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Novel Regenerated Solvent Extraction Processes for the Recovery of Carboxylic Acids or Ammonia from Aqueous Solutions
Part I. Regeneration of Amine-Carboxylic Acid Extracts

L.J. Poole* and C.J. King

(*Ph.D. Thesis)

March 1990

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NOVEL REGENERATED SOLVENT EXTRACTION PROCESSES FOR THE RECOVERY OF CARBOXYLIC ACIDS OR AMMONIA FROM AQUEOUS SOLUTIONS

PART I. REGENERATION OF AMINE-CARBOXYLIC ACID EXTRACTS

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by

Loree J. Poole

ABSTRACT

Two novel regenerated solvent extraction processes are examined. The first process has the potential to reduce the energy costs inherent in the recovery of low-volatility carboxylic acids from dilute aqueous solutions. The second process has the potential for reducing the energy costs required for separate recovery of ammonia and acid gases (e.g. CO_2 and H_2S) from industrial sour waters.

The recovery of carboxylic acids from dilute aqueous solution can be achieved by extraction with tertiary amines. An approach for regeneration and product recovery from such extracts is to back-extract the carboxylic acid with a water-soluble, volatile tertiary amine, such as trimethylamine. The resulting trimethylammonium carboxylate solution can be concentrated and thermally decomposed, yielding the product acid and the volatile amine for recycle.

Experimental work was performed with lactic acid, succinic acid, and fumaric acid. Equilibrium data show near-stoichiometric recovery of the carboxylic acids from an organic solution of Alamine 336 into aqueous solutions of trimethylamine. For fumaric and succinic acids, partial

evaporation of the aqueous back extract decomposes the carboxylate and yields the acid product in crystalline form. The decomposition of aqueous solutions of trimethylammonium lactates was not carried out to completion, due to the high water solubility of lactic acid and the tendency of the acid to self-associate.

The separate recovery of ammonia and acid gases from sour waters can be achieved by combining steam-stripping of the acid gases with simultaneous removal of ammonia by extraction with a liquid cation exchanger. The use of di-2,4,4-trimethylpentyl phosphinic acid as the liquid cation exchanger is explored in this work.

Batch extraction experiments were carried out to measure the equilibrium distribution ratio of ammonia between an aqueous buffer solution and an organic solution of the phosphinic acid (0.2N) in Norpar 12. The concentration-based distribution ratios increase from 0.11 to 0.46 as the aqueous phase pH increases from 7.18 to 8.15. Regeneration of the organic extractant solution was carried out by stripping at elevated temperatures to remove the ammonia, with 99% recovery of the ammonia being obtained at 125°C.

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PREFACE

The research presented in this dissertation is a study of two novel regenerated solvent extraction processes. The feasibility of each process is explored through experimental work designed to simulate process steps.

In the first process, carboxylic acids of low volatility are recovered from dilute aqueous solution by extraction with tertiary amines. The organic extract is then regenerated by back-extraction of the acid into aqueous amine solution, followed by thermal decomposition of the alkylammonium carboxylates. The principal applications are for the recovery of organic acids from fermentation broths and waste streams. This process is examined in Chapters 1 through 6.

In the second process, ammonia is recovered from aqueous buffer solutions in the pH range 7.5-9.5 by extraction with an organic liquid cation exchanger. The organic extract is then regenerated by stripping at elevated temperature to remove the ammonia. The principal application is for the treatment of industrial sour waters. This process is examined in Chapters 7 through 12.

PART I. REGENERATION OF AMINE-CARBOXYLIC ACID EXTRACTS

CHAPTER 1. INTRODUCTION

The regeneration of amine-carboxylic acid extracts is a necessary step in the recovery of carboxylic acids from dilute aqueous solutions by extraction with tertiary (e.g., trioctyl) amines. The need to recover carboxylic acids from dilute aqueous solutions arises in many industrial processes. One important example is the production of organic acids by fermentation, in which a major cost is the recovery and purification of the product. Another application is in the processing of aqueous industrial waste or recycle streams.

1.1 Acids Examined

The acids examined in this work are lactic acid, succinic acid, and fumaric acid. Their formulas and properties are given in Table 1-1. These acids were chosen because they have strong potential for being produced commercially by fermentation (1,2,3). In order for large-scale industrial production of these acids by fermentation to be economically feasible, energy efficient process schemes for recovery of the acids from the broth must be developed (4,5,6).

The production of chemicals by fermentation generally results in dilute aqueous solutions of the product; the product is present at less than 10 wt.% concentration, and usually substantially lower (6). The optimum pH for a particular fermentation process varies according to the particular

Table 1-1. Lactic Acid, Succinic Acid, and Fumaric Acid

Acid	Formula	pK_{HA} (7) (at 25°C)	Solubility in H_2O (at 25°C)
Lactic	CH_3-CHOH-COOH	3.85	>11.55 mol/l (8)
Succinic	HOOC-CH_2-CH_2-COOH	4.21, 5.60	0.65 mol/l (9)
Fumaric (*trans*-Butenedioic)	HOOC-CH=CH-COOH	3.10, 4.60	0.048 mol/l (9)

microorganism and substrate used; however, for most fermentations, the pH of the broth must be at or above the first pK_a of the acid.

The recovery of fermentation product organic acids has traditionally been accomplished by the precipitation of the calcium salt of the acid. The salt is formed by the addition of calcium hydroxide to the fermentation broth. The salt crystals precipitate out of solution and are filtered and washed. The salt is then converted to the free acid form by the addition of aqueous sulfuric acid. Calcium sulfate precipitates out of solution and is removed by filtration. The aqueous solution containing the free organic acid is then purified by techniques such as carbon treatment and ion exchange. Acid crystals are recovered from the purified solution upon evaporation of the water. (1)

At the present time, citric acid is the only commodity chemical that is primarily manufactured using a fermentation process (10,11). An alternative acid recovery process in which citric acid is extracted from the fermentation broth into an organic amine solution has recently come into large-scale use (11). The organic extract is regenerated by back-extraction of the acid into water at an elevated temperature. Citric acid crystals are then obtained through evaporative crystallization.

There is a large market for citric acid; it is widely used in the food and pharmaceutical industries (3) and is increasingly being used as a detergent builder (12,13,14). In 1981, the U.S. production of citric acid was 235 million pounds (15).

1.1.1 Lactic Acid

Currently, about half of the world production of lactic acid is by fermentation (16). Before 1950, lactic acid was produced in the United States primarily by fermentation (1); after 1950, production shifted to a chemical synthesis route based on the hydrolysis of lactonitrile (16). Today, the United States imports most of the domestic market demand. In the industrial production of lactic acid by fermentation, concentrations of 12-15 wt.% can be obtained at a pH of between 5 and 7, depending on the microorganism used (16). Lactic acid can be produced at higher concentrations than other fermentation product acids.

More than 50% of all lactic acid produced is used in the food industry, as a food acidulent and as a preservative (16). Lactic acid is also used in the pharmaceutical industry (16) and has potential to be widely used in the manufacture of biodegradable plastics (2,16). The market demand for lactic acid in the U.S. in 1985 was approximately 50 million pounds (2).

1.1.2 Succinic Acid

Succinic acid is not currently being produced commercially by fermentation. Commercial production of succinic acid is generally by the hydrogenation of maleic anhydride or fumaric acid, which are produced by vapor phase oxidation of benzene, butene, or butane with oxygen over V_2O_3 catalyst (3). Currently, all U.S. production is butane-based (17). Studies of

the fermentative production of succinic acid are being carried out in Japan (3,18,19).

Succinic acid is used in the manufacture of foods and pharmaceuticals, as an intermediate in the synthesis of complex organic compounds, and in the manufacture of resins, pesticides, and other products (3). U.S. production of succinic acid is of the order of one million pounds per year (4).

1.1.3 Fumaric Acid

In the past, fumaric acid has been produced by fermentation in the United States (1). At the present time it is produced by the catalytic oxidation of butane in the vapor phase; either directly or by the initial production of maleic acid followed by isomerization to form fumaric acid (3,17). The fermentative production of fumaric acid resulted in solutions of pH 5 to 6.5 with approximately 3.2 wt.% fumaric acid (20).

In the United States, the major uses of fumaric acid are in the manufacture of paper size resins (40% of use), as a food acidulent (20%), and in the manufacture of unsaturated polyester resins (15%). Due to its lower price, fumaric acid (77.5 cents per pound) competes with citric acid (83.5-89.5 cents per pound [21]) as a food acidulent; however, the lower solubility of fumaric acid limits its use. The current U.S. production capacity for fumaric acid is 39 million pounds per year. The market demand in the U.S. in 1988 was approximately 31 million pounds. (22,23)

1.2 Separation from Dilute Aqueous Solution

Separation by conventional distillation is not economically favorable because the carboxylic acids have low volatilities relative to water. Since the acids are present at low concentration, there would be a high energy cost due to the need to vaporize large quantities of water. Furthermore, there would be no separation of the product acid from other high-boiling impurities.

Separation of the acid from aqueous solution by extraction with conventional solvents is difficult because the aqueous-phase activity coefficient of the acid is low due to its hydrophilicity and its ionic character. In previous investigations, extraction by reversible chemical complexation has been found to be a favorable method for the removal of carboxylic acids from dilute aqueous solution (24,25).

1.3 Extraction by Reversible Chemical Complexation

In extraction by reversible chemical complexation, the extractant pulls the solute into the solvent phase by forming a complex with a functional group of the solute. As long as the stoichiometric ratio is favorable, this complex formation often enables a higher distribution ratio of the acid into the solvent phase than can be achieved using extraction with conventional solvents. The extractant is dissolved in an organic solvent or diluent. Diluents which have functional groups can interact with the complex and

affect the distribution ratio of the acid between the aqueous and organic phases.

Long-chain aliphatic amines have been found to be good extractants for carboxylic acids (25,26,27). Alamine 336 (a long-chain tertiary amine, Henkel Corp.) has been used as the extractant in this work because of low water solubility, thermal stability, and commercial availablity. Methyl isobutyl ketone (MiBK) is used as the diluent.

Extraction of an acid by reversible chemical complexation can be described by the following reaction, in which B is the extractant in the organic phase and A is the un-ionized acid (originally present in the aqueous phase):

$$pA\ (\text{aqueous}) + qB\ (\text{organic}) = A_pB_q\ (\text{organic}) \qquad (1\text{-}1)$$

Reversible complexation is driven by the amount of un-ionized acid in the aqueous solution and is therefore favored at low pH, the optimum pH being related to the pK_a of the acid.

The heterogeneous equilibrium constant for the reaction, $K_{p,q}$, can be defined as follows:

$$K_{p,q} = \frac{[A_pB_q]_{org}}{[A]_{aq}^{p}\,[B]_{org}^{q}} \qquad (1\text{-}2)$$

In MiBK diluent, and for the particular acids being examined, carboxylic acid/Alamine 336 complexes with more than one acid molecule per molecule

of amine are formed (24). Table 1-2 gives the values of the equilibrium constants determined by Tamada (24) for the systems examined in this work.

1.4 Regeneration Methods

Once the acid has been extracted into the organic solvent phase, a second step or series of steps is needed to recover the acid in product form and to regenerate the solvent phase so that it can be recycled back to the extractor. Distillation can be used for sufficiently volatile carboxylic acids, such as acetic (25), but is not suitable for the much less volatile acids considered here. Two possible regeneration methods (27) studied in more detail by Tamada (24) involve swings of temperature and/or diluent composition. In these methods, the acid is back-extracted into an aqueous phase by taking advantage of the change in the equilibrium distribution ratio that occurs with changes in temperature and/or composition of the diluent.

1.4.1 Temperature Swing

It has been found that the values of the equilibrium constants decrease with an increase in temperature (24,27). Therefore a process can be run, as shown in Figure 1-1, in which the extraction takes place at ambient temperature and back-extraction into water takes place at a higher temperature. The end-product is a somewhat more concentrated aqueous solution of the acid which can be sent to an evaporative crystallizer. In the production of citric acid by fermentation, recovery of the product can

Table 1-2.
Equilibrium Constants for
Carboxylic Acid/Alamine 336 (0.3M) in MiBK Systems

($K_{p,q}$ values have units of $[mol/l]^{1-(p+q)}$)

	log ($K_{p,q}$) at 25°C				
(p,q) =	(1,1)	(1,2)	(2,1)	(2,2)	(3,1)
Lactic Acid	1.31	---	1.52	---	1.17
Succinic Acid	1.39	---	1.91	---	---
Fumaric Acid	---	4.33	4.81	7.49	---

(from Tamada, 1989)

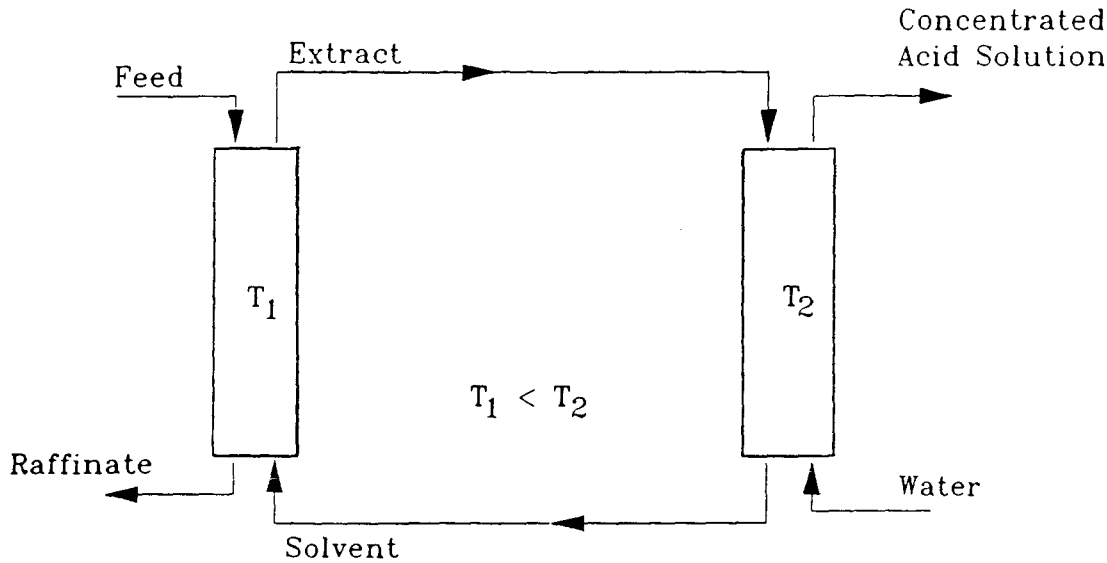


Figure 1-1. Temperature-Swing Regeneration

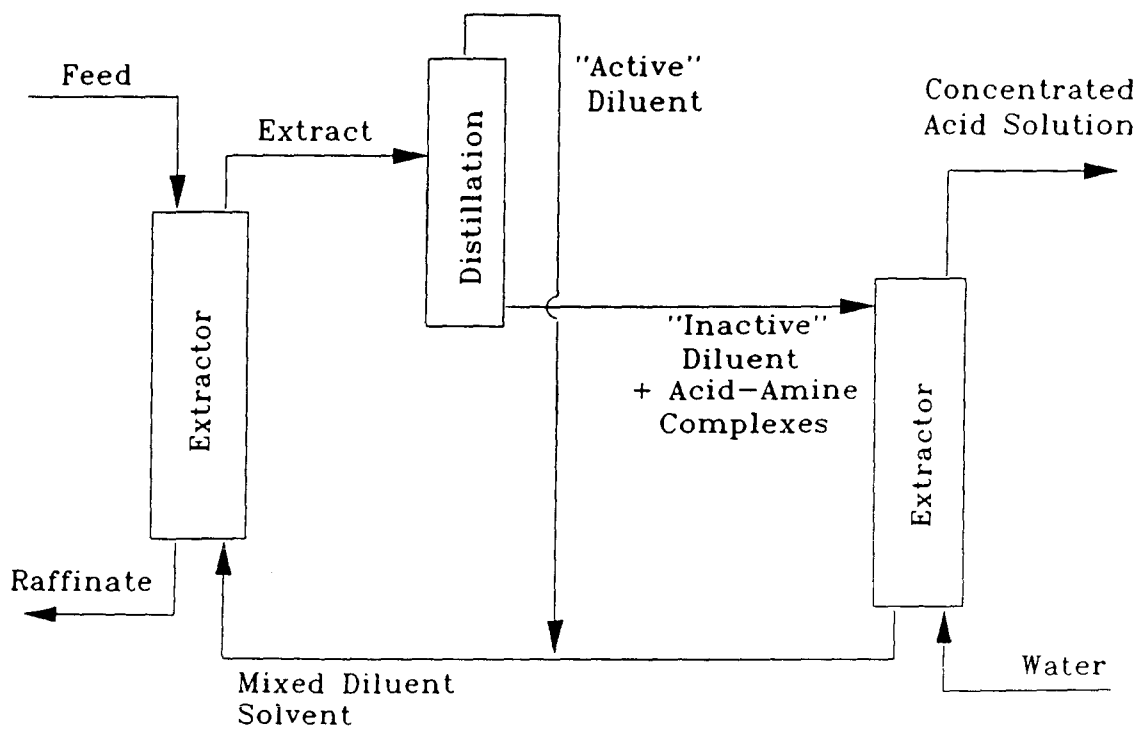


Figure 1-2. Diluent-Swing Regeneration

be obtained by extraction into a solvent mixture of trilaurylamine, n-octanol and a C_{10} or C_{11} isoparaffin, followed by back-extraction of the acid into water at an elevated temperature (27).

1.4.2 Diluent Composition Swing

The type of diluent that is used affects the structures of the complexes that are formed between the acid and the extractant, as well as the values of the equilibrium constants. A change in the composition of the diluent will change the overall equilibrium distribution of the acid between the aqueous and organic phases. In one form of diluent-swing regeneration, as shown in Figure 1-2, the diluent used in the solvent stream entering the extractor is a combination of two components; one that promotes the forward extraction and one that is an inert diluent. When the solvent stream enters the regenerator, the diluent consists of only the inert component. The composition of the diluent is altered between the extractor and the regenerator by use of a distillation column.

A desirable goal for both of these regeneration processes, temperature-swing and diluent-swing, is to increase the concentration of the carboxylic acid in the aqueous phase. The diluent-swing process can incorporate the temperature-swing effects (by running the two columns at different temperatures) to achieve a greater concentration of the acid.

1.4.3 Displacing Acid

Another regeneration alternative is one proposed by Rückl et. al. (28) for the recovery of citric acid. A tertiary amine extractant in an organic diluent is used to extract citric acid from an aqueous feed stream. The organic solvent phase containing the citric acid is then contacted in a reextraction column with an aqueous phase containing a volatile acid, e.g., acetic acid. There is a transfer of citric acid and acetic acid between the two phases. The acetic acid is then removed from the solvent phase by distillation and recycled back to the reextraction column. The regenerated solvent phase can be reused to extract citric acid from the aqueous feed stream.

1.4.4 Precipitation

Starr (29) has explored a regeneration method in which extracted acids with low solubility in water, e.g. fumaric acid, are recovered from the organic phase by precipitation from the extract. The organic extract solution is heated and precipitation of the acid occurs as the volatile diluent is driven off.

1.4.5 pH-Swing

Regeneration of amine-carboxylic acid extracts can be achieved by back-extraction of the acid into an aqueous solution of a strong base such as NaOH; however, this approach results in a salt of the acid rather than

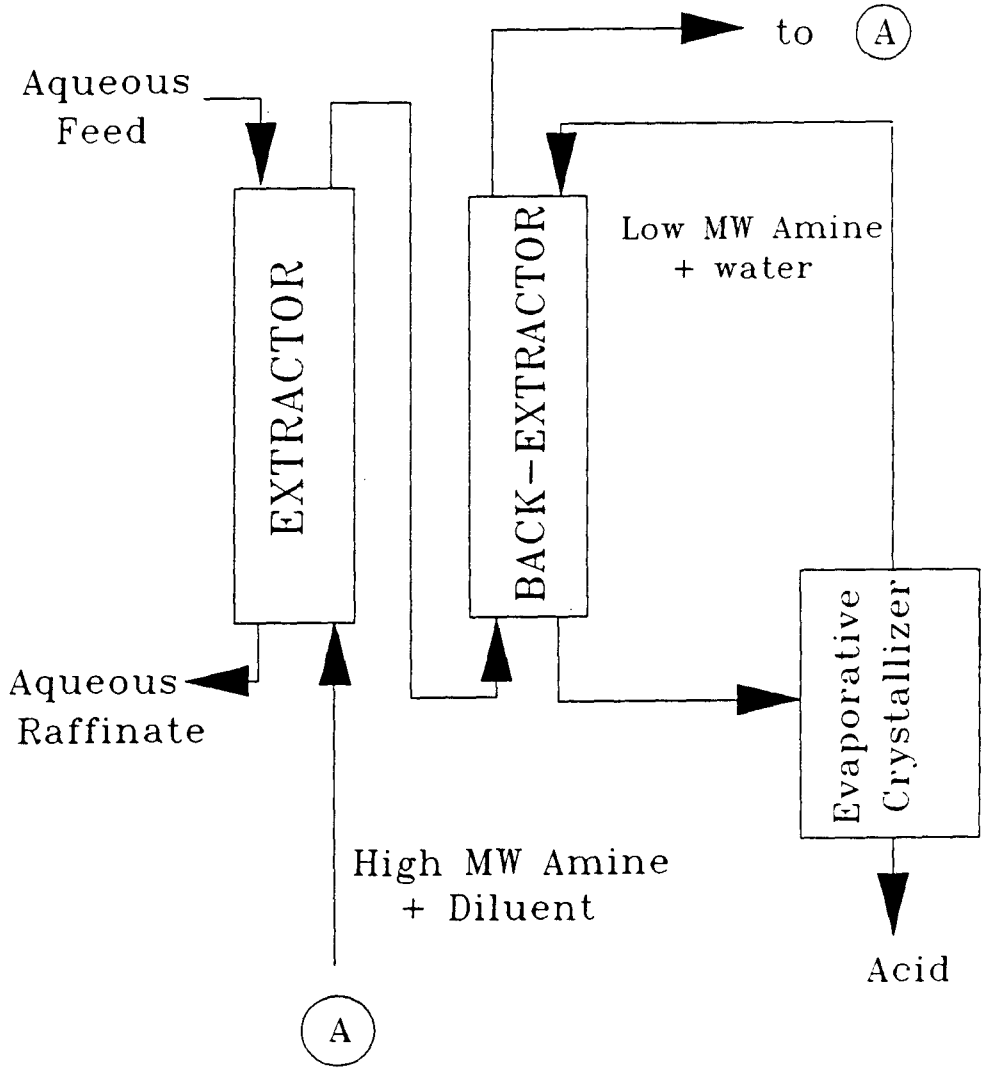
what is usually the desired product of the pure acid. Another acid could be added to the aqueous solution of the salt to convert the salt back to the free acid form. However, this regeneration method has the disadvantages of consuming both an acid and a base and producing a salty waste stream.

1.4.6 pH-Swing with a Volatile Base

In this work, a regeneration method involving recycle of a volatile base is examined. As shown in Figure 1-3, the acid is back-extracted from the loaded organic phase into an aqueous trimethylamine solution. The aqueous solution of the trimethylammonium salt is then heated to drive off the water and the trimethylamine, leaving the acid in crystalline form. Trimethylamine can then be recycled, thereby avoiding costs for make-up chemicals and disposal of by-products.

In order to determine the feasibility of this regeneration method, experiments were carried out in three areas. The results of experiments in which the acids were back-extracted from organic amine solutions into aqueous solutions of trimethylamine are discussed in Chapter 4. Chapter 5 discusses the results of concentration and heating experiments in which the water and trimethylamine are driven off from aqueous solutions of the trimethylammonium carboxylates, as well as the work done in washing and further purification of the crystalline acid product. The experimental procedures and analytical methods used are described in Chapter 3.

Figure 1-3. Regeneration using Recycle of a Volatile Base



In Chapter 2, the criteria used in selecting trimethylamine as the volatile base to be used in the process are reviewed. In Chapter 6, the economic viability of this regeneration method is examined and compared to that of other regeneration alternatives.

REFERENCES

1. Lockwood, L.B., "Production of Organic Acids by Fermentation", in Microbial Technology, 2nd ed., Vol. 1, Peppler, H.J., and Perlman, D., Eds., Academic Press, Chapter 11, 356-387 (1979).

2. Lipinsky, E.S. and Sinclair, R.G., "Is Lactic Acid a Commodity Chemical?", Chem. Eng. Prog., 26-32 (August, 1986).

3. Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., John Wiley & Sons, New York (1979). "Maleic Anhydride, Maleic Acid, and Fumaric Acid", Vol. 14; "Hydroxycarboxylic Acids", Vol. 13; "Succinic Acid and Succinic Anhydride", Vol. 21.

4. Kertes, A.S. and King, C.J., "Extraction Chemistry of Fermentation Product Carboxylic Acids", Biotech. Bioeng., 28, 269-282 (1986).

5. Nauman, E.B., "An Overview of Biochemical Engineering", in Advanced Biochemical Engineering, John Wiley & Sons, Chapter 1, 1-12 (1987)

6. Busche, R.M., "Recovering Chemical Products from Dilute Fermentation Broths, Biotechnol. Bioeng. Symp. No. 13, John Wiley & Sons, 597-615 (1983).

7. Lange's Handbook of Chemistry, 13th ed., Dean, J.A., Ed., McGraw-Hill, New York (1985).

8. Holten, C.H., Lactic Acid: Properties and Chemistry of Lactic Acid and Derivatives, Verlag Chemie (1971).

9. The Merck Index, 10th ed., Windholz, M., Ed., Merck & Co., Inc., Rahway, New Jersey (1983).

10. Meers, J.L., and Milsom, P.E., "Organic Acids and Amino Acids", in Basic Biotechnology, Bu'Lock, J., and Kristiansen, B., Eds., Academic Press, Chapter 13, 359-383 (1987).

11. National Research Council, "Commercializing Biotechnology", in Separation & Purification, Critical Needs and Opportunities, National Academy Press, Chapter 4, Section 1, 21-28 (1987).

12. "Detergent Newsfront", Chemical Marketing Reporter, p. 25 (Aug. 15, 1988).

13. Boutique, J.P., Nijs-Brams, H., and Fakoukakis, E., "Built Liquid Detergents", Eur. Pat. Appl. EP 212723 A2 (Mar. 4, 1987); Chem. Abstr. Vol. 106, No. 158352h (1987).

14. Flores Luque, V., Cohen, L., and Trujillo, F., "Alternatives to Sodium Tripolyphosphate in Detergent Formulations. I. Replacement by Citric Acid or its Sodium Salt", Ing. Quim., 19(219), 145-149 (1987); Chem. Abstr. Vol. 107, No. 136367k.

15. Ng, T.K., Busche, R.M., McDonald, C.C., and Hardy, R.W.F., "Production of Feedstock Chemicals", Science, 219, 733-740 (Feb. 11, 1983).

16. Vick Roy, T.B., "Lactic Acid", in Comprehensive Biotechnology, Vol. 3, Pergamon Press, Chapter 38, 761-776 (1985).

17. "Maleic Running Full", Chemical Marketing Reporter, p. 3 (Sept. 5, 1988).

18. Sato, M., Nakahara, T., and Yamada, K., "Fermentative Production of Succinic Acid from *n*-Paraffin by *Candida brumptii* IFO 0731", Agri. Biol. Chem., 36, 1969-1974 (1972).

19. Kaneuchi, C., Seki, M., and Komagata, K., "Production of Succinic Acid from Citric Acid and Related Acids by *Lactobacillus* Strains", Appl. Environ. Microbiol., Vol. 54, No. 12, 3053-3056 (1988).

20. Kane, J.H., Finlay, A., and Amann, P.F., "Production of Fumaric Acid", U.S. Patent No. 2,327,191 (Aug. 17, 1943); referenced in Prescott, S.C., and Dunn, C.G., Industrial Microbiology, 3rd ed., McGraw-Hill (1959).

21. "Chemical Prices", Chemical Marketing Reporter, p. 36 (June 5, 1989).

22. "Chemical Profile: Fumaric Acid", Chemical Marketing Reporter (July 3, 1989).

23. "Chemical Profile: Fumaric Acid", Chemical Marketing Reporter (Aug. 11, 1986).

24. Tamada, J.A., "Extraction of Carboxylic Acids by Amine Extractants", Ph.D. Dissertation, Department of Chemical Engineering, University of California, Berkeley (1989). LBL-25571.

25. Ricker, N.L., Pittman, E.F., and King, C.J., "Solvent Extraction with Amines for Recovery of Acetic Acid from Dilute Aqueous Industrial Streams", J. Separ. Proc. Technol., Vol. 1, No. 2, 23-30 (1980).

26. Wardell, J.M. and King, C.J., "Solvent Equilibria for Extraction of Carboxylic Acids from Water", J. Chem. Eng. Data, Vol. 23, No. 2, 144-148 (1978).

27. Baniel, A.M., Blumberg, R., Hajdu, K., "Recovery of Acids from Aqueous Solutions", U.S. Patent No. 4,275,234 (June 23, 1981); Chem. Abstr. Vol. 97, No. 109557 (1982).

28. Rückl, W., Siebenhofer, M., and Marr, R., "Separation of Citric Acid from Aqueous Fermentation Solutions by Extraction-Reextraction Processes", Int. Solv. Extr. Conf. (ISEC '86), Preprints, Vol. III, DECHEMA, Munich, Germany, III-653 to III-658 (1986).

29. Starr, J.N., Chemical Engineering Department, University of California, Berkeley, personal communication (1989).

CHAPTER 2. SELECTION OF THE VOLATILE BASE

This chapter discusses the criteria used in selecting an appropriate volatile base for back-extraction of carboxylic acids. Various classes of low molecular weight amine compounds are examined with respect to the desired characteristics of the volatile base. Low molecular weight tertiary amines possess the desired characteristics, with trimethylamine being suitable for exploratory use in the regeneration process.

2.1 Desired Characteristics

The regeneration method examined in this work involves back-extraction of the acid into an aqueous solution of a volatile base, followed by concentration and thermal decomposition of the resulting salt. The base used must be water-soluble, have a substantially higher volatility than that of the acid, and not form a thermodynamically irreversible bond with the acid. The base must have sufficient basic strength to compete effectively with the organic extractant (Alamine 336) for the acid. The base must be thermally stable at whatever temperature is required to crack the salt.

2.2 Ammonia

Ammonia is a relatively strong (pK_b = 4.75 at 25°C [1]), water-soluble, volatile base. However, the heating of a solution of ammonia and a carboxylic acid results in amide formation (2). Upon further heating, nitrile

formation occurs (3). Shukla et al. (4) prepared lactamide by passing a stream of dry ammonia through molten lactic acid at 150°C:

$$CH_3\text{-}CHOH\text{-}COOH + NH_3 \xrightarrow{150^\circ C} CH_3\text{-}CHOH\text{-}CONH_2 + H_2O \qquad (2\text{-}1)$$

In the present work, lactamide was produced by heating a concentrated aqueous solution of ammonium lactate. An aqueous solution containing 6.28M ammonium lactate was heated at 120°C for 30 minutes. Samples of the solution were analyzed before and after heating by high performance liquid chromatography (HPLC) using an organic acid analysis column (Biorad AMINEX Ion Exclusion HPX-87H) and a differential refractometer detector (Waters, R401). Fifteen percent of the lactic acid was converted to lactamide during the heating process.

Ammonia is therefore not a desirable choice for the volatile base because it forms a covalent bond with the acid. The covalent amide bond can be broken by reaction with nitrous acid (2):

$$R\text{-}CONH_2 + HNO_2 \xrightarrow{H_2SO_4} R\text{-}COOH + N_2 + H_2O \qquad (2\text{-}2)$$

or hydrolysis of the amide can be catalyzed by acid or base under "vigorous conditions" (2,5):

$$R\text{-}CONH_2 \xrightarrow[H_2O]{H_2SO_4} R\text{-}COOH + NH_3 \qquad (2\text{-}3)$$

The first approach consumes nitrous acid and does not regenerate ammonia. The second would be expensive in practice.

2.3 Primary and Secondary Amines

Primary and secondary amines would also react with carboxylic acids to form amides under the anticipated conditions of the regeneration process. Mitchell and Reid (3) formed amides by passing dimethylamine gas through heated aliphatic acids. Again, the production of a covalent bond makes these compounds undesirable for use as the volatile base.

2.4 Tertiary Amines

Tertiary amines cannot form amides with carboxylic acids. Urbas (6,7) discusses the cracking of various trialkylammonium salts, with the tertiary amine being either tributylamine or dicyclohexylmethylamine and the acid being either acetic, propionic, butyric, lactic, or citric acid. Depending on the relative volatilities, either the amine or the acid was driven off from concentrated aqueous solutions of the trialkylammonium salt or from a chloroform extract of the salt.

In the regeneration method examined in this work, the first step is the back-extraction of the acid from the organic solvent phase into the aqueous basic solution. It is desirable that the acid be concentrated during this step. From this standpoint, the best low molecular weight tertiary amine for use in this process is the one which is the most water soluble; i.e., trimethylamine. Trimethylamine is commercially available as a 25 wt.% aqueous solution.

Trimethylamine (TMA) also has the desired characteristics of high volatility (b.p. = 2.9°C [1]), and strong basicity (pK_b = 4.1 at 25°C [8]). The thermal stability of TMA was explored by Kaufman (9) who found that thermal decomposition (loss of a methyl group) occurs above 350°C (9,10). As will be seen, that high a temperature is not required to crack the trialkylammonium salts of TMA and succinic acid or fumaric acid.

In the carboxylic acid recovery process shown in Figure 1-3, TMA is to be recycled from the evaporative crystallizer to the back-extraction column. The evaporative crystallizer should be run under a nitrogen atmosphere and/or at temperatures low enough so that oxidation of TMA will not occur. The conditions under which oxidation of TMA can occur were investigated by Jones and Gesser (10) and Cullis and Waddington (11).

Cullis and Waddington (11) carried out gaseous oxidation of TMA at temperatures of 165°C and 170°C using initial partial pressures of: 100 mm TMA with 100 mm O_2; 50 mm TMA with 250 mm O_2; and other combinations. The reaction products were formaldehyde and dimethylamine. Jones and Gesser (10) carried out the oxidation of TMA at 200°C with initial partial pressures of 50 mm O_2 and 200 mm of an equilmolar mixture of TMA and deuterated TMA.

REFERENCES

1. CRC Handbook of Chemistry and Physics, 65th ed., CRC Press, Inc., Boca Raton, Florida (1984).

2. Streitwieser Jr., A., and Heathcock, C.H., Introduction to Organic Chemistry, Macmillan, New York (1976). "Carboxylic Acids", Chapter 17; "Derivatives of Carboxylic Acids", Chapter 18.

3. Mitchell, J.A., and Reid, E.E., "The Preparation of Aliphatic Amides", J. Am. Chem. Soc., Vol. 53, 1879-1883 (May, 1931).

4. Shukla, V.A., Shroff, J.J., and Srivastava, H.C., "A Convenient Laboratory Technique for the Preparation of α-Hydroxy Acid Amides", Indian J. Chem Educ., Vol. 4, No. 1, 26 (1974).

5. Cox, J.D., and Pilcher, G., Thermochemistry of Organic and Organometallic Compounds, Academic Press, New York (1970). Chapter 6.

6. Urbas, B., "Recovery of Acetic Acid from a Fermentation Broth", U.S. Patent No. 4,405,717 (Sept. 20, 1983).

7. Urbas, B., "Recovery of Organic Acids from a Fermentation Broth", U.S. Patent No. 4,444,881 (Apr. 24, 1984).

8. The Merck Index, 10th ed., Merck & Co., Inc., Rahway, New Jersey (1983).

9. Kaufman, R.G., "The Thermal Decomposition of Trimethylamine", Ph.D. Dissertation, The Catholic University of America (1962).

10. Jones, P.W., and Gesser, H.D., "Formation of Hydrogen from Amine Oxidation and Pyrolysis", Combustion and Flame, Vol. 19, 134 (1972).

11. Cullis, C.F., and Waddington, D.J., "The Gaseous Oxidation of Tertiary Aliphatic Amines, II. Trimethylamine", Proc. Roy. Soc. A, Vol. 246, 91-98 (1958).

CHAPTER 3. EXPERIMENTAL PROCEDURES AND EQUIPMENT

Three types of experiments were performed:

1. experiments in which the acids were back-extracted from organic amine solutions into aqueous solutions of trimethylamine;

2. concentration and heating experiments in which the water and trimethylamine were driven off from aqueous solutions of the trimethylammonium carboxylates; and

3. experiments aimed at washing and further purifying the crystalline acid product.

This chapter describes the experimental procedures and analytical methods used in these experiments.

3.1 Reagents Used

The reagents used and their sources are given in Table 3-1. Distilled water that had been passed through a Milli-Q water purification system (Millipore Corp.) was used to dilute the lactic acid and trimethylamine (TMA) solutions when necessary and to make aqueous solutions of succinic and fumaric acid. The 25 wt.% aqueous TMA solution was stored in the original 3.5 liter glass container at 4°C to prevent volatilization of the TMA. Before each use, the aqueous TMA solution was brought to room temperature, and the TMA concentration was measured by first adding an excess of 6N H_2SO_4 to a 5 ml sample of the TMA solution and then back-titrating with 0.1N NaOH. Methyl red was used as an indicator.

Table 3-1.
Source and Description of Chemicals Used

Compound	Supplier	Description
Alamine 336	Henkel Corp.	3° amine, C_8-C_{10} straight chain
Fumaric acid (crystalline)	Aldrich, Inc.	99% purity
Lactic acid	Mallinckrodt, Inc.	85 wt.% aqueous solution
Methyl isobutyl ketone (MiBK)	Aldrich, Inc.	99.7% purity
Succinic acid (granular)	Mallinckrodt, Inc.	analytical grade
Trimethylamine (TMA)	Aldrich, Inc.	25 wt.% aqueous solution (manufactured by adding 99% anhydrous TMA to water)

3.2 Equipment

High performance liquid chromatography (HPLC) analysis was carried out using a Spectra-Physics SP 8000B chromatograph and a differential refractometer detector (Waters, R401). Either an organic acid analysis column (Biorad AMINEX Ion Exclusion HPX-87H) or a C_{18} Radial-Pak μ-Bondapak column (Waters) contained in a radial compression module (Waters, RCM-100) was used. The mobile phase was 0.01N H_2SO_4.

Gas chromatography (GC) analysis was carried out using a Varian model 3700 chromatograph with an FID detector and a Hewlett-Packard 3390A integrator. Samples (1 μl) were injected into a GC column packed with 5% silicone 0V-17 on acid-washed, DMCS-treated, 80/100 mesh Chromosorb W (Alltech Associates). The column was 5 ft. stainless steel tubing with an outer diameter of 1/8 in. The injector temperature was 290°C. The column temperature was held at 35°C for 2 minutes and then increased to 240°C at a rate of 10°C/min. Nitrogen was used as the carrier gas.

Aqueous phase pH values were determined using an Orion 701A pH meter equipped with an Orion semimicro Ross pH electrode. Flasks containing two-phase extraction systems were placed in a shaker bath--either a Fisher Scientific, Versa-Bath S or a Lab-Line, Orbit Water Bath Shaker.

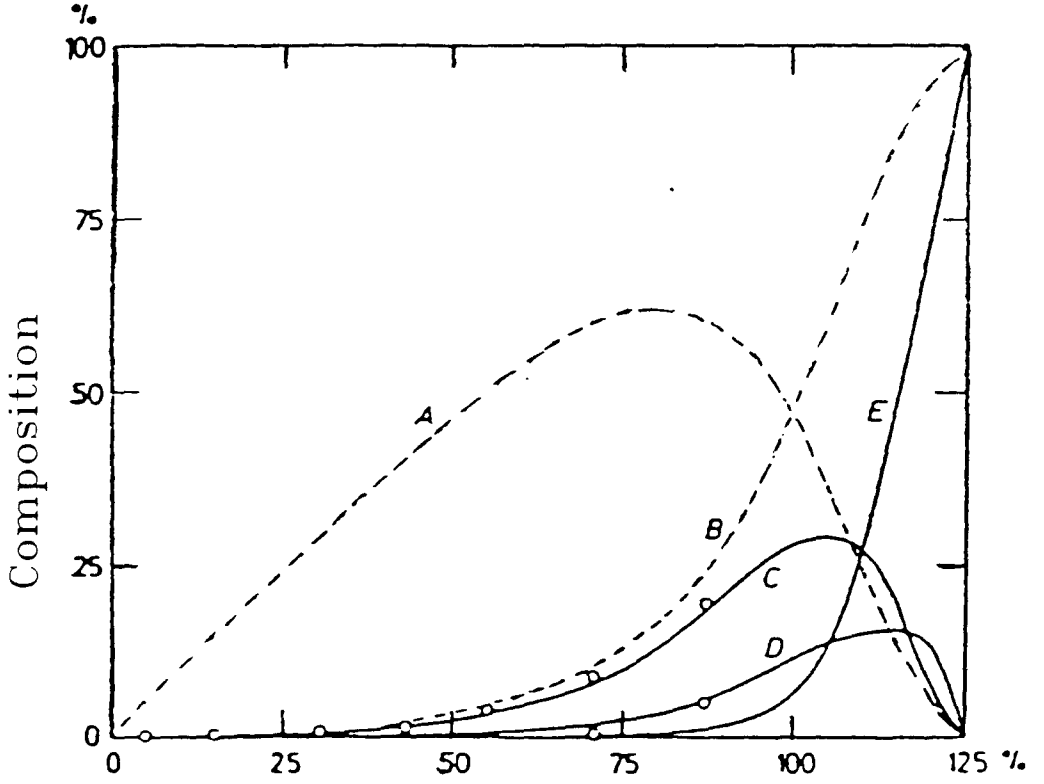
3.3 Dilution and Heating of Aqueous Lactic Acid Solutions

Lactic acid forms intermolecular esters in concentrated aqueous solution. The hydroxyl group on the 2nd carbon reacts with the acidic COOH group of another acid to form lactoyllactic acid. Reaction with additional acid molecules results in polymer formation. Figure 3-1 shows the equilibrium composition of aqueous lactic acid solutions of varying concentrations (1).

Below 20 wt.%, primarily the lactic acid monomer is present. (At 30 wt.% total lactic acid, 0.86 wt.% lactoyllactic acid is present; while at 15 wt.% total lactic acid, only 0.55 wt.% lactoyllactic acid is present.) If an aqueous solution of the monomer is desired, it can be produced by dilution of the 85 wt.% aqueous solution. However, the kinetics of hydrolysis of the esters are slow. It has been found that heating of the diluted solution increases the rate of hydrolysis and that the equilibrium composition can be reached by boiling the freshly diluted solution for 12 hours. (1)

In the present work, 2.0M lactic acid in water was made by dilution of the 85 wt.% aqueous solution. The resulting solution was boiled with total reflux for 12 hours. The complete hydrolysis of the esters was confirmed by HPLC analysis using both the organic acid analysis column and the C_{18} column.

Figure 3-1.
Equilibrium Composition of Aqueous Lactic Acid
(from Holten [1])



Concentration in wt % in terms of equivalent quantities of lactic acid

A: Free lactic acid
B: Total polylactic acids
C: Lactoyllactic acid (dimer)
D: Lactoyllactoyllactic acid (trimer)
E: Sum of higher polylactic acids

3.4 Preparation of Amine-Carboxylic Acid Extracts for use in Back-Extraction Experiments

Before the back-extraction experiments could be performed, it was necessary to prepare the organic amine-carboxylic acid extracts. This was done at 25°C by contacting equal volumes of an aqueous solution of the acid with an organic solution of 0.3M Alamine 336 in methyl isobutyl ketone (MiBK), using the experimental results of Tamada (2) or Starr (3) as a guide to predicting the resultant concentration of acid in the organic phase.

For lactic acid, the two phases were contacted in a separatory funnel and then transferred to Erlenmeyer flasks which were placed in a 25°C shaker bath. The flasks were left in the bath (set at approximately 40 oscillations per minute) for 2 days to allow the phases to settle. Vigorous shaking in a separatory funnel of an aqueous solution of succinic acid with the organic amine solution was found to result in emulsion formation; therefore, for both succinic acid and fumaric acid, the two phases were placed directly in Erlenmeyer flasks. The flasks were put in a 25°C shaker bath set at approximately 80 oscillations per minute for 2 to 3 days to allow transfer of the acid to occur across the interface.

In order to obtain sufficiently high final concentrations of fumaric acid, it was necessary for the amount of fumaric acid present initially to exceed the aqueous solubility limit. Thus, when the flasks were placed in the shaker bath, the aqueous phase contained undissolved fumaric acid crystals. As the fumaric acid was transferred from the aqueous to the

organic phase, these crystals dissolved into the aqueous (bottom) phase.

Upon removal of the flasks from the shaker bath, the phases were separated by removal of each phase by pipet. The pH of the aqueous phase was measured. The amount of acid remaining in the aqueous phase was determined by titration with 0.01N or 0.1N NaOH, using phenolphthalein as an indicator. The concentration of acid in the organic phase was determined by two-phase titration with 0.01N or 0.1N NaOH, using phenolpthalein as an indicator. A blank titration of 0.3M Alamine 336 in MiBK was also performed. Material balances were within 1-2.5%.

3.5 Back-Extraction Experiments

Experiments were carried out in which the acid was back-extracted from the Alamine 336 extract into aqueous solutions of varying TMA concentration. These back-extraction experiments were performed at 25°C. The two phases were contacted in a separatory funnel using an organic to aqueous phase ratio of 8/3 (v/v). The two phases were then transferred to Erlenmeyer flasks. The flasks were placed in a 25°C shaker bath for 2 days to allow the phases to settle.

Upon removal of the flasks from the shaker bath, the phases were separated by pipet. GC analysis of the organic phase was used to determine if any TMA had been transferred from the aqueous to the organic phase, and if so how much. The pH of the aqueous phase was measured, and the concentration of acid in the aqueous phase was determined by

HPLC analysis using the C_{18} column.

The concentration of acid remaining in the organic phase was determined by HPLC analysis of a NaOH extract of the organic phase. The C_{18} column was used. The NaOH extract was obtained by contacting a 5 ml sample of the organic phase with 10 ml of 0.3N, 0.34N or 0.53N NaOH in a centrifuge tube. The two phases were contacted by stirring with a magnetic stir bar. The two phase system was then centrifuged for 30 minutes at 2000 rpm to separate the phases. The NaOH solution was concentrated enough to effect essentially complete transfer of the acid from the organic phase to the aqueous phase, as verified by tests in which acid was back-extracted from organic solutions of known acid concentration.

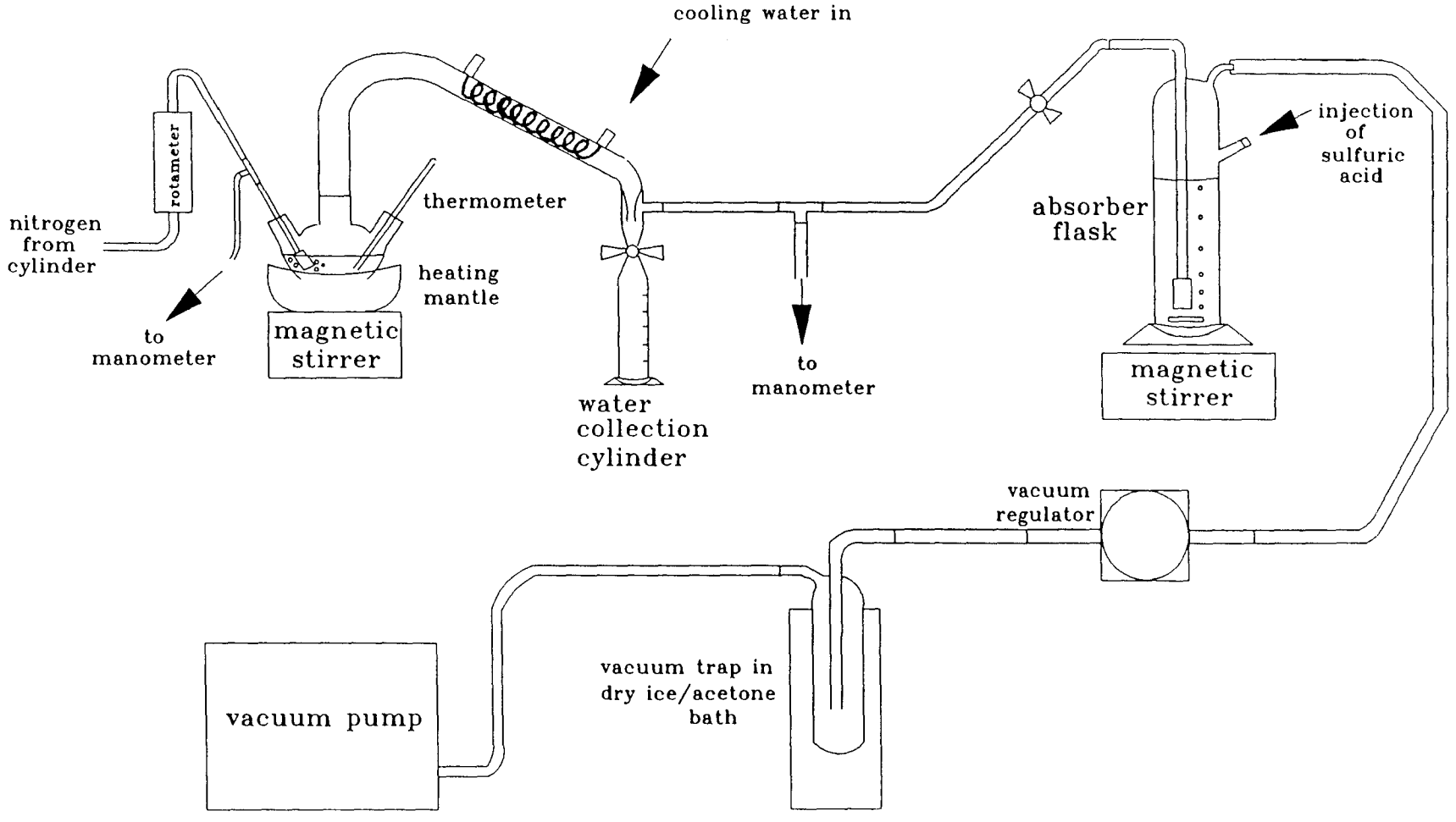
3.6 Concentration and Thermal Decomposition of Alkylammonium Carboxylates

Aqueous solutions of trimethylammonium carboxylates were heated to vaporize the water and TMA and recover the carboxylic acid in crystalline form. The heating was performed under nitrogen to prevent possible oxidation of the TMA. The apparatus used in these experiments is shown in Figure 3-2.

The aqueous solution (60 ml) was placed in a 3-neck 100 ml round-bottom flask and stirred with a magnetic stir bar. The flask was heated using a heating mantle (Glas-Col Apparatus Co.) attached to a voltage regulator (The Superior Electric Co., Powerstat). The water was driven off

Figure 3-2.

Apparatus for Thermal Cracking Experiments



from the solution, and collected in a graduated cylinder. The TMA was collected in an absorber flask containing dilute H_2SO_4.

During the experiment, the rates of evolution of water and TMA were to be determined; therefore, the heating was performed under vacuum to permit separate recovery of water and TMA for data-taking purposes. Under vacuum, after the TMA was removed from solution, it absorbed only slightly (see below) in the water that was present in the condenser and in the graduated cylinder.

At the beginning of an experimental run, the absorber flask was filled with 400 ml of H_2SO_4 concentrated enough to neutralize 10% of the TMA initially present in the aqueous trimethylammonium carboxylate solution. Methyl red was added to the solution to serve as an indicator. When 10% of the TMA had been absorbed, the solution changed in color from red to clear. At this point, the time was recorded and then 5 ml of concentrated H_2SO_4 (80 times the concentration of the initial absorber solution) were injected into the absorber flask, causing the solution to return to red in color. This process was repeated throughout the experimental run.

Nitrogen was bubbled through the aqueous trimethylammonium carboxylate solution. The nitrogen flow rate was measured with a rotameter encased in a plastic shield (Omega Engineering, Inc., model FL-111). To keep the system under vacuum, a General Electric 1/4 hp vacuum pump and a vacuum regulator (Weiss) were used.

Throughout the experimental run, the volume of water collected was recorded, as a function of time. The pressure in the system was monitored with a mercury manometer at two points -- after the rotameter; and after the cylinder used to collect the water. Any fluctuations in the rotameter reading were recorded.

The temperature of the aqueous trimethylammonium carboxylate solution was monitored throughout the run. The temperature was allowed to increase gradually (reflecting the increase in boiling temperature of the solution) until a point was reached when most of the water had been removed. At this point, a sharp increase in temperature was observed. In order to prevent thermal decomposition of the acid itself, the voltage regulator was adjusted as needed to keep the temperature below 130°C.

At the end of the run, a sample of the water collected was titrated with 0.03N H_2SO_4 in order to determine the amount of TMA that had absorbed into the water. When the experiment was conducted under vacuum (absolute pressure of system ranging between 14 and 15 in. Hg), less than 2% of the total TMA was present in the water. A sample of the final absorber solution was titrated with 0.01N or 0.1N NaOH in order to determine the amount of TMA that had been absorbed between the last color change and the end of the experimental run.

The moles of TMA collected versus time, volume of water collected versus time, and nitrogen flow rate were used to determine the partial pressures of water vapor and TMA over the aqueous trimethylammonium

carboxylate solution as functions of temperature and of the concentrations of salt and free acid in solution. These values may be close to equilibrium, but no special efforts were made to assure that. The data were also used to determine rates of TMA and water removal from the solution as functions of time.

3.7 Washing and Further Purification of Acid Crystals

After an experimental run in which a trimethylammonium carboxylate salt (of either succinic acid or fumaric acid) was concentrated and thermally decomposed as described above, there remained behind a mixture-- light-yellow in color -- of acid crystals, water, and residual TMA. Various techniques were used to wash and further purify the crystals.

One method tried was to hold the mixture at 120°C under vacuum for 6 hours, in an attempt to drive off the remaining water and TMA from the mixture. However, this treatment resulted in solidification of the viscous liquid containing the acid crystals. An elemental analysis of this material was carried out to determine its composition and in particular the amount of residual TMA. The amount of residual TMA determined by this method was confirmed by a material balance (i.e., the amount of TMA originally present in the aqueous solution, minus that amount collected in the absorber flask and the water collection flask).

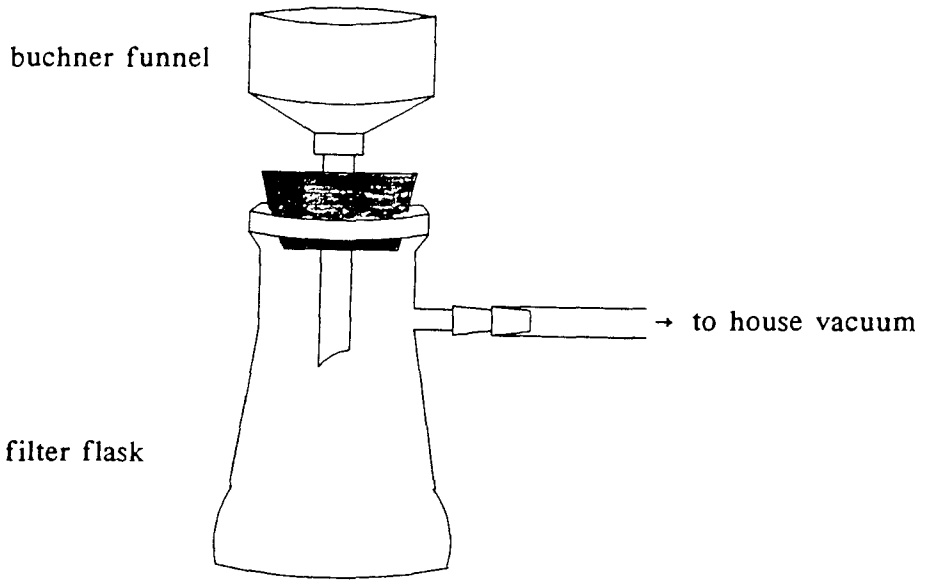
The elemental analysis of the solidified material was conducted by V. Tashinian of the Microanalytical Laboratory, College of Chemistry, at the

University of California, Berkeley. The carbon, hydrogen, and nitrogen contents were measured. The analysis method involved use of a Perkin-Elmer Model 240 Elemental Analyzer in which samples were burned with an excess of oxygen to form CO_2 from carbon, H_2O from hydrogen, and N_2 from nitrogen. The concentrations of these compounds were determined using a thermal conductivity detector.

Another method used to clean the crystals was to wash the mixture with various organic solvents. The mixture was transferred to a piece of filter paper (Whatman, #50) contained in a buchner funnel. The buchner funnel was placed on top of a filter flask as shown in Figure 3-3. The mixture was washed with solvent until the crystals were white in color. The crystals were then dried and weighed and sent to the Microanalytical Laboratory for elemental analysis.

The disadvantage of this washing method was that in order to clean the crystals effectively, it was necessary to use solvents in which the acid had a significant solubility. During the washing process, a portion of the acid crystals dissolved into the solvent and was washed through the filter paper. The solvent was evaporated under vacuum from the solvent/acid mixture present in the filter flask, and then the acid crystals were scraped off the bottom of the filter flask. These crystals were then placed on the filter paper and washed to obtain a subsequent batch of purified crystals. This process had to be repeated up to 6 times (generating 6 separate batches of crystals, each batch weighing between 5-30% of the total acid) in order to obtain a good (greater than 70 wt.%) recovery of the acid in

Figure 3-3.
Equipment used to wash the Acid Crystals



purified crystalline form.

The third, and most successful, method used to treat the crystals was to dissolve the mixture in MiBK, then drive off the solvent, water, and residual TMA by heating under vacuum. The mixture was first dissolved in acetone and then transferred to the filter flask used previously. The buchner funnel was placed on the flask and then the acetone was removed by suction through the vacuum line.

The material (acid, water, and TMA) left behind after the acetone was removed was dissolved in approximately 200 ml of MiBK. The filter flask was placed on a combination heater/stirrer (Thermolyne, Nuova II), and the solution was stirred with a magnetic stir bar. The solution was heated to 80°C, and, as the solvent evaporated, it was pulled through the vacuum line. The crystals that remained after the solvent was removed were dry; there was no visual evidence of water being present. The crystals were collected and sent to the Microanalytical Laboratory for elemental analysis.

REFERENCES

1. Holten, C.H., Lactic Acid: Properties and Chemistry of Lactic Acid and Derivatives, Verlag Chemie, Chapter XI, 192-231 (1971).

2. Tamada, J.A., "Extraction of Carboxylic Acids by Amine Extractants", Ph.D. Dissertation, Department of Chemical Engineering, University of California, Berkeley (1989). LBL-25571.

3. Starr, J.N., Department of Chemical Engineering, University of California, Berkeley, personal communication (1989).

CHAPTER 4. RESULTS OF THE BACK-EXTRACTION EXPERIMENTS

This chapter discusses the experimental results for the back-extraction of lactic, succinic, and fumaric acids from organic extract solutions into aqueous trimethylamine (TMA) solutions. The extract solutions consisted of the acid, the extractant, and the diluent. The extractant was Alamine 336 (Henkel), a tertiary amine with aliphatic chains of 8 to 10 carbons in length, and the diluent was methyl isobutyl ketone (MiBK). During the back-extraction experiments, the concentration of acid in the initial organic phase was held constant while the TMA concentration was varied. For all three acids, essentially 100% of the acid was back-extracted into the aqueous phase at conditions in which there was one molecule of TMA for every equivalent weight of acid. This indicates that the basicity of the aqueous TMA is much stronger than that of the organic Alamine 336.

4.1 Modeling of the Back-Extraction

The back-extraction of the acid from the organic phase into an aqueous solution of trimethylamine can be modeled by solving simultaneously the chemical equilibrium and mass balance equations that describe the system. The chemical equilibrium equations describe the complex formation that occurs in the organic phase as discussed in Section 3 of Chapter 1, and the dissociation of the acid and of TMA in the aqueous phase.

The solubility of the acid in the amine-free diluent can be accounted for by use of the partition coefficient, P, which is defined as follows:

$$P = \frac{\text{concentration of uncomplexed acid in organic phase}}{\text{concentration of un-ionized acid in aqueous phase}} \qquad (4\text{-}1)$$

where both concentrations have units of moles per liter. The partition coefficients for the three acids between water and MiBK are given in Table 4-1.

Table 4-1.
Partition Coefficients for Water/MiBK Systems at 25°C

Acid	P
Lactic	0.11 (1)
Succinic	0.19 (1)
Fumaric	2.2 (2)

The organic solvent phase used in the back-extraction experiments consisted of 0.3M Alamine 336 in MiBK. Acid is present in the organic extract solution as a result of two interactions, acid-diluent and acid-amine. The acid concentration resulting from the acid-diluent interaction is taken to be equal to the product of the partition coefficient, the concentration of un-ionized acid in the aqueous phase, and a correction factor, Φ. The correction factor assumed and used in this work is the volume fraction diluent in the solvent mixture.

4.1.1 Lactic Acid

The back-extraction at 25°C of lactic acid from the organic extract solution into aqueous TMA solutions is described by the following equations:

(i) Equations describing transfer of lactic acid between aqueous and organic phases (1):

$$HA + \overline{A336} = \overline{(HA)A336} \qquad \log K_{1,1} = 1.31 \tag{4-2}$$

$$2HA + \overline{A336} = \overline{(HA)_2A336} \qquad \log K_{2,1} = 1.52 \tag{4-3}$$

$$3HA + \overline{A336} = \overline{(HA)_3A336} \qquad \log K_{3,1} = 1.17 \tag{4-4}$$

$$P_1 = \text{partition of lactic acid between water and MiBK} = \frac{\overline{(HA)}}{(HA)} = 0.11 \tag{4-5}$$

where HA denotes the un-ionized acid, A336 denotes the extractant (Alamine 336), the overbar denotes the organic phase, and the $K_{p,q}$ values are the equilibrium constants of the complex formation as determined by Tamada (1) and listed in Table 1-2.

(ii) Equations describing equilibria in the aqueous phase:

$$HA = H^+ + A^- \qquad -\log K_a = 3.85 \ (3) \tag{4-6}$$

$$R_3NH^+ = R_3N + H^+ \qquad -\log K_a = 9.8 \ (3) \tag{4-7}$$

$$(H^+) + (R_3NH^+) = (A^-) + (OH^-) \tag{4-8}$$

where R_3N denotes TMA and Equation 4-8 describes the charge balance in the aqueous phase. The parentheses in Equations 4-5 and 4-8 denote

concentrations.

The concentration of un-ionized acid in the aqueous phase can be expressed as the product of the total acid in the aqueous phase and the quantity α_1, where:

$$\alpha_1 = \frac{1}{1 + \frac{K_{a,acid}}{(H^+)}} \tag{4-9}$$

Then the mass balance for the lactic acid can be written as follows:

0 =	Total Acid in System	-	Acid in Organic Phase	-	Acid in Aqueous Phase

$$0 = [HA]_{init} - K_{1,1}[B](HA) - 2K_{2,1}[B](HA)^2 - 3K_{3,1}[B](HA)^3$$

$$-\Phi P_1(HA) - WS(HA)/\alpha_1 \tag{4-10}$$

where the first term is the initial concentration of acid in the organic phase, the parentheses denote concentrations in the aqueous phase, the brackets denote concentrations in the organic phase, B denotes the uncomplexed Alamine 336 molecule, Φ is equal to the volume fraction of MiBK (0.85) in the organic solvent, and WS is equal to the water to solvent ratio (3/8) used in the back-extraction experiments.

The mass balance for the Alamine 336 (essentially all present in the organic phase) can be written as follows:

Uncomplexed A336 = Total A336 - Complexed A336

$$[B] = [B_{total}] - K_{1,1}[B](HA) - K_{2,1}[B](HA)^2 - K_{3,1}[B](HA)^3 \qquad (4\text{-}11)$$

or:

$$[B] = \frac{[B_{total}]}{1 + K_{1,1}(HA) + K_{2,1}(HA)^2 + K_{3,1}(HA)^3} \qquad (4\text{-}12)$$

Equation 4-12 can be substituted into Equation 4-10 to give a mass balance for the acid in terms of only two unknown values, the pH of the aqueous raffinate (incorporated into α_1) and the concentration of un-ionized acid in the aqueous phase. A computer program (given in Appendix C) was used to solve the resulting equation for (HA) at set pH values using a Newton Raphson minimization routine.

For each pH value, the recovery of the acid into the aqueous phase was calculated as:

$$\text{Recovery} = \frac{WS(HA)/\alpha_1}{[HA]_{init}} \qquad (4\text{-}13)$$

and the ratio of moles of TMA to moles of acid originally present in the organic phase was calculated where:

$$(R_3N)_{total} = (R_3N) + (R_3NH^+) = (R_3NH^+)/\beta \qquad (4\text{-}14)$$

where:

$$\beta = \frac{1}{1 + \frac{K_{a,R3NH^+}}{(H^+)}} \qquad (4\text{-}15)$$

and the value of (R_3NH^+) is determined using Equations 4-6 and 4-8. In this manner, a theoretical back-extraction curve for lactic acid was generated as shown in Figure 4-1.

4.1.2 Succinic Acid

The back-extraction at 25°C of succinic acid from the organic extract solution into aqueous TMA solutions is described by the following equations:

(i) Equations describing transfer of succinic acid between aqueous and organic phases (1):

$$H_2A + \overline{A336} \rightleftharpoons \overline{(H_2A)A336} \qquad \log K_{1,1} = 1.39 \qquad (4\text{-}16)$$

$$2H_2A + \overline{A336} \rightleftharpoons \overline{(H_2A)_2A336} \qquad \log K_{2,1} = 1.91 \qquad (4\text{-}17)$$

$$P_2 = \text{partition of succinic acid between water and MiBK} = \frac{\overline{(H_2A)}}{(H_2A)} = 0.19 \qquad (4\text{-}18)$$

where H_2A denotes the un-ionized succinic acid, the overbar denotes the organic phase, and the $K_{p,q}$ values are the equilibrium constants of the complex formation as determined by Tamada (1) and listed in Table 1-2.

(ii) Equations describing equilibria in the aqueous phase:

$$H_2A \rightleftharpoons H^+ + HA^- \qquad -\log K_{a1} = 4.21\ (3) \qquad (4\text{-}19)$$

$$HA^- \rightleftharpoons H^+ + A^{2-} \qquad -\log K_{a2} = 5.60\ (3) \qquad (4\text{-}20)$$

$$R_3NH^+ \rightleftharpoons R_3N + H^+ \qquad -\log K_a = 9.8\ \ (3) \qquad (4\text{-}21)$$

$$(H^+) + (R_3NH^+) = 2(A^{2-}) + (HA^-) + (OH^-) \qquad (4\text{-}22)$$

Equation 4-22 describes the charge balance in the aqueous phase. The parentheses in Equations 4-18 and 4-22 denote concentrations.

The concentration of un-ionized succinic acid in the aqueous phase can be expressed as the product of the total succinic acid in the aqueous phase and the quantity α_2, where:

$$\alpha_2 = \frac{1}{1 + \dfrac{K_{a1}}{(H^+)} + \dfrac{K_{a1}K_{a2}}{(H^+)^2}} \qquad (4\text{-}23)$$

Then the mass balance for the succinic acid can be written as follows:

0 =	Total Acid in System	-	Acid in Organic Phase	-	Acid in Aqueous Phase

$$0 = [H_2A]_{init} - K_{1,1}[B](H_2A) - 2K_{2,1}[B](H_2A)^2$$

$$-\Phi P_2(H_2A) - WS(H_2A)/\alpha_2 \qquad (4\text{-}24)$$

where the first term is the initial concentration of acid in the organic phase, the parentheses denote concentrations in the aqueous phase, the

brackets denote concentrations in the organic phase, B denotes the uncomplexed Alamine 336 molecule, Φ is equal to the volume fraction of MiBK (0.85) in the organic solvent, and WS is equal to the water to solvent ratio (3/8) used in the back-extraction experiments.

The mass balance for the Alamine 336 (essentially all present in the organic phase) can be written as follows:

Uncomplexed A336 = Total A336 - Complexed A336

$$[B] = [B_{total}] - K_{1,1}[B](H_2A) - K_{2,1}[B](H_2A)^2 \qquad (4\text{-}25)$$

or:

$$[B] = \frac{[B_{total}]}{1 + K_{1,1}(H_2A) + K_{2,1}(H_2A)^2} \qquad (4\text{-}26)$$

Equation 4-26 can be substituted into Equation 4-24 to give a mass balance for the acid in terms of only two unknown values, the pH of the aqueous raffinate (incorporated into α_2) and the concentration of un-ionized acid in the aqueous phase. A computer program (given in Appendix C) was used to solve the resulting equation for (H_2A) at set pH values using a Newton Raphson minimization routine.

For each pH value, the recovery of the acid into the aqueous phase was calculated as:

$$\text{Recovery} = \frac{WS(H_2A)/\alpha_2}{[H_2A]_{init}} \qquad (4\text{-}27)$$

and the ratio of moles of TMA to moles of acid originally present in the organic phase was calculated where, as before (Equation 4-14):

$$(R_3N)_{total} = (R_3N) + (R_3NH^+) = (R_3NH^+)/\beta \qquad (4\text{-}28)$$

and the value of (R_3NH^+) is determined using Equations 4-19, 4-20, and 4-22 (β was defined in Equation 4-15). In this manner, a theoretical back-extraction curve for succinic acid was generated as shown in Figure 4-2.

4.1.3 Fumaric Acid

The back-extraction at 25°C of fumaric acid from the organic extract solution into aqueous TMA solutions is described by the following equations:

(i) Equations describing transfer of fumaric acid between aqueous and organic phases (1):

$$H_2A + \overline{2A336} \rightleftharpoons \overline{(H_2A)(A336)_2} \qquad \log K_{1,2} = 4.33 \qquad (4\text{-}29)$$

$$2H_2A + \overline{A336} \rightleftharpoons \overline{(H_2A)_2A336} \qquad \log K_{2,1} = 4.81 \qquad (4\text{-}30)$$

$$2H_2A + \overline{2A336} \rightleftharpoons \overline{(H_2A)_2(A336)_2} \qquad \log K_{2,2} = 7.49 \qquad (4\text{-}31)$$

$$P_3 = \text{partition of fumaric acid between water and MiBK} = \frac{\overline{(H_2A)}}{(H_2A)} = 2.2 \qquad (4\text{-}32)$$

where H_2A denotes the un-ionized fumaric acid, the overbar denotes the organic phase, and the $K_{p,q}$ values are the equilibrium constants of the complex formation as determined by Tamada (1) and listed in Table 1-2.

(ii) Equations describing equilibria in the aqueous phase:

$$H_2A \rightleftharpoons H^+ + HA^- \qquad -\log K_{a1} = 3.10\ (3) \tag{4-33}$$

$$HA^- \rightleftharpoons H^+ + A^{2-} \qquad -\log K_{a2} = 4.60\ (3) \tag{4-34}$$

$$R_3NH^+ \rightleftharpoons R_3N + H^+ \qquad -\log K_a = 9.8\ \ (3) \tag{4-35}$$

$$(H^+) + (R_3NH^+) = 2(A^{2-}) + (HA^-) + (OH^-) \tag{4-36}$$

Equation 4-36 describes the charge balance in the aqueous phase. The parentheses in Equation 4-32 and 4-36 denote concentrations.

The concentration of un-ionized fumaric acid in the aqueous phase can be expressed as the product of the total fumaric acid in the aqueous phase and the quantity α_3, where:

$$\alpha_3 = \frac{1}{1 + \dfrac{K_{a1}}{(H^+)} + \dfrac{K_{a1}K_{a2}}{(H^+)^2}} \tag{4-37}$$

where $K_{a,1}$ and $K_{a,2}$ are the acid dissociation constants of fumaric acid, as given in Equations 4-33 and 4-34. Then the mass balance for the fumaric acid can be written as follows:

0 =	Total Acid in System	-	Acid in Organic Phase	-	Acid in Aqueous Phase

$$0 = [H_2A]_{init} - K_{1,2}[B]^2(H_2A) - 2K_{2,1}[B](H_2A)^2 - 2K_{2,2}[B]^2(H_2A)^2$$

$$-\Phi P_3(H_2A) - WS(H_2A)/\alpha_3 \tag{4-38}$$

where the first term is the initial concentration of acid in the organic phase, the parentheses denote concentrations in the aqueous phase, the brackets denote concentrations in the organic phase, B denotes the uncomplexed Alamine 336 molecule, Φ is equal to the volume fraction of MiBK (0.85) in the organic solvent, and WS is equal to the water to solvent ratio (3/8) used in the back-extraction experiments.

The mass balance for the Alamine 336 (essentially all present in the organic phase) can be written as follows:

Uncomplexed A336 = Total A336 - Complexed A336

$$[B] = [B_{total}] - 2K_{1,2}[B]^2(H_2A) - K_{2,1}[B](H_2A)^2 - 2K_{2,2}[B]^2(H_2A)^2 \qquad (4\text{-}39)$$

Equation 4-39 is second order in terms of [B] and can be solved for [B] using the quadratic equation. The positive root of Equation 4-39 is:

$$[B] = \frac{-K_{2,1}(H_2A)^2 - 1}{2\{2K_{1,2}(H_2A) + 2K_{2,2}(H_2A)^2\}} + \frac{\sqrt{\{K_{2,1}(H_2A)^2 + 1\}^2 + 4[B_{total}]\{2K_{1,2}(H_2A)+2K_{2,2}(H_2A)^2\}}}{2\{2K_{1,2}(H_2A) + 2K_{2,2}(H_2A)^2\}} \qquad (4\text{-}40)$$

Equation 4-40 can be substituted into Equation 4-38 to give a mass balance for the acid in terms of only two unknown values, the pH of the aqueous raffinate (incorporated into α_3) and the concentration of un-ionized acid in the aqueous phase. This equation is of the form:

$$f\{pH,(H_2A)\} = 0 \qquad (4\text{-}41)$$

Two computer programs were used sequentially to solve this equation for

(H_2A) at set pH values. In the first program, at a given pH value, the value of the function, f, was calculated for a range of (H_2A) values in order to determine an interval within which the function is equal to zero. The interval is bounded by two (H_2A) values, one that results in a negative value for f and one that results in a positive value for f. In the second program, for the selected pH value, a bisection routine was used to determine the value of (H_2A) within this interval for which f is equal to zero. These two computer programs, "second" and "fumaric", are given in Appendix C.

For each pair of pH and (H_2A) values, the recovery of the acid into the aqueous phase was calculated as:

$$\text{Recovery} = \frac{WS(H_2A)/\alpha_3}{[H_2A]_{init}} \tag{4-42}$$

and the ratio of moles of TMA to moles of acid originally present in the organic phase was calculated where, as before (Equation 4-14):

$$(R_3N)_{total} = (R_3N) + (R_3NH^+) = (R_3NH^+)/\beta \tag{4-43}$$

and the value of (R_3NH^+) is determined using Equations 4-33, 4-34, and 4-36 (β was defined in Equation 4-15). In this manner, a theoretical back-extraction curve for fumaric acid was generated as shown in Figure 4-3.

4.2 Results of the Back-Extraction Experiments

Figure 4-1 shows the experimental data for the back-extraction of lactic acid from a solution of 0.3M Alamine 336 in MiBK into aqueous solutions of TMA. The theoretical curve generated using the computer program is also shown. Essentially complete removal of the acid from the organic phase is achieved when one mole of TMA is present for every mole of acid. There is reasonable agreement between theory and experiment.

Figure 4-2 shows similar results for the back-extraction of succinic acid. Succinic acid is a di-carboxylic acid; complete removal is achieved when two moles of TMA are present for every mole of succinic acid. The data compare favorably with the predicted curve.

The data for the back-extraction of fumaric acid are shown in Figure 4-3. Fumaric acid is a di-carboxylic acid, and complete removal is achieved when two moles of TMA are present for every mole of fumaric acid. Again, the data compare favorably with the predicted curve.

The experimental results for all three acids show that the ionized, aqueous TMA is a much stronger base than the complexing, organic Alamine 336, i.e., the shapes of the curves correspond to the available aqueous TMA pairing stoichiometrically with the back-extracted acid, even when this results in a very low acid concentration in the organic phase.

Figure 4-1.
Back-extraction of Lactic Acid from 0.3M Alamine 336 in MiBK into Aqueous Solutions of Varying TMA Concentration

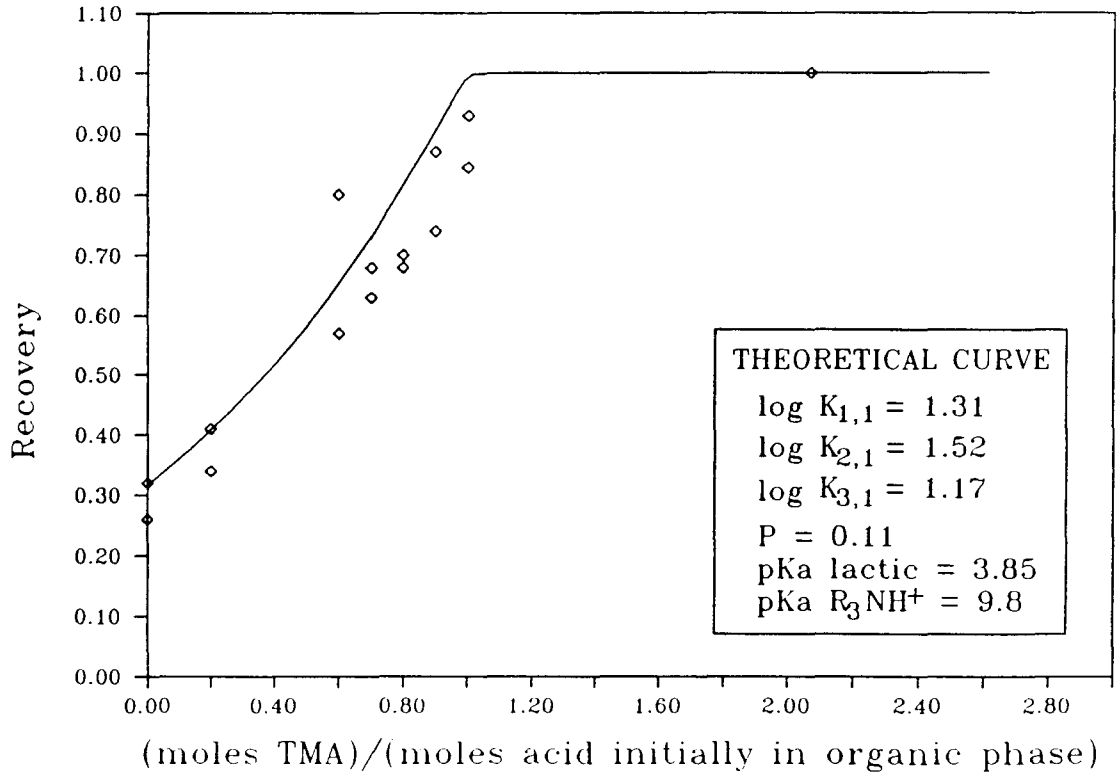


Figure 4-2.
Back-extraction of Succinic Acid from 0.3M Alamine 336 in MiBK into Aqueous Solutions of Varying TMA Concentration

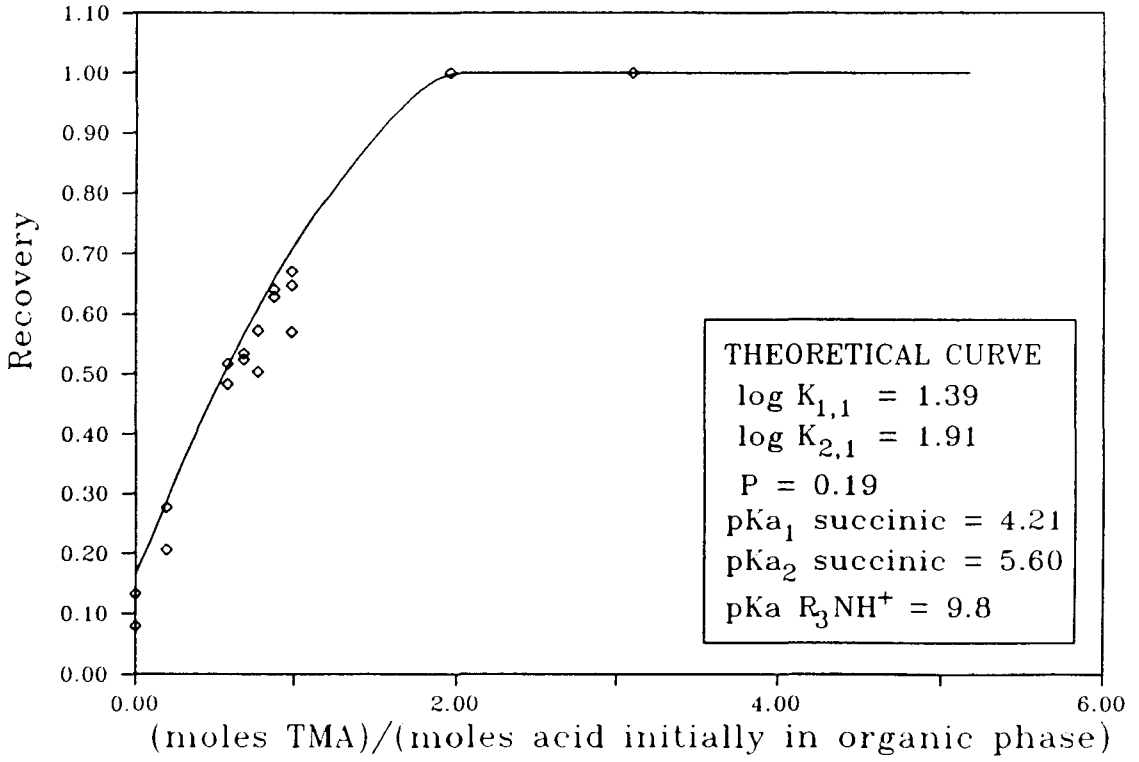
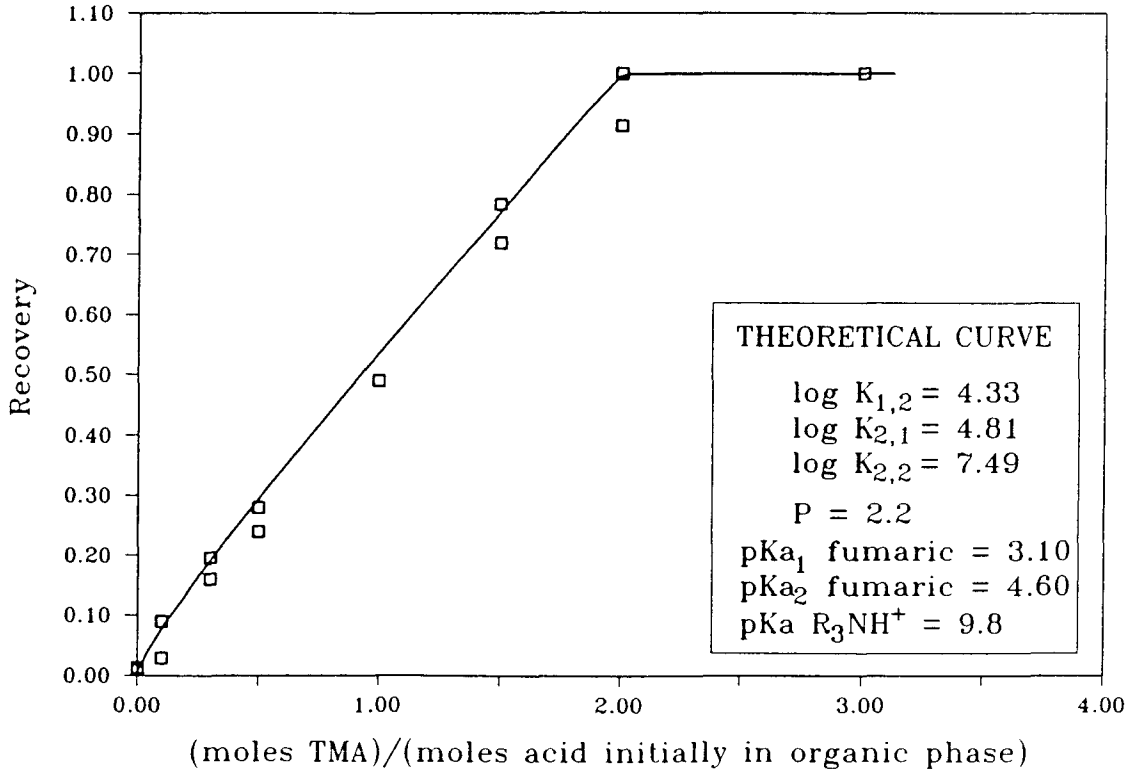


Figure 4-3.
Back-extraction of Fumaric Acid from 0.3M Alamine 336 in MiBK into Aqueous Solutions of Varying TMA Concentration



In the back-extraction experiments, TMA did not partition significantly (greater than 0.0005 wt.%) into the organic phase at molar ratios of TMA to acid less than or equal to the ratio required to achieve 100% removal of the acid from the organic phase. Under these conditions, essentially all of the TMA is ionized and paired with the acid. For example, in an aqueous solution containing 2 moles of TMA for every mole of succinic acid, less than 2 mol.% of the TMA is in the un-ionized form (see results of computer programs, Appendix C). Essentially only the un-ionized TMA will partition into the organic phase.

When TMA was present in excess of the ratio required to achieve 100% removal of the acid from the organic phase, transfer of TMA into the organic phase occurred as shown in Table 4-2; the larger the excess of TMA, the greater the amount transferred into the organic phase.

Table 4-2.
TMA Transferred to Organic Phase

	(moles TMA/moles acid) in system	TMA present in organic phase (wt.%)
Lactic Acid	2.1	2.5
Succinic Acid	3.1	1.4
Fumaric Acid	3.0	0.55

REFERENCES

1. Tamada, J.A., "Extraction of Carboxylic Acids by Amine Extractants", Ph.D. Dissertation, Department of Chemical Engineering, University of California, Berkeley (1989). LBL-25571.

2. Starr, J.N., Department of Chemical Engineering, University of California, Berkeley, personal communication (1989).

3. Lange's Handbook of Chemistry, 13th ed., Dean, J.A., Ed., McGraw-Hill, New York (1985).

CHAPTER 5. RESULTS OF THE THERMAL REGENERATION EXPERIMENTS

This chapter discusses the results of concentration and heating experiments in which water and trimethylamine are driven off from aqueous solutions of trimethylammonium carboxylates. For both succinic acid and fumaric acid, removal of water and trimethylamine was essentially complete, leaving behind the acid in crystalline form. The results of work done to wash and further purify these crystals are also discussed.

5.1 Thermal Regeneration Experiments

As shown in the carboxylic acid recovery process diagram (Figure 1-3), water and trimethylamine (TMA) are to be removed from aqueous solutions of TMA and a low-volatility carboxylic acid. In this final step of the recovery process, complete removal of TMA is desired in order to generate the acid in product form. The regenerated back-extractant (the TMA) is to be recycled within the process. The apparatus used in the thermal regeneration experiments was discussed in Chapter 3, Section 6.

5.1.1 Lactic Acid

As discussed in Chapter 3, Section 3, lactic acid forms intermolecular esters in concentrated aqueous solution. Lactic acid also has a high solubility in water. As an aqueous solution of lactic acid is concentrated by heating, crystalline lactic acid does not precipitate out of solution, but rather the viscosity of the solution increases steadily as polymerization of

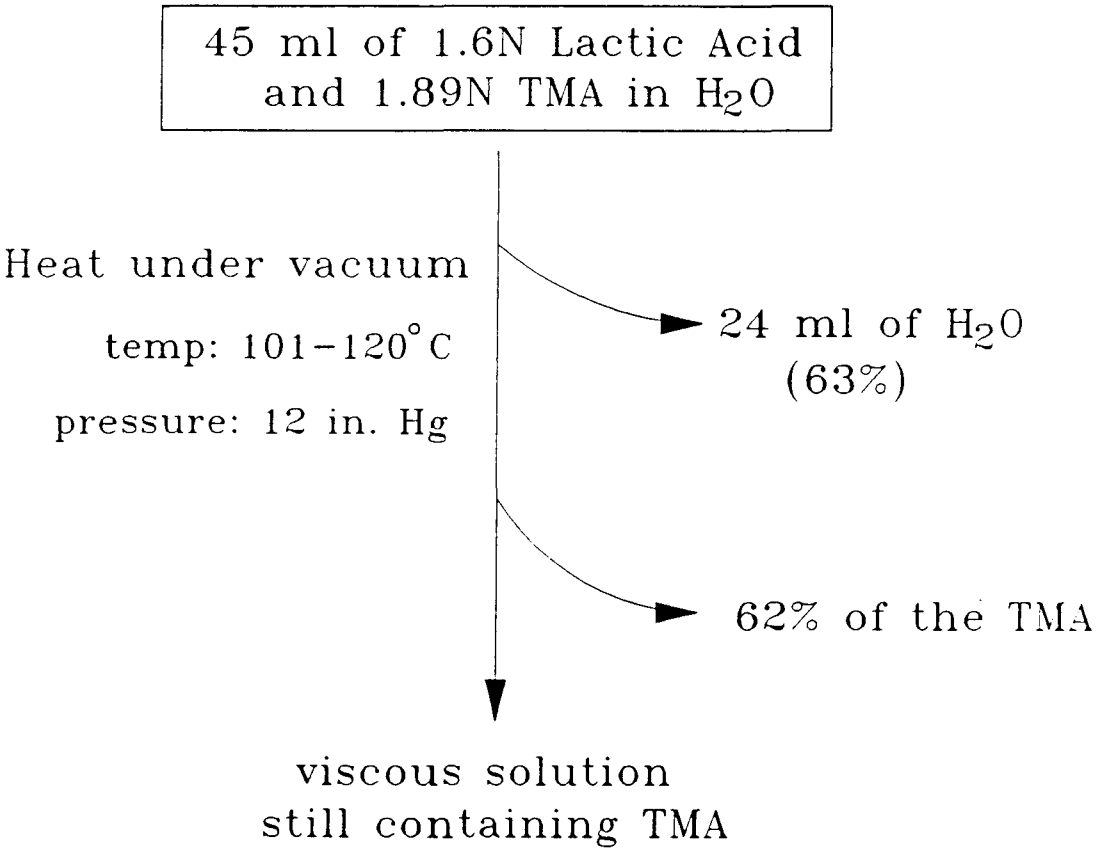
the lactic acid molecules occurs. This effect was illustrated in Figure 3-1.

Crystalline lactic acid is usually obtained by fractional vacuum distillation of the commercial syrup (85-90 wt.% lactic acid) which contains both free lactic acid and polymeric forms (1,2). The free lactic acid is removed overhead in the distillation. The middle fraction is collected and cooled in an ice bath whereupon lactic acid crystals form. If separation of the optical isomers is desired, this crystalline material (or the distillate itself, without prior cooling) is then dissolved in an equal volume of a mixture of equal parts of ethyl and isopropyl ethers (1,2,3). Fractional crystallization separates the less soluble L-lactic acid from the mixture of L- and DL-lactic acid.

Crystalline lactic acid is not thermodynamically stable at room temperature. If held at room temperature, the crystalline acid "will spontaneously commence intermolecular reactions with the formation of water and esters" (1). Lactic acid is offered commercially as aqueous solutions of varying assay strengths. The general assay levels are 44, 50, 80, and 88 wt.% lactic acid (4,5).

In the thermal regeneration experiments carried out with aqueous solutions of trimethylammonium lactate, the goal was to remove essentially all the TMA, leaving behind a concentrated aqueous solution of lactic acid and lactic acid polyesters, similar to the commercial syrup. Figure 5-1 summarizes the results of the experiments. Only 62% of the TMA present in the initial aqueous solution was removed, leaving behind a viscous

Figure 5-1.
Heating of Lactic Acid/TMA/H_2O Solutions



aqueous solution of lactic acid and TMA, and also, no doubt, TMA/lactate and lactic acid polyesters. It is possible that after a large portion of the water and TMA are removed, the formation of intermolecular esters could prevent further TMA removal due to transport limitations. Also, the increasing ratio of lactic acid to TMA in the residue probably serves to suppress the volatility of TMA, because of the chemical interaction between lactic acid and TMA.

5.1.2 Succinic Acid and Fumaric Acid

Figure 5-2a shows the rates of water and TMA removal from an aqueous TMA/succinate salt solution initially containing 2 moles of TMA for every mole of succinic acid. Figure 5-2b shows the temperature rise during the experimental run. The temperature rise initially corresponds to the rise in boiling point of the solution. The temperature is held constant at 112°C at the end of the run, as was discussed in Chapter 3.

Although TMA is more volatile than water, it is held in solution due to complexation or ion-pair formation with the acid. The salt is decomposed when a high enough temperature is reached and/or as crystallization of the acid occurs, driving the decomposition reaction. TMA is released after most of the water has been removed. The extra release of TMA at the start of the experimental run (as shown in Figure 5-2a) occurred because there was a slight excess of TMA present in the initial aqueous solution.

Figure 5-2.
Concentration and Decomposition of a TMA/Succinate Salt
(starting with a 0.6M aqueous solution of the di-salt of the acid)

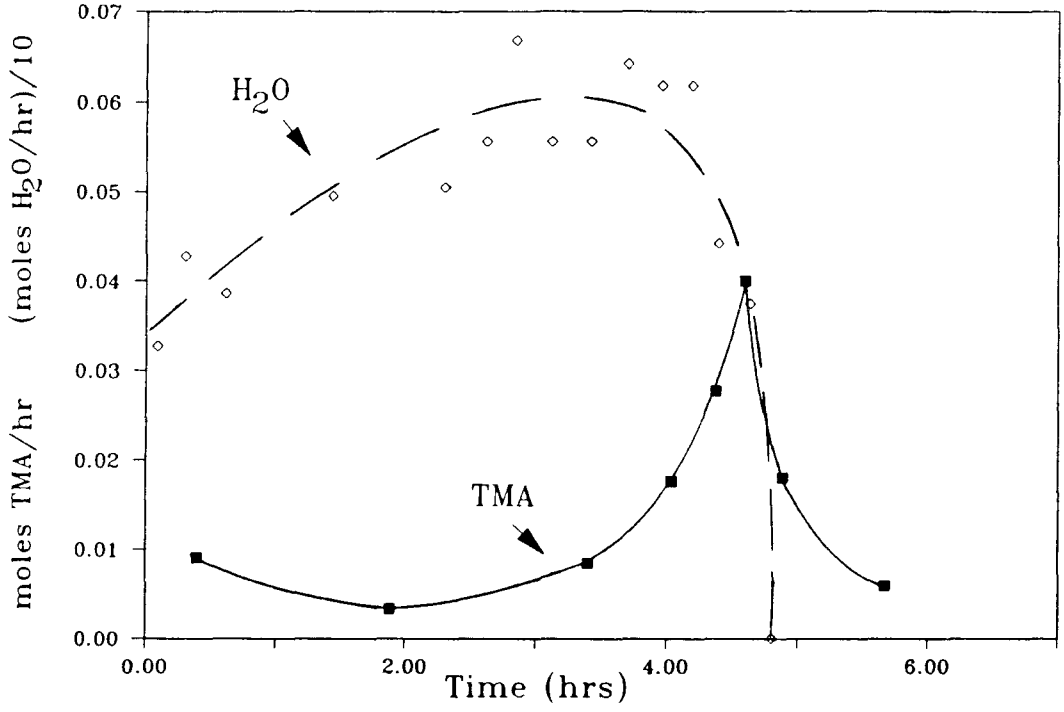


Figure 5-2a. Rate of Removal of H_2O and TMA with Time

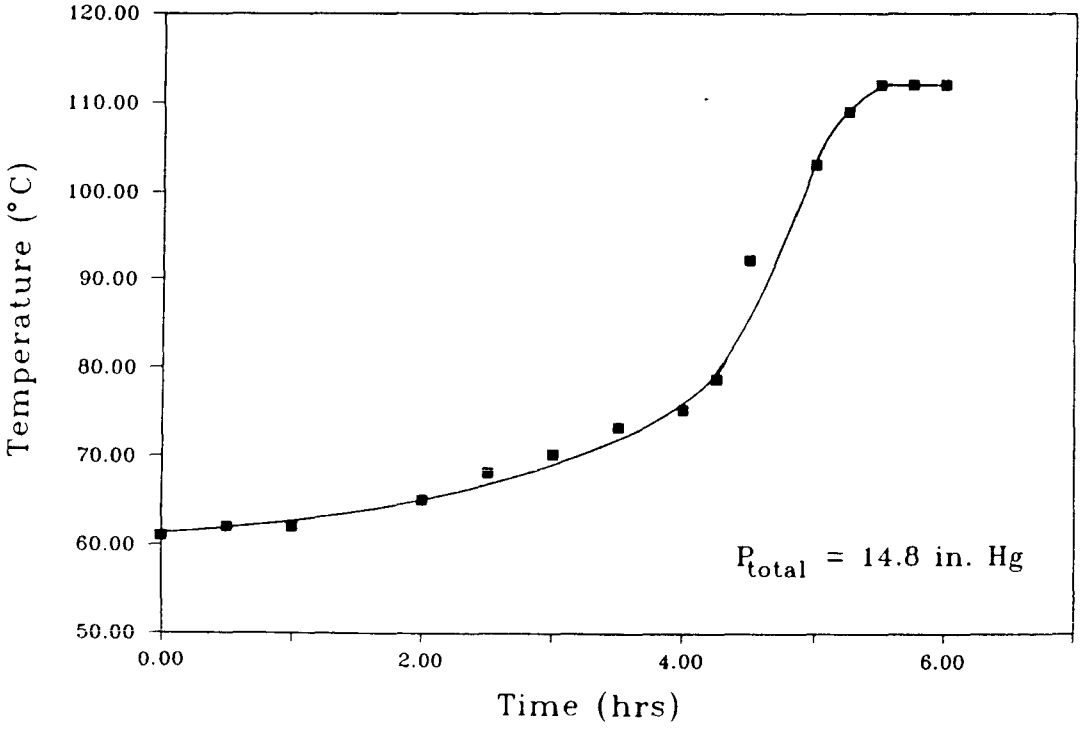


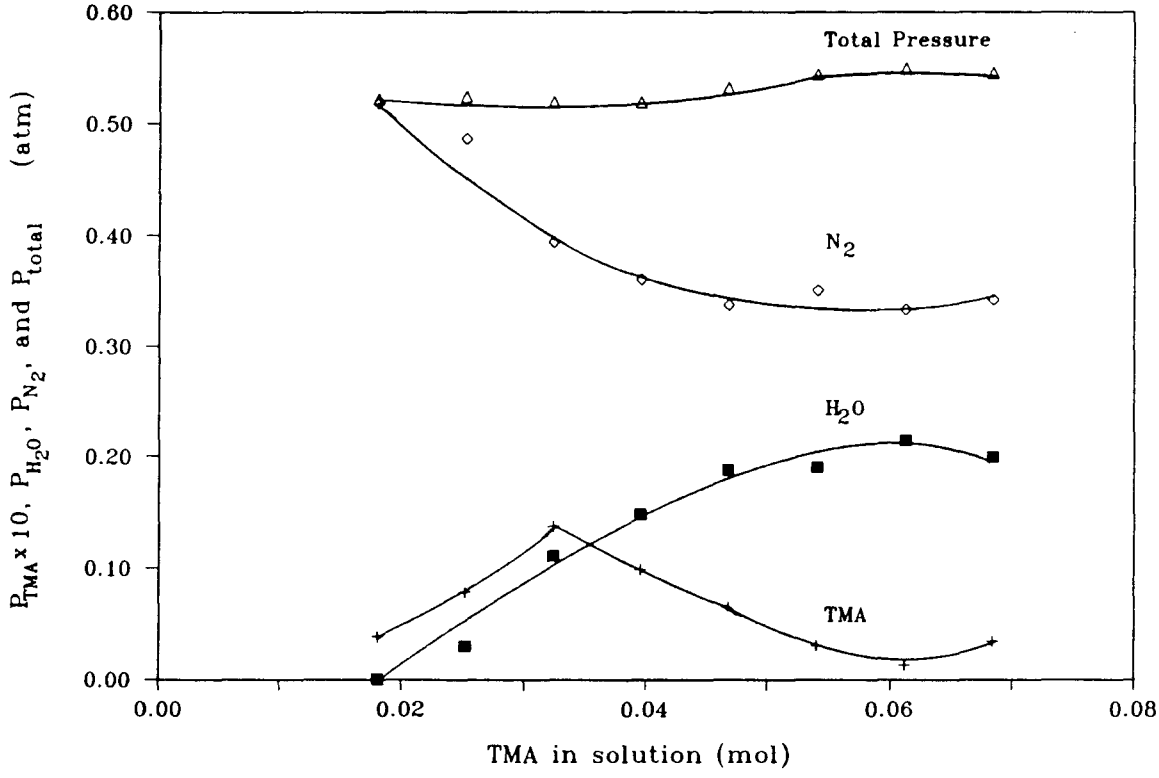
Figure 5-2b. Variation of Temperature with Time

The data shown in Figure 5 are from the fifth experimental run conducted with a TMA/succinate salt solution. The results of all experimental runs are reported in Appendix A. As explained in Chapter 3, experimental run #5 was conducted under vacuum for data-taking purposes. Under these conditions, the solution started boiling at 61°C and at the end of the run, the temperature was held at 112°C. Experimental run #3 was conducted at slightly above atmospheric pressure (1.07 atm), and boiling commenced at 101°C. The temperature in the heating flask at the end of run #3 was equal to 172°C. It is necessary to keep the temperature in the heating flask considerably below the decomposition temperature of the acid (235°C for succinic acid, 230°C for fumaric acid [6]).

The partial pressures of TMA, water, and nitrogen above the solution as a function of TMA left in solution are shown in Figure 5-3. These data are from experimental run #6. The partial pressure values for TMA and water are functions of the nitrogen flow rate used during the experimental run. The nitrogen flow rate used (0.0137-0.0158 moles/min) in experimental runs #5 and #6 was high enough to purge the heating flask continually of vaporized water and TMA.

The rates of water and TMA removal shown in Figure 5-2a are functions of the rate at which heat is supplied to the heating flask. Although the values of the data points shown in Figures 5-2a and 5-3 are functions of the experimental conditions, the order in which water and TMA are vaporized, illustrated in these figures, is a characteristic of the TMA/water/carboxylic acid system.

Figure 5-3.
Partial Pressures above Succinic Acid/TMA/H_2O System during Thermal Regeneration Experimental Run



Figures 5-4a and 5-4b show the results of the thermal regeneration experiments carried out with aqueous solutions of the di-trimethylammonium salt of fumaric acid. As with succinic acid, the TMA is released after most of the water is removed, and again an end-product containing the acid in crystalline form is obtained.

5.2 Washing and Purification of Crystalline Product

At the end of an experimental run in which a salt of TMA and succinic acid or fumaric acid was concentrated and thermally decomposed, there remained in the heating flask a mixture (yellowish in color) of water, acid crystals, dissolved acid, and residual TMA. Various methods described in Chapter 3 were used to wash and further purify the acid crystals. Depending on the washing technique used, recoveries of between 67% and 77% purified succinic acid crystals were achieved.

The first two treatment methods (washing with acetone and chloroform, and washing with acetone and carbon tetrachloride) served to separate the acid crystals from the viscous aqueous solution consisting of TMA and dissolved acid present in roughly equilmolar amounts. The third treatment method -- dissolution of the mixture of solid crystals and aqueous solution into methyl isobutyl ketone (MiBK), followed by evaporation of the MiBK --yielded the highest recovery of succinic acid and was used to treat the fumaric acid crystals. A recovery of 81% of the purified fumaric acid crystals was obtained. With improved washing techniques, it is possible that an even greater percent recovery can be achieved.

Figure 5-4.
Concentration and Decomposition of a TMA/Fumarate Salt
(starting with a 0.1M aqueous solution of the di-salt of the acid)

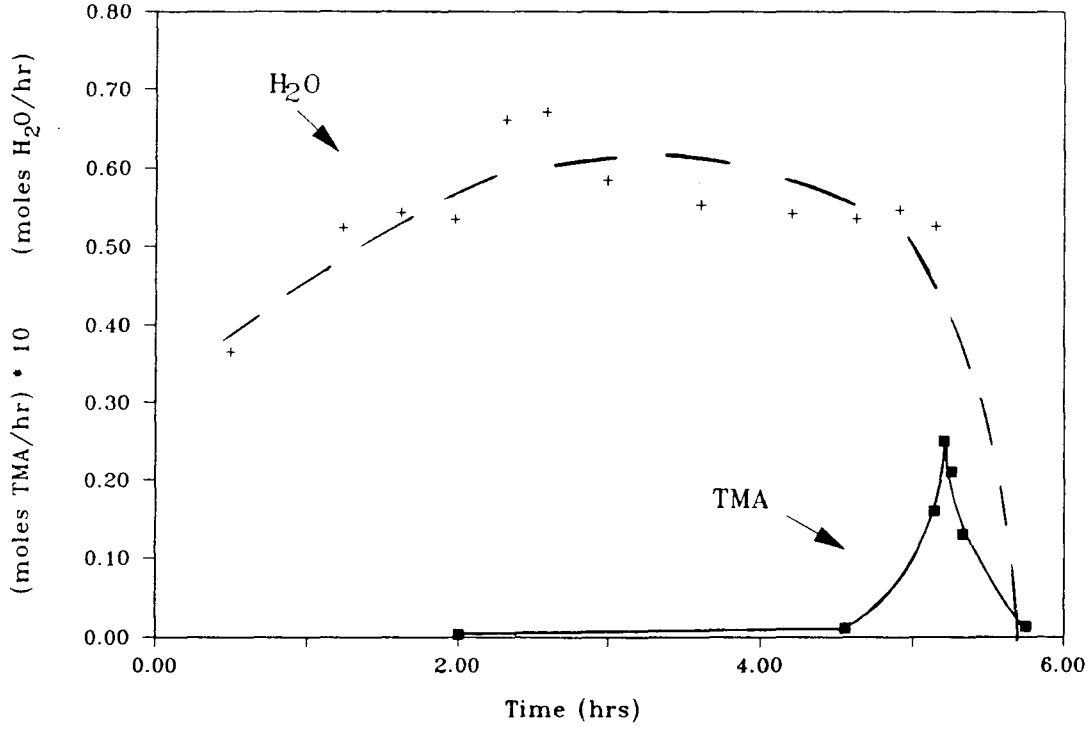


Figure 5-4a. Rate of Removal of H_2O and TMA with Time

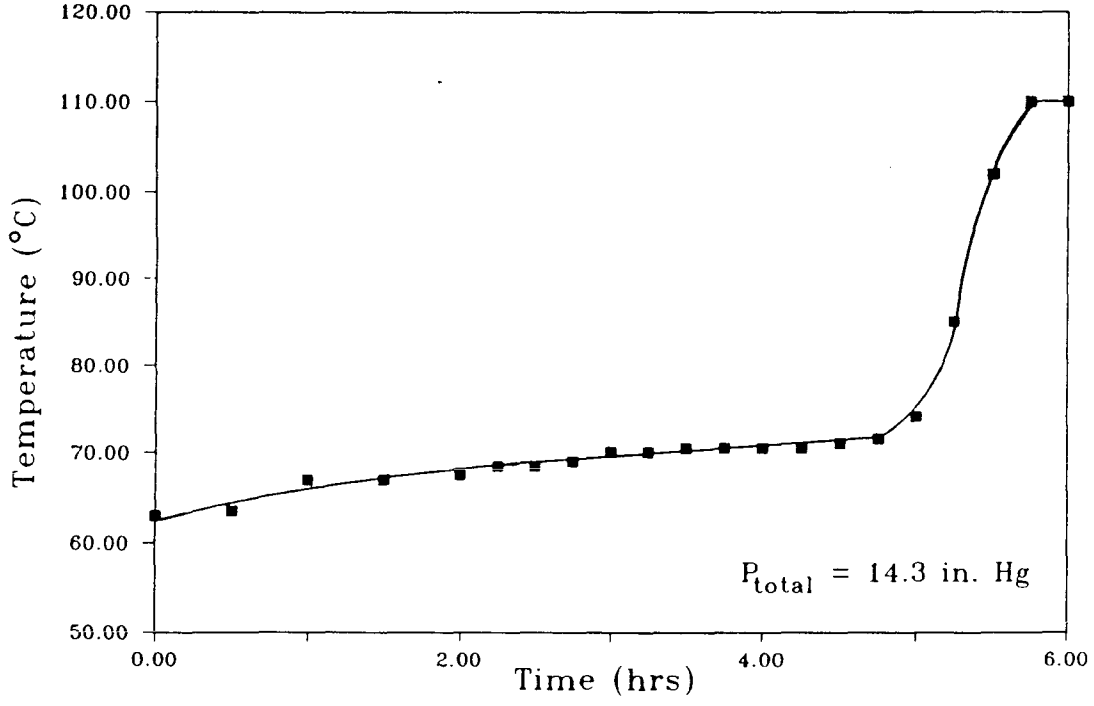


Figure 5-4b. Variation of Temperature with Time

The preliminary work done to determine the best method of washing the crystals was performed on succinic acid crystals from a number of different thermal regeneration experiments. The composition of the mixture remaining in the heating flask at the end of a typical succinic acid experimental run was 40.5 wt % C, 6.6 wt % H, and 3.6 wt % N. The ratio of moles of TMA per mole of acid in the overall mixture (solid crystals and aqueous solution) was therefore equal to 0.4. Table 5-1 shows the degree to which the various washing techniques removed this residual TMA.

Three successive recrystallizations of the succinic acid from MiBK resulted in relatively pure (containing between 0.05 and 0.11 wt % N) crystals. The fumaric acid crystals were recrystallized from MiBK only one time and were of lower purity (containing 0.61 wt % N). Apparently successive recrystallizations are required to remove the residual TMA.

Dissolution of the concentrated TMA/water/carboxylic acid mixture into MiBK serves to lower the concentrations of the 1-1 TMA/acid salt ($R_3NH^+HA^-$) and of the un-ionized TMA (R_3N) and the un-ionized carboxylic acid (H_2A). In addition, in an MiBK diluent, the un-ionized form of the TMA molecule would be favored. The combination of these two effects would drive the reaction for the formation of the TMA/acid ion pair:

$$R_3N + H_2A = R_3NH^+HA^- \tag{5-1}$$

with:

$$K = \frac{(R_3NH^+HA^-)}{(R_3N)\,(H_2A)} \tag{5-2}$$

Table 5-1. Washing of Succinic and Fumaric Acid Crystals

Treatment	Composition of Crystals (wt %)			TMA/Acid in crystals	Recovery (wt %)
	%C	%H	%N	(moles/moles)	
SUCCINIC ACID					
Washed with acetone and chloroform	40.2	5.1	0.09-0.16	0.008-0.014	67.0
Washed with acetone and carbon tetrachoride	40.4-40.7	5.2-5.3	0.17-0.28	0.014-0.024	67.5
Recrystallized from MiBK (3 times)	41.1-42.4	5.3-5.5	0.05-0.11	0.004-0.009	77.0
FUMARIC ACID					
Recrystallized from MiBK (1 time)	42.1	4.0	0.61	0.05	81.0

to the left, thereby increasing the proportion of TMA that is present in volatile form.

After dissolution of the mixture into MiBK, the solution was heated under vacuum to remove the solvent. As the solvent was removed from the mixture, the water and a portion of the TMA were also removed, leaving behind crystalline acid as well as a small amount of solid TMA/acid salt. Successive recrystallizations served to break apart this salt and liberate TMA.

It is possible that the TMA remaining in solution after the heating and concentration of an aqueous solution of TMA and lactic acid could be removed by this dissolution/heating technique, leaving behind a mixture of the free acid and polymeric forms of the acid. Urbas (7) states that the trialkylammonium salt of lactic acid and either tributylamine or dicyclohexylmethylamine can be thermally decomposed to obtain the acid and the tertiary amine; however, no experimental details are given. Further studies on the separation of TMA from aqueous solutions of ·TMA and lactic acid are left for future work.

REFERENCES

1. Holten, C.H., Lactic Acid: Properties and Chemistry of Lactic Acid and Derivatives, Verlag Chemie (1971).

2. Borsook, H., Huffman, H.M., and Liu, Yun-Pu, "The Preparation of Crystalline Lactic Acid", J. Biol. Chem., 102, 449-460 (1933).

3. Krebs, H.A. and Sakami, W., "L(+)-Lactic Acid", Biochemical Preparations, 8, 75-59 (1961).

4. Smith, G.D., Fritz, R.M., King, G.R., and Maute, R.L., "Lactic Acid and Its Derivatives", in Encyclopedia of Industrial Chemical Analysis, Vol. 15, Snell, D.F., and Ettre, L.S., Eds., Interscience Publishers, New York (1972).

5. "Chemical Prices", Chemical Marketing Reporter (January 8, 1990).

6. The Merck Index, Windholz, M., Ed., 10th ed., Merck & Co., Inc., Rahway, New Jersey (1983).

7. Urbas, B., "Recovery of Organic Acids from a Fermentation Broth", U.S. Patent No. 4,444,881 (Apr. 24, 1984).

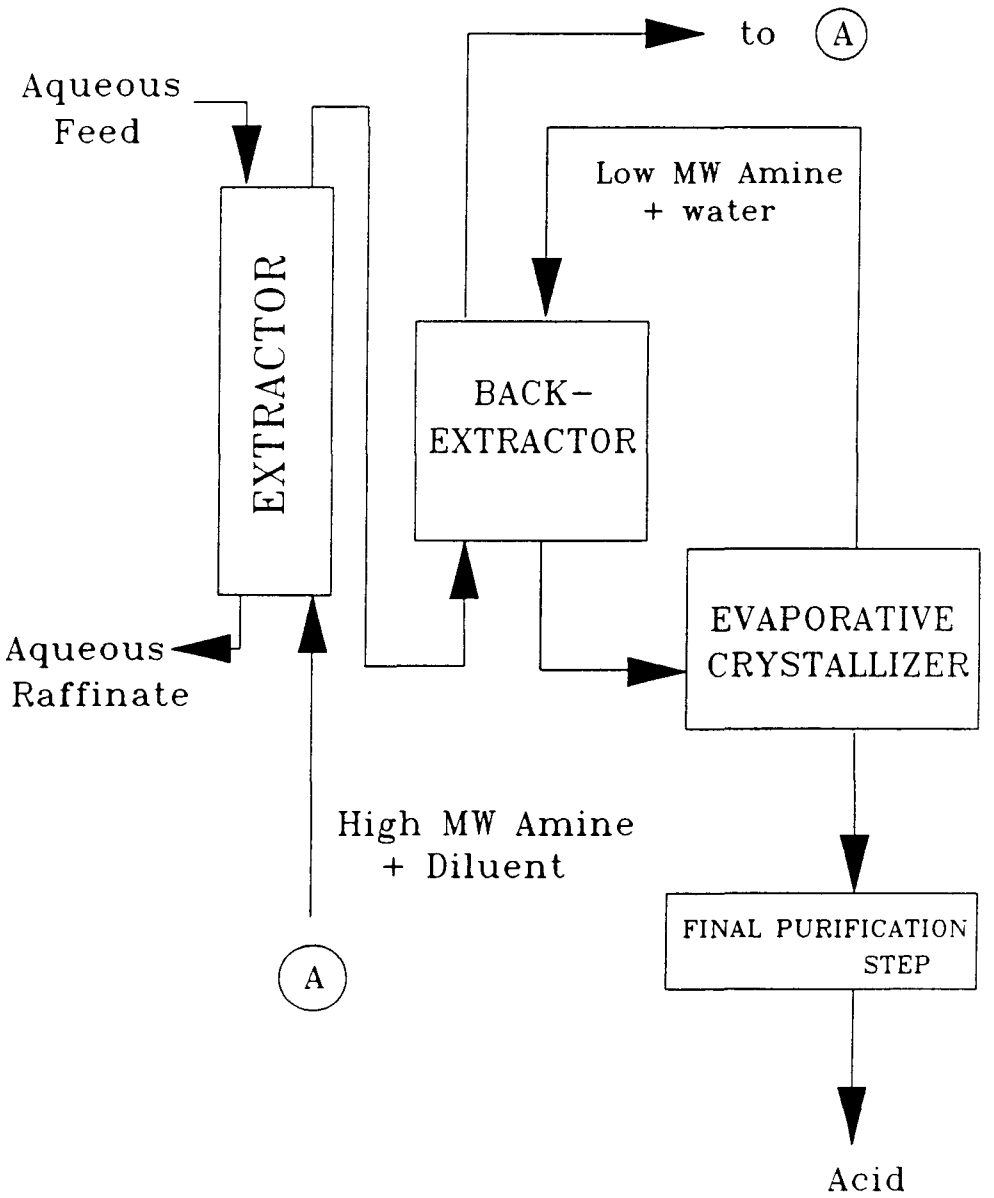
CHAPTER 6. PROCESS DESIGN CONSIDERATIONS

This chapter examines the implications of the experimental results reported in previous chapters, for the design of a carboxylic acid recovery process in which back-extraction into and recycle of a volatile base is the method of regeneration of the amine-carboxylic acid extract. Each step of the process is first examined separately, and then the economic viability of this regeneration method is compared to that of the temperature-swing and diluent composition-swing regeneration methods.

6.1 The Carboxylic Acid Recovery Process

A process diagram for the recovery of low-solubility carboxylic acids from dilute aqueous solutions using the regeneration method explored in this work is shown in Figure 6-1. The acid is extracted by reversible chemical complexation from the aqueous feed into an organic solution of a tertiary amine extractant. The acid is then back-extracted from the loaded organic phase into an aqueous trimethylamine (TMA) solution. The aqueous solution of the trimethylammonium salt is heated in an evaporative crystallizer to drive off the water and the TMA, which are recycled to the process. The acid product is then sent to a final purification step.

Figure 6-1. Carboxylic Acid Recovery Process



6.1.1 Extraction of the Carboxylic Acid by a Tertiary Amine Extractant

The first step of the carboxylic acid recovery process is the extraction of the acid into the solvent phase to produce an amine-carboxylic acid extract and a relatively acid-free aqueous raffinate. Figure 6-2 shows a McCabe-Thiele operating diagram for the extraction at 25°C of succinic acid from dilute aqueous solution into 0.3M Alamine 336 in methyl isobutyl ketone (MiBK). The vertical axis is the concentration of acid in the organic phase while the horizontal axis is the concentration of acid in the aqueous phase. The equilibrium curve was determined experimentally by Tamada (1).

In a McCabe-Thiele operating diagram, the equilibrium curve relates the compositions of the two streams leaving a stage in a multi-stage extraction process. The operating curve relates the compositions of streams flowing past each other between stages. Three stages are shown on the diagram in Figure 6-2. For dilute solutions, the operating curve is a straight line with a slope equal to the water to solvent flow ratio (W/S). (2)

During the extraction process, the equilibrium curve must lie above the operating line. Limiting conditions occur at points where the equilibrium curve and operating line intersect. These 'pinch points' usually occur at the ends of a multi-stage extractor as is shown in Figure 6-2; however, depending on the shape of the equilibrium curve, internal pinch points may occur. (2)

Figure 6-2. Extraction of Succinic Acid from Aqueous Solution into 0.3M Alamine 336 in MiBK

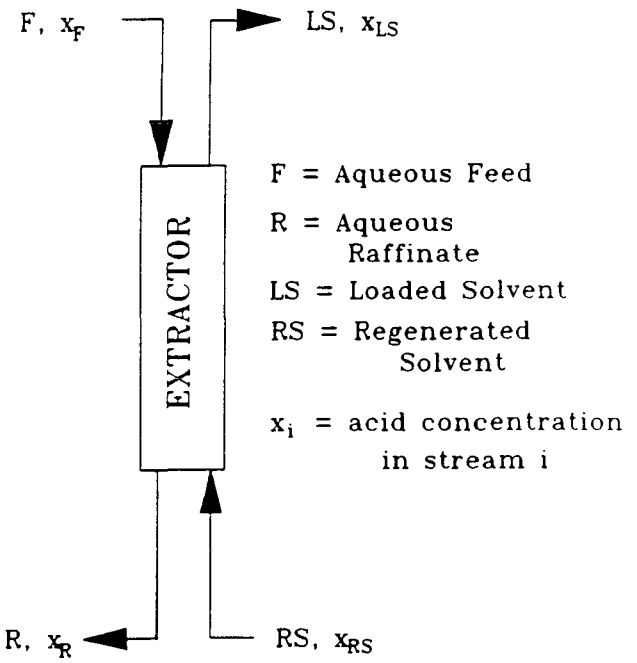


Figure 6-2a. Multi-Stage Extractor

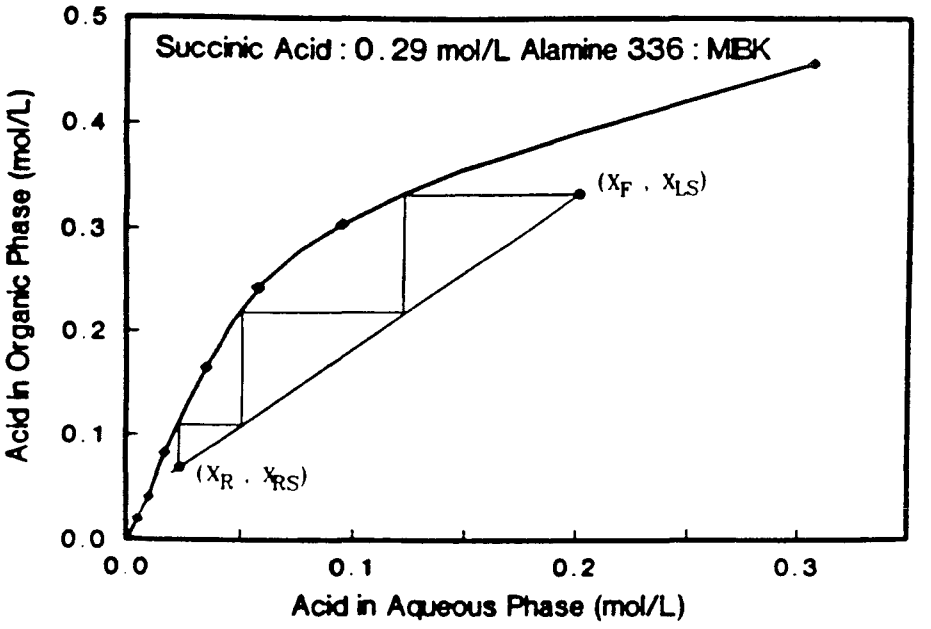


Figure 6-2b. McCabe-Thiele-Type Process Diagram Including Equilibrium Curve for Succinic Acid at 25°C Organic Phase: 0.3M Alamine 336 in MiBK (from Tamada [1])

The endpoints of the operating line are the pairs of compositions in the streams passing each other at each end of the column. The locations of these points are dictated by the feed composition, the desired removal of the acid from the feed, and the flow ratio used in the extractor. Flow ratios for industrial extractors are typically in the range $1 < W/S < 10$ (2).

Figures 6-3 and 6-4 show equilibrium curves for the extraction at 25°C of lactic acid (1) and fumaric acid (3) from dilute aqueous solution into 0.3M Alamine-336 in MiBK. A thorough discussion of the extraction of carboxylic acids by amine extractants, including the effects of changes in temperature or diluent composition on the shape of the equilibrium curve, is given by Tamada (1).

For succinic acid or fumaric acid, vigorous mixing of an aqueous acid solution with an organic solution of Alamine 336 in MiBK results in emulsion formation. Therefore, the multi-stage extractor used in the process should be one that suppresses emulsion formation by either allowing only gentle mixing and/or promoting phase separation.

6.1.2 Back-Extraction of the Acid into Aqueous TMA Solution

Due to the strong basicity of TMA, nearly complete removal of the acid from the organic extract solution can be achieved when one mole of TMA is present for every equivalent weight of acid. Figures 6-5 and 6-6 show equilibrium curves for fumaric acid partitioning between an organic phase of 0.3M Alamine 336 in MiBK and an aqueous phase of 0.4M TMA or

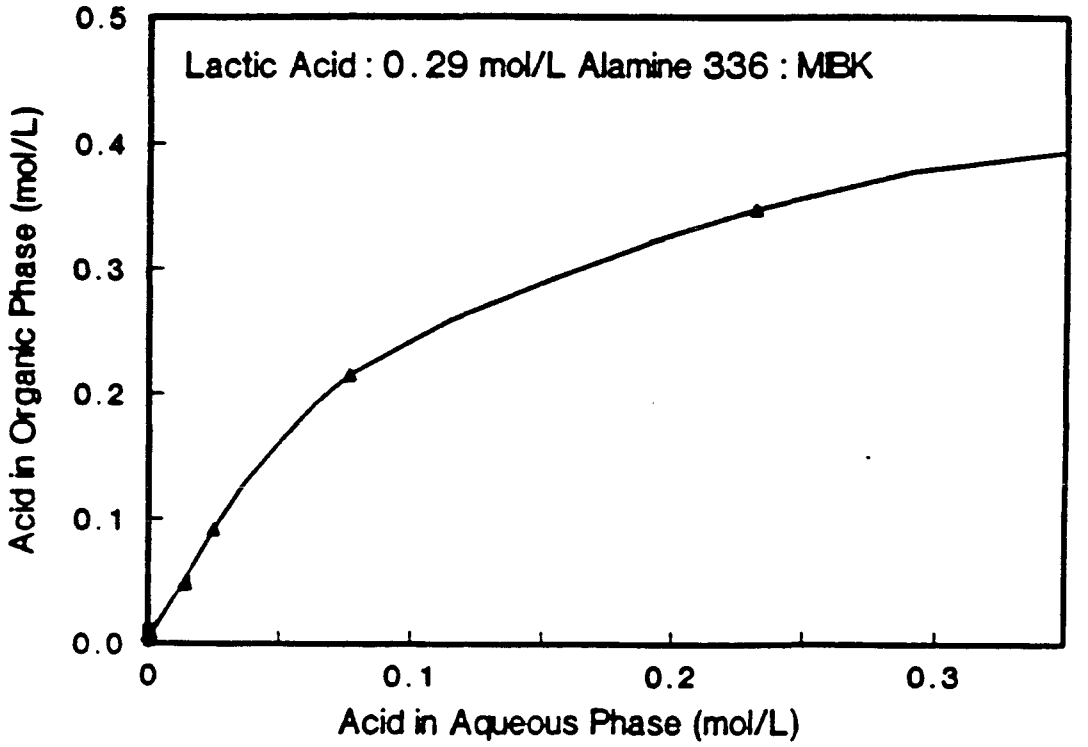


Figure 6-3. Equilibrium Curve for Lactic Acid at 25°C
Organic Phase: 0.3M Alamine 336 in MiBK
(from Tamada [1])

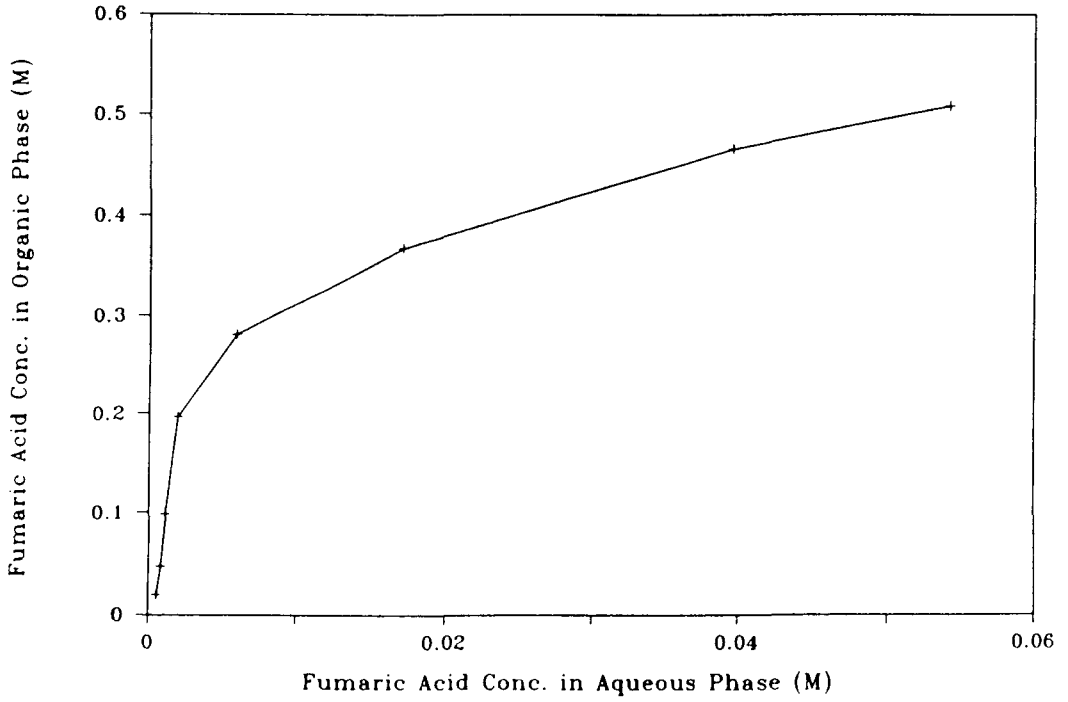


Figure 6-4. Equilibrium Curve for Fumaric Acid at 25°C
Organic Phase: 0.3M Alamine 336 in MiBK
(from Starr [3])

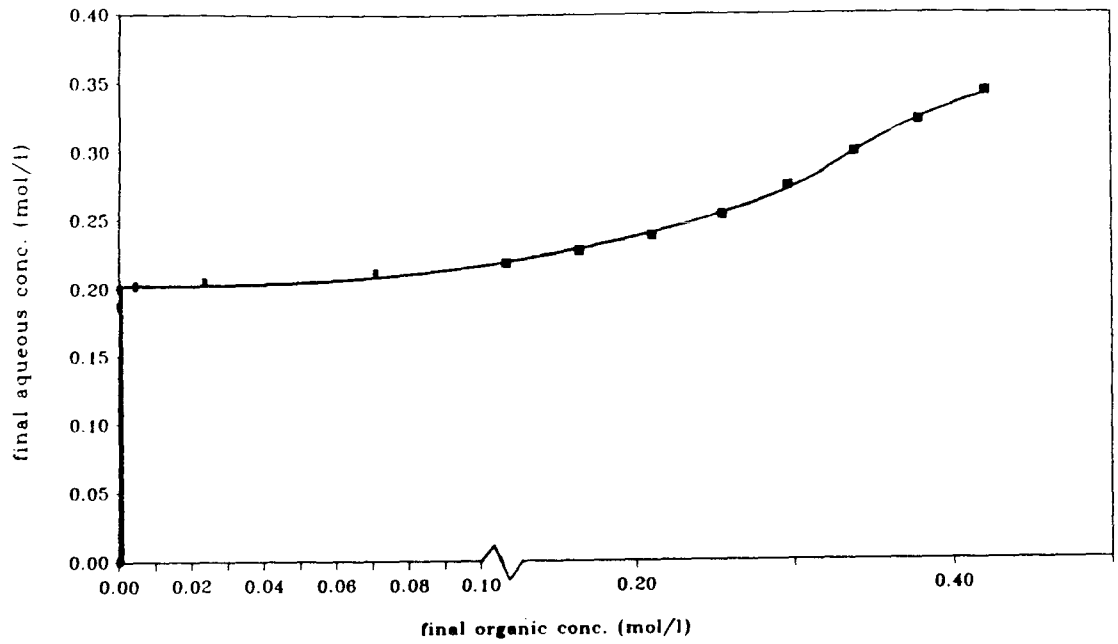


Figure 6-5. Equilibrium Curve for Fumaric Acid at 25°C
Organic Phase: 0.3M Alamine-336 in MiBK
Aqueous Phase: 0.4M TMA
(Calculated using computer programs: "second" and "equilf", given in Appendix C)

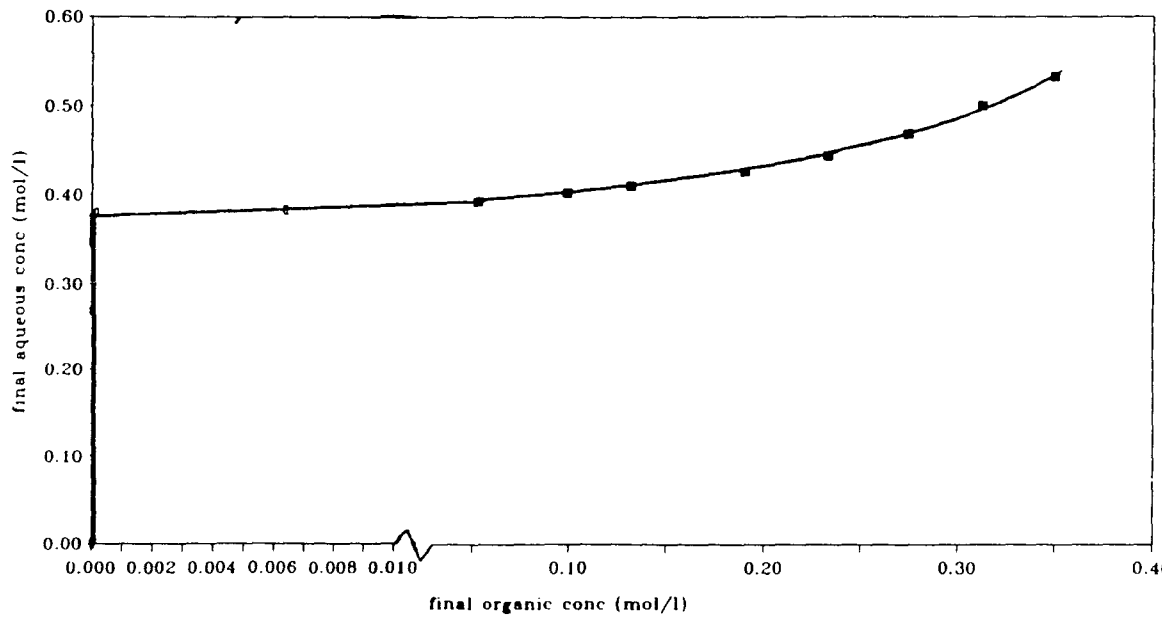


Figure 6-6. Equilibrium Curve for Fumaric Acid at 25°C
Organic Phase: 0.3M Alamine 336 in MiBK
Aqueous Phase: 0.76M TMA
(Calculated using computer programs: "second" and "equilf")

0.76M TMA (the vertical axis being the concentration of acid in the aqueous phase). When fumaric acid is present in an amount equal to or less than 1/2 the amount of TMA, essentially all of the acid will be present in the aqueous phase. When fumaric acid is present in an amount greater than 1/2 the amount of TMA, it will partition between the organic and aqueous phases.

A counter-current multi-stage extractor should not be used to carry out the back-extraction of the acid into aqueous TMA solution. In a counter-current multi-stage extractor, the exiting acid-depleted organic phase would contact an entering aqueous TMA phase containing little or no acid, and as discussed in Chapter 4, TMA transfer into the organic phase would occur. The organic phase would leave the extractor saturated with TMA and another process step would be required to remove the TMA.

In general, there is little incentive to use a multi-stage extractor for two-phase systems with equilibrium curves of the shape shown in Figures 6-5 and 6-6, because due to the shape of the equilibrium curve each additional stage used in an extractor would serve to increase the concentration of the solute in the extractant phase to only a small degree. In this particular case, the equilibrium curves shown would not be valid for the entire length of a counter-current column, due to the change in TMA concentration in the aqueous phase.

Therefore, a one-stage extractor should be used for the back-extraction of acid from the organic phase into aqueous TMA solution. Emulsion

formation was not encountered during the experimental work done with these two-phase systems, and thus a standard mixer/settler extractor could probably be used.

Typical phase ratios for industrial one-stage extractors range from 0.1 to 10. These ratios can be achieved by recycle of one of the phases, if necessary. Since it is desirable to concentrate the acid during this back-extraction step, the organic to aqueous (S/W) phase ratio should be greater than 1. To avoid TMA transfer to the organic phase, the product of the concentration of TMA and the flowrate for the aqueous phase should be somewhat less than or equal to the product of the concentration -- in terms of equivalent weight per volume -- of the acid and the flowrate for the organic solvent phase leaving the forward extractor.

Although 100% recovery of the acid from the organic extract solution can be achieved without TMA transfer to the organic phase, for control purposes, a recovery of about 90% could be used, thereby allowing for slight fluctuations in the acid concentration of the organic solvent stream leaving the forward extractor. The acid not removed from the organic phase would be sent back through the forward extractor. A significant decrease in the concentration of acid in the feed to the carboxylic acid recovery process would require a corresponding decrease in the TMA concentration and/or aqueous-phase flowrate in order to avoid TMA transfer to the organic phase.

The maximum concentration of acid attainable in the final aqueous phase depends on the solubility of TMA in water at the temperature and pressure of operation. Although the solubility of TMA in water at 20°C and atmospheric pressure is approximately equal to 41 wt.% (4,5), TMA is commercially available as a 25 wt.% aqueous solution. This commercial product has a density of 0.933 g/ml at 20°C (4) and therefore has a TMA concentration of 3.95 mol/l.

6.1.3 Degree of Concentration of the Acid

The economic feasibility of the carboxylic acid recovery process depends in part on the degree of concentration of acid that can be achieved during the forward and back-extraction steps; i.e., on the amount of water that must be removed in the evaporative crystallizer. For a given acid, if a recycle stream is not to be used in the back-extractor, then the degree of concentration that can be achieved depends on the maximum possible concentration of extractant in the organic solvent phase (which in turn is dependent on the diluent used), the maximum solubility of TMA in water, and the flow ratios permissible in industrial equipment. If one allows for the possibility of recycle to the back-extractor of a portion of the aqueous stream leaving the back-extractor, then the degree of concentration that can be achieved depends only on the solubility of TMA in water at the temperature and pressure of operation. The conditions that would require recycle of the aqueous phase in the back-extractor are discussed in Section 2.2 of this chapter.

A sample calculation follows for the degree of concentration attainable during the recovery of succinic acid from dilute solution when the organic solvent phase consists of Alamine 336 in a MiBK diluent and the aqueous feed solution is 3 wt. % succinic acid. The calculation is summarized in Table 6-1. According to Tamada (1,6), 1.0M Alamine 336 in MiBK is the maximum concentration that should be used in the extraction due to problems of third-phase formation and high solvent viscosity at higher concentrations.

For the forward extractor, the assumption of infinite stages was used; the loaded organic solvent stream leaving the extractor is then in equilibrium with the aqueous feed solution and likewise the organic solvent stream entering the extractor is in equilibrium with the aqueous raffinate stream leaving the extractor. For the back-extractor, in order to obtain the maximum concentration of acid in the aqueous TMA solution, the acid recovery from the organic phase was set at 100%. The regenerated organic solvent, containing essentially no acid, is sent back to the forward extractor. Since this regenerated organic solvent stream is in equilibrium with the acid-depleted aqueous raffinate, essentially 100% removal of the acid from the aqueous feed can occur in the forward extractor.

The concentration of succinic acid in the organic phase leaving the forward extractor is calculated as follows:

$$[H_2A] = K_{1,1}[B](H_2A) + 2K_{2,1}[B](H_2A)^2 + \Phi P(H_2A) \qquad (6\text{-}1)$$

where H_2A denotes the succinic acid, B denotes the uncomplexed Alamine

Table 6-1. Sample Calculation for Degree of Concentration of Succinic Acid

FORWARD EXTRACTOR

Aqueous Feed: 3 wt % succinic acid (0.250M)
pH = 2.49

Inlet Organic Solvent Stream: 1.0M Alamine 336 in MiBK

Aqueous Raffinate: water containing little acid

Outlet Organic Solvent Stream: 1.35M succinic acid and 1.0M Alamine 336 in MiBK

Water/Solvent Flow Ratio: 5.40

BACK-EXTRACTOR

Initial Organic Phase: 1.35M succinic acid and 1.0M Alamine 336 in MiBK

Initial Aqueous Phase: 3.95M TMA

Final Organic Phase: 1.0M Alamine 336 in MiBK

Final Aqueous Phase: 1.97M succinic acid and 3.95M TMA

Solvent/Water Phase Ratio: 1.46

Concentration Factor: 1.97/0.250 = 7.88

336 molecule, the parentheses denote concentrations in the aqueous phase, the brackets denote concentrations in the organic phase, the $K_{p,q}$ values are the equilibrium constants of the complex formation as listed in Table 1-2, Φ is equal to the volume percent of MiBK (0.50) in the organic solvent, and P (0.19) is the partition coefficient for succinic acid between water and MiBK as given in Table 4-1.

In order to solve Equation 6-1, the values of [B] and (H_2A) must first be calculated as follows:

$$[B] = \frac{[B_{total}]}{1 + K_{1,1}(H_2A) + K_{2,1}(H_2A)^2} \tag{6-2}$$

$$(H_2A) = \frac{(H_2A_{total})}{1 + \frac{K_{a,1}}{(H^+)} + \frac{K_{a,1}K_{a,2}}{(H^+)^2}} \tag{6-3}$$

where the numerator in Equation 6-3 is the concentration (0.250M) of succinic acid in the aqueous feed solution, $K_{a,1}$ and $K_{a,2}$ are the first and second dissociation constants ($10^{-4.21}$ and $10^{-5.60}$) of succinic acid, and (H^+) is the hydrogen ion concentration ($10^{-2.49}$) in the aqueous feed solution as determined experimentally.

As shown in Table 6-1, the concentration of acid in the loaded organic phase was calculated to be 1.35M. A material balance for the succinic acid can be used to calculate the water/solvent flow ratio in the forward extractor. This value, 5.40, is within the desired range.

In the back-extractor, the commercially available 25 wt. % (3.95M) aqueous TMA solution is used as the aqueous phase. The phase ratio is set so that the number of moles of TMA in the back-extractor is equal to twice the number of moles of succinic acid, so as to obtain 100% recovery of the acid from the organic phase while at the same time avoiding transfer of TMA to the organic phase. This solvent/water phase ratio is equal to 1.46, which is within the desired range. The acid concentration in the final aqueous phase is then equal to half the TMA concentration or 1.97M.

The degree of concentration achieved during the forward and back-extraction steps is equal to the final aqueous acid concentration (1.97M) divided by the acid concentration in the aqueous feed solution (0.250M). In this example, the degree of concentration -- or concentration factor -- is equal to 7.88, or approximately 8. In order to obtain a greater degree of concentration, a more concentrated aqueous TMA solution must be used.

6.1.4 Thermal Decomposition of the Trimethylammonium Carboxylates

After the carboxylic acid has been back-extracted into an aqueous solution of TMA, the aqueous solution of the trimethylammonium carboxylate is heated in an evaporative crystallizer to drive off the water and TMA. As discussed in Chapter 2, oxidation of TMA during this step is undesirable. The evaporative crystallizer should be run under a nitrogen atmosphere and/or at a temperature low enough so that oxidation of TMA will not occur. The temperature should also be kept considerably below the thermal decomposition temperature of the carboxylic acid (235°C for

succinic acid, 230°C for fumaric acid [7]).

The energy consumption for this heating and concentration step is given by the sum of the sensible heat required to raise the temperature of the aqueous trimethylammonium carboxylate solution to the initial boiling temperature, the sensible heat required to sustain boiling as the boiling temperature increases during concentration, and the latent heat required to vaporize the water. For a given weight of acid product, the higher the concentration of the initial aqueous trimethylammonium carboxylate solution, the lower the energy consumption during this step.

6.1.5 Final Purification Step

As discussed in Chapter 5, a final purification step is needed to remove residual TMA from the crystalline acid product. This step could consist of dissolution in MiBK, or another solvent, of the material left at the end of the evaporative crystallization step followed by heating (possibly under vacuum) to drive off the MiBK, and the residual TMA and water. If this method is used, a vapor stream of MiBK, TMA, and water would be produced.

In order to avoid chemical consumption, separation of the MiBK (or other solvent) from the vapor stream would be required so that the MiBK could be reused in this purification step, and the TMA and water could be recycled to the back extractor. This separation could be achieved by passing the MiBK/TMA/water vapor stream through a condenser. If the

system is under sufficient vacuum (see Chapter 3, Section 6) the TMA will remain in the vapor phase. The MIBK and water will condense and can be collected in a trap. Once condensed, the MiBK and the water will form two different phases and can be separated by decantation. Stripping can be used to remove residual MiBK from the water phase, if this is necessary. The TMA vapor stream can then be passed through water under atmospheric pressure to allow absorption to occur, producing an aqueous TMA solution.

6.2 Comparison of pH-Swing Regeneration to Temperature-Swing Regeneration and Diluent Composition-Swing Regeneration

This work examines a carboxylic acid recovery process in which regeneration of an amine-carboxylic acid extract is achieved by back-extraction of the acid into an aqueous solution of a volatile base followed by a heating and concentration step to obtain the acid product. In Chapter 1, Section 4, alternative regeneration methods were discussed. Two of the regeneration methods, temperature-swing and diluent composition-swing also consist of a back-extraction step which would need to be followed by a heating and concentration step in order to obtain the acid in product form.

Important factors in determining the economic viability of a process are the energy consumption, chemical consumption, and capital and other operating costs of the process. Table 6-2 compares these three regeneration methods with regard to these factors. All three regeneration methods involve full recycle of chemicals; the only chemical consumption would be through entrainment, solubility, or degradation losses.

Table 6-2. Comparison of pH-Swing, Temperature-Swing and Diluent Composition-Swing Regeneration Methods

PROCESS STEP	PROCESS COST	REGENERATION METHOD
Back-extraction:	Energy Consumption:	Temperature-Swing:
		energy required to raise the temperature of the inlet streams to the back-extractor
		Diluent Composition-Swing:
		energy required to alter the diluent composition through distillation
	Capital and other Operating Costs:	Temperature-Swing:
		1. multi-stage extractor 2. heat-exchanger
		Diluent Composition-Swing:
		1. multi-stage extractor 2. distillation column
		pH-Swing:
		1. one-stage extractor
Concentration: (including removal of TMA for pH-swing)	Energy Consumption:	Temperature-Swing:
		depends on the concentration of acid achieved during back-extraction; upon the sensitivity to temperature of the equilibrium curve for the acid.

Table 6-2. (Continued)

PROCESS STEP	PROCESS COST	REGENERATION METHOD
Concentration: (including removal of TMA for pH-swing)	Energy Consumption:	Diluent Composition-Swing: depends on the concentration of acid achieved during back-extraction; upon the sensitivity to diluent composition of the equilibrium curve for the acid.
		pH-Swing: depends on the concentration of acid achieved during back-extraction; on the solubility of TMA in water at the temperature and pressure of operation
	Capital and other Operating Costs:	all methods: essentially the same
Final Purification:		pH-Swing process only:
	Energy Consumption:	energy required to drive off solvent, residual water, TMA
	Capital and other Operating costs:	1. evaporative crystallizer 2. condenser

6.2.1 Energy Consumption

During the back-extraction step, the energy consumption would be higher for the temperature-swing and diluent composition-swing regeneration methods than for the pH-swing regeneration. In temperature-swing regeneration (see Figure 1-1), energy would be required to raise the temperature of the inlet streams to the back-extractor; however, some of this energy could be provided by heat exchange between the loaded organic solvent stream and the regenerated organic solvent stream. In diluent composition-swing regeneration (see Figure 1-2) energy is required to alter the diluent composition by distillation.

After the back-extraction step, all three regeneration methods have a concentration and heating step during which water (water and TMA for the pH-swing process) is removed to generate the acid in product form--either in crystalline form or as a concentrated aqueous solution. The energy consumption during this step would depend on the degree of concentration of the acid that had already been achieved during the forward and back-extraction steps; i.e. on the amount of further concentration required. The degree of concentration of acid that can be attained during the forward and back-extraction steps is compared below for the three regeneration methods.

The pH-swing regeneration method requires a final purification step that is not needed for the temperature-swing or diluent composition-swing methods. The energy consumption for this step is given by the sum of the

sensible heat required to raise the temperature of the MiBK/TMA/water/acid mixture to the boiling point of MiBK (117-118°C at atmospheric pressure [7]), and the heat required to vaporize the MiBK and the water.

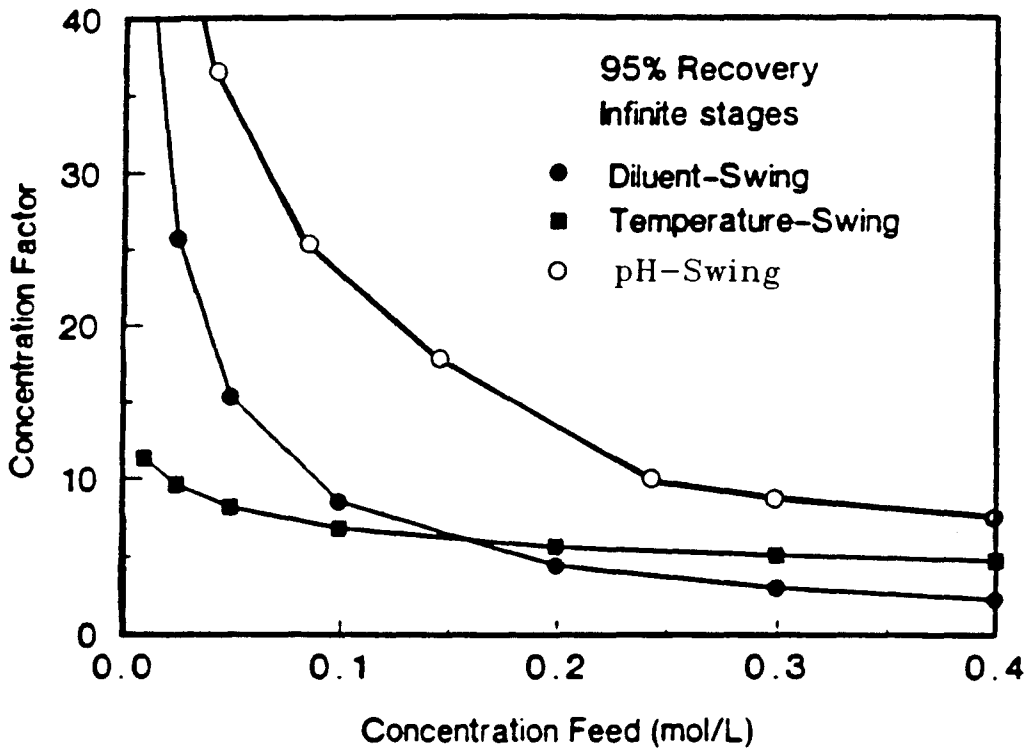
6.2.2 Comparision of Degree of Concentration

The degree of concentration of the acid that can be achieved during the forward and back-extraction steps was compared by Tamada (1) for the temperature-swing and diluent composition-swing processes. The degree of concentration (concentration factor) is shown in Figure 6-7 as a function of the acid concentration of the aqueous feed to the carboxylic acid recovery process. These curves were generated for aqueous feed solutions of succinic acid.

The organic solvent phase used in the temperature-swing process was 0.3M Alamine 336 in MiBK. For the diluent composition-swing process, the organic solvent phase used in the forward extractor consisted of 15% (v/v) Alamine 336 (0.3M Alamine 336), 55% (v/v) chloroform, and 30% (v/v) heptane, while the organic solvent phase used in the back-extractor consisted of 30% (v/v) Alamine 336 (0.6M Alamine 336), 10% (v/v) chloroform, and 60% (v/v) heptane.

Also shown in Figure 6-7 is the degree of concentration attainable when pH-swing regeneration is used. This curve was calculated as detailed in Section 1.3 of this chapter. The organic solvent phase used in the calculations was 0.3M Alamine 336 in MiBK. The following assumptions of

Figure 6-7. Comparison of the Maximum Possible Concentration Factor for Temperature- (1), Diluent Composition- (1) and pH-Swing Regeneration



Tamada (1) were used in the calculations: infinite stages in the forward extractor; and 95% recovery of the acid from the aqueous feed. The pH values for aqueous solutions of succinic acid -- needed to solve equation 6-3 -- of varying concentration were taken from Tamada (1).

During the back-extraction step, the commercially available (3.95M) aqueous TMA solution was used for the calculations involving the higher values of aqueous feed concentration. However, below about 0.05M succinic acid in the aqueous feed, the concentration of acid in the loaded organic phase was low enough that if 3.95M TMA was used, the phase ratio (W/S) in the back-extractor would need to be less than 0.1 in order to prevent TMA transfer into the organic phase. (Higher values for the phase ratio would result in 2-phase systems in which there was an excess of TMA--greater than the amount required to recover 100% of the acid from the organic phase.) Therefore, for low concentrations of acid in the aqueous feed solution, the phase ratio in the back-extractor was set at 0.1, and TMA solutions less concentrated than 3.95M were used.

For feed solutions below about 0.05M succinic acid, a recycle stream of the aqueous TMA phase could be used in the back-extractor to achieve W/S equal to or greater than 0.1. This use of a recycle stream would prevent the necessity of using TMA solutions less concentrated than 3.95M, and would thereby result in concentration factors for feed solutions below 0.05M succinic acid greater than those shown in Figure 6-7.

In order to determine the TMA concentration needed (or for higher values of aqueous feed concentration, the phase ratio needed) in the back-extraction step, the following equation was used:

$$[H_2A] \times \text{TMA to acid ratio required to achieve desired recovery in the back-extractor} = (TMA) \times W/S \qquad (6\text{-}4)$$

where $[H_2A]$ is the concentration of acid in the loaded organic phase leaving the forward extractor, (TMA) is the aqueous TMA concentration, and the TMA/acid ratio needed was determined from Figure 4-2. The recovery of acid obtained in the forward extractor was set at 95% as given by Tamada (1); therefore, the recovery of acid in the back-extractor is that needed to produce a regenerated organic phase with a succinic acid concentration in equilibrium with the concentration of succinic acid in the aqueous phase leaving the forward extractor.

For the range of feed concentrations shown in Figure 6-7, the concentration factor is highest for the pH-swing regeneration method. The energy required during the concentration and heating step of the carboxylic acid recovery process would therefore be lowest for a process using pH-swing regeneration.

6.2.3 Capital and Operating Costs

The capital costs for the back-extraction step of the carboxylic acid recovery process using pH-swing regeneration would probably be the lowest of the three regeneration methods due to the lower capital costs for a one-

stage extractor than for the multi-stage extractors that would be needed for the other two regeneration methods. In addition, the temperature-swing regeneration would include capital costs for a heat-exchanger, while diluent composition-swing regeneration would include the capital and operating costs of the distillation column. However, the pH-swing regeneration method must bear the capital and operating costs of the equipment needed for the final purification step, which is not required when the other two regeneration methods are used.

6.3 Summary and Conclusions

A carboxylic acid recovery process is proposed in which regeneration of an amine-carboxylic acid extract is achieved by back-extraction of the acid into an aqueous solution of trimethylamine. The resultant aqueous solution is concentrated by evaporation and the trimethylammonium carboxylate is decomposed thermally, yielding the volatile trimethylamine for recycle and the acid in product form.

The feasibility of this process has been explored through experimental work with lactic acid, succinic acid, and fumaric acid. Process calculations using data from forward and back-extraction experiments show that a high degree of concentration of the acid can be achieved by extraction with a high molecular-weight tertiary amine in an organic diluent, followed by back-extraction into aqueous trimethylamine solution. Experiments involving the thermal decomposition of the trimethylammonium carboxylates yielded approximately 80% recovery of succinic acid and fumaric acid in crystalline

form. These recovery fractions can probably be increased. The experimental results and an examination of the overall process design demonstrate that the carboxylic acid recovery process examined in this work should be viable for acids of low volatility.

REFERENCES

1. Tamada, J.A., "Extraction of Carboxylic Acids by Amine Extractants", Ph.D. Dissertation, Department of Chemical Engineering, University of California, Berkeley (1989). LBL-25571.

2. King, C.J., Separation Processes, 2nd ed., McGraw-Hill, Inc. (1980).

3. Starr, J.N., Department of Chemical Engineering, University of California, Berkeley, personal communication (1989).

4. Industrial Solvents Handbook, 3rd ed., Flick, E.W., Ed., Noyes Data Corporation (1985).

5. Lange's Handbook of Chemistry, 13th ed., Dean, J.A., Ed., McGraw-Hill, Inc. (1985).

6. Tamada, J.A., Department of Chemical Engineering, Massachusetts Institute of Technology, personal communication (1989).

7. The Merck Index, 10th ed., Windholz, M., Ed., Merck & Co., Inc., Rahway, New Jersey (1983).

APPENDIX A. EXPERIMENTAL DATA

A.1 Back-Extraction Experiments

This section gives the experimental results for the back-extraction of lactic, succinic, and fumaric acids from organic extract solutions into aqueous trimethylamine (TMA) solutions.

Table A-1. Back-Extraction of Lactic Acid

Initial Organic Phase: 0.71M lactic acid and 0.3M Alamine 336 in methyl isobutyl ketone (MiBK)

Organic to Aqueous (S/W) Phase Ratio: 8/3 (v/v)

TMA in Initial Aqueous Phase (M)	Final Aqueous pH	Lactic Acid in Final Aqueous Phase (M)	Lactic Acid in Final Organic Phase (M)
0	2.04	0.61	0.465
0.38	3.77	0.78	0.413
1.14	4.87	1.52	0.272
1.33	5.27	1.28	0.234
1.51	5.42	1.32	0.213
1.70	5.96	1.40	0.0916
1.89	6.28	1.60	0.0511
3.92	9.62	2.11	--

Table A-2. Back-Extraction of Succinic Acid

Initial Organic Phase: 0.45M succinic acid and 0.3M Alamine 336 in methyl isobutyl ketone (MiBK)

Organic to Aqueous (S/W) Phase Ratio: 8/3 (v/v)

TMA in Initial Aqueous Phase (M)	Final Aqueous pH	Succinic Acid in Final Aqueous Phase (M)	Succinic Acid in Final Organic Phase (M)
0	2.61	0.16	0.415
0.23	4.40	0.33	0.357
0.69	5.06	0.58	0.217
0.81	5.16	0.63	0.210
0.93	5.26	0.69	0.223
1.04	5.35	0.76	0.160

Initial Organic Phase: 0.44M succinic acid and 0.3M Alamine 336 in methyl isobutyl ketone (MiBK)

Organic to Aqueous (S/W) Phase Ratio: 8/3 (v/v)

TMA in Initial Aqueous Phase (M)	Final Aqueous pH	Succinic Acid in Final Aqueous Phase (M)	Succinic Acid in Final Organic Phase (M)
1.16	5.53	0.76	0.19
2.30	7.06	1.2	--
3.70	9.44	1.2	--

Table A-3. Back-Extraction of Fumaric Acid

Initial Organic Phase: 0.286M fumaric acid and 0.3M Alamine 336 in methyl isobutyl ketone (MiBK)

Organic to Aqueous (S/W) Phase Ratio: 8/3 (v/v)

TMA in Initial Aqueous Phase (M)	Final Aqueous pH	Fumaric Acid in Final Aqueous Phase (M)	Fumaric Acid in Final Organic Phase (M)
0	2.82	0.0072	0.282
0.076	3.96	0.0685	0.277
0.229	4.33	0.150	0.240
0.381	4.54	0.215	0.217
0.762	4.95	0.635	0.145
1.14	5.27	0.597	0.080
1.52	6.22	0.697	--
2.29	9.39	0.763	--

A.2 Thermal Regeneration Experiments

This section gives the experimental results of concentration and heating experiments in which water and trimethylamine are driven off from aqueous solutions of trimethylammonium carboxylates.

A.2.1 Preliminary Regeneration Experiments conducted with Aqueous Trimethylammonium Succinate Solutions

Table A-4. Regeneration Run #1

Initial Aqueous Solution: 60 ml of 0.6M succinic acid and 1.2M TMA

Treatment: The solution was heated under vacuum.
No nitrogen stream was used.
Temperature of solution: 80°C - 126°C
Pressure of System: 7 - 12 in. Hg

Final Conditions:

1. heating flask contained viscous yellowish liquid mixed with white crystals.
   The crystals consisted of 40.55 wt.% C, 5.17 wt.% H, and 0.61 wt.% N.
   The liquid contained approximately 20% of the initial TMA.

2. water collection flask contained 38.2 ml of TMA/water (43.7% of the initial TMA).

3. absorber flask contained 30.6% of the initial TMA.

Table A-5. Regeneration Run #2

Initial Aqueous Solution: 60 ml of 0.6M succinic acid and 1.2M TMA

Treatment: The solution was heated at 1.05 atm.
A nitrogen stream was used.
Temperature of solution: 99°C - 220°C

Final Conditions:

1. heating flask contained dark brown solid material; decomposition of the succinic acid had probably occurred.

Table A-6. Regeneration Run #3

Initial Aqueous Solution: 60 ml of 0.6M succinic acid and 1.2M TMA

Treatment: The solution was heated at 1.07 atm.
A nitrogen stream was used.
Temperature of solution: 101°C - 172°C

Final Conditions:

1. heating flask contained viscous yellowish liquid mixed with white crystals.
2. water collection flask contained 43 ml of TMA/water (3.6% of the initial TMA).
3. absorber flask contained 32% of the initial TMA.

Conclusion: TMA was lost through leaks in the experimental apparatus.

Table A-7. Regeneration Run #4

Initial Aqueous Solution: 60 ml of 0.6M succinic acid and 1.2M TMA

Treatment: The solution was heated under vacuum.
A nitrogen stream was used.
Temperature of solution: 64°C - 112°C
Pressure of system: 13 - 17 in. Hg

Final Conditions:

1. heating flask contained viscous yellowish liquid mixed with white crystals.
2. water collection flask contained 46.9 ml of TMA/water (2% of the initial TMA).
3. absorber flask contained 80% of the initial TMA.

A.2.2 Thermal Regeneration Experiments conducted with Aqueous Trimethylammonium Succinate and Trimethylammonium Fumarate

Table A-8. Regeneration Run #5

Initial Aqueous Solution: 60 ml of 0.6M succinic acid and 1.2M TMA

Treatment: The solution was heated under vacuum.
Nitrogen flowrate: 0.0137 - 0.0158 moles/min
Temperature of solution: 61°C - 112°C
Pressure of system: 14.8 in. Hg

Final Conditions:

1. heating flask contained viscous yellowish liquid mixed with white crystals.
2. water collection flask contained 43.5 ml of TMA/water (1% of the initial TMA).
3. absorber flask contained 80% of the initial TMA.

Table A-8. (continued)

Time (hrs)	cumulative volume (ml) of H_2O collected	cumulative moles of TMA collected
0	0	0
0.17	1	
0.43	3	
0.79	5.5	0.0072
2.08	17	
2.52	21	
2.72	23	
2.80	24	
2.90	25	
2.97	26	0.0144
3.07	27	
3.17	28	
3.27	29	
3.35	30	
3.46	31	
3.57	32	
3.63	33	
3.75	34	
3.83	35	0.0216
3.93	36	
3.98	37	
4.10	38	
4.20	39	
4.24	39.5	0.0288
4.28	40	
4.42	41	
4.48	41.5	
4.50	41.75	0.0360
4.55	42	
4.68	43	0.0432
4.76	43.5	
5.08	43.5	0.0504
6.26	43.5	0.0574

Table A-9. Regeneration Run #6

Initial Aqueous Solution: 60 ml of 0.6M succinic acid and 1.2M TMA

Treatment: The solution was heated under vacuum.
Nitrogen flowrate: 0.0137-0.0158 moles/min
Temperature of solution: 61°C - 121.5°C
Pressure of system: 14.9 in. Hg

Final Conditions:

1. heating flask contained viscous yellowish liquid mixed with white crystals.
2. water collection flask contained 44.75 ml of TMA/water (1.25% of the initial TMA).
3. absorber flask contained 80% of the initial TMA.

Time (hrs)	cumulative volume (ml) of H_2O collected	cumulative moles of TMA collected
0	0	0
0.13	1	
0.62	5	
0.80	7	
0.87		0.0072
1.15	10	
1.46	13	
1.74	16	
2.26	21	
2.48	23	
2.63	25	
2.92	28	
3.02		0.0144
3.23	31	
3.54	34	
3.81	37	
3.90		0.0216
4.27	41	
4.29		0.0288
4.51	43	
4.57		0.0360
4.69	44	
4.79		0.0432
4.88	44.75	
4.94	44.75	
5.26		0.0504
6.26		0.0575

Table A-10. Regeneration Run #7

Initial Aqueous Solution: 60 ml of 0.1M fumaric acid and 0.2M TMA

Treatment: The solution was heated under vacuum.
Nitrogen flowrate: 0.0137-0.0158 moles/min
Temperature of solution: 63°C - 124°C
Pressure of system: 14.3 in. Hg

Final Conditions:

1. heating flask contained viscous orange/yellow liquid mixed with white crystals.
2. water collection flask contained 49.5 ml of TMA/water (1.24% of the initial TMA).
3. absorber flask contained 68.2% of the initial TMA.

Time (hrs)	cumulative volume (ml) of H_2O collected	cumulative moles of TMA collected
0	0	0
0.99	6.5	
1.33	10	
1.91	15	
2.44	21	
2.84	25	
3.26	30	
3.74	34	
3.96	37	
4.00		0.0012
4.35	40.5	
4.69	44	
4.98	47	
5.10		0.0024
5.175		0.0036
5.22		0.0048
5.25	49.5	
5.28		0.0060
5.37		0.0072
6.125	49.5	0.0082

APPENDIX B. NOMENCLATURE

Chapter 1

pK_{HA}	$-\log_{10}$(acid dissociation constant)
A	unionized acid
B	extractant
p	stoichiometric coefficient for the number of acid molecules per complex
q	stoichiometric coefficient for the number of extractant molecules per complex
K_{pq}	apparent stepwise equilibrium constant for association of *p* acid and *q* extractant molecules
$[A_pB_q]_{org}$	concentration of the *(p,q)* complex in the organic phase, mol/L
$[A]_{aq}$	concentration of the unionized acid in the aqueous phase, mol/L
$[B]_{org}$	concentration of the extractant in the organic phase, mol/L

Chapter 4 and Chapter 6

P	partition coefficient
HA	unionized carboxylic acid
H_2A	unionized di-carboxylic acid
A336	extractant (Alamine 336)
K_{pq}	apparent stepwise equilibrium constant for association of *p* acid and *q* extractant molecules
K_a	acid dissociation constant
pK_a	$-\log_{10}$(acid dissociation constant)
R_3N	trimethylamine
$[HA]_{init}$	initial concentration of acid in the organic phase, mol/L

$[B_{total}]$	total concentration of extractant in the organic phase, mol/L
B	uncomplexed extractant molecule
Φ	volume fraction of diluent in the solvent phase
WS	water to solvent phase ratio (v/v)

Chapter 5

R_3N	trimethylamine
H_2A	unionized di-carboxylic acid
K	equilibrium constant for the reaction: $R_3N + H_2A = R_3NH^+HA^-$

APPENDIX C. COMPUTER PROGRAMS

This appendix gives the computer programs used to model the partitioning of either lactic, succinic, or fumaric acid between an organic solution of Alamine 336 in methyl isobutyl ketone (MiBK) and aqueous trimethylamine solutions. The equations describing these systems and the numerical methods used to solve the equations were discussed in Chapter 4, Section 1. The computer programs used for lactic and succinic acid were written using the software package, Lotus 123 (Lotus Development Corp., 1983). The computer programs used for fumaric acid were written in the FORTRAN computing language.

C.1 Lactic Acid

The theoretical curve shown in Figure 4-1 was plotted using the results given in columns K and L below. The equations used to generate the numbers in columns B through N are given after the table of results. The variable z is the loading -- the number of moles of acid per mole of Alamine 336 -- in the initial organic phase.

(REGEN31.WK1)

simulation of regeneration by back extraction with tma

pKb = 9.80
K11 = 20.42
K21 = 33.11
K31 = 14.79
BTOT = 0.30
pKa1 = 3.85
pKa2 = 12.00

FOR Z = 2.37
(W/S) = 0.38
D = 0.09

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
	guess pH	1/alpha H2A	1/alpha1 HA-	1/alpha2 A=	Guess H2A	df/dx	F	New Guess H2A	Aq Acid (All frms	TMA Added	TMA per Init Ac	% Acid Recvr'd	Load corrected	log(A)
21	10.00	1.4E+06	1.0E+00	1.0E+02	1.3E-06	5.3E+05	0.00000	1.3E-06	1.90	4.95	2.61	1.00	0.00	-5.87
	9.00	1.4E+05	1.0E+00	1.0E+03	1.4E-05	5.3E+04	0.00000	1.4E-05	1.90	2.20	1.16	1.00	0.00	-4.87
	8.00	1.4E+04	1.0E+00	1.0E+04	1.3E-04	5.3E+03	0.00000	1.3E-04	1.89	1.92	1.01	1.00	0.00	-3.87
	7.00	1.4E+03	1.0E+00	1.0E+05	1.3E-03	5.5E+02	0.00000	1.3E-03	1.87	1.88	0.99	0.99	0.03	-2.87
	6.50	4.4E+02	1.0E+00	3.2E+05	4.1E-03	1.9E+02	0.00000	4.1E-03	1.83	1.83	0.96	0.97	0.08	-2.39
	6.25	2.5E+02	1.0E+00	5.6E+05	7.1E-03	1.1E+02	0.00000	7.1E-03	1.79	1.78	0.94	0.94	0.13	-2.15
	6.00	1.4E+02	1.0E+00	1.0E+06	1.2E-02	7.2E+01	0.00000	1.2E-02	1.73	1.72	0.91	0.91	0.21	-1.91
	5.80	9.0E+01	1.0E+00	1.6E+06	1.9E-02	5.2E+01	0.00000	1.9E-02	1.66	1.64	0.87	0.88	0.29	-1.73
	5.60	5.7E+01	1.0E+00	2.6E+06	2.8E-02	3.9E+01	0.00000	2.8E-02	1.58	1.55	0.82	0.83	0.39	-1.56
	5.50	4.5E+01	1.0E+00	3.2E+06	3.4E-02	3.4E+01	0.00000	3.4E-02	1.54	1.50	0.79	0.81	0.45	-1.47
	5.40	3.6E+01	1.0E+00	4.1E+06	4.1E-02	3.0E+01	0.00000	4.1E-02	1.49	1.45	0.76	0.78	0.51	-1.39
	5.20	2.3E+01	1.0E+00	6.6E+06	6.0E-02	2.4E+01	0.00000	6.0E-02	1.39	1.33	0.70	0.73	0.63	-1.22
	5.00	1.5E+01	1.1E+00	1.1E+07	8.6E-02	2.1E+01	0.00000	8.6E-02	1.29	1.20	0.63	0.68	0.76	-1.07
	4.80	9.9E+00	1.1E+00	1.8E+07	1.2E-01	1.8E+01	0.00000	1.2E-01	1.18	1.06	0.56	0.62	0.89	-0.92
	4.60	6.6E+00	1.2E+00	3.0E+07	1.6E-01	1.7E+01	0.00000	1.6E-01	1.08	0.92	0.48	0.57	1.02	-0.78
	4.40	4.5E+00	1.3E+00	5.1E+07	2.2E-01	1.6E+01	0.00000	2.2E-01	0.99	0.77	0.41	0.52	1.13	-0.66
	4.00	2.4E+00	1.7E+00	1.7E+08	3.4E-01	1.6E+01	0.00000	3.4E-01	0.83	0.48	0.25	0.44	1.34	-0.46
	3.60	1.6E+00	2.8E+00	7.0E+08	4.6E-01	1.7E+01	0.00000	4.6E-01	0.71	0.26	0.13	0.38	1.48	-0.34
	3.00	1.1E+00	8.1E+00	8.1E+09	5.6E-01	1.8E+01	0.00000	5.6E-01	0.63	0.08	0.04	0.33	1.58	-0.25
	2.50	1.0E+00	2.4E+01	7.4E+10	5.9E-01	1.8E+01	0.00000	5.9E-01	0.61	0.02	0.01	0.32	1.60	-0.23
	2.00	1.0E+00	7.2E+01	7.2E+11	6.0E-01	1.8E+01	0.00000	6.0E-01	0.60	0.00	0.00	0.32	1.61	-0.22

```
B21: (S1) 1+10^(A21-$B$10)+10^(2*A21-$B$10-$B$11)
C21: (S1) 1+10^($B$10-A21)+10^(A21-$B$11)
D21: (S1) 1+10^($B$10+$B$11-2*A21)+10^($B$11-A21)
E21: (S1) +H21
F21: (S1) 4*$B$8*B21*$B$18*E21^3+3*(B21*$B$18*$B$7-B$9*B$17*B$8+3*$B$9*$B$8)
*E21^2+2*($B$6*B21*$B$18-B$17*B$9*B$7+2*$B$7*$B$9)*E21+(B21*$B$18-B$17*B$9*B$6+$
B$9*$B$6+B$19)
G21: (F5) ($B$8*B21*$B$18)*E21^4+(B21*$B$18*$B$7-B$17*B$9*B$8+3*$B$9*$B$8)*E
21^3+($B$6*B21*$B$18-B$9*B$17*B$7+2*$B$7*$B$9)*E21^2+(B21*$B$18-B$17*B$9*B$6+$B$
9*$B$6+B$19)*E21-$B$17*$B$9
H21: (S1) +E21-G21/F21
I21: +H21*B21
J21: (1+10^(A21-B$5))*(-10^-A21+10^(A21-14)+I21/C21+2*I21/D21)
K21: (F2) +J21/$B$17/$B$9*$B$18
L21: (F2) +I21/($B$9*$B$17)*$B$18
M21: +B$17*(L21-1)
N21: @LOG(H21)
```

C.2 Succinic Acid

The theoretical curve shown in Figure 4-2 was plotted using the results given in columns K and L below. The equations used to generate the numbers in columns B through N are the same as those given above for lactic acid. The variable z is the loading -- the number of moles of acid per mole of Alamine 336 -- in the initial organic phase.

(REGEN31.WK1)

simulation of regeneration by back extraction with tma

pKb =	9.80	
K11 =	24.55	24.55
K21 =	81.28	81.28
K31 =	0.00	0.00
BTOT =	0.30	
pKa1 =	4.21	
pKa2 =	5.60	

FOR Z = 1.50
(W/S) = 0.38
D = 0.16

21	A	B	C	D	E	F	G	H	I	J	K	L	M	N
	guess pH	1/alpha H2A	1/alpha1 HA-	1/alpha2 A=	Guess H2A	df/dx	F	New Guess H2A	Aq Acid (All frms	TMA Added	TMA per Init Ac	% Acid Recvr'd	Load corrected	log(A)
	10.00	1.5E+10	2.5E+04	1.0E+00	7.7E-11	5.8E+09	0.00000	7.7E-11	1.20	6.20	5.17	1.00	0.00	-10.11
	9.00	1.5E+08	2.5E+03	1.0E+00	7.7E-09	5.8E+07	0.00000	7.7E-09	1.20	2.78	2.32	1.00	0.00	-8.11
	8.00	1.6E+06	2.5E+02	1.0E+00	7.7E-07	5.8E+05	0.00000	7.7E-07	1.20	2.43	2.03	1.00	0.00	-6.11
	7.00	1.6E+04	2.6E+01	1.0E+00	7.4E-05	6.1E+03	0.00000	7.4E-05	1.20	2.35	1.96	1.00	0.00	-4.13
	6.50	1.7E+03	8.9E+00	1.1E+00	6.8E-04	6.7E+02	0.00000	6.8E-04	1.19	2.24	1.87	0.99	0.02	-3.17
	6.25	6.0E+02	5.5E+00	1.2E+00	1.9E-03	2.4E+02	0.00000	1.9E-03	1.16	2.11	1.76	0.97	0.05	-2.71
	6.00	2.2E+02	3.5E+00	1.4E+00	5.1E-03	9.9E+01	0.00000	5.1E-03	1.11	1.89	1.57	0.92	0.12	-2.29
	5.80	1.0E+02	2.6E+00	1.6E+00	1.0E-02	5.5E+01	0.00000	1.0E-02	1.03	1.64	1.37	0.86	0.22	-1.99
	5.60	5.0E+01	2.0E+00	2.0E+00	1.8E-02	3.4E+01	0.00000	1.8E-02	0.92	1.35	1.13	0.77	0.35	-1.74
	5.50	3.6E+01	1.8E+00	2.3E+00	2.4E-02	2.8E+01	0.00000	2.4E-02	0.86	1.21	1.01	0.72	0.42	-1.62
	5.40	2.6E+01	1.7E+00	2.7E+00	3.0E-02	2.4E+01	0.00000	3.0E-02	0.80	1.07	0.89	0.67	0.50	-1.52
	5.20	1.5E+01	1.5E+00	3.8E+00	4.6E-02	1.8E+01	0.00000	4.6E-02	0.68	0.81	0.68	0.56	0.65	-1.34
	5.00	8.7E+00	1.4E+00	5.6E+00	6.5E-02	1.5E+01	0.00000	6.5E-02	0.57	0.60	0.50	0.47	0.79	-1.19
	4.80	5.5E+00	1.4E+00	8.9E+00	8.6E-02	1.3E+01	0.00000	8.6E-02	0.47	0.44	0.37	0.40	0.91	-1.06
	4.60	3.7E+00	1.5E+00	1.5E+01	1.1E-01	1.2E+01	0.00000	1.1E-01	0.40	0.32	0.26	0.33	1.00	-0.97
	4.40	2.6E+00	1.7E+00	2.7E+01	1.3E-01	1.1E+01	0.00000	1.3E-01	0.34	0.22	0.19	0.28	1.07	-0.89
	4.00	1.6E+00	2.6E+00	1.1E+02	1.6E-01	9.8E+00	0.00000	1.6E-01	0.26	0.10	0.09	0.22	1.17	-0.79
	3.60	1.2E+00	5.1E+00	5.1E+02	1.8E-01	9.3E+00	0.00000	1.8E-01	0.23	0.05	0.04	0.19	1.22	-0.74
	3.00	1.1E+00	1.7E+01	6.9E+03	1.9E-01	9.0E+00	0.00000	1.9E-01	0.21	0.01	0.01	0.17	1.24	-0.71
	2.50	1.0E+00	5.2E+01	6.6E+04	2.0E-01	8.9E+00	0.00000	2.0E-01	0.20	0.00	0.00	0.17	1.25	-0.71

C.3 Fumaric Acid

```
FILE: SECOND   DATA     A   VM/XA SP2 - CMS Release 5.5 3/11/90 8806A

C THIS PROGRAM WAS USED TO DETERMINE (H2A) VALUES THAT BOUND AN INTERVAL
C WITHIN WHICH F(PH,(H2A)), I.E., EQUATION 4-41, IS EQUAL TO ZERO.
C
      INTEGER K
      DOUBLE PRECISION PH,ALPHA,X,AFREE,BFREE,ATOT,Y,KF,KS,
     *   KT,SOL,KAF,KAS,SW,HPLUS,BTOT,BB,AA,ANEW,FA,AEQ
     *   RATIO,THATOT,ANSWER
C
C THE PROGRAM WAS RUN AT SET VALUES OF AQUEOUS-PHASE PH.
      READ(5,*) PH
      HPLUS=10.**(0.-PH)
C
C VALUES OF THE EQUILIBRIUM CONSTANTS, ACID DISSOCIATION CONSTANTS
C AND PARTITION COEFFICIENT ARE SET
      KF=10.**4.33
      KS=10.**4.91
      KT=10.**7.49
      KAF=10.**(0.-3.10)
      KAS=10.**(0.-4.60)
      SOL=2.2D0
      SOL=SOL*0.8500
C
C THE INITIAL CONCENTRATION OF EXTRACTANT AND OF ACID IN THE ORGANIC
C PHASE AND THE ORGANIC TO AQUEOUS PHASE RATIO ARE SET
      BTOT=0.3D0
      ATOT=0.07500
      WRITE(6,*) 'ATOT EQUALS',ATOT
      SW=8.D0/3.D0
C
C ALPHA (EQUATION 4-37) IS CALCULATED
      ALPHA=1./(1.+KAF/HPLUS+(KAF*KAS/(HPLUS**2.)))
C
C X IS THE INITIAL GUESS FOR THE CONCENTRATION OF THE TOTAL AMOUNT OF
C ACID IN THE AQUEOUS PHASE AT EQUILIBRIUM
C
      X=0.15
C ANEW IS THE INITIAL GUESS FOR THE CONCENTRATION OF UNIONIZED ACID
C IN THE AQUEOUS PHASE, I.E., (H2A), AS CALCULATED BELOW
         ANEW=ALPHA*X
      WRITE(6,*) 'PH IS',PH,'HPLUS IS',HPLUS
      WRITE(6,*) 'ALPHA IS', ALPHA, 'GUESS IS', X
C
C IN THIS LOOP, VALUES OF F (EQUATION 4-41) ARE CALCULATED FOR
C VARYING VALUES OF (H2A)
      DO 10 K=1,100
         AFREE=ANEW
         WRITE(6,*) 'AFREE EQUALS',AFREE
         AEQ=AFREE/ALPHA
         WRITE(6,*) '      AEQ EQUALS',AEQ
C
C THE CONCENTRATION OF UNCOMPLEXED EXTRACTANT IS CALCULATED
         BFREE=(0.-(KS*(AFREE**2.)+1))+
     * ((KS*(AFREE**2.)+1.)**2.+4*BTOT*(2.*KF*AFREE+2*KT*(AFREE**2.)))
     * **0.5
         BFREE=BFREE/(4.*(KF*AFREE+KT*(AFREE**2.)))
```

```
      WRITE(6,*) 'BEREF EQUALS',BEREF
C
C THE VALUE OF F (EQUATION 4-41) IS CALCULATED
      BB=KF*(BEREF**2.)*SW+SOL*SW+1./ALPHA
      AA=2.0*KS*BEREF*SW+2.*KT*(BEREF**2.0)*SW
      FA=((0.-BB)+((BB**2.)+4.*ATOT*SW*AA)**0.5)/(2*AA)-AEREF
      WRITE(6,*) '          FA EQUALS',FA
      IF (FA .GE. 0.) WRITE(6,*) '     FA IS POSITIVE'
C
C THE TOTAL CONCENTRATION OF TRIMETHYLAMINE (ALL IN THE AQUEOUS PHASE)
C IS CALCULATED
      TMATOT=(1.+10.**(PH-9.81))*(10.**(PH-14.)-(10.**(0.-PH))+
     * (10**(0.-3.10))*ANEW*(10**PH)+2*(10.**(0.-4.60-3.10+2*PH)*ANEW))
      WRITE(6,*) 'TMATOT EQUALS',TMATOT
C
C THE RATIO OF MOLES OF TMA TO MOLES OF ACID IN THE SYSTEM IS
C CALCULATED
      RATIO=(TMATOT/ATOT)/SW
      WRITE(6,*) 'RATIO EQUALS',RATIO
      IF (FA .LT. 0.) GO TO 20
      WRITE(6,*) '     '
C
C A NEW GUESS FOR THE CONCENTRATION OF THE TOTAL AMOUNT OF ACID
C IN THE AQUEOUS PHASE IS SET
      AEQ=AEQ+0.01
C
C A NEW GUESS FOR THE CONCENTRATION OF UNIONIZED ACID IN THE
C AQUEOUS PHASE IS SET, AS CALCULATED BELOW
      ANEW=AEQ*ALPHA
10    CONTINUE
20    CONTINUE
      WRITE(6,*) 'LAST ANEW EQUALS',ANEW
      WRITE(6,*) 'K EQUALS',K
      STOP
      END
```

FILE: FUMARIC DATA A VM/XA SP2 - CMS Release 5.5 1/11/90 8806A

```
C THIS PROGRAM WAS USED TO GENERATE THE THEORETICAL BACK-EXTRACTION
C CURVE SHOWN IN FIGURE 4-3
C
      INTEGER K,N
      DOUBLE PRECISION PH,ALPHA,AFREE,BFREE,ATOT,Y,TOL,KF,KS,
     *   KT,SOL,KAF,KAS,SW,HPLUS,BTOT,BB,AA,Z,FA,FY,
     *   RATIO,TMATOT,ANSWER,UPPER,LOWER,BY,BBY,AAY,TEST,
     *   TLOWER,TUPPER,RECOVER
C
C VALUES OF THE EQUILIBRIUM CONSTANTS, ACID DISSOCIATION CONSTANTS,
C AND PARTITION COEFFICIENT ARE SET
      KF=10.**4.33
      KS=10.**4.81
      KT=10.**7.49
      KAF=10.**(0.-3.10)
      KAS=10.**(0.-4.60)
      SOL=2.200
      SOL=SOL*0.85
      TOL=0.0000001
C
C THE INITIAL CONCENTRATION OF EXTRACTANT AND OF ACID IN THE ORGANIC
C PHASE AND THE ORGANIC TO AQUEOUS PHASE RATIO ARE SET
      BTOT=0.300
      ATOT=0.2857500
      SW=8.00/3.00
C
C IN THIS LOOP, PH VALUES ARE SET.  THE UPPER- AND LOWER-BOUND VALUES
C FOR THE TOTAL CONCENTRATION OF ACID IN THE AQUEOUS PHASE AS
C DETERMINED IN THE PROGRAM, "SECOND", ARE READ IN
      DO 30 N=1,16
        READ(5,*) PH,TLOWER,TUPPER
        HPLUS=10.**(0.-PH)
        WRITE(6,*) '     '
        WRITE(6,*) 'PH EQUALS',PH,'HPLUS EQUALS',HPLUS
        WRITE(6,*) 'PARTITION EQUALS',SOL
C
C ALPHA (EQUATION 4-37) IS CALCULATED
        ALPHA=1./(1.+KAF/HPLUS*(KAF*KAS/(HPLUS**2.)))
        WRITE(6,*) 'ALPHA IS', ALPHA
        WRITE(6,*) 'GUESSES ARE',TLOWER,TUPPER
C
C IN THIS LOOP, FOR THE SET VALUE OF PH, EQUATION 4-41 IS SOLVED, I.E.,
C THE VALUE OF (H2A) THAT RESULTS IN F = 0 IS DETERMINED.
      DO 10 K=1,100
C
C THE UPPER- AND LOWER-BOUND VALUES OF (H2A) ARE CALCULATED
        LOWER=ALPHA*TLOWER
        UPPER=ALPHA*TUPPER
         AFREE=LOWER
C
C  CALCULATING F(A), I.E., F[PH,(H2A:LOWER)], EQUATION 4-41
C
         BFREE=(0.-(KS*(AFREE**2.)+1))+
     * ((KS*(AFREE**2.)+1.)**2.+4*BTOT*(2.*KF*AFREE+2*KT*(AFREE**2.)))
     * **0.5
```

```
      BFREE=BFREE/(4.*(KF*AFREE+KT*(AFREE**2.)))
      BB=KF*(BFREE**2.)*SW+SOL*SW+1./ALPHA
      AA=2.0*KS*BFREE*SW+2.*KT*(BFREE**2.0)*SW
      FA=((0.-BB)+((BB**2.)+4.*ATOT*SW*AA)**0.5)/(2*AA)-AFREE
C
C  CALCULATING FY, I.E., F(PH,(H2A:UPPER/2+LOWER/2)), EQUATION 4-41
C
      Y=LOWER+(UPPER-LOWER)/2.
      BY=(0.-(KS*(Y**2.)+1))+
     * ((KS*(Y**2.)+1.)**2.+4*ATOT*(2.*KF*Y+2*KT*(Y**2.)))
     * **0.5
      BY=BY/(4.*(KF*Y+KT*(Y**2.)))
      BBY=KF*(BY**2.)*SW+SOL*SW+1./ALPHA
      AAY=2.0*KS*BY*SW+2.*KT*(BY**2.0)*SW
      FY=((0.-BBY)+((BBY**2.)+4.*ATOT*SW*AAY)**0.5)/(2*AAY)-Y
      IF (FY .EQ. 0.) GO TO 21
C
C  COMPARING OLD AND NEW GUESSES
C
      Z=(TUPPER-TLOWER)/2.
      IF (Z .LE. TOL) GO TO 24
      TEST=FA*FY
C
C A NEW VALUE OF EITHER THE LOWER- OR UPPER-BOUND IS SET
      IF (TEST .GT. 0.) TLOWER=Y/ALPHA
      IF (TEST .LT. 0.) TUPPER=Y/ALPHA
10    CONTINUE
      WRITE(6,*) 'DOESN''T WORK, K EQUALS',K
21    CONTINUE
      WRITE(6,*) 'FY EQUALS ZERO'
24    CONTINUE
      WRITE(6,*) 'ITERATIONS EQUALS',K
      WRITE(6,*) 'AFREE EQUALS',Y
C
C THE TOTAL AQUEOUS-PHASE CONCENTRATION OF ACID AT EQUILIBRIUM IS
C CALCULATED AS (H2A)/ALPHA, BELOW
      ANSWER=Y/ALPHA
      WRITE(6,*) 'ATOT,EQ,AQ EQUALS',ANSWER
C
C THE TOTAL CONCENTRATION OF TRIMETHYLAMINE (ALL IN THE AQUEOUS
C PHASE) IS CALCULATED
      TMATOT=(1.+10.**(PH-9.81))*((10**(PH-14.))-(10**(0.-PH))+
     *  (10**(0.-3.10)))*Y*(10**PH)+2*(10.**(0.-4.60-3.10+2*PH)*Y))
      WRITE(6,*) 'TMATOT EQUALS',TMATOT
C
C THE RATIO OF MOLES OF TMA TO MOLES OF ACID IN THE SYSTEM IS
C CALCULATED
      RATIO=(TMATOT/ATOT)/SW
      WRITE(6,*) 'RATIO EQUALS',RATIO
      RECOVER=(ANSWER/ATOT)/SW
      WRITE(6,*) 'RECOVERY EQUALS',RECOVER
30    CONTINUE
      STOP
      END
```

Input to the program, "fumaric" :

9.56	0.760	0.763
9.39	0.760	0.763
9.20	0.760	0.763
9.00	0.760	0.763
8.00	0.760	0.763
7.00	0.756	0.762
6.22	0.707	0.712
5.27	0.700	0.712
5.00	0.237	0.241
4.95	0.218	0.222
4.70	0.138	0.140
4.60	0.113	0.115
4.54	0.099	0.103
4.33	0.064	0.068
3.96	0.028	0.032
2.82	0.004	0.007

Output from the program, "fumaric" :

```
PH EQUALS  9.56000000000000005      HPLUS EQUALS 0.27542287033381662 6E-09
PARTITION EQUALS  1.87000005245208722
ALPHA IS 0.380185805558739118E-11
GUESSES ARE 0.759999999999999995       0.762999999999999998
ITERATIONS EQUALS          15
AFREE EQUALS 0.290081734834267825E-11
ATOT,EQ,AQ EQUALS 0.762999908447265479
TMATOT EQUALS  2.38417483681268627
RATIO EQUALS  3.12883836852058561
RECOVERY EQUALS  1.00131221581005958

PH EQUALS  9.38999999999999990      HPLUS EQUALS 0.407380277804112837E-09
PARTITION EQUALS  1.87000005245208722
ALPHA IS 0.831751545956632751E-11
GUESSES ARE 0.759999999999999995       0.762999999999999998
ITERATIONS EQUALS          15
AFREE EQUALS 0.634626353415782408E-11
ATOT,EQ,AQ EQUALS 0.762999908447265590
TMATOT EQUALS  2.10618450724493989
RATIO EQUALS  2.76402166305110208
RECOVERY EQUALS  1.00131221581005980

PH EQUALS  9.19999999999999996      HPLUS EQUALS 0.630957344480193315E-09
PARTITION EQUALS  1.87000005245208722
ALPHA IS 0.199521523019987217E-10
GUESSES ARE 0.759999999999999995       0.762999999999999998
ITERATIONS EQUALS          15
AFREE EQUALS 0.151957468535213842E-10
ATOT,EQ,AQ EQUALS 0.761609405517576110
TMATOT EQUALS  1.89711979264111497
RATIO EQUALS  2.48965852052639747
RECOVERY EQUALS 0.999487408815716669
```

```
PH EQUALS  9.00000000000000000      HPLUS EQUALS 0.100000000000000001E-08
PARTITION EQUALS  1.87000005245208722
ALPHA IS 0.501166043545598904E-10
GUESSES ARE 0.759999999999999995       0.762999999999999998
ITERATIONS EQUALS          15
AFREE EQUALS 0.381733847117881006E-10
ATOT,EQ,AQ EQUALS 0.761688323974608825
TMATOT EQUALS  1.75929563952453250
RATIO EQUALS  2.30878692850988521
RECOVERY EQUALS 0.999590976344631024

PH EQUALS  8.00000000000000000      HPLUS EQUALS 0.100000000000000002E-07
PARTITION EQUALS  1.87000005245208722
ALPHA IS 0.500988545660584509E-08
GUESSES ARE 0.759999999999999995       0.762999999999999998
ITERATIONS EQUALS          15
AFREE EQUALS 0.381743440993960973E-08
ATOT,EQ,AQ EQUALS 0.761980377197264136
TMATOT EQUALS  1.54725679461296739
RATIO EQUALS  2.03052072783853976
RECOVERY EQUALS 0.999974248290372861

PH EQUALS  7.00000000000000000      HPLUS EQUALS 0.999999999999999955E-07
PARTITION EQUALS  1.87000005245208722
ALPHA IS 0.499200391302131503E-06
GUESSES ARE 0.756000000000000005       0.761999999999999997
ITERATIONS EQUALS          16
AFREE EQUALS 0.379426132963017077E-06
ATOT,EQ,AQ EQUALS 0.760067779541015329
TMATOT EQUALS  1.51947029464512817
RATIO EQUALS  1.99405550478363260
RECOVERY EQUALS 0.997464277612880992

PH EQUALS  6.21999999999999997      HPLUS EQUALS 0.602559586074357777E-06
PARTITION EQUALS  1.87000005245208722
ALPHA IS 0.177704296609843232E-04
GUESSES ARE 0.707000000000000003       0.711999999999999994
ITERATIONS EQUALS          16
AFREE EQUALS 0.126280321293523223E-04
ATOT,EQ,AQ EQUALS 0.710620529174804547
TMATOT EQUALS  1.40492894214835329
RATIO EQUALS  1.84373876922356073
RECOVERY EQUALS 0.932572872932814365

PH EQUALS  5.27000000000000002      HPLUS EQUALS 0.537031796370252712E-05
PARTITION EQUALS  1.87000005245208722
ALPHA IS 0.118942745931729504E-02
GUESSES ARE 0.699999999999999997       0.711999999999999994
ITERATIONS EQUALS          17
AFREE EQUALS 0.846872242138577722E-03
ATOT,EQ,AQ EQUALS 0.711999908447265531
TMATOT EQUALS  1.29707635230576912
RATIO EQUALS  1.70219993740914588
RECOVERY EQUALS 0.934383081951792024

PH EQUALS  5.00000000000000000      HPLUS EQUALS 0.999999999999999997E-05
PARTITION EQUALS  1.87000005245208722
ALPHA IS 0.357195560435231768E-02
GUESSES ARE 0.237000000000000002       0.241000000000000006
ITERATIONS EQUALS          16
AFREE EQUALS 0.858596401548687412E-03
ATOT,EQ,AQ EQUALS 0.240371520996093616
TMATOT EQUALS 0.410821451237148999
RATIO EQUALS 0.539135762778410771
RECOVERY EQUALS 0.315448190283587421
```

```
PH EQUALS  4.94999999999999996      HPLUS EQUALS 0.11220184543019635 6E-04
PARTITION EQUALS  1.87000005245208722
ALPHA IS 0.434247165188559377E-02
GUESSES ARE 0.217999999999999999       0.222000000000000003
ITERATIONS EQUALS          16
AFREE EQUALS 0.959611757861260372E-03
ATOT,EQ,AQ EQUALS 0.220982849121093616
TMATOT EQUALS 0.372105065538926041
RATIO EQUALS 0.488326857662632577
RECOVERY EQUALS 0.290003739004059860

PH EQUALS  4.69999999999999996      HPLUS EQUALS 0.199526231496887998E-04
PARTITION EQUALS  1.87000005245208722
ALPHA IS 0.109975514125581365E-01
GUESSES ARE 0.137999999999999998       0.139999999999999999
ITERATIONS EQUALS          15
AFREE EQUALS 0.153965652652087007E-02
ATOT,EQ,AQ EQUALS 0.139999938964843723
TMATOT EQUALS 0.215607469649707520
RATIO EQUALS 0.282949435235836641
RECOVERY EQUALS 0.183726954022104622

PH EQUALS  4.60000000000000009      HPLUS EQUALS 0.251188643150957948E-04
PARTITION EQUALS  1.87000005245208722
ALPHA IS 0.155652975329168908E-01
GUESSES ARE 0.113000000000000003       0.115000000000000005
ITERATIONS EQUALS          15
AFREE EQUALS 0.179000826625507528E-02
ATOT,EQ,AQ EQUALS 0.114999938964843729
TMATOT EQUALS 0.169790777826511460
RATIO EQUALS 0.222822543079411364
RECOVERY EQUALS 0.150918555071973395

PH EQUALS  4.54000000000000004      HPLUS EQUALS 0.288403150312660563E-04
PARTITION EQUALS  1.87000005245208722
ALPHA IS 0.190365389721107621E-01
GUESSES ARE 0.990000000000000047E-01  0.102999999999999994
ITERATIONS EQUALS          16
AFREE EQUALS 0.195011007016773400E-02
ATOT,EQ,AQ EQUALS 0.102440368652343669
TMATOT EQUALS 0.147241998412571518
RATIO EQUALS 0.193230969045369447
RECOVERY EQUALS 0.134436179333784336

PH EQUALS  4.33000000000000007      HPLUS EQUALS 0.467735141287198128E-04
PARTITION EQUALS  1.87000005245208722
ALPHA IS 0.368969418562646086E-01
GUESSES ARE 0.640000000000000013E-01  0.680000000000000049E-01
ITERATIONS EQUALS          16
AFREE EQUALS 0.245567119098119227E-02
ATOT,EQ,AQ EQUALS 0.665548706054686634E-01
TMATOT EQUALS 0.664486551669359088E-01
RATIO EQUALS 0.113449678696766282
RECOVERY EQUALS 0.873423498759431233E-01

PH EQUALS  3.95999999999999996      HPLUS EQUALS 0.109647819614318512E-03
PARTITION EQUALS  1.87000005245208722
ALPHA IS 0.100969936798364399
GUESSES ARE 0.279999999999999997E-01  0.319999999999999998E-01
ITERATIONS EQUALS          16
AFREE EQUALS 0.311219000201320815E-02
ATOT,EQ,AQ EQUALS 0.308229370117187413E-01
TMATOT EQUALS 0.327660850492828620E-01
RATIO EQUALS 0.430001116132321011E-01
RECOVERY EQUALS 0.404500485718093678E-01
```

```
PH EQUALS  2.8200000000000006      HPLUS EQUALS 0.15135612484362079 3E-02
PARTITION EQUALS  1.8700000524520 8722
ALPHA IS 0.65209595058106995 0
GUESSES ARE 0.40000000000000008E-02  0.70000000000000015E-02
ITERATIONS EQUALS          15
AFREE EQUALS 0.36874824021856812 5E-02
ATOT,EQ,AQ EQUALS 0.56548156738281188 4E-02
TMATOT EQUALS 0.48588864462021969 1E-03
RATIO EQUALS 0.63764913992154815 0E-03
RECOVERY EQUALS 0.74210179446563238 9E-02
```

```
FILE: EQUILF   DATA     A    VM/XA SP2 - CMS Release 5.5 1/11/90 8806A

C THIS PROGRAM WAS USED TO GENERATE THE EQUILIBRIUM CURVES SHOWN IN
C FIGURES 6-5 AND 6-6
C
      INTEGER K,N
      DOUBLE PRECISION PH,ALPHA,AFREE,BFREE,ATOT,Y,TOL,KF,KS,
     *   KT,SOL,KAF,KAS,SW,HPLUS,BTOT,BB,AA,Z,FA,FY,
     *   RATIO,TMATOT,ANSWER,UPPER,LOWER,PY,BBY,AAY,TEST,
     *   TLOWER,TUPPER,RECOVER,TOLL,TESTR,O,DIF,TTUPPER,TTLOWER
C
C VALUES OF THE EQUILIBRIUM CONSTANTS, ACID DISSOCIATION CONSTANTS,
C AND PARTITION COEFFICIENT ARE SET
      KF=10.**4.33
      KS=10.**4.81
      KT=10.**7.49
      KAF=10.**(0.-3.10)
      KAS=10.**(0.-4.60)
      SOL=2.200
      SOL=SOL*0.8500
      TOL=0.0000001
      TOLL=0.00001
C
C THE INITIAL CONCENTRATION OF EXTRACTANT IN THE ORGANIC PHASE AND
C THE ORGANIC TO AQUEOUS PHASE RATIO ARE SET
      BTOT=0.300
      SW=8.00/3.00
C
C THE PH, AMOUNT OF ACID IN THE SYSTEM, AND THE UPPER- AND LOWER-
C BOUND VALUES AS DETERMINED IN THE PROGRAM, "SECOND", ARE READ IN
      READ(5,*) ATOT,PH,TTLOWER,TTUPPER,DIF
C
C IN THIS LOOP, EQUATION 4-41 IS SOLVED FOR THE GIVEN VALUES OF TOTAL
C ACID AND AQUEOUS-PHASE PH
      DO 30 N=1,100
        HPLUS=10.**(0.-PH)
        WRITE(6,*) '     '
        WRITE(6,*) 'ATOT EQUALS',ATOT
        WRITE(6,*) 'PH EQUALS',PH,'HPLUS EQUALS',HPLUS
        WRITE(6,*) 'PARTITION EQUALS',SOL
C
C ALPHA (EQUATION 4-37) IS CALCULATED
        ALPHA=1./(1.+KAF/HPLUS+(KAF*KAS/(HPLUS**2.)))
        WRITE(6,*) 'ALPHA IS', ALPHA
        WRITE(6,*) 'GUESSES ARE',TTLOWER,TTUPPER
        TLOWER=TTLOWER
        TUPPER=TTUPPER
      DO 10 K=1,100
C
C THE VALUES OF (H2A), I.E., AQUEOUS-PHASE UNIONIZED ACID CONCENTRATION,
C ARE CALCULATED
         LOWER=ALPHA*TLOWER
         UPPER=ALPHA*TUPPER
          AFREE=LOWER
C
C  CALCULATING F(A), I.E., EQUATION 4-41, WITH (H2A) = LOWER
C
```

```
          BFREE=(0.-(KS*(AFREE**2.)+1))+
     * ?(KS*(AFREE**2.)+1.)**2.+4*ATOT*(2.*KF*AFREE+2*KT*(AFREE**2.)))
     * **0.5
          BFREE=BFREE/(4.*(KF*AFREE+KT*(AFREE**2.)))
          BB=KF*(BFREE**2.)*SW+SOL*SW+1./ALPHA
          AA=2.0*KS*BFREE*SW+2.*KT*(BFREE**2.0)*SW
          FA=((0.-BB)+((BB**2.)+4.*ATOT*SW*AA)**0.5)/(2*AA)-AFREE
C
C  CALCULATING FY, I.E., EQUATION 4-41, WITH (H2A) = LOWER/2 + UPPER/2
C
          Y=LOWER+(UPPER-LOWER)/2.
          BY=(0.-(KS*(Y**2.)+1))+
     * ?(KS*(Y**2.)+1.)**2.+4*ATOT*(2.*KF*Y+2*KT*(Y**2.)))
     * **0.5
          BY=BY/(4.*(KF*Y+KT*(Y**2.)))
          BBY=KF*(BY**2.)*SW+SOL*SW+1./ALPHA
          AAY=2.0*KS*BY*SW+2.*KT*(BY**2.0)*SW
          FY=((0.-BBY)+((BBY**2.)+4.*ATOT*SW*AAY)**0.5)/(2*AAY)-Y
          IF (FY .EQ. 0.) GO TO 21
C
C  COMPARING OLD AND NEW GUESSES
C
          Z=(UPPER-LOWER)/2.
          IF (Z .LE. TOL) GO TO 24
          TEST=FA*FY
C
C A NEW VALUE FOR EITHER THE UPPER OR LOWER BOUND IS SET
          IF (TEST .GT. 0.) LOWER=Y/ALPHA
          IF (TEST .LT. 0.) UPPER=Y/ALPHA
10     CONTINUE
          WRITE(6,*) 'DOESN''T WORK, K EQUALS',K
21     CONTINUE
          WRITE(6,*) 'FY EQUALS ZERO'
24      CONTINUE
          WRITE(6,*) 'ITERATIONS EQUALS',K
          WRITE(6,*) 'AFREE EQUALS',Y
C
C THE TOTAL CONCENTRATION OF ACID IN THE AQUEOUS PHASE AT EQUILIBRIUM
C IS CALCULATED
          ANSWER=Y/ALPHA
          WRITE(6,*) 'ATOT,EQ,AQ EQUALS',ANSWER
C
C THE TOTAL CONCENTRATION OF TRIMETHYLAMINE (ALL IN THE AQUEOUS
C PHASE? IS CALCULATED
          TMATOT=(1.+10.**(PH-9.81))*((10**(PH-14.))-(10**(0.-PH))+
     *   (10**(0.-3.10))*Y*(10**PH)+?*(10.**(0.-4.60-3.10+2*PH)*Y))
          WRITE(6,*) 'TMATOT EQUALS',TMATOT
C
C THIS VALUE OF TMA CONCENTRATION IS COMPARED TO THE DESIRED VALUE,
C WHICH, IN THIS EXAMPLE, IS 0.76 MOL/L
          Q=DABS(TMATOT-0.76)
          IF (Q .LE. TOLL) GO TO 34
          TESTR=TMATOT-0.76
C
C IF THE CALCULATED TMA CONCENTRATION IS NOT THE DESIRED VALUE, THE
```

```
C VALUE OF THE AQUEOUS-PHASE PH IS ADJUSTED, AND THE CALCULATIONS ARE
C REPEATED
          IF (TESTR .GT. 0.) PH=PH-DTF
          IF (TESTR .LT. 0.) GO TO 36
30        CONTINUE
          WRITE(6,*) 'DOESN''T WORK, N =',N
36        CONTINUE
          WRITE(6,*) 'DOESN''T WORK, TESTR =',TESTR
34        CONTINUE
          WRITE(6,*) 'TMATOT EQUALS',TMATOT
C
C THE RATIO OF MOLES OF TMA TO ACID IN THE SYSTEM IS CALCULATED
          RATIO=(TMATOT/ATOT)/SW
          WRITE(6,*) 'RATIO EQUALS',RATIO
          RECOVER=(ANSWER/ATOT)/SW
          WRITE(6,*) 'RECOVERY EQUALS',RECOVER
          STOP
          END
```