Canada) or Aldrich (Milwaukee, WI, USA). Alkleen C and sodium alkyl sulphonate was supplied by Hoechst Canada (Montreal, QC, Canada). All buffers were obtained from Beckman (Fullerton, CA, USA). All other chemicals and solvents were purchased commercially from either Aldrich (Milwaukee, WI, USA), Sigma (St. Louis, MO, USA) or Fisher Scientific (Ottawa, ON, Canada) in the highest purity available, and were used without further purification.

6.2.1.1 Capillary Electrophoresis (CE)

The capillary electrophoresis studies were carried out using a Beckman P/ACE system 2100 (Fullerton, CA, USA) equipped with a variable wavelength absorbance detector. The fused silica capillaries used were from Polymicro Technologies (Phoenix, AZ, USA) with 57 cm (50 cm to detector) $\times$ 75 μm i.d. $\times$ 375 μm o.d.

All experiments for sodium alkyl sulphonate were performed at 25.0 ± 0.1 °C and an applied voltage of (+20 kV). Injection was at the anodic end in the pressure mode with an injection time of 2 seconds. The analysis was done with indirect UV detection at 214 nm.

All experiments for Turkey Red Oil were performed at 35.0 ± 0.1 °C and a constant voltage of (+20 kV), unless otherwise stated. The samples were injected in the pressure mode for 10 seconds. The analytes were detected by UV-visible absorbance at 200 nm. Further, the electropherograms were acquired and stored on a personal computer using the Beckman Gold System (version 7.11). The sample data rate was 2/second.

Procedure

A stock solution of sodium alkyl sulphonate (1g/L) and Turkey Red Oil (1 g/L) was prepared in deionized water. Stock sample solutions of castor oil (12 g/L), ricinoleic acid (1 g/L), oleic acid (1 g/L), and linoleic acid (1 g/L) were prepared in methanol. All stock solutions were stored at 4 °C to prevent chemical decomposition. These stock solutions of Turkey Red Oil and the fatty acids were then diluted in 0.01 M NaOH, since the real industrial water samples were basic (pH ~ 12). All CE buffers and samples were prepared daily from the stock solutions and ultrasonicated for 20 minutes before use to remove dissolved air. Each day before starting the analysis, the capillary was rinsed with 0.1 M NaOH and water for 5 minutes. Between each run the capillary was flushed with 0.1 M NaOH, water and the running buffer for 1 minute.

The number of theoretical plates N (Kuhn and Hoffstetter-Kuhn, 1993 [2]) for each analyte was calculated using the following equation:

$$N = 5.54 \left[\frac{t'_R}{W_{\frac{1}{2}}} \right]^2 \quad (6.3)$$

The parameters in equation (6.4) are: t'_R is the migration time of the solute, $W_{1/2}$ is the peak width at half height. Electroosmotic mobilities or EOF (μ_{eo}) were calculated using the following equation (6.2) (Kuhn and Hoffstetter-Kuhn, 1993 [2]):

$$\mu_{eo} = \frac{L_T L}{t_{eo} V}$$

The electrophoretic mobilities (μ_{ep}) of solutes were calculated from the following equation (Kuhn and Hoffstetter-Kuhn, 1993 [2]):

$$\mu_{ep} = \mu_{eo} + \frac{L_T L}{t_{ep} V} \quad (6.4)$$

Finally corrected peak area (CPA) is the peak area normalized with respect to the migration time (Peak Area/Migration Time).

6.2.1.2 Gas Chromatography - Mass Spectrometry

For the purpose of comparison of analytical methods, GC-MS studies were performed. These were carried out using a Varian 3400 - Saturn II GC-MS equipped with DB - 5 column (30 m $\times$ 0.25 mm i.d. $\times$ 0.25 μ m film thickness; Chromatographic Specialties, J & W). The GC temperature program included an initial temperature of 150 $^{\circ}$ C, followed by 10 $^{\circ}$ C/min ramp to 200 $^{\circ}$ C, followed by a second ramp of 6 $^{\circ}$ C/min to a final temperature of 300 $^{\circ}$ C, which was held for 3 minutes. The conditions for the injection port include: an injection temperature of 300 $^{\circ}$ C, and an injection volume of 2 μ L. The total analysis time was 26 minutes. For detection purposes a mass selective

detector with electron impact ionization set at a mass range of 50 to 650 AMU was used. These setting were used both for the analysis of sulphonated anionic surfactants as well as sulphonated castor oil.

Procedure

Sulphonated Anionic Surfactants: Analysis of sulphonated castor oil using GC-MS requires a derivatization step using an ion-pairing agent (Field *et al.*, 1992, and Vogel, 1978 [5] [6]). A standard solution of 0.5 M ion-pairing agent tetrabutylammonium hydrogen sulphate ($\text{N}(\text{Bu})_4^+ \text{HSO}_4^-$) was prepared at room temperature. A standard solution of 15 $\mu\text{g}/\text{mL}$ of both surfactants (alkel sodium sulphonate and sulphonated castor oil) was also prepared at room temperature. At this time 0.5 mL of the ion-pairing agent was added to 3 mL of the surfactant solution (15 $\mu\text{g}/\text{mL}$). Subsequently a liquid-liquid extraction using 2 mL of chloroform (CHCl_3) was performed three times by shaking for 30 seconds. The chloroform extracts were then collected, combined and concentrated on a rotary evaporator. This concentrated extract was then dissolved in 1 mL of chloroform and 2 μL of sample injected to the GC-MS equipment for analysis.

6.3 Result and Discussion

6.3.1 Analysis of Alkleen C (Sodium Alkyl Sulphonate)

The analysis by CE of sodium alkyl sulphonate (0.5 g/L), the anionic portion of Alkleen C was carried out using the same procedure as described by Heinig *et al.*, 1996 [7]. The procedure provided in this reference was for the analysis of linear alkyl benzene sulphonates. However, in this study, since the sodium alkyl sulphonates do not contain a benzene ring, direct UV detection can not be used.

The sodium alkyl sulphonates are a by-product from a chemical process. This surfactant is a mixture of straight and branched alkyl sulphonates ($C_7 - C_{13}$). Therefore, in this study the detection of these surfactants for the CE analysis was done through indirect UV detection at 214 nm.

Best results were obtained using 100 mM phosphate at pH 6.8 and 5 mM dodecylbenzene sulphonate (DBS) which was added for indirect UV detection. Further, this buffer contained 20 mM α -cyclodextrin and 30% acetonitrile.

Under these conditions several peaks were obtained (Appendix D, Figure (D.1)). The GC-MS studies using the ion-pairing agent (Field *et al.*, 1994 [5]) also resulted in several peaks as represented by Figure (D.2) of Appendix D.

As described, the sodium alkyl sulphonate is a mixture of several alkyl sulphonates. Further, there were no internal standards available for this product. As a result, the identification and quantification of each peak was problematic.

Analysis of real industrial water using either method (CE or GC-MS) was not carried out since the fresh process water samples containing the Alkleen C surfactant was not available. The industrial water samples available only contained Turkey Red Oil surfactant; hence method development using CE instrumentation for the analysis of this surfactant was initiated.

6.3.2 Method Development, Analysis of Turkey Red Oil

There are several steps involved with CE method development (Heiger *et al.*, 1997 [8]). Figure (6.4) provides the considerations taken for the analysis of Turkey Red Oil. The first important consideration in this study was the choice of detection. Since the UV detection feature was available on the CE apparatus, it was needed to determine whether the samples contained UV-Vis chromophores.

In the event of lack of an UV absorbing chromophore, it is necessary to add a component to the electrolyte for indirect UV analysis. Other information such as the sample's ionic character (anionic, nonionic and cationic) and its solubility in water is of great importance. This will aid in the choice of buffer and hence further pH and concentration optimization. The choices of experimental conditions such as capillary length, temperature, applied voltage, and injection time in our investigation were made on the bases of literature reviews, as well as preliminary experimental runs. The separation was then further optimized by the addition of buffer additives as well as choosing the best condition (temperature, injection time, voltage). Once the best separation is achieved, experiments on data analysis and reproducibility could be started.

Figure (6.4): CE method development flow chart.

6.3.3 Choice of Separation Conditions

Turkey Red Oil, a product of sulphonation of castor oil, is a complex mixture of sulphonated and non-reacted C₁₈-fatty acids, Table (5.1) (McMurry, 1986 [9]). All components are expected to be anionic in a basic solution due to the dissociation of sulphonic and carboxylic functional groups. As they have similar and high mass-to-charge ratio, their absolute mobilities are less than the electroosmotic flow (EOF), resulting in a net mobility towards cathode (normal polarity) in the investigated system. Indirect UV analysis was also performed at 214 nm, using sodium dodecyl benzene sulphonate (SDBSA) as the carrier in the buffer. The indirect UV gave inconclusive results; however, some peaks were observed using direct UV detection. Since most of the components in Turkey Red Oil (Table (5.1)) contain double bonds, direct UV detection at 200 nm was used.

Optimization of the separation was achieved through testing the migration behavior of an alkaline solution of Turkey Red Oil (0.5 g/L). Different variables that affect separation such as electrolyte composition (concentration, pH, addition of modifiers), applied voltage, and temperature were examined with respect to an improvement of peak efficiency, resolution, and achieving the shortest analysis time.

A series of buffers were selected and tested to determine the most suitable electrolyte. The initial concentration of 20 mM for the buffer was chosen since literature studies indicate such buffer concentrations for the separation of fatty acids. All these experiments were performed at 25 °C and an applied voltage of 20 kV. Table (6.1) provides a list of the investigated buffers.

The best results in terms of fast migration time and high resolution were obtained with the Tris buffer at pH 8. The high electrolyte pH values provides high effective electrophoretic mobility of the solutes in the CE analysis.

Figure (6.5): CE analysis of sulphonated castor oil. Capillary of 57 cm $\times$ 75 μ m i.d. (50 cm to detector). Buffer: 20 mM Tris, pH 8, 20 kV, 35 $^{\circ}$ C, 10 second injection, 200 nm direct UV detection.

Under these conditions three peaks could be detected. In addition, the largest peak, presumably ricinoleic acid, was very broad. Using a Tris buffer at pH 7 and pH 9 did not improve the separation. The injection was in the pressure mode for 2 seconds. Further experiments indicated that an injection time of 10 seconds actually provided better

results; hence, this injection time was thus chosen for further analysis. Figure (6.5) provides a sample chromatogram under these conditions.

Table (6.1): Investigated Buffers.

Buffers		Concentration	Observation
Acetate	pH = 4.5	20.0 mM	Slow EOF, castor oil insoluble
Citrate/MES	pH = 6.0		castor oil insoluble
Phosphate	pH = 5.9		Poor resolution and peak separation
	pH = 6.8		"
	pH = 7.2		"
	pH = 8.5		"
Tris	pH = 8.0		<i>Good resolution and Peak separation</i>
Tricine	pH = 8.0		Low resolution
Borate	pH = 9.0		Low sensitivity
MES	pH = 6.0		"

MES (4-morpholineethanesulfonic acid monohydrate).

Tris (hydroxymethyl aminomethane).

Tricine (N-[Tr(hydroxymethyl)methyl]glycine).

A thorough study of the literature on the analysis of sulphonated surfactants as well as fatty acids indicates experimental temperatures ranging from 25 to 40 °C. Temperature investigations indicated that best separations were accomplished at 35 °C. Figure (6.6) and (6.7) are representations of the variations of plate efficiency and mobility changes of the compounds with respect to temperature.

Figure (6.6): Effect of temperature on plate efficiency (N). 20 mM Tris buffer pH 8, 20 kV, 35 °C, 10 second injection, 200 nm direct UV detection.

Figure (6.7): Effect of temperature on mobilities. 20 mM Tris buffer pH 8, 20 kV, 35 °C, 10 second injection, 200 nm direct UV detection.

Figure (6.6) shows that the best plate efficiency was reached at 35 °C, with no further changes at 40 °C. This is partly due to lower buffer viscosity, shorter migration time and lower adsorption of analytes on to the capillary wall. Figure (6.7) indicates that the mobilities of peaks 1, 2 and 3 decreased with increasing temperature. An overall improvement in the separation could be observed at 35 °C as compared to 25 °C. Thus in the subsequent stages of the method development a temperature of 35 °C was used.

6.3.4 Buffer Additives

There are several types of buffer additives normally used in CE analysis. Organic solvents are often added to the buffers in order to enhance the separation of compounds, and in some cases to increase solubilities. However in the case of castor oil (fatty acids), literature studies (Gutnikov *et al.*, 1994 [10]) report that the addition of organic solvents may not be of great advantage. For example, the fatty acids have low or negligible solubilities in acetonitrile.

6.3.4.1 Organic Solvents

Tetrahydrofuran has great solvent capacity but it attacks the latex caps of the CE sample vials. Other reports indicate that the content of the organic solvent in the electrolyte must be kept as low as possible. An increase in the solvent content will result in the lowering of the EOF and hence effects on the migration times of the components (Roland-Assad and Gareil, 1995 [11]).

Attempts to improve separation in the presence of organic solvents were disappointing. Addition of acetonitrile or methanol into the buffer slowed the EOF, and

resulted in longer migration times and broadened peaks without improving the separation. In addition, a slight decrease in the sensitivity of the direct detection at 200 nm was observed in the presence of methanol.

6.3.4.2 Cyclodextrins

The other type of buffer additives are cyclodextrins (CD's). Several types of CD's are commercially available. Here six different CDs with varying cavity sizes and rim substitutions were investigated. Cyclodextrins are well known for their potential to increase the apparent aqueous solubility of low polarity compounds. They can be added to separation buffers to increase the selectivity and efficiency of the CE separation (Kuhn and Hoffstetter-Kuhn, 1993 [2]).

An important characteristic of CDs is their ability to form inclusion complexes with a wide variety of guest molecules. When uncharged cyclodextrins are added to the buffer system, they migrate with the electroosmotic flow. When inclusion complexation occurs between neutral CDs and negatively charged analytes, the electrophoretic mobility of the CD-analyte complexes is lower (shorter migration time) than that of the uncomplexed analyte. The better the molecular fit into the CD cavity, the stronger this complexation, and hence the faster the analytes migrate towards the detector.

Among the CDs tested were the natural α -CD, β -CD, γ -CD. The derivatized CDs were dimethyl- β -CD (DM- β -CD), trimethyl- β -CD (TM- β -CD) and hydroxypropyl- β -CD (HP- β -CD). A total of 5 mM of each of these compounds were added in turn to the aqueous Tris buffer and the peak shapes and the plate efficiencies were analyzed. In the presence of any studied CD, four peaks could be detected.

The addition of CD strongly affected the electrophoretic mobility of two peaks migrating before the last peak. It seems likely that the peak before the largest peak is separated into two peaks. In addition, all these peaks (before the last peak) migrate at the shorter time, which suggests complexation by the studied CDs (Figure 6.8a). The migration time of the last peak was only slightly decreased by addition of any CDs into the Tris buffer. However, in the presence of the substituted cyclodextrins, the number of theoretical plates per meter (N/m) for this peak increased more than 4 times (Figure 6.8b). This is probably due to improved mobility match between the analyte and the background electrolyte.

Among the substituted CDs, the best separation efficiency of the last peak was observed with DM- β -CD (N/m = ~ 45000). However, the shape of other peaks broadened. The overall improvement in all peak shapes was obtained with the addition of HP- β -CD. For further improvements of the separation efficiency, the optimum concentrations of HP- β -CD and a Tris buffer were investigated. The influence of various concentrations of HP- β -CD on the separation efficiency was studied in the range of 2.5 – 12.5 mM.

Figures (6.9 and 6.10) are graphical representations of plate efficiencies and peak mobilities with respect to the concentration of HP- β -CD added to the buffer. Upon increasing the CD concentration, the peak shapes (width at half height) improved continuously with an optimum concentration of 7.5 mM.

Figure (6.8): Effect of various cyclodextrins at a concentration of 5 mM on (a) The electrophoretic mobility of Turkey Red Oil components, (b) The number of theoretical plates per meter of peak 4 (presumably ricinoleic acid). Electrolyte, 20 mM Tris pH 8.0; capillary, 57 cm x 75 μ m (50 cm Effective Length); 10 second injection in the pressure mode; applied voltage (+20 kV); detection direct 200 nm; temperature 35 °C.

Figure (6.9): Effect of HP- β -CD concentration on plate efficiency. 20 mM Tris buffer pH 8, 20 kV, 35 °C, 10 second injection, 200 nm direct UV detection.

Figure (6.10): Effect of HP- β -CD concentrations on the peak mobilities. 20 mM Tris buffer pH 8, 20 kV, 35 °C, 10 second injection, 200 nm direct UV detection.

An increase in migration time for the last peak was observed at this concentration. This indicates that a decrease in EOF is responsible for the observed increase in migration time and that the inclusion is not occurring between this solute and HP- β -CD.

6.3.5 Buffer Concentration

All of the experimental studies carried out used 20 mM Tris buffer at pH 8. However at this point a search for the best buffer concentration was carried out. The best initial guess for the buffer concentration will be between 10-50 mM. At higher buffer concentrations (>50 mM) there will be larger currents, and an EOF will be generated which will result in poor separations. Concentrations lower than 10 mM will not be suitable due to lower currents, lower EOF and longer separation times. Use of higher concentrations of the Tris buffer at pH 8.0 containing 7.5 mM HP- β -C led to slightly better efficiencies; however, an increase in the migration time and electrophoretic current is also observed.

The plate efficiency determination with respect to buffer concentration was found to be at a maximum at 30 mM. Hence, based on the above described results, the highest performance with respect to separation efficiency and analysis time was achieved with 30 mM Tris (pH=8.0) buffer containing 7.5 mM HP- β -CD.

6.3.6 Optimization of Injection Time and Voltage

Optimization of the injection time was carried out while using the optimum buffer concentration of 30 mM Tris pH 8, 7.5 mM HP- β -CD, and 35 °C. The injection times of 2, 5, 10, 15, and 20 seconds were examined; the best injection time was found to be 10

seconds. Higher injection times showed better sensitivity of the separated peaks, but decreased the peak efficiency and peak resolution. A second study was also carried out in order to determine the best applied voltage. The conditions of the buffer were still 30 mM Tris pH 8, 7.5 mM HP- β -CD, 35 °C, and the injection time 10 seconds. The applied voltages of 18, 20, 22, and 24 kV were studied; and the optimum voltage of 20 was chosen. Figure (6.11) provides the optimized chromatogram for the analysis of sulphonated castor oil or Turkey Red Oil ($\approx$ 75% sulphonated).

Figure (6.12) is the representation of the CE chromatogram obtained for the standard solution of castor oil (100% nonsulphonated). Further CE analysis of the standard solutions of the single acids, the major components of castor oil (ricinoleic acid 87%, oleic acid 7%, and linoleic acid 2%), indicate the same retention time as peak 1.

6.3.7 Peak Identification

The identification of the Turkey Red Oil peaks without pure standards is problematic. The only available standards were the Castor Oil and the single fatty acids.

Since castor oil is the complex combination of different C₁₈ fatty acids (Table 5.1), the following assumptions were made. If the sulphonation is with the hydroxyl group and not with the double bonds, sulphonated ricinoleic acid should be detected as a major peak using direct UV detection. Additionally, all castor oil components are supposed be in basic solutions in the form of free acids. As represented by Table (5.1), the major component of castor oil is ricinoleic acid (87%), the only fatty acid bearing an OH group.

Figure (6.11): Optimized chromatogram of sulphonated castor oil. Buffer: 30 mM Tris pH 8, 7.5 mM HP- β -CD, 35 °C, 20 kV and 10 second injection in the pressure mode.

Figure (6.12): CE chromatogram for standard solution of castor oil. Buffer: 30 mM Tris pH 8, 7.5 mM HP- β -CD, 35 °C, 20 kV and 10 second injection in the pressure mode.

The other minor unsaturated acids are linoleic and oleic, which are non-hydroxylated fatty acids. As a result of the above simplified assumptions, four peaks (oleic, linoleic, ricinoleic and sulphonated ricinoleic acids) should be detected with direct UV detection. Saturated acids such as palmitic and stearic acids (minor components) with low UV absorptivity will not be detected with direct UV detection.

The results obtained from the analysis of castor oil (Figure (6.12)) and single fatty acids (no data shown) indicates that all components of castor oil are not resolved under the CE conditions used, and that they migrate almost with the EOF. Thus, Peak 1 in Figure (6.11) belongs to the non-reacted castor oil components.

The largest peak, Peak 4 (Figure (6.11)) probably belongs to the sulphonated ricinoleic acid, because it is not obtained with Castor Oil and the single fatty acids. In addition, Peak 4 migrates at longer migration time (more negative electrophoretic mobility) which indicates an increased negative charge due to the sulphonated group when compared to castor oil components. Peaks 2 and 3 belong to other components of Turkey Red Oil, which at the present time are not identified. Thus, further evaluation of the method was based on the performance of Peaks 1 and 4 as major components of Turkey Red Oil. Peak 1 represents the total non-reacted castor oil content and Peak 4 represents an anionic surfactant.

6.3.8 Performance Characteristics

Special attention was next devoted to the aspects related to method validation, such as linearity, precision and detection limits. The quantitative applicability of the method for the determination of Turkey Red Oil was evaluated at six different concentrations

over the range of 0.05 to 1 g/L. The calibration graphs for Peak 1 and Peak 4, as representative peaks, were established with the corrected peak area. The corrected peak area is the peak area normalized with respect to migration time. Good linearity in terms of corrected peak area response was obtained.

The data for regression analysis of the total Turkey Red Oil and for its Peak 1 and Peak 4 calibration curves are provided in Table (6.2). A linear relationship between corrected peak area and concentration of total components of castor oil was also obtained. It is worth noting that the sensitivity (slope and calibration plots) obtained for the total analysis of castor oil agree well with that obtained for the total Turkey Red Oil (Table 6.2).

Table (6.2): Regression data for the calibration curves.

	Slope (CPA*/Conc.)	Intercept	r²
Peak 1	14.24	0.07	0.9990
Peak 4	31.34	-0.51	0.9979
Total Peak **	52.53	0.01	0.9991
Castor Oil	50.56	0.48	0.9990

*CPA - Corrected Peak Area (Peak Area/Migration Time).

** Total Peak includes all four detected peaks in Turkey Red Oil.

In order to determine the repeatability (within-day precision) of the method, replicate injections (n=18) of 0.5 g/L of the Turkey Red Oil were made. In Table (6.3), the average values and relative standard deviations (R.S.D.s) are given for the migration

time and corrected peak area. Relatively stable migration times (during two days of replicate experiments) were obtained when the capillary was rinsed with sodium hydroxide after each run as described in the experimental section (Figure 6.13).

Table (6.3): Precision of the CE migration time and corrected peak area (CPA).

	Migration Time [min] Mean	R.S.D. [%]	CPA Mean	R.D.S. [%]
Peak 1 ^{a)}	3.96	1.3	7.75	2.5
Peak 4 ^{a)}	7.03	2.3	15.67	4.3
Peak 1 ^{b)}	4.05	0.3	8.35	3.1
Peak 4 ^{b)}	7.32	0.6	15.06	2.1
Peak 1 ^{c)}	3.99	1.5	7.95	4.5
Peak 4 ^{c)}	7.12	2.7	15.47	4.1

a) n = 18 (day 1); ^{b)} n = 9 (day 2); ^{c)} n = 27

However, it was found that the migration time (especially for peak 4) increased over the lifetime of the capillary. The observed variance in migration time between days is probably affected by any changes of the capillary surface that affect the electroosmotic flow. Therefore, it is better to rely on relative migration times, since its reproducibility was found to be much better. Detection limits based on a signal-to-noise ratio of 3 for Peak 1 (total castor oil compounds) and Peak 4 (sulphonated ricinoleic acid) were estimated to be 10 µg/mL and 25 µg/mL, respectively.

(a)

(b)

Figure (6.13): Reproducibility of (a) Migration time and (b) Corrected peak area of 27 replicate injections of 0.5 g/L Turkey Red Oil obtained during two successive days (18 injection for day 1 and 9 injections for day 2). Conditions are the same as Figure (6.11, and 6.12).

6.3.9 Application

The applicability of the developed methods to real industrial process water was next investigated. Process water (Tank 701) and discharge wastewater (Tank 601) samples obtained from BA Banknote Inc. (Ottawa, Canada) were analyzed (Figure (2.1)). The analysis of process samples is important for quality control considerations. Environmental concern is the motivation for the analysis of discharge wastewater.

Figure (6.14) represents a typical electropherogram of the diluted process water (Tank 701) sample. As it can be seen, the process water contains additional components (presumably dyes from the cleaning process) which are well separated from the Turkey Red Oil components. No major matrix interferences were observed with the analysis of Turkey Red Oil spiked in this sample (Figure 6.14a). The recoveries for the two diluted aliquots of the process water spiked with 0.1 g/L and 0.5 g/L of Turkey Red Oil standard were 90% and 106% respectively.

The Turkey Red Oil concentration based on the determination of Peak 4 was found to be 1.6 g/L, which agrees well with that obtained by GC-MS (1.5 g/L) using tetrabutylammonium hydrogen sulphate as an ion pairing agent (results are presented in Appendix E). However, the method sensitivity is not satisfactory to monitor surfactant levels in a waste effluent stream (Tank 601).

Figure (6.14): Electropherogram of twenty five-fold dilution of an industrial water sample from BA Banknote Inc. (Tank 701), (a) Unspiked and (b) Spiked with 0.5 g/L standard Turkey Red Oil. Conditions are the same as in Figure (6.11, and 6.12).

6.4 Conclusions

The analysis of sodium alkyl sulphonate (anionic portion of Alkleen C) was carried out using the CE method developed by Heinig *et al.* 1996 [7]. These CE analyses were done using indirect UV detection by adding dodecylbenzene sulphonate (DBS) to the buffer. Several peaks were observed using this method of analysis, as well as analyses using GC-MS. However, due to the unavailability of the internal standards for this surfactant, peak identification was not possible.

Furthermore, this chapter also described the development and validation of capillary electrophoresis method with direct UV detection for the analysis of Turkey Red Oil components. Successful validation of the method demonstrated acceptable levels of recovery, precision, and detector linearity to monitor surfactant level in a process water. However, the method sensitivity is not satisfactory to monitor surfactant level in a waste effluent stream. Application of solid-phase extraction as a preconcentration step can further lower the detection limits of the developed procedure.

Apart from the already recognized economical advantages such as the rapidity of the separation, the low cost of fused silica capillaries and the negligible consumption of chemicals, CE shows a great potential in the determination of Turkey Red Oil component distribution in Industrial water with no sample preconcentration other than dilution. This makes it an attractive complement/alternative to conventional techniques.

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Chapter 7

7. Conclusions

This chapter provides a summary of the conclusions arrived at from experiments for the pH adjustment of industrial process streams using gases and on a newly developed capillary electrophoresis analytical method for the determination of surfactants in industrial process water of BA Banknote Inc.

7.1 Summary of Conclusions

7.1.1 pH Adjustments

Simple experimental studies using CO₂ gas and compressed air for the purpose of temporary pH adjustment indicate that CO₂ gas can be used successfully to lower the pH of industrial process water. This gas can replace the use of highly corrosive acids such as H₂SO₄. However, in the cases where a temporary pH adjustment was required, there were serious limitations to the use of compressed air to remove carbon dioxide from the solution and hence to raise the pH. Since compressed air contains a small concentration of CO₂ gas, it was thought that this might have affected the reversibility of the process. It

was found that the dyes present in the process streams did not affect the pH reversibility process.

Results on the model solutions ($\text{pH} < 8$) indicated that temporary pH adjustment using these gases is possible, but only in a reasonable time. For solutions with pH above 9, the degassing process becomes very slow.

As expected, gases were less soluble in aqueous solutions at higher temperatures, and an increase in the rate of CO_2 removal from the solution was noted with an increase in temperature. The CO_2 was more soluble in solutions at lower temperatures; therefore, lowering of the pH of solutions was faster at lower temperatures.

A preliminary comparative study of the use of different gases for the purpose of pH adjustment was carried out. It was found that the use of CO_2 gas for this purpose was better as compared to other gases such as SO_2 and NH_3 . The variation of the pH of the solution with these gases was more rapid due to their higher solubilities in aqueous solutions and their pH effects were more difficult to reverse. These gases are also rather toxic, where as CO_2 is not only environmentally friendly but also economically attractive.

An attempt was made to numerically predict the time variation of the concentration of H^+ ion, which was found experimentally at different temperatures. The predictions of this concentration and the other carbonated species in the solution required the values of the rate constants k_d and k_{-d} for dissolution of CO_2 into water. Since these rate constants had not previously been determined, the predictions were done with initial guesses for k_d . Using a computer program modeling the time dependence of pH, k_d could be determined with an error of approximately $\pm 15\%$. However, in the cases where the system is

bubbled with N₂ gas, the predictions of the computer model is slightly different as compared to the experimental data. This is most probably due to some simplifying assumptions.

The apparent activation energy for the forward and reverse reaction of CO₂ (g) $\rightleftharpoons$ CO₂ (aq) was found to be – 47 kJ/mol and – 27 kJ/mol, respectively. Results from mass transfer calculations indicate reasonable agreement with the experimentally determined flux of CO₂ entering the water.

7.1.2 Analysis of Surfactant

The analysis of sodium alkyl sulphonate (the anionic portion of Alkleen C) was carried out using a capillary electrophoresis (CE) method developed using indirect UV detection by adding dodecylbenzene sulphonate (DBS) to the buffer. Several peaks were observed using both methods of analysis (CE and GC-MS); however, no peak identification was possible due to the unavailability of internal standards.

A method using CE with direct UV detection was also developed for the analysis of Turkey Red Oil components. This method demonstrated acceptable levels of recovery, precision, and detector linearity to monitor surfactant level in process water of BA Banknote Inc. However, the method sensitivity is not satisfactory to monitor surfactant levels in a waste effluent stream, which enters the environment. Further improvements in the sensitivity of this method are needed in order to compare the limits of discharge with the ones accepted by the OMEE.

7.2 Future Contributions

There are several other aspects in this research project that would be of interest for further investigation.

7.2.1 pH Adjustments

The process of increasing and decreasing of the pH of solutions using gases could be studied in more detail in order to refine the relations for mass transfer. The suitability of this process could also be examined for other industries where common acids and bases are being used as a means of pH adjustment. The processes by which the rate of solution degassing (removal of CO_2) could be optimized can be investigated. The developed computer model, which predicts the rate of pH change (concentration of H^+ ion) with respect to time, could be further upgraded for the degassing process. In this program, the term used for the concentration of CO_2 (g) is not totally equal to zero. It is actually a combination of the pressure of N_2 and CO_2 gas together. The computer program can also be modified for the solutions with $8 < \text{pH} < 10$. The differential equations within the model can be modified using the appropriate reactions for this pH range to carry out predictions of $[\text{H}^+]$ for these cases. There is also a great potential to make the degassing of CO_2 more rapid.

7.2.2 Analysis of Surfactants

The analysis of Alkleen C was not further investigated since there were no internal standards available for the anionic portion (sodium alkyl sulphonate) of this surfactant. The analysis of Alkleen C using the method developed only gave separation of some of

the peaks. In addition, the industrial process water (BA Banknote Inc.) containing this surfactant was not available since this industry had changed to using Turkey Red Oil surfactant. In a future study, the nonionic portion (nonyl phenol polyglycol) of this surfactant could be analyzed by a CE analytical method already developed (Heinig *et al.* 1996 [6], page 179).

The analysis of Turkey Red Oil surfactant with CE indicated that this method was not sensitive enough for monitoring the levels of this surfactants entering the environment. Methods such as solid-phase extraction can be used as a preconcentration step. This can help to further lower the detection limits of the developed procedure.

Finally, the study of analysis of Alkleen C and Turkey Red Oil surfactants can be extended to the examination of the levels of these surfactant in the sludge which is sent to landfill. The absorption of these surfactants into the soil and their rate of biodegradability is of importance, as is the rate of desorption from soil and movement in the environment.

Appendix A

Calibration of the Rotameter

A Matheson Gas products Rotameter or flow meter (model Matheson Gas Products, Model 7630T-602)) was used to determine the volumetric gas flow rate for pH adjustment studies using gases. The calibration of this rotameter was carried out by passing the gases through the rotameter and then through the bubble flow meter. In this process a timer was used to record the time for different volumes of gas. The calibration conditions were a temperature of 298 K (25 ± 2 °C) and a gas pressure of 1.2 atm.

The volumetric readings for both CO₂ and N₂ gases are provided in Tables (A.1 and A.2). The calibration curves are presented in Figures (A.1 and A.2). The plots are both straight lines and the corresponding equation of the lines are (Q in mL/s):

$$\text{For CO}_2 \text{ gas} \quad Q_{\text{CO}_2} = 0.139 * (\text{index}) - 0.555 \quad (r^2 = 0.99) \quad (\text{A.1})$$

$$\text{For N}_2 \text{ gas} \quad Q_{\text{N}_2} = 0.159 * (\text{index}) - 1.182 \quad (r^2 = 0.99) \quad (\text{A.2})$$

In the course of this research, rotameter readings between 40 and 50 were used. These rotameter readings correspond to gas flow rates of 6.4 mL/s and 6.7 mL/s for CO₂ and N₂ gases respectively.

Table (A.1): Calibration data for the rotameter using CO₂ gas at 298 K ($25 \pm 2^\circ\text{C}$).

Rotameter Reading (± 0.2)	Gas Flow Rate (± 0.2 mL/s)
12	1.5
15	1.7
25	2.9
29	3.4
38	4.7
48	6.3
56	7.5
62	8.4
67	9.0
78	10.4
81	10.9
96	12.5
111	14.7
113	15.2
125	17.0
128	17.5
150	20.7

Table (A.2): Calibration data for the rotameter using N₂ gas at 298 K (25 ± 2°C).

Rotameter Reading (± 0.2)	Gas Flow Rate (± 0.2 mL/s)
4.5	0.62
14	1.3
15	1.9
22.5	2.4
25	2.5
32	3.4
39	4.3
43	5.2
52	6.6
56	7.5
65.5	9.1
76	10.7
80	11.6
86	12.3
93	13.9
98	14.8
109	15.8
115	16.6

Figure (A.1): Calibration curve for the rotameter using CO₂ gas at 298 K (25 ± 2 °C).

Figure (A.2): Calibration curve for the rotameter using N₂ gas at 298 K (25 ± 2 °C).

Appendix B

Temporary pH Adjustment Studies Using Other Gases (SO₂ and NH₃)

A study was carried out in order to investigate the use of gases such as SO₂ and NH₃ for the purpose of temporary pH adjustment. The results are compared to those obtained using CO₂ gas and are presented in Figure (B.1).

As described in section 3.6.6 the Henry's law constant for NH₃ is much higher than for the other two gases SO₂ and CO₂;

$$K_H(\text{NH}_3) \gg K_H(\text{SO}_2) > K_H(\text{CO}_2)$$

As a result, the degassing process for the NH₃ dissolved in water will be slower as shown Figure (B.1). One would expect that the solution would degas after some time (pH decreases). However, by bubbling with N₂ gas this pH did not decrease; on the contrary, it increased.

Figure (B.1): A comparison of pH adjustment using different gases.

Appendix C

Computer Programs for the Determination of Rate Constants in the Carbonated Systems.

This section provides the computer programs (Fortran 77) developed to predict the rate constant k_d and k_{-d} for the carbonated system. In addition, this program predicts the change in concentration of species CO_2 (aq), H_2CO_3 , H^+ and HCO_3^- when bubbling with CO_2 gas (lowering the pH) as well as when sparging with N_2 gas (increasing the pH).

The differential equations which represent the system of temporary pH adjustment using gases (Chapter 4, section 4.6.1) are solved using the numerical method developed by the German mathematicians Runge and Kutta. The fourth order Runge-Kutta method is widely used in computer solutions to differential equations. This method has been used extensively for solving such sets of differential equations efficiently (Gerald and Wheatley, 1989 [18], chapter 4).

```

Cc-----
cc
cc                                CO2 Program
cc
cc    This program will determine the rate constants for carbonated
cc    systems at 297K and an initial guess for kd.
cc
cc    Case: Bubbling with CO2 Gas at 297 K (22 °C), Data analysis
cc
cc    CA(0)=initial concentration of CO2 (aq)
cc    CB(0)=initial concentration of H2CO3
cc    CHO3(0)=initial concentration of HCO3-
cc    CH(0)=initial concentration of H+
cc    t0 = initial time
cc
cc    CA(I)= determined concentration of CO2 (aq)
cc    CB(I)= determined concentration of H2CO3
cc    CHO3(I)=determined concentration of HCO3-
cc    CH(I)= Determined concentration of H+
cc
cc    h= Step Change                      dt= Change in time
cc
cc    The rate constants are:              The equilibrium constants are:
cc    kh = kh          k-h = kmh          K(Henry) = khien
cc    kl = kl          k-l = kml          KW (ionization of H2O) = W
cc    kd = kd          k-d = kmd
cc
cc-----
cc
cc    Implicit Double Precision (A-H, O-Z)
cc    Real kh, kmh, kml, kl, khien, kd, kmd, W, CA0, CA, CB0, CB, h, t0,
cc    +      CH0, CH, CHO30, CHO3, FCA, FCB, FCC
cc
cc    External FCA
cc    External FCB
cc    External FCC
cc
cc    Common /Block1/kd, kmd, kh, kmh, kl, kml
cc    Common /Block2/CB0
cc    Common /Block3/CA0
cc    Common /Block4/CH0
cc    Common /Block5/CHO30
cc    Common /Block6/CH
cc
cc    kh=1.320D0
cc    kmh=624.0D0
cc    kml=4.26e12
cc    khien=3.84e-02
cc    kd=58.4e-04
cc    kmd=(kd/khen) * (1.0+ (kh/kmh) )
cc    kl=(4.14e-07) *kml* ( (kmh/kh)+1.0D0)
cc    W=10** (-14.16690D0)
cc    CA0=0.0D0
cc    CB0=0.0D0
cc    CHO30=0.0D0
cc    CH0=8.93e-08
cc    t0=0.0
cc    h=3.00e-05

```

```

      A0=10000
cc      print1,'kd','kmd'
      print2, kd, kmd
      print3, 'Time (min)', 'CO2(aq)', 'H2CO3', 'H+', 'HCO3-'
      print4, t0, CA0, CB0, CH0, CHO30
cc-----
cc
      Do 10 I=1,2100000
cc
      Call RK4TH1(FCA,t0,h,CA0,CA)
      Call RK4TH2(FCB,t0,h,CB0,CB)
      Call RK4TH3(FCC,t0,h,CHO30,CHO3)
cc
      t0=t0+h
      CA0=CA
      CB0=CB
      CH=CHO3+(W/CH0)
      CHO30=CHO3
      CH0=CH
cc
      A=(A0)*10
      If(I.eq.A) then
        Print4, t0, CA, CB, CH, CHO3
        A0=10000+A0
      EndIf
cc
10      continue
cc
3      format(1x,a10,2x,a12,8x,a5,9x,a3,12x,a5)
4      format(e12.3,2x,e12.3,2x,e12.3,2x,e12.3,3x,e12.3)
1      format(1x,a5,15x,a5)
2      format(2x,e12.3,5x,e12.3)
      stop
      end
cc-----
cc
      Real Function FCA(CA0,t0)
      Implicit Double Precision (A-H, O-Z)
      Real kd,kmd,kh,kmh,k1,kml,CA0,t0,CB0
cc
      Common /Block1/kd,kmd,kh,kmh,k1,kml
      Common /Block2/CB0
cc
      FCA=1.25D0*kd+(kmh*CB0)-(kh+kmd)*CA0
cc
      Return
      End
cc-----
cc
      Real Function FCB(CB0,t0)
      Implicit Double Precision (A-H, O-Z)
      Real kd,kmd,kh,kmh,k1,kml,CA0,t0,CH0,CHO30,CB0
cc
      Common /Block1/kd,kmd,kh,kmh,k1,kml
      Common /Block3/CA0
      Common /Block4/CH0

```

```

Common /Block5/CHO30
cc
      FCB=kh*CA0+(kml*CH0*CHO30)-(kmh+k1)*CB0
cc
      Return
      End
cc-----
cc
      Real Function FCC(CHO30,t0)
cc      Implicit Double Precision (A-H, O-Z)
      Real kd,kmd,kh,kmh,k1,kml,CB0,t0,CH0,CA0
cc
      Common /Block1/kd,kmd,kh,kmh,k1,kml
      Common /Block2/CB0
      Common /Block3/CA0
      Common /Block4/CH0
cc
      FCC=k1*(CB0)-(kml*CH0*CHO30)
cc
      Return
      End
cc-----
cc
      Subroutine RK4TH1(FCA,t0,h,CA0,CA)
      Real FCA,t0,h,CA0,CA,AK1,AK2,AK3,AK4
cc
      AK1=h * FCA(CA0,t0)
      AK2=h * FCA(CA0+AK1/2.0,t0+h/2.0)
      AK3=h * FCA(CA0+AK2/2.0,t0+h/2.0)
      AK4=h * FCA(CA0+AK3,t0+h)
      CA=CA0+(AK1+2.0*AK2+2.0*AK3+AK4)/6.0
cc
      Return
      end
cc-----
cc
      Subroutine RK4TH2(FCB,t0,h,CB0,CB)
      Real FCB,t0,h,CB0,CB,BK1,BK2,BK3,BK4
cc
      BK1=h * FCB(CB0,t0)
      BK2=h * FCB(CB0+BK1/2.0,t0+h/2.0)
      BK3=h * FCB(CB0+BK2/2.0,t0+h/2.0)
      BK4=h * FCB(CB0+BK3,t0+h)
cc
      CB=CB0+(BK1+2.0*BK2+2.0*BK3+BK4)/6.0
cc
      Return
      End
cc-----
cc
      Subroutine RK4TH3(FCC,t0,h,CHO30,CH03)
      Real FCB,t0,h,CHO30,CH03,CK1,CK2,CK3,CK4,CH0,CH
cc
      Common /Block4/CH0
      Common /Block6/CH
cc
      CK1=h * FCC(CHO30,t0)

```

```

      CK2=h * FCC(CHO30+CK1/2.0,t0+h/2.0)
      CK3=h * FCC(CHO30+CK2/2.0,t0+h/2.0)
      CK4=h * FCC(CHO30+CK3,t0+h)
cc
      CHO3=CHO30+(CK1+2.0*CK2+2.0*CK3+CK4)/6.0
cc
      CH=CH0+(CK1+2.0*CK2+2.0*CK3+CK4)/6.0
cc
      Return
      End

```

(April 15th, 1998)

```

Cc-----
cc                                     N2 Program
cc
cc      This program will determine the concentration of species
cc      CO2(aq), H2CO3, H+ and HCO3- for the systems at 297K when
cc      bubble with N2 gas. The determined kd and k-d are the ones
cc      found by the CO2 program..
cc
cc      Case: Bubbling with N2 Gas at 297 K (22 °C), Data analysis
cc
cc      CA(0)=initial concentration of CO2 (aq)
cc      CB(0)=initial concentration of H2CO3
cc      CHO3(0)=initial concentration of HCO3-
cc      CH(0)=initial concentration of H+
cc      t0 = initial time
cc
cc      CA(I)= determined concentration of CO2 (aq)
cc      CB(I)= determined concentration of H2CO3
cc      CHO3(I)=determined concentration of HCO3-
cc      CH(I)= Determined concentration of H+
cc
cc      h= Step Change                      dt= Change in time
cc
cc      The rate constants are:              The equilibrium constants are:
cc      kh = kh          k-h = kmh          K(Henry) = khi
cc      k1 = k1          k-1 = km1          KW (ionization of H2O) = W
cc      kd = kd          k-d = kmd
cc
Cc-----

cc
cc      Implicit Double Precision (A-H, O-Z)
cc      Real kh, kmh, km1, k1, khi, kd, kmd, W, CA0, CA, CB0, CB, h, t0,
cc      +      CH0, CH, CHO30, CHO3, FCA, FCB, FCC
cc
cc      External FCA
cc      External FCB
cc      External FCC
cc
cc      Common /Block1/kd, kmd, kh, kmh, k1, km1
cc      Common /Block2/CB0
cc      Common /Block3/CA0
cc      Common /Block4/CH0
cc      Common /Block5/CHO30
cc      Common /Block6/CH
cc
cc      kh=1.32D0
cc      kmh=624.0D0
cc      km1=4.26e12
cc      khi=3.84e-02
cc      kd=58.4e-04
cc      kmd=(kd/khi) * (1.0D0 + (kh/kmh))
cc      k1=(4.14e-07) * km1 * ((kmh/kh) + 1.0D0)
cc      W=10**(-14.1669D0)
cc      CA0=4.02e-02
cc      CB0=8.50e-05
cc      CHO30=1.25e-04

```

```

CH0=1.25e-04
t0=0.0
h=3.00e-05
A0=5000
cc
    print1,'kd','kmd'
    print2, kd, kmd
    print3, 'Time (min)', 'CO2(aq)', 'H2CO3', 'H+', 'HCO3-'
    print4, t0, CA0, CB0, CH0, CHO30
cc
cc-----
cc
    Do 10 I=1,1800000
cc
        Call RK4TH1(FCA,t0,h,CA0,CA)
        Call RK4TH2(FCB,t0,h,CB0,CB)
        Call RK4TH3(FCC,t0,h,CHO30,CHO3)
cc
            t0=t0+h
            CA0=CA
            CB0=CB
            CH=CHO3+(W/CH0)
            CHO30=CHO3
            CH0=CH
cc
            A=(A0)*10
            If(I.eq.A) then
                Print4, t0, CA, CB, CH, CHO3
                A0=5000+A0
            EndIf
cc
10    continue
cc
3    format(1x,a10,2x,a12,8x,a5,9x,a3,12x,a5)
4    format(e12.3,2x,e12.3,2x,e12.3,2x,e12.3,3x,e12.3)
1    format(1x,a5,15x,a5)
2    format(2x,e12.3,5x,e12.3)
cc
    stop
    end
cc-----
cc
    Real Function FCA(CA0,t0)
    Implicit Double Precision (A-H, O-Z)
    Real kd,kmd,kh,kmh,k1,kml,CA0,t0,CB0
cc
    Common /Block1/kd,kmd,kh,kmh,k1,kml
    Common /Block2/CB0
cc
        FCA=0.0D0*kd+(kmh*CB0)-(kh+kmd)*CA0
cc
    Return
    End
cc-----
cc
    Real Function FCB(CB0,t0)
    Implicit Double Precision (A-H, O-Z)

```



```

      Real kd,kmd,kh,kmh,k1,km1,CA0,t0,CH0,CHO30,CB0
cc
      Common /Block1/kd,kmd,kh,kmh,k1,km1
      Common /Block3/CA0
      Common /Block4/CH0
      Common /Block5/CHO30
cc
      FCB=kh*CA0+(km1*CH0*CHO30)-(kmh+k1)*CB0
cc
      Return
      End

```

```

cc-----
cc
      Real Function FCC(CHO30,t0)
cc      Implicit Double Precision (A-H, O-Z)
      Real kd,kmd,kh,kmh,k1,km1,CB0,t0,CH0,CA0
cc
      Common /Block1/kd,kmd,kh,kmh,k1,km1
      Common /Block2/CB0
      Common /Block3/CA0
      Common /Block4/CH0
cc
      FCC=k1*(CB0)-(km1*CH0*CHO30)
cc
      Return
      End

```

```

cc-----
cc
      Subroutine RK4TH1(FCA,t0,h,CA0,CA)
      Real FCA,t0,h,CA0,CA,AK1,AK2,AK3,AK4
cc
      AK1=h * FCA(CA0,t0)
      AK2=h * FCA(CA0+AK1/2.0,t0+h/2.0)
      AK3=h * FCA(CA0+AK2/2.0,t0+h/2.0)
      AK4=h * FCA(CA0+AK3,t0+h)
cc
      CA=CA0+(AK1+2.0*AK2+2.0*AK3+AK4)/6.0
cc
      Return
      end

```

```

cc-----
cc
      Subroutine RK4TH2(FCB,t0,h,CB0,CB)
      Real FCB,t0,h,CB0,CB,BK1,BK2,BK3,BK4
cc
      BK1=h * FCB(CB0,t0)
      BK2=h * FCB(CB0+BK1/2.0,t0+h/2.0)
      BK3=h * FCB(CB0+BK2/2.0,t0+h/2.0)
      BK4=h * FCB(CB0+BK3,t0+h)
cc
      CB=CB0+(BK1+2.0*BK2+2.0*BK3+BK4)/6.0
cc
      Return
      End

```

```

cc-----
cc
      Subroutine RK4TH3(FCC,t0,h,CHO30,CHO3)

```

```

      Real FCB,t0,h,CHO30,CHO3,CK1,CK2,CK3,CK4,CH0,CH
cc
      Common /Block4/CH0
      Common /Block6/CH
cc
      CK1=h * FCC(CHO30,t0)
      CK2=h * FCC(CHO30+CK1/2.0,t0+h/2.0)
      CK3=h * FCC(CHO30+CK2/2.0,t0+h/2.0)
      CK4=h * FCC(CHO30+CK3,t0+h)
cc
      CHO3=CHO30+(CK1+2.0*CK2+2.0*CK3+CK4)/6.0
cc
      CH=CH0+(CK1+2.0*CK2+2.0*CK3+CK4)/6.0
cc
      Return
      End

```

(April 15th, 1998)

Appendix D

CE and GC-MS Analysis of Surfactant Alkleen C

This appendix provides the capillary electrophoresis (CE) and gas chromatography-mass spectrometry (GC-MS) chromatograms for the surfactant Alkleen C. Since there were no internal standards available for this surfactant, peak identification and quantification was problematic. Figures (D.1) and (D.2) are representations of CE and GC-MS chromatograms respectively.

Since Alkleen C is produced as a by-product of a chemical process, it is a mixture of various branched and non-branched alkyl sulphonate in combination with nonylphenol polyglycol ether (NPPE). Hoeschst Canada Inc. the producer of this surfactant provided a sample of the alkyl sulphonate portion of this surfactant. However, internal standards for each of the alkyl sulphonate (branched or non-branched) was not available. As a result, during the CE analysis of this product several peaks have been obtained between the 5 to 8 minutes run time that can not be identified (Figure (D.1)). The GC-MS analysis of this compound also provided peaks between 6 and 15 minutes of total run time, which could not be identified individually (Figure (D.2)).

NAME
 DATA 20ACD
 METHOD LAS

CHAN LEV REP TYPE DIRECTORY
 A 1 1 Orig C:\GOLD\SYSTEMDATA\OBSA1\
 C:\GOLD\SYSTEM\

TIME DATE
 INJECTION 15:47:34 26 MAR 1997
 ANALYSIS 16:17:38 26 MAR 1997
 REPORT 09:27:17 1 APR 1997

Figure (D.1): CE chromatogram of surfactant Alkleen C.
 100 mM phosphate buffer pH 6.8, 5 mM dodecyl benzenesulfonate,
 20 mM α -cyclodextrin, 30% acetonitrile and indirect UV detection.

Chromatogram Plot

File: C:\ROCID\S1

Date: Jul-15-1997 13:16:05

Comment: S1

Scan No: 300

Retention Time: 5:00

RIC: 0

Mass Range: 0 - 0

Plotted: 300 to 1000

Range: 1 to 1560

100% = 1323487

Figure (D.2): GC-MS chromatogram of surfactant Alkleen C.

Appendix E

GC-MS Analysis of Surfactant Turkey Red Oil, Standard Solutions and Industrial Water

The GC-MS analyses of Turkey Red oil (sulphonated castor oil) are presented in this section. For the analysis of both standard solutions and industrial process water an ion-pairing agent was used. Using the ion pairing agent tetrabutylammonium hydrogen sulfate (Field et al., 1992 [5], page 179), GC-MS analysis gives a concentration of 1.5 g/L of Turkey Red Oil in Tank 701 (Figure 2.1). Analysis of the effluent stream (Tank 601, Figure 2.1) was not successful using this method due to formation of precipitate upon the addition of the ion-pairing agent.

Figure (E.1) represents the GC-MS analysis of a standard solution of Turkey Red Oil. Figure (E.2) provides the GC-MS analysis of Tank 701. In all studies an injection volume of 2 μ L was used. As it could be observed from Figure (E.1), there is only one peak for the ion-paired Turkey Red-Oil at around 16 minutes of run time. When the same analysis procedure was done for Tank (701) a small peak with the same retention time was observed. The quantification of these peaks was done using total ions.

Scan No: 558 Retention Time: 9:10 RIC: 183243 Mass Range: 50 - 282
Plotted: 558 to 1158 Range: 1 to 1568 100% = 626712

Figure (E.1): GC-MS analysis of standard solution of Turkey Red Oil.

Scan No: 552 Retention Time: 9:12 RIC: 94618 Mass Range: 50 - 281
Plotted: 550 to 1150 Range: 1 to 1568 100% = 373845

Figure (E.2): GC-MS analysis of Tank 701.