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Scott M. Husson and C. Judson King

Environmental Energy Technologies Division

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REGENERATION OF LACTIC AND SUCCINIC ACID-LADEN BASIC SORBENTS BY LEACHING WITH A VOLATILE BASE IN AN ORGANIC SOLVENT

by

Scott M. Husson and C. Judson King

Department of Chemical Engineering
University of California

and

Environmental Energy Technologies Division
Lawrence Berkeley National Laboratory
Berkeley, California 94720

September 1997

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Regeneration of Lactic and Succinic Acid-Laden Basic Sorbents by Leaching with a Volatile Base in an Organic Solvent

Scott M. Husson
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Abstract

Recovery of carboxylic acids from aqueous solutions using reversible chemical complexation with basic polymeric sorbents affords an energy-efficient separation technique. If an appropriate method of regeneration for such sorbents, allowing recovery and reuse of all agents, is utilized, this separation technique can also avoid production of waste salts and net consumption of chemical agents. Leaching with an organic solution of a volatile base was explored as a method of regenerating tertiary amine and pyridyl sorbents. Experimental data are presented which show that regeneration efficiency correlates with the non-aqueous basicity of the regenerant as measured by the Gutmann donicity scale. Essentially complete regeneration of lactic acid-laden Dowex MWA-1 was achieved when 8-10 moles of trimethylamine were present for every mole of adsorbed acid; adequate (over 70%) regeneration was obtained at a molar ratio of 2:1. The resulting trimethylamine-lactic acid complex can be thermally decomposed fully when trimethylamine is employed in an organic solvent instead of in water. A likely cause of the incomplete thermal decomposition of trimethylammonium lactate in previous, water-based systems is the aqueous environment in which the decomposition was performed.

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1. Introduction

Carboxylic acids are important chemicals of commerce. They also appear as desired or contaminating constituents of a wide range of aqueous process streams. There are many instances where it is important to remove and/or recover carboxylic acids from aqueous solutions. Examples include product recovery in the manufacture of chemicals from biomass by fermentation and both product recovery and processing of aqueous wastes in the petrochemical, chemical, pulp and paper industries. There are also applications in other industries based upon biological materials, such as corn wet milling and processing of grains and food oils. Acids commonly of interest are acetic, formic, succinic, adipic, fumaric, maleic, malic, citric and lactic acids. There is strong industrial interest in lactic acid as a precursor to biodegradable plastics.

1.1 Separation Techniques

Present separation techniques for removal and recovery of carboxylic acids from dilute aqueous solutions are energy-intensive and therefore expensive. Some, such as the classical method for recovery of citric and lactic acids by precipitation of calcium salts and those requiring regeneration by leaching with an aqueous solution of a strong base, also consume large volumes of chemicals (e. g., sulfuric acid and lime) and create large volumes of waste (e. g., calcium sulfate). Recovery technology using reversible chemical complexation with agents such as polymeric sorbents with amine functionalities can reduce energy consumption substantially. If an appropriate method of regeneration, allowing recovery and reuse of all agents, is utilized, such processes can also avoid production of waste salts and net consumption of chemical agents.

1.2 Separation by Reversible Chemical Complexation

Previous researchers (Kertes and King, 1986; Tamada, et al., 1990; Yabannavar and Wang, 1987, 1991; Yang, et al., 1987; Garcia and King, 1989) have shown that extraction and adsorption by reversible chemical complexation are effective for recovery of carboxylic acids from dilute aqueous solutions. Amine-based extractants and adsorbents sustain uptake capacity for carboxylic acids from solutions at pH above the pK_{a1} of the acid, where the acid exists mostly as the carboxylate anion. Agents such as carbon dioxide can be used in conjunction with these complexing agents to avoid the problem of pH-rise and, therefore, to sustain uptake capacity at $pH>pK_{a1}$ (Husson and King, 1997). However, these strongly basic complexing agents require correspondingly strong methods for regeneration (Tung and King, 1992, 1994).

1.3 Regeneration Methods

1.3.1 pH-swing

One approach to regenerating strongly basic extractants and adsorbents is leaching with an aqueous solution of a strong base (e.g., NaOH or $Ca(OH)_2$) to form the carboxylate salt. A strong acid (e.g., H_2SO_4) must then be added to liberate the carboxylic acid product. This approach necessarily consumes chemicals and produces a waste salt by-product. Kulprathipanja and Strong (1990) provide an example of a carboxylic acid recovery process utilizing pH-swing regeneration. This patent discloses a process for adsorption of citric acid by adsorbents containing tertiary amine or pyridyl functionalities, with regeneration using an aqueous solution of sodium, potassium or ammonium hydroxide, yielding the respective sodium, potassium or ammonium citrate. Treatment of these citrates with a strong acid would yield the free citric acid form, but again consumes an acid and a base and produces a waste salt stream.

1.3.2 pH-swing Using a Volatile Base

A second approach involves leaching with an aqueous solution of a volatile base, such as trimethylamine (TMA) (Poole and King, 1991, 1995). The resulting trimethylammonium carboxylate can be decomposed thermally, yielding acid product and recovering the TMA, available for recycle. For sparingly soluble acids, such as succinic and fumaric, partial evaporation of the aqueous trimethylammonium carboxylate solution results in precipitation of the acid product (Poole and King, 1991). However, for lactic acid, which is highly soluble in water and self associating, the thermal decomposition of trimethylammonium lactate is incomplete (Poole and King, 1991), leaving about 0.6 mols TMA/mol lactic acid under the conditions used.

1.3.3 Solvent Leaching

Several investigators have developed carboxylic acid recovery schemes using ion exchange and/or adsorption, with regeneration of the acid-laden resin by solvent leaching. Kulprathipanja (1988) discloses the use of styrene-divinylbenzene resins to adsorb citric acid with regeneration by water or by a mixture of acetone and water. Similarly, Kawabata (1982) discloses the use of adsorbents containing pyridyl functional groups combined with regeneration by leaching with an organic solvent such as an alcohol or a ketone. In each of these processes, the carboxylic acid is adsorbed from an aqueous solution at pH below the pK_{a1} of the acid. Frierman et al. (1987) investigated solvent leaching as a method of regeneration for activated carbons and both basic and non-functionalized polymeric adsorbents loaded with acetic acid. The organic solvents used included ketones, esters, methanol, dimethyl sulfoxide, diisopropyl ether, toluene and undecane. Sorbents containing amine functional groups gave incomplete regeneration by solvent leaching under the conditions used.

1.4 General Research Objective

The various methods used heretofore to recover carboxylic acids have presented limitations and thus offer opportunities for improvement. It is accordingly a general objective of this research to provide an efficient process for the recovery of carboxylic acids from aqueous solutions which neither consumes large amounts of chemicals nor generates waste chemical streams.

1.5 Proposed Process

In the process under consideration, the carboxylic acid is first removed from an aqueous feed stream by a solid phase adsorption technique with a basic sorbent. The sorbed carboxylic acid is then recovered by contacting the sorbent phase with an organic solution of a volatile base that is sufficiently basic in comparison with the sorbent. This "back-extracts" or solubilizes the carboxylic acid into the organic phase as an acid/base complex. The organic solution containing the acid/base complex is heated to decompose the complex fully to yield the carboxylic acid product. The volatile base can be recovered overhead and recycled. Chapter addresses various process considerations. A patent application covering this process has been filed with the U.S. Patent and Trademark Office.

This process can be viewed as an improvement in the process for carboxylic acid recovery from solid sorbents in which the acid is converted into an aqueous solution of alkylammonium carboxylate, which is then thermally decomposed. A likely cause of the incomplete thermal decomposition of alkylammonium carboxylates of the more soluble and associating acids recovered from the solid sorbent in the work of Poole and King (1991) is the aqueous environment in which the decomposition was carried out. An aqueous environment promotes ionization of the alkylammonium carboxylate

salt, thereby suppressing the volatility of the alkylamine and stabilizing the alkylammonium carboxylate salt in the liquid phase. Employing a volatile base (e.g., an alkylamine) in an organic solvent instead of in water results in complete decomposition of the acid/base complex during the heating step. The volatile base in this process is not limited to alkylamines.

The importance of the solvent can be understood by examining the process of acid-base ionization. Equation 1.5-1 shows the equilibria involved when an acid, HA, and base, B, are placed together in solution (Popovych and Tomkins, 1981):

$$\underset{(1)}{HA + B} \leftrightarrow \underset{(2)}{HA \cdots B} \leftrightarrow \underset{(3)}{A^{\delta-} \cdots BH^{\delta+}} \leftrightarrow \underset{(4)}{A^{-} + BH^{+}} \qquad (1.5\text{-}1)$$

Initially, the acid and base exist in molecular form (1). In equilibrium with the unassociated acid and base molecules is the loosely associated acid-base complex resulting from hydrogen bonding (2). The degree of complex formation depends on whether the solvent is more effective at stabilizing the individual molecules or the acid-base complex. If the acid-base interaction is strong, there may be partial charge transfer within this complex (3). For solvents of high dielectric constant (e.g., water) the charge transfer will be complete, and fully solvated ions will exist in solution (4). Thus, for a given acid and base, the degree of ionization is a function of the solvent dielectric constant. The strength of interaction increases from (1) to (4). The goal is to choose a solvent with a low dielectric constant (e.g., an organic solvent) which stabilizes the free acid more effectively than the acid-base complex. This serves to drive the equilibrium in Equation 1.5-1 towards the left, in the direction of the more loosely associated complexes.

In the organic solvent, the basicity of the regenerant material is reflected primarily through Lewis acid/Lewis base (e.g., hydrogen bonding) interactions, rather than through protonation (ionization) as is the case for the alkylamine carboxylates in an aqueous solution. Suppression of ionization in the organic solution promotes thermal decomposition of the acid/base complex.

After removal of the volatile base through thermal decomposition and vaporization, product carboxylic acid can be recovered by evaporative crystallization from the organic solvent or by other means. Alternatively, if an aqueous concentrate is the desired product, the carboxylic acid can be transferred from the organic solvent to water in a dual-feed distillation, provided that the acid is sufficiently soluble and the organic solvent is sufficiently miscible with water at distillation temperatures.

2. Experimental Materials and Methods

2.1 Materials

2.1.1 Chemical Reagents

Table 2.1-1 lists the chemical reagents used in this work along with their sources.

TABLE 2.1-1
Chemical Reagents and Their Sources

Chemical	Source	Description
Lactic acid	Aldrich	85+% in water, A.C.S. reagent grade
Succinic acid	Aldrich	99+%, A.C.S. reagent grade
Methyl ethyl ketone	Fisher Scientific	
Methyl isobutyl ketone	Sigma-Aldrich	99.5+%, HPLC grade
Trimethylamine	Matheson	Anhydrous
Piperidine	Aldrich	99%
Dimethyl sulfoxide	American Burdick & Jackson	
Pyridine	Mallinckrodt	Analytical reagent
Acetonitrile	Baxter	
Methanol	Fisher Scientific	A.C.S. reagent grade
Sodium hydroxide	Aldrich	A.C.S. reagent grade
Hydrochloric acid	Fisher Scientific	37+% in water, A.C.S. reagent grade
Sulfuric acid	Fisher Scientific	A.C.S. reagent grade
Karl Fisher reagent	GFS Chemicals	methanol-free, ketone compatible
Karl Fisher titrant	GFS Chemicals	2 mg/mL
Westvāco WV-B activated carbon	Westvāco Chemical Division	Wood-based

All aqueous solutions were prepared from distilled water which had been passed through a Milli-Q water purification system (Millipore Corp.).

The 85+wt.% commercial grade lactic acid contains both lactic acid monomers and significant amounts of intermolecular esters. Below about 20 wt.%, the solution contains primarily the acid monomer (Holten, 1971). The 85+wt.% lactic acid solution was diluted with water to approximately 15 wt.% and boiled under constant reflux for at least 12 hours to hydrolyze any lactic acid polymers. Boiling the solution was necessary to increase the rate of hydrolysis of the intermolecular esters (Holten, 1971). Complete hydrolysis of the esters was confirmed by high-performance liquid chromatography (HPLC).

2.1.2 Polymeric Sorbents

The polymeric sorbents utilized are listed in Table 2.1-2 with their manufacturers and structures.

TABLE 2.1-2
Polymeric Sorbents and Their Sources (Dow, 1983; Reilly, 1989; Rohm & Haas, 1981)

Sorbent	Manufacturer	Polymer Matrix	Functional Groups	Mesh Size
Dowex MWA-1	Dow Chemical Co.	Polystyrene-divinylbenzene	~90% 3° amine ~10% 4° ammonium	20-50
Amberlite IRA-35	Rohm & Haas Corporation	Acrylic	3° amine	16-50
Reillex 425	Reilly Industries, Inc.	Poly(4-vinyl pyridine)	Pyridine	18-50

All of the sorbents are commercially available and all are macroreticular. Prior to use, the sorbents were washed repeatedly with aqueous hydrochloric acid, aqueous sodium hydroxide, water and

methanol in that order. The sorbents were further purified by Soxhlet extraction with methanol for at least 24 hours. Prior to use, the sorbents were dried to constant weight in a vacuum oven (VWR Scientific, Inc., Model 1410D) at 60°C and 15-25 kPa. The activated carbon, Westvāco WV-B was used as received.

2.1.3 Regenerant Solutions

In order to vary the amount of regenerant base in contact with the acid-laden sorbent while maintaining a fixed solution to sorbent ratio, the regenerant base was diluted in an organic solvent. The organic solvent also provided a liquid phase for trimethylamine (TMA), which is a gas at 25°C. In the case of TMA, the regenerant solution was prepared by bubbling gaseous TMA in methyl ethyl ketone (MEK) or methyl isobutyl ketone (MiBK). Organic-phase water concentrations were measured by Karl Fischer titration using a methanol-free, ketone-compatible Karl Fischer reagent and Karl Fisher titrant. A methanol-free solvent was used to avoid formation of ketals and water by reaction of ketones with methanol. Methanol was replaced by 2-methoxyethanol, which reacts with ketones at an insignificant rate (MacLeod, 1991). Typical organic-phase water concentrations were $<5\times10^{-4}$ g H_2O/g solution.

2.2 Methods

2.2.1 Preparation of Acid-Laden Sorbent for Regeneration

To prepare acid-laden sorbent for regeneration, known weights of dry sorbent (typically 0.5 g) and acid solution (typically 5.0 g) were contacted in 20-mL scintillation vials sealed with Teflon®-lined caps. The vials were placed in a constant-temperature, reciprocating shaker bath (Fisher Scientific, Versa-Bath® S) at 25°C and 120 RPM for at least 24 hours. Previous studies of sorption of lactic

acid on Dowex MWA-1 showed that equilibrium was reached within the experimental error in one hour (Tung and King, 1994). Aqueous-phase acid concentrations were determined by HPLC using a Bio-Rad Aminex HPX-87H strong cation-exchange column or a Bio-Rad Fast-acid Analysis column, a 0.01 N H_2SO_4 mobile phase, and an ultraviolet detector (Hewlett-Packard, Series 1050) operating at 210 nm.

Total solution uptakes were determined by weighing the sorbent samples following centrifugation in a 15-mL, coarse grade, fritted glass funnel enclosed within a plastic centrifuge tube. The centrifuge (Damon/IEC, Model HN-SII) was operated for 8 minutes at 2000 RPM. These conditions are sufficient to remove nearly all of the interstitial and adhering bulk liquid (Frierman, 1983).

To maintain an essentially anhydrous environment during regeneration, the sorbed water was removed from the "wet" acid-laden sorbent by drying to constant weight in a vacuum oven at 60°C and 50-60 kPa. The extremely low volatility of lactic and succinic acids ensured that losses of acid during this drying step were insignificant in comparison to the total acid uptake.

2.2.2 Sorbent Regeneration

Regeneration isotherms were generated by contacting "dry" acid-laden sorbent with organic base solutions in 20-mL scintillation vials sealed with Teflon®-lined caps. The vials were placed in a constant-temperature shaker bath at 25°C and 120 RPM for at least 24 hours. The solution-to-sorbent phase ratio for regeneration of Dowex MWA-1 and Amberlite IRA-35 was generally 29-30 mL/g; the phase ratio for regeneration of Reillex 425 was 5-6 mL/g. For experiments using TMA, the initial TMA concentrations were determined by HPLC using a Bio-Rad Aminex HPX-72-O

organic base-analysis column, a 0.01 N NaOH mobile phase, and an ultraviolet detector (Hewlett-Packard, Series 1050) operating at 214 nm. To determine the remaining amount of sorbed acid following regeneration, the acid concentration in the regenerant solution was measured by HPLC.

2.2.3 Thermal Cracking of Acid/Amine Complex

The apparatus used for thermal cracking of the TMA-lactic acid complex is depicted in Figure 2.2-1. The organic solution containing lactic acid, TMA and MEK was placed in a 3-neck, 100-mL, round-bottom flask equipped with a magnetic stir bar, thermometer, and a heating mantle (Glas-Col Apparatus Co.) attached to a voltage regulator (The Superior Electric Co.). The experiments were performed at atmospheric pressure, and nitrogen was sparged into the solution to prevent possible oxidation of the TMA. The solution was boiled under total reflux. The TMA evolved was carried to an absorber flask containing dilute H_2SO_4 and agitated by a magnetic stirrer.

The rate of evolution of TMA was monitored by absorption into dilute H_2SO_4 containing methyl red as the indicator. At the beginning of a run, the absorber flask was filled with 500-mL of H_2SO_4 solution concentrated enough to neutralize about 25% of the TMA initially present in the TMA-lactic acid solution. When 25% of the TMA had been absorbed, the solution changed color from red to yellow. At this point, the time was recorded and 5-mL of a concentrated solution of H_2SO_4 (enough to neutralize another 10% of the TMA) was injected into the absorber flask. This process was repeated throughout the experiment, adding enough H_2SO_4 to neutralize 10% of the TMA with each injection. A sample of the final absorber solution was titrated with 0.0794 N NaOH to determine the amount of TMA that had been absorbed between the last color change and the end of the experimental run. The amount of TMA remaining in the lactic acid solution was determined by

HPLC.

2.2.4 Product Purification

Treatment of the final acid solution with activated carbon was examined as a purification technique to remove colored impurities. A sample of the lactic acid solution following thermal cracking was contacted with a known weight of Westvāco WV-B carbon for 1 minute. A second, aqueous sample was prepared by transferring the acid from the organic solution to water by evaporation with water addition. This sample was also contacted with activated carbon. The two solutions were filtered to remove carbon fines. Changes in solution color were examined visually and spectrophotometrically. Absorbance spectra were measured using a spectrophotometer (Varian, Cory UV-Vis) operating between 380 and 800 nm.

2.2.5 Fixed-bed Regeneration

Fixed-bed regeneration of carboxylic acid-laden sorbent by leaching with an organic solution of trimethylamine (TMA) was investigated to assess the kinetics of the regeneration process.

Figure 2.2-2 shows a schematic representation of the apparatus used for the fixed-bed regeneration experiments. A known dry mass of Dowex MWA-1 sorbent was pre-wet with methanol and fed as a slurry to a 1cm I.D. x 30 cm length Chromaflex® (Kontes) glass column. The outlet tubing at the bottom of the column was elevated to avoid drainage of the methanol from the bed. Additional methanol was added to fill the column completely. Pure water was fed to the column via PTFE tubing connected to an adjustable plunger at the top of the column to displace the methanol from the sorbent. All solutions were delivered to the top of the column with a Masterflex® (Cole-Parmer Co.)

peristaltic pump at a controlled volumetric flow rate of 1.8 mL/min. Prior to methanol displacement, the inlet tubing and the plunger were filled with water, and the adjustable plunger at the top of the column was positioned to minimize the mixing volume above the sorbent bed. Effluent samples from the column were collected over specified time intervals in glass scintillation vials using a fraction collector (LBK-Produkter AB).

During the acid adsorption (i.e., sorbent loading) step, a 2 wt.% aqueous lactic acid solution was fed to the column. Effluent samples were collected over 3-minute intervals into 20-mL scintillation vials. Lactic acid concentrations in the effluent samples were measured by HPLC, as already described.

When the sorbent bed was fully loaded (i.e., had reached its adsorption capacity), the flow of acid solution was stopped, and pure MEK or acetone was fed to the column to displace the remaining water in the sorbent bed. This switch in feed solution marked the beginning of the water-displacement step. During this period, the fraction sizes were adjusted to ensure that rapid changes in acid and water concentration could be monitored with precision. The sequence of collection times was 14 samples at 50 s, 7 samples at 1 min, 7 samples at 2 min. Water contents of the samples were measured by Karl Fischer titration with the methanol-free, ketone-compatible solvent. An effluent density profile was also measured by weighing known sample volumes using an Eppendorf pipet.

When water concentrations in the effluent reached values less than 1 wt.%, the flow of pure ketone was stopped, and a solution of TMA in MEK was fed to the column to regenerate the lactic acid-laden sorbent. TMA concentrations of 2.8 wt.% and 10.1 wt.% were investigated. The sequence of collection times during regeneration was 14 samples at 50 s, 7 samples at 1 min, 7 samples at 2

min, 7 samples at 3 min, 7 samples at 4 min. TMA concentrations in the effluent were measured by HPLC using a Bio-Rad Aminex HPX-72-O organic base column. Minor losses of TMA from the collected samples may have occurred despite efforts to seal each sample immediately following the completed collection interval. Losses during the early stages of regeneration should be less significant because the presence of carboxylic acid in the samples suppresses the volatility of the TMA. In addition, the sampling time intervals were smaller at the beginning of regeneration.

3. Selection of the Organic Base and Solvent

The organic base should supply a sufficiently large driving force for regeneration of the sorbent. In addition to competing effectively with the basic sites of the sorbent for the acid, the base must be removable from the sorbent under conditions which will not degrade the sorbent. The base should be sufficiently different in volatility to be easily removed from the acid following sorbent regeneration. To aid the selection of appropriate organic bases, linear free-energy relations were developed to correlate regeneration capacity of various regenerants in terms of their non-aqueous basicity as measured by the Gutmann donicity scale.

3.1 Linear Free-energy Relations (LFER) (Jensen, 1980)

A useful empirical tool for predicting reactivity trends for a series of related reactions is a linear free-energy relation (LFER). The importance of such a relation is that given a knowledge of the reactivity trends of a related reaction series, it can predict reactivity trends for the reaction series of interest. A reaction series may correspond to the reactions of a single species with a substrate whose structure is varied via different substitutions or to the reactions of a single substrate with a series of attacking reagents. Examples of these types of reaction series are regeneration of various acid-laden sorbents with a single regenerant species and regeneration of a single acid-laden sorbent by various regenerant species, respectively.

An example of an LFER is the correlation between the logarithms of the equilibrium constants for two reaction series, α and β for a common species, i:

$$\ln K_i^{\alpha} = a \ln K_i^{\beta} + b \qquad (3.1\text{-}1)$$

where a and b are parameters characteristic of species i. Recognizing the relationship between the equilibrium constant and the standard Gibbs free-energy change for each reaction, Equation 3.1-1 can be rewritten as a true LFER:

$$\Delta g_i^{\alpha} = a' \, \Delta g_i^{\beta} + b' \qquad (3.1\text{-}2)$$

The free-energy change for each reaction is a combination of enthalpic and entropic contributions:

$$\Delta g_i^{\alpha} = \Delta h_i^{\alpha} - T \, \Delta s_i^{\alpha} \qquad (3.1\text{-}3)$$

Within a reaction series, the absolute changes in the Gibbs free-energy are not of concern, but rather the relative changes in Gibbs free-energy of two closely related reactions. Equation 3.1-3 can be written in differential form:

$$\delta\Delta g_i^{\alpha} = \delta\Delta h_i^{\alpha} - T \, \delta\Delta s_i^{\alpha} \qquad (3.1\text{-}4)$$

A frequent assumption (Hammett, 1940) is that the reactions within a given reaction series have similar entropy changes:

$$\delta\Delta s_i^{\alpha} = 0 \qquad (3.1\text{-}5)$$

With this assumption, Equation 3.1-2 can be written in terms of changes in enthalpy, rather than in terms of changes in Gibbs free-energy. The significance of this assumption can be demonstrated using the concept of the Gutmann donor number for correlating regenerant basicity.

3.2 Gutmann Donor Number (Gutmann, 1978)

Donor numbers were developed to correlate the properties of an acidic solute in a variety of donor

solvents with the coordinating ability of a given solute (i.e., its Lewis basicity). Gutmann's reference acid is $SbCl_5$ because (1) it forms 1:1 molar adducts with all donor molecules, (2) it allows complete adduct formation with very weak donors when it is in excess, (3) its Sb-Cl bonds are not easily heterolyzed; ionization equilibria can be neglected. The donor number of the donor solvent is given as the negative of the enthalpy of reaction of a highly diluted solution of the solvent, D, and $SbCl_5$ in 1,2-dichloroethane:

$$D + SbCl_5 \leftrightarrow D\text{-}SbCl_5 \qquad -\Delta h = DN_{D\text{-}SbCl_5} \tag{3.2-1}$$

The important assumption of the donor number approach to correlating solvent basicity is that the relative order of solvent base strengths found in the $SbCl_5$ system remains unchanged for other acids (Jensen, 1980). Therefore, the enthalpy of formation of a given acid-base adduct is linearly related to the donor number of the base:

$$-\Delta h_{D\text{-}A} = c\ DN_{D\text{-}SbCl_5} + d \tag{3.2-2}$$

where constants c and d are characteristic of the acid, A, and the reaction conditions. Using Equations 3.1-2, 3.1-3, 3.1-4, 3.1-5 and the relationship between Δg and ln(K), we can express the equilibrium constant for formation of the acid-base adduct in terms of the solvent donor number:

$$\ln K_{D\text{-}A} = c'\ DN_{D\text{-}SbCl_5} + d' \tag{3.2-3}$$

If the isentropic assumption of Equation 3.1-5 is valid, a plot of $\ln(K_{D\text{-}A})$ versus the DN of a series of donor solvents will give a straight line characteristic of the acid and the reaction conditions.

3.3 Effect of Regenerant Basicity on Regeneration

The ability of an organic solvent to regenerate an acid-laden sorbent depends on its basicity and the

strength of the acid-base interaction. The overall reaction controlling the regeneration process is the formation of an acid(HA)-base(R) adduct:

$$HA + R \leftrightarrow HA\text{-}R \tag{3.3-1}$$

with an equilibrium constant, $K_{D\text{-}A}$. This reaction assumes a (1,1) acid-base complex. For an adsorption/regeneration system, this reaction is the product of two independent reactions. The first reaction is reaction of an acid molecule with a basic site on the sorbent(S) to create an adsorbed acid molecule:

$$HA + S \leftrightarrow HA\text{-}S \tag{3.3-2}$$

The second reaction is that between a regenerant molecule and an adsorbed acid molecule. The ideal exchange model can be used to describe regeneration of acid-laden polymeric sorbents by strongly basic regenerant solvents. This model assumes that one or more regenerant molecules compete with a basic site on the sorbent for an acid molecule:

$$HA\text{-}S + n\,\overline{R} \leftrightarrow \overline{HA\text{-}R_n} + S \tag{3.3-3}$$

where HA is an acid molecule, S is a basic site on the sorbent, R is a regenerant molecule, and overbars denote species in the solvent phase. Again, the assumption is made that only (1,1) acid-base complexes are formed (i.e., n = 1). The overall equilibrium constant, $K_{D\text{-}A}$, is simply the product of the equilibrium constants for each independent reaction. The equilibrium constant for Equation 3.3-3 can be written:

$$K_R = \frac{\overline{a_{HA\text{-}R}}\; a_S}{a_{HA\text{-}S}\; \overline{a_R}} \tag{3.3-4}$$

In order to calculate values for K_R, an assumption concerning the species activity coefficients is

necessary. For dilute liquid solutions, the ratio of activity coefficients can be assumed to be constant. The equilibrium constant can now be rewritten in terms of species concentrations:

$$K_R = \frac{\overline{[HA-R]}\ [S]}{[HA-S]\ \overline{[R]}} \tag{3.3-5}$$

Values of K_R are calculated from Equation 3.3-5 in the limit that the organic phase concentrations approach zero. Various organic bases with differing Lewis basicity as measured by DN_{SbCl_5} were chosen as regenerants to examine the usefulness of Equation 3.2-3. Since the overall equilibrium constant of Equation 3.3-1 is the product of the individual adsorption and regeneration equilibrium constants, and since the adsorption equilibrium constant is independent of the regenerant utilized, K_{D-A} in Equation 3.2-3 can be replaced by K_R.

3.4 Effect of Sorbent Basicity on Regeneration

By analogy to the relation between $\ln(K_R)$ and solvent donor number for regeneration of a single acid-laden sorbent with various regenerants, one would expect that $\ln(K_R)$ is linearly related to an energy term characteristic of sorbent basicity for a given regenerant solvent. If an effective donor number can be assigned to each sorbent, then the relation in Equation 3.2-3 can be used.

One approach to assigning an effective sorbent donor number is to use the donor number of the sorbent's most basic functional group. This approach warrants caution since the surrounding polymer matrix influences the basicity of a functional group. As an example, both Dowex MWA-1 and Amberlite IRA-35 have tertiary amine functionality. However, Amberlite IRA-35 is more strongly basic than Dowex MWA-1 based on apparent pK_a (Gustafson, 1970). The lower basicity of Dowex MWA-1 can be attributed to the base-weakening styrene ring adjacent to the amine group (Gustafson,

1970). Amberlite IRA-35 has an aliphatic, rather than an aromatic, backbone and thus, has a higher basicity.

Effective donor numbers for Reillex 425 and Amberlite IRA-35 were assigned based on their most basic functional groups: pyridine for Reillex 425 and triethylamine for Amberlite IRA-35. Because the styrene ring on Dowex MWA-1 serves to weaken its basicity, an alternative method for assigning a donor number was used. Following Equation 3.3-4, for $K_R = 1$ and $n = 1$, the sorbent basicity is matched by the regenerant basicity. If the donor number of a regenerant which gives $K_R = 1$ is known, then the donor number of the sorbent is also known.

3.5 Combined Effects of Regenerant and Sorbent Basicity on Regeneration

The regenerability of an acid-laden sorbent relates to both regenerant and sorbent basicity through an equation of the form of Equation 3.2-3. Therefore, a more useful LFER accounts for both solvent and sorbent basicity:

$$\ln K_R = c'' \, \Delta DN_{D\text{-}SbCl_5} + d'' \qquad (3.5\text{-}1)$$

where $\Delta DN_{D\text{-}SbCl_5}$ represents the difference in $DN_{D\text{-}SbCl_5}$ between the regenerant and the sorbent.

3.6 Selection of the Organic Solvent

The organic base can be deployed in an organic solution. The solvent for this solution is selected to satisfy the following criteria. The solvent should (1) not react irreversibly with the acid, the organic base, or the sorbent, (2) be easily removed from the sorbent under conditions which do not degrade the sorbent, (3) be sufficiently different in volatility to be easily removed from the acid, (4) have a

high solubility for the organic base. Under circumstances where the acid and the base interact strongly to form an acid/base complex (e.g., amine regenerants), the solvent should have a boiling point high enough for the complex decomposition reaction to occur at a reasonable rate and low enough to prevent side reactions (e.g., production of lactoyllactic acid). It is also preferable if the solvent solvates the acid more effectively than it does the acid-amine complex. Using these criteria, suitable solvents can be selected from ketones, ethers, esters and aldehydes. Aldehydes can be reactive in a number of ways which may limit their use. Alcohols can also be used but do pose the problem that they can form esters with the desired acids.

Ketones were chosen as solvents, with methyl ethyl ketone (MEK), methyl isobutyl ketone (MiBK) being the two solvents used. They do not react irreversibly with carboxylic acids or with organic bases. Ketones will likely stabilize the uncomplexed acid more effectively than the acid-base complex, thereby favoring the formation of the uncomplexed acid and amine. Stabilization of the acid can occur by hydrogen bonding of the carboxylate -OH of the acid with the carbonyl oxygen of the ketone. No such stabilization is likely for the complexed acid, although the α-OH group of lactic acid could potentially act as a hydrogen bonding site. However, it may be speculated that there is internal hydrogen bonding of the α-OH group of lactic acid with the carboxylate group. This speculation is supported by the negligible overloading behavior during amine extraction of lactic acid, which would occur through hydrogen bonding of a second acid molecule with the carboxylate group of the first acid (Tamada, 1989). In addition, an internally-bonded structure for α-hydroxyisobutyric acid has been found by NMR experiments (Mori et al., 1969).

MEK and MiBK are most preferred because their normal boiling points (80°C and 116°C,

respectively) are high enough for the complex decomposition reaction to occur at a reasonable rate and low enough to minimize side reactions (e.g., production of lactoyllactic acid and/or acid-sugar caramelization reactions) which occur at temperatures above 120°C (Windholz, 1983; Vickroy, 1985). Other ketone solvents could be used with complex decomposition performed under vacuum or at elevated pressures; however, atmospheric pressure affords the most economical process conditions.

4. Results and Discussion

4.1 Sorbent Regeneration

4.1.1 Lactic Acid-laden Sorbent

Table 4.1-1 lists the organic bases chosen for the sorbent regeneration studies based on the criteria outlined in Section 3.

TABLE 4.1-1
Organic bases chosen as sorbent regenerants

Organic Base	Gutmann Donor Number	B.P., °C at 1 atm. (Windholz, 1983)
Acetonitrile	14.1	81.6
Dimethyl sulfoxide (DMSO)	29.8	189.0
Pyridine	33.1	115-116
Piperidine	51.0	106.0
Trimethylamine (TMA)	60.0	2.9

Figures 4.1-1 to 4.1-5 show the experimental data for batch leaching of lactic acid from Dowex MWA-1 by varying amounts of each of the organic bases listed in Table 4.1-1. All organic solutions were prepared using MEK as the organic solvent. Figure 4.1-6 shows the regeneration ability of pure MEK. The data in Figures 4.1-1 to 4.1-5 were corrected for regeneration of MEK alone. This correction assumes that the organic-phase acid concentration is the sum of two binary interactions, acid-organic base and acid-MEK on a mole fraction basis. In these figures, percent regeneration refers to the percentage of the composite uptake of lactic acid recovered from the sorbent during regeneration. The composite uptake is defined as:

$$q = \frac{W_0 \, (x_i - x_f)}{m} \qquad (4.1\text{-}1)$$

where W_0 is the initial mass of solution, m is the mass of sorbent used, and x_i and x_f are the initial and final weight fractions of solute in solution. The composite uptake is a measure of the selective uptake of the solute over the solvent and is equivalent to a surface excess (Kipling, 1965). The percent regeneration at 0 mols base/mol adsorbed acid corresponds to leaching with pure MEK using a 30 mL/g MEK to sorbent ratio.

In all cases, less than 100% regeneration was achieved for all base to acid ratios. The inability of the organic bases to regenerate the basic sites of the sorbent fully probably reflects the quarternary ammonium content of the sorbent (Gustafson, et al., 1970). The data indicate that for all regenerants other than piperidine and TMA, a large amount of solvent, yielding highly dilute effluent solutions, would be necessary to achieve a percent regeneration of sorbed acid high enough to be considered for use in a process with continuous acid recovery.

Values of K_R were calculated according to Equation 3.3-5 and plotted versus organic-phase regenerant concentration. The data were extrapolated to zero regenerant concentration to determine the value of K_R at infinite dilution. Table 4.1-2 lists the values of K_R for regeneration of lactic acid-laden Dowex MWA-1 by the regenerants used.

TABLE 4.1-2
Values of K_R for regeneration of lactic acid-laden polymeric sorbents

Sorbent	Regenerant (in MEK)	K_R
Dowex MWA-1	Acetonitrile	0.008
Dowex MWA-1	Dimethyl sulfoxide	0.033
Dowex MWA-1	Pyridine	0.024
Dowex MWA-1	Piperidine	19.57
Dowex MWA-1	Trimethylamine	9.51
Amberlite IRA-35	Trimethylamine	0.184
Reillex 425	Trimethylamine	60.52

Figure 4.1-7 shows a plot of $\ln(K_R)$ versus DN, as suggested by Equation 3.2-3, for regeneration of lactic acid-laden Dowex MWA-1 by various regenerants. A least-squares regression of the data was used to evaluate the slope and intercept. From this regression, an effective donor number for Dowex MWA-1 of 44.5 was found to give K_R=1.

Figure 4.1-8 compares the experimental data for leaching of three lactic acid-laden sorbents by organic solutions of TMA in MEK. Again, percent regeneration was corrected for by regeneration of pure MEK alone as shown in Figure 4.1-6. For Reillex 425, Dowex MWA-1 and Amberlite IRA-35, pure MEK gives about 10-11%, 3-4% and 1-2% regeneration, respectively, for the phase ratios used. As anticipated, regeneration efficiency was inversely related to sorbent basicity. Values of K_R were measured as previously described and are listed in Table 4.1-2.

Figure 4.1-9 shows a plot of $\ln(K_R)$ versus ΔDN, where ΔDN is the difference in donor number between the regenerant and the sorbent, for regeneration of lactic acid-laden sorbents. The line

represents the LFER between $\ln(K_R)$ and ΔDN for regeneration of lactic acid-laden Dowex MWA-1 by various regenerants shown in Figure 4.1-7. The consistency of fit validates the usefulness of LFERs for analysis and prediction of regeneration of acid-laden sorbents by organic bases which are based upon sorbent and regenerant donor numbers.

4.1.2 Succinic Acid-laden Sorbent

Table 4.1-3 shows the results for leaching succinic acid from Dowex MWA-1 at two concentrations of organic TMA. In this table, percent regeneration refers to the percentage of the composite uptake of succinic acid recovered from the sorbent during regeneration. Only two points were obtained for this isotherm, because at high TMA concentrations succinic acid began to precipitate from the regenerant solution.

TABLE 4.1-3
Regeneration of succinic acid-laden Dowex MWA-1 by solvent leaching with TMA.

TMA concentration, wt.%	% regeneration
0.1	2.6
0.4	9.5

Two possible explanations for acid precipitation were explored. The first explanation was based on the presumption that the presence of TMA would enhance succinic acid solubility in the organic phase.

Precipitation of succinic acid at high TMA concentrations can be rationalized by considering the solubility of succinic acid in pure MiBK (i.e., in the absence of TMA). This solubility is 0.03 mol/L

for an anhydrous solution (Starr and King, 1992). Examination of the samples in which succinic acid precipitated in the current study showed that precipitation occurred in samples in which the amount of acid removed from the sorbent exceeded its solubility in pure MiBK.

The role of TMA in the process might have been to enhance the rate at which succinic acid was removed from the sorbent, by increasing the solubility-based driving force. In the absence of TMA, precipitation of the acid from the regenerant solution would eventually happen. However, because of the low solubility of succinic acid in pure MiBK, the driving force for regeneration of the sorbent would be quite low. TMA would serve to enhance the solubility of succinic acid in MiBK by forming the acid-base adduct. If, following regeneration, the TMA was vaporized, the solubility of the succinic acid would fall, and precipitation would occur. Precipitation of succinic acid during regeneration could then be attributed to losses of TMA from the sample scintillation vials. Teflon®-lined caps were used to prevent losses of TMA; however, the vibrations caused by the shaker bath may have loosened the vials and allowed TMA to escape.

Subsequent studies focused on measuring the enhanced solubility of succinic acid in MiBK for various concentrations of TMA. Solutions of TMA in MiBK were contacted with excess succinic acid in 125-mL vials with Teflon-lined crimp caps at 25°C for at least 8 days to reach equilibrium. The organic-phase acid concentration was determined by high-performance liquid chromatography (HPLC).

The results of this study showed no increase in the organic-phase acid concentration with increased TMA concentration. Thus, a second explanation of acid precipitation was postulated, namely that

the TMA was reacting with succinic acid to form a *solid* acid-base adduct with a lower solubility in MiBK than for the acid alone. To test this hypothesis, a solution of succinic acid dissolved in MiBK was contacted with a solution of TMA in MiBK. Upon contact, a white precipitate formed. This solid was washed with pure MiBK over a Hirsch funnel and subjected to elemental analysis. This analysis was performed by the Microanalytical Laboratory, College of Chemistry, at the University of California at Berkeley using a Perkin Elmer Model 2400 Elemental Analyzer. Table 4.1-4 compares the experimental composition of the solid precipitate to the theoretical composition for a 1:1 TMA:succinic acid adduct.

TABLE 4.1-4
Elemental analysis of precipitate formed during addition of TMA to a solution of succinic acid in MiBK. Values are atomic %.

Element	% Theoretical	% Experimental
C	47.46	45.00
H	8.47	8.54
N	7.90	7.01

The chemical analysis supports the hypothesis that the solid was the acid-base adduct rather than the pure acid. To determine whether the pure acid could be recovered from the acid-base adduct, the solid was heated in a vacuum oven at a temperature above 150° C and 15-20 kPa overnight. The final solid was also analyzed for chemical composition. Table 4.1-5 compares the experimental composition of the solid to the theoretical composition for pure succinic acid.

TABLE 4.1-5
Elemental analysis of the solid following heating of the initial precipitate above 150° C and 15-20 kPa overnight. Values are atomic %.

Element	% Theoretical	% Experimental
C	40.68	40.82
H	5.12	5.36
N	0.00	0.33

Based on these results, it appears that the pure acid can be recovered by thermal cracking of the solid acid-base adduct.

The results of this work are important, because they provide the final step in a process to recover succinic acid from aqueous solution using basic polymeric sorbents. Organic solutions of TMA can be used to regenerate acid-laden sorbent. Following regeneration, TMA can be vaporized from the resultant precipitate, resulting in precipitation of the acid product. This process could also be used for other acids with limited solubility in the organic diluent.

Using an organic solution of TMA for regeneration of succinic acid-laden sorbents has two advantages over regeneration with an aqueous solution of TMA. Precipitation of the TMA-succinic acid complex from the organic solution means that the acid can be recovered by heating a small amount of solid material to vaporize the TMA, without incurring the energy penalty for sensible heat to raise the temperature of the entire solution. When regeneration is done with aqueous TMA, the entire regenerant solution must be heated to vaporize the TMA.

The low solubility of the TMA-acid complex in the organic solvent (<0.03 mol/L in MiBK) means

that a high percentage of the succinic acid can be recovered in solid form. The higher acid solubility in water (0.65 mol/L), means that evaporation of some water would be necessary to recover the same percentage of acid, provided that similar volumes of organic and aqueous regenerant solutions are needed to regenerate the acid-laden sorbent fully. Evaporation of water is undesirable because of its high latent heat of vaporization.

4.2 Thermal Cracking

In the TMA-lactic acid thermal cracking experiments, essentially 100% of the total TMA initially present was recovered overhead. There was no odor of TMA left in the residual liquid. This result was confirmed by HPLC analysis of the final solution; TMA was absent in the chromatogram.

Figure 4.1-10 presents the results of a typical thermal cracking experiment performed at atmospheric pressure under a nitrogen atmosphere. The rate of evolution of TMA is high during the initial stages of cracking, where the concentration of TMA (in the form of the acid:TMA adduct) is high. The rate decreases as the concentration of TMA in solution decreases. This result may be associated with a lower driving force for the cracking reaction at low concentrations of TMA.

The cracking temperature may also affect the rate of evolution of TMA. Although thermal decomposition of the acid-base adduct was complete in the previous studies, the thermal cracking step took about 150 minutes to reach completion. This residence time is undesirable for a process to recover lactic acid continuously from solution. It may be possible to increase the cracking rate by increasing the cracking temperature. An increased cracking temperature could be achieved by operating at an elevated pressure or by selection of a higher boiling organic diluent. The overall

cracking time could also be decreased by heating the solution at a higher rate initially. To test the effects of increasing the cracking temperature and the heating rate, two cracking experiments were performed replacing the MEK organic solvent with MiBK. In the first experiment, temperature increased gradually from 25°C to the solution boiling point at 116°C. In the second experiment, temperature was ramped to 116°C in under 5 minutes. Figure 4.1-11 shows that essentially 100% recovery of TMA was achieved for both experiments. The data clearly indicate that the cracking rate increases with increasing temperature. By running the reaction at a higher temperature initially, complete vaporization of TMA was achieved in 30-40 minutes, a significant improvement over the previous time of 150 minutes.

Discoloration of the final solution was a problem; the solution turned yellow upon heating at 80° C and 116°C. The intensity of the discoloration was less for the solution run at higher temperatures initially. Several possible causes of this discoloration exist; however, the most likely source of color is a caramelization reaction involving lactic acid and/or trace amounts of sugar and/or TMA. Discoloration of lactic acid upon heating is common, and usually occurs in the presence of residual sugars (Vickroy, 1985). Thus, the discoloration observed in the final solution may be due to interactions between trace amounts of residual sugars present in the original lactic acid and/or TMA and/or lactic acid. Alternatively, the yellow color may be associated with the formation of lactic acid lactate (lactoyllactic acid), which can be prepared by heating lactic acid at 120 °C for 10 hours (Windholz, 1983). By decreasing the residence time for the thermal cracking step, formation of colored by-products through the above mentioned caramelization or esterification reactions may also be reduced.

Treatment of the final acid solution with activated carbon was effective for eliminating colored impurities; the final solution was not discernibly colored following this treatment. Figure 4.1-12 shows the absorbance spectra for the organic and aqueous lactic acid solutions. Comparing the spectra for carbon purified and non-purified samples confirms that carbon adsorption was effective for eliminating colored impurities from solution.

In a commercial process, it is desirable for a carbon adsorbent used for decolorization to exhibit low uptake capacity for lactic acid. Several investigators have measured uptake capacities for lactic acid on activated carbon (Bartell and Miller, 1923; Linner and Gortner, 1935). The capacities range from 0.72-1.01 mmol/g for the carbons studied. However, these studies did not address the effect of carbon type on acid uptake. Exploiting surface chemistry properties of various carbons may result in acid uptakes much lower than those previously recorded (Kilduff and King, 1996). Chinn and King (1997) recently discovered that lactic acid uptake values are inversely related to the degree of surface oxidation for Calgon Filtrasorb 400 carbon. Uptake capacities for the least highly oxidized samples ranged from 1.1-2.7 mmol/g, while those for the most highly oxidized samples ranged from 0.8-1.7 mmol/g. This result suggests that carbons with a high natural oxygen content (e.g., wood-based carbons) might further reduce acid uptake.

Since an aqueous acid product is often desired, water could be added to the final cracking solution following complete removal of TMA. The remaining organic solvent could be stripped from the solution to produce an aqueous lactic acid solution, perhaps containing some polymers, but similar to the commercial 85 wt.% syrup. Alternatively, if the solution is dilute enough and the acid is soluble enough, the acid could be transferred from the organic solvent to water in a dual-feed

distillation.

4.3 Fixed-bed Regeneration

Figure 4.1-13 shows the concentration profiles for lactic acid, water and TMA during the first fixed-bed experiment. In this experiment, MEK was used as the organic displacer during the water displacement step, and a 2.8 wt.% TMA regenerant solution in MEK was used during the regeneration step. During the loading step, lactic acid began to break through at about 30 minutes and reached its feed concentration at about 108 minutes. The composite and individual uptakes during this step were calculated from the breakthrough curve to be 0.381g/g and 0.400 g/g, respectively. Both values differ by <4% from the values measured in batch adsorption experiments.

During the water-displacement step, the acid and water concentrations dropped sharply as the interstitial fluid was displaced from the sorbent bed. The acid concentration declined to an asymptotic value of c/c_0=0.05, which corresponds to the fact that the MEK had some regeneration capacity for lactic acid-laden sorbent. The amount of lactic acid removed from the column during this step corresponds to all of the interstitial and non-selectively sorbed acid, plus 10.0% of the selectively sorbed acid. The water concentration reached a plateau value of 13-15 wt.% between 118 and 133 minutes before decreasing to <1 wt.% around 160 minutes. The plateau can be attributed to the limited solubility of water in MEK. At 118 minutes, essentially all of the interstitial water has been displaced from the column. The remaining water resides within the sorbent particles and must diffuse through the pores to reach the bulk solution. The driving force for transport of water from the pores is the difference between the bulk solution water concentration and the solubility limit of water in MEK (12-13 wt.% at 25°C (Kartzmark, 1986)). When the bulk solution is saturated with water,

there is no driving force for transport of water from the pores.

To test this reasoning, a second experiment was performed using acetone as the organic displacer. If the plateau in water concentration is associated with solubility-limited transport of water, there should be no plateau in the water concentration profile during water displacement by acetone, since acetone and water are completely miscible. Figure 4.1-14 compares the water profiles for miscible displacement with acetone and partially-miscible displacement with MEK. Displacement by acetone shows no plateau in water concentration and reduces the water concentration to <1 wt.% at approximately 140 minutes.

During the regeneration step, TMA began its breakthrough at about 160 minutes. At that time, the lactic acid concentration also began to increase, reaching a maximum concentration 2.6 times the aqueous feed value at about 180 minutes, before dropping to zero at about 210 minutes. The amount of lactic acid removed from the sorbent during this step corresponds to 82.2% of the selectively sorbed acid. The total amount of acid removed during the water displacement and regeneration steps corresponds to 92.2% of the selectively held acid. This value compares closely to the 90-91% removal value obtained in batch regeneration studies. The inability of the TMA to regenerate the sorbent fully is a consequence of its inability to regenerate strongly-basic, quaternary ammonium sites. Computing from the TMA breakthrough curve, the amount of TMA needed to regenerate the sorbent corresponds to 1.7 mol TMA/mol acid. This regenerant/acid ratio is considerably lower than the value of 8 found during batch regeneration. The low ratio found in this study results from the continuous removal of acid:amine adducts, thereby shifting the equilibrium in favor of regeneration.

The acid focusing effect during regeneration results from the shift in adsorption equilibrium to favor desorption when TMA is introduced in the feed. This focusing effect serves to concentrate the acid with respect to its initial aqueous feed concentration. Focusing has been described by Wankat and co-workers (Busbice and Wankat, 1975; Wankat, 1990) and occurs when there exists some thermodynamic variable (in this case, TMA concentration) which, when changed, causes a large change in the amount of solute adsorbed.

The average acid concentration in the effluent samples between 160 and 194 minutes was 3.2 wt.%--1.6 times the initial aqueous feed concentration. Since the amount of acid regenerated is related to the amount of TMA introduced to the column, increasing the concentration of the regenerant should increase the concentration of the acid in the effluent. To verify this prediction, a second experiment was performed with a 10.1 wt.% TMA regenerant solution. Figure 4.1-15 compares the acid concentration profiles during regeneration for the two TMA concentrations studied. Increasing the TMA feed concentration produced a much sharper acid peak, exceeding six times the feed concentration. The average acid concentration in the effluent between 160 and 175 minutes was 5.9 wt.%--almost 3 times higher than the initial aqueous concentration.

In addition to concentrating the acid, regeneration with an organic solution replaces the initial solvent, water, with an organic solvent having a much lower heat of vaporization. From an energy savings standpoint, this solvent exchange is advantageous since isolation of the acid will likely require vaporization of the solvent.

Figure 4.1-16 shows a typical TMA concentration profile during regeneration. Whereas the

concentration following breakthrough should level off to the feed concentration, the measured concentrations were only about 80-90% of the feed concentration. The low concentrations likely correspond to TMA losses from the collection vials. Losses of TMA from the samples do not appear to affect the measured acid concentrations significantly, since the fixed-bed data match closely with batch regeneration data.

5. Process Considerations

5.1 Overall Process

For an overall process, the carboxylic acids are first removed from the aqueous stream by a solid phase adsorption technique with a basic sorbent. The sorbed carboxylic acid is then recovered by contacting the sorbent phase with an organic solution of a volatile base, such as a low-molecular-weight amine. This "back-extracts" or solubilizes the carboxylic acid into the organic extraction phase as an amine/carboxylic acid complex. When this organic solution is heated, this complex decomposes completely to yield the carboxylic acid which can then be recovered. The amine is also regenerated and can be recycled. Thus, a process is achieved which consumes no substantial amount of chemicals and generates no substantial amount of waste by-product. The process is illustrated in Figure 5.1-1. Other process configurations may be used as well to implement the concept. Examples include the rotating-valve "Sorbex" process of UOP, Inc. (de Rosset et al., 1981; Broughton, 1985), and various multi-bed processes.

5.1.1 Sorbent Bed

In Figure 5.1-1 an aqueous feed stream containing the carboxylic acid is fed to the contactor containing a bed of solid polymeric sorbent. This sorbent is a relatively basic material (e.g., tertiary amine or pyridyl sorbents), which selectively adsorbs the carboxylic acid from the acid-rich aqueous feed and produces an acid-lean aqueous effluent. This effluent can be suitably monitored until a breakthrough in carboxylic acid level is noted, indicating that the sorbent has removed its capacity of acid. At this point, the aqueous feed and effluent lines are closed via valves. An organic solution of a low molecular weight amine is then fed to the contactor. The amine reacts with the sorbed carboxylic acid to form an amine/carboxylic acid complex, which is soluble in the organic solvent

phase. The regenerated sorbent can then be reused.

During the regeneration step, it is generally desirable to use a relatively concentrated solution of alkylamine to minimize contacting residence time. For this purpose, gaseous alkylamines can be dissolved in the organic solution under pressure.

As illustrated in Figure 4.1-5, the completeness of desorption depends at least in part upon the amount of amine employed during the regeneration cycle. At least one equivalent of amine should be employed for each equivalent of acid being desorbed.

5.1.2 Decomposing Zone

The solution of amine/carboxylic acid complex in an organic solvent is fed to a decomposing zone. There, heat (and optionally reduced pressure) is applied to decompose the complex into the corresponding amine and carboxylic acid. As the decomposition progresses, either the free acid or the amine, or both, are removed, driving the decomposition forward and permitting a more complete decomposition of the complex and recovery of the acid. If, as is usually the case, the amine is more volatile than the acid, it can be taken off overhead, typically in combination with the organic solvent. The mixture of solvent and amine can be condensed and recycled. A particular advantage of this process is that this decomposition can be carried out to completion with minimal loss of amine or acid. In prior water-based systems, this decomposition could not be carried to completion for highly water-soluble carboxylic acids such as lactic acid.

It is generally preferred to carry out the decomposition step in an oxygen-free or reduced-oxygen

environment (e.g., under a nitrogen gas blanket) to minimize oxidation of the amine, which can occur at elevated temperatures (Cullis and Waddington, 1958).

The acid which is freed by this decomposition and amine/solvent removal is taken from the decomposition zone either as crystals or as a liquid acid or as a highly saturated solution, depending upon the tendency of the carboxylic acid to crystallize. The carboxylic acid can be recovered from this product and subjected to purification steps as needed.

5.2 Water Content During Regeneration

The processing advantages provided by the present regeneration technique are maximized if the water content is minimized in the amine/carboxylic acid-containing solution during decomposition. Thus, it is advantageous to rinse the solid sorbent with a solvent to remove residual water prior to contacting the solid sorbent with the organic solution of amine. The solvent can be, but is not limited to, the organic diluent used to solubilize the amine. The displacement can be a miscible displacement or an immiscible displacement as shown in Figure 4.1-14. A second function of this rinse step is to remove any non-selectively sorbed compounds present in the aqueous feed (e.g., sugars) that could otherwise interfere with acid purification. The rinse phase can be treated such as by distillation to separate out water and provide the solvent in dry form for recycle.

5.3 Selection of Amine

5.3.1 Desired Characteristics

An important element of this research is the use of an organic solution of an amine as the desorbent material. The amine can be a mono-, di- or trialkylamine. It is selected to have substantial solubility

in the organic solvent phase. Of these materials, the trialkyamines offer an advantage of not being capable of forming amides with the recovered acids.

5.3.2 Trimethylamine

Of the trialkylamine materials, preference is given to trimethylamine (TMA) for several reasons. First, it is the most common and least expensive of these materials. It has a high solubility in organic solvents and thus allows a concentrated desorbent solution to be formed. It is also the most volatile of the trialkylamines (b.p. 2.9°C) and thus, upon decomposition of the trimethylamine/carboxylic acid complexes, can be removed overhead by distillation with the least amount of heating of the organic regenerant solution. Other trialkylamines containing up to about 6 or even 8 total carbon atoms--for example methyldiethylamine, triethyamine, dimethyl-n-propylamine and the like--may be used. Monoalkylamines of up to 6 carbon atoms and dialkylamines of up to about 8 total carbon atoms can also be used as long as their potential for side reactions is kept in mind. Mixtures of amines can be used.

5.4 Selection of the Solid-Phase Adsorbent

The organic solution of amine is used to resolubilize carboxylic acid adsorbed onto a solid adsorbent. These solid phase materials include basic, polymeric ion exchange resins such as pyridyl, pyridinium and amine group-containing resins.

6. Conclusions

Lactic and succinic acid-laden polymeric sorbents can be regenerated by leaching with an organic solution of a volatile base. Regeneration efficiency correlates with the non-aqueous basicity of the regenerant as measured by the Gutmann donicity scale. Lactic acid-laden Dowex MWA-1 was 90-91% regenerated when 8-10 moles of trimethylamine (TMA) were present for every mole of adsorbed acid; adequate (over 70%) regeneration was obtained at a molar ratio of 2:1. The inability of the TMA to regenerate the sorbent fully is a consequence of its inability to regenerate strongly-basic, quaternary ammonium sites. Upon repeated use, the sorbent should sustain about 90% of its initial capacity, an acceptable figure.

The resulting TMA-lactic acid complex can be cracked thermally to yield acid product and TMA, available for recycle. For lactic acid, the cracking reaction is essentially 100% complete when regeneration is performed by leaching with an organic solution of TMA, rather than an aqueous solution of TMA. A likely cause of the incomplete thermal decomposition of trimethylammonium lactate in previous, water-based systems is the aqueous environment in which the decomposition was performed.

Acknowledgment

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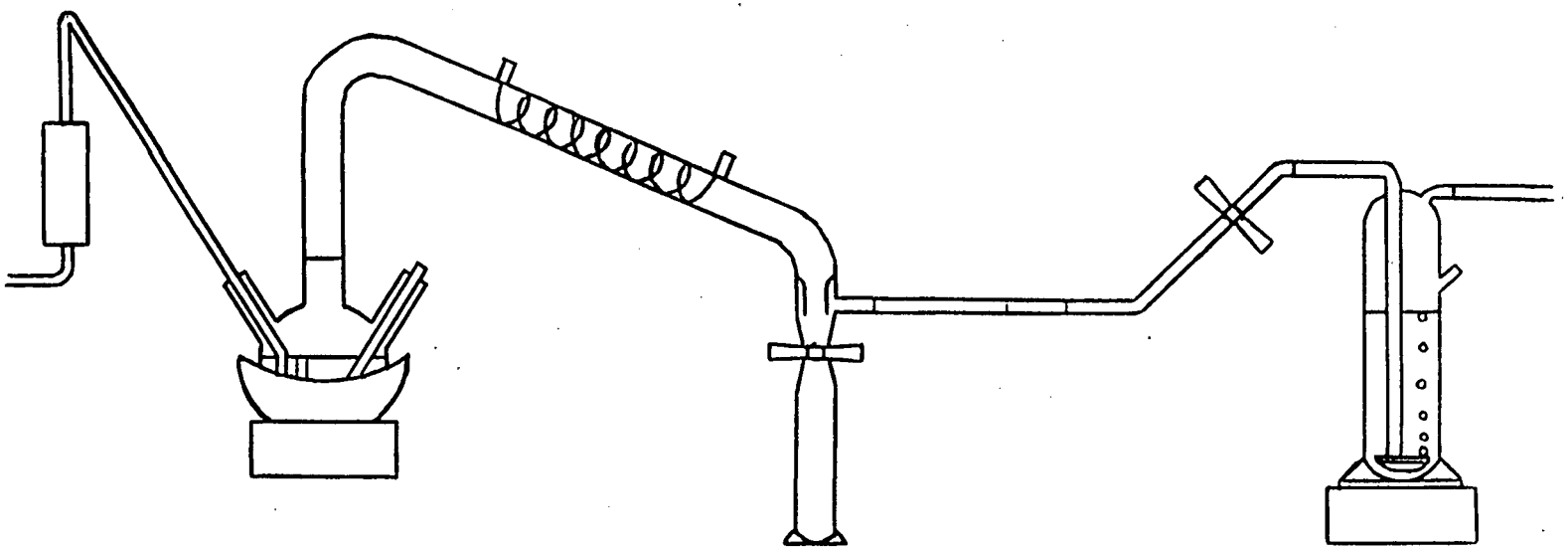


Figure 2.2-1. Schematic representation of the apparatus used in the thermal cracking experiments.

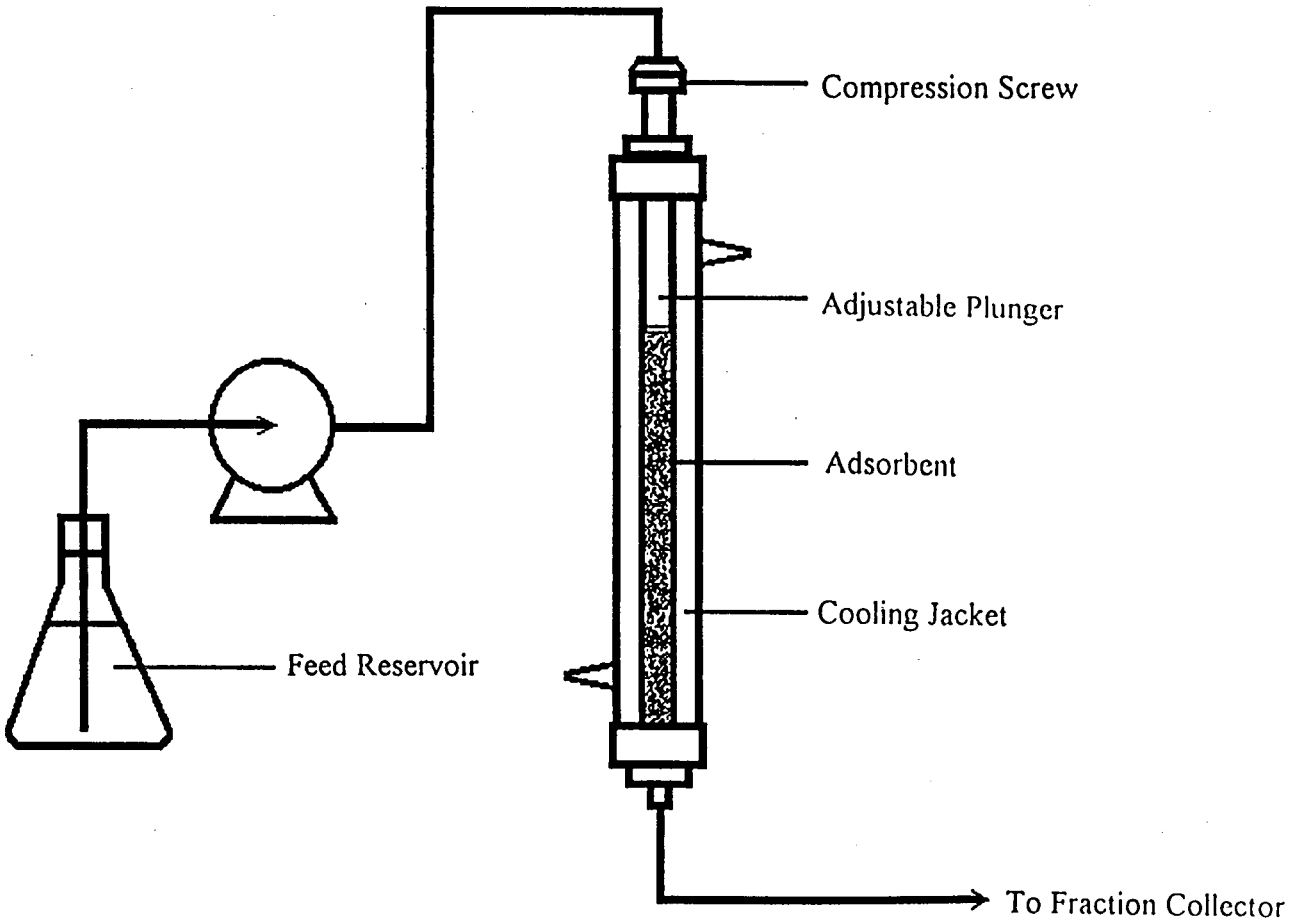


Figure 2.2-2. Schematic representation of the apparatus used in the fixed-bed regeneration experiments.

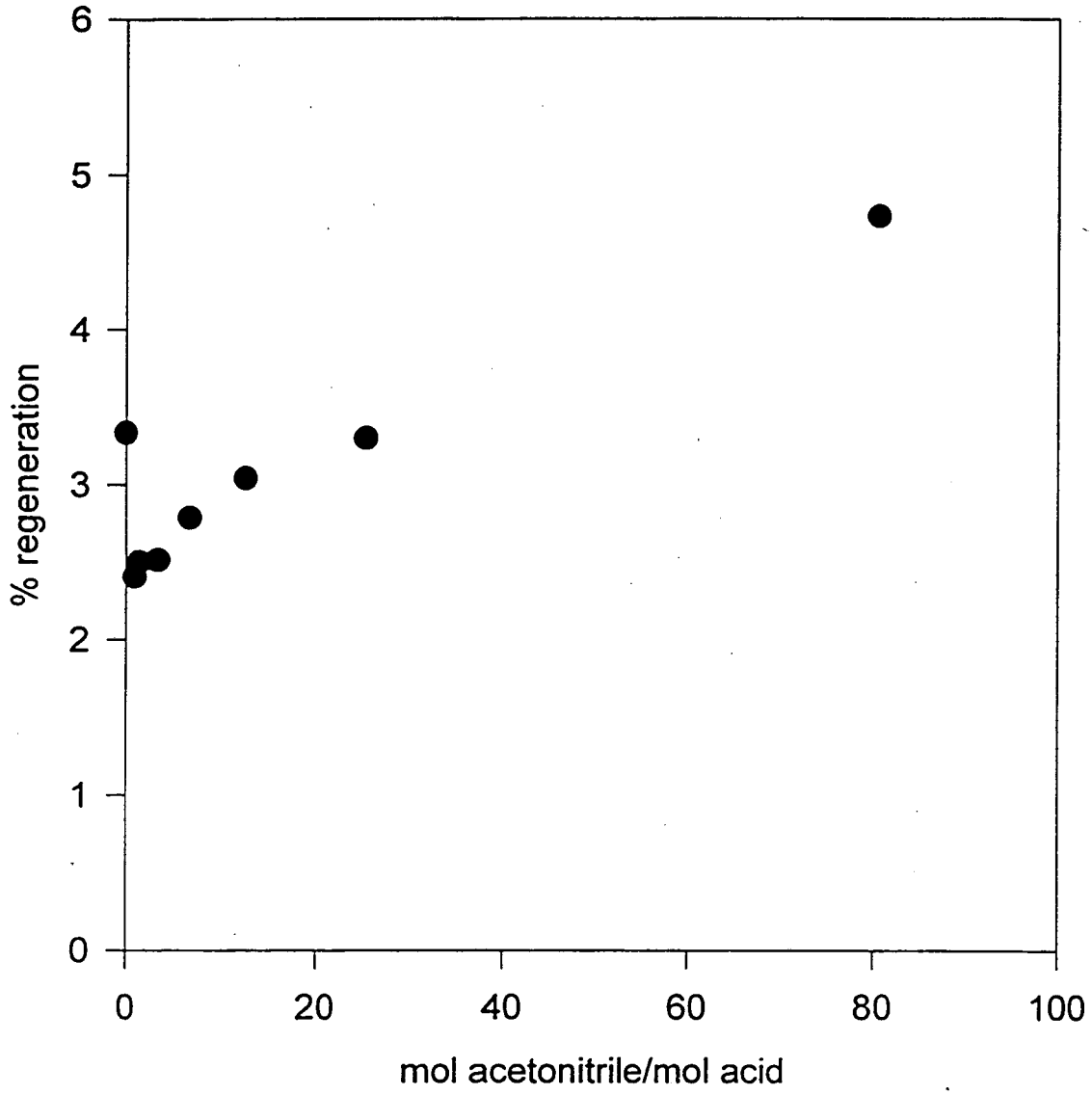


Figure 4.1-1. Leaching of lactic acid-laden Dowex MWA-1 by organic solutions of acetonitrile in methyl ethyl ketone at 25°C.

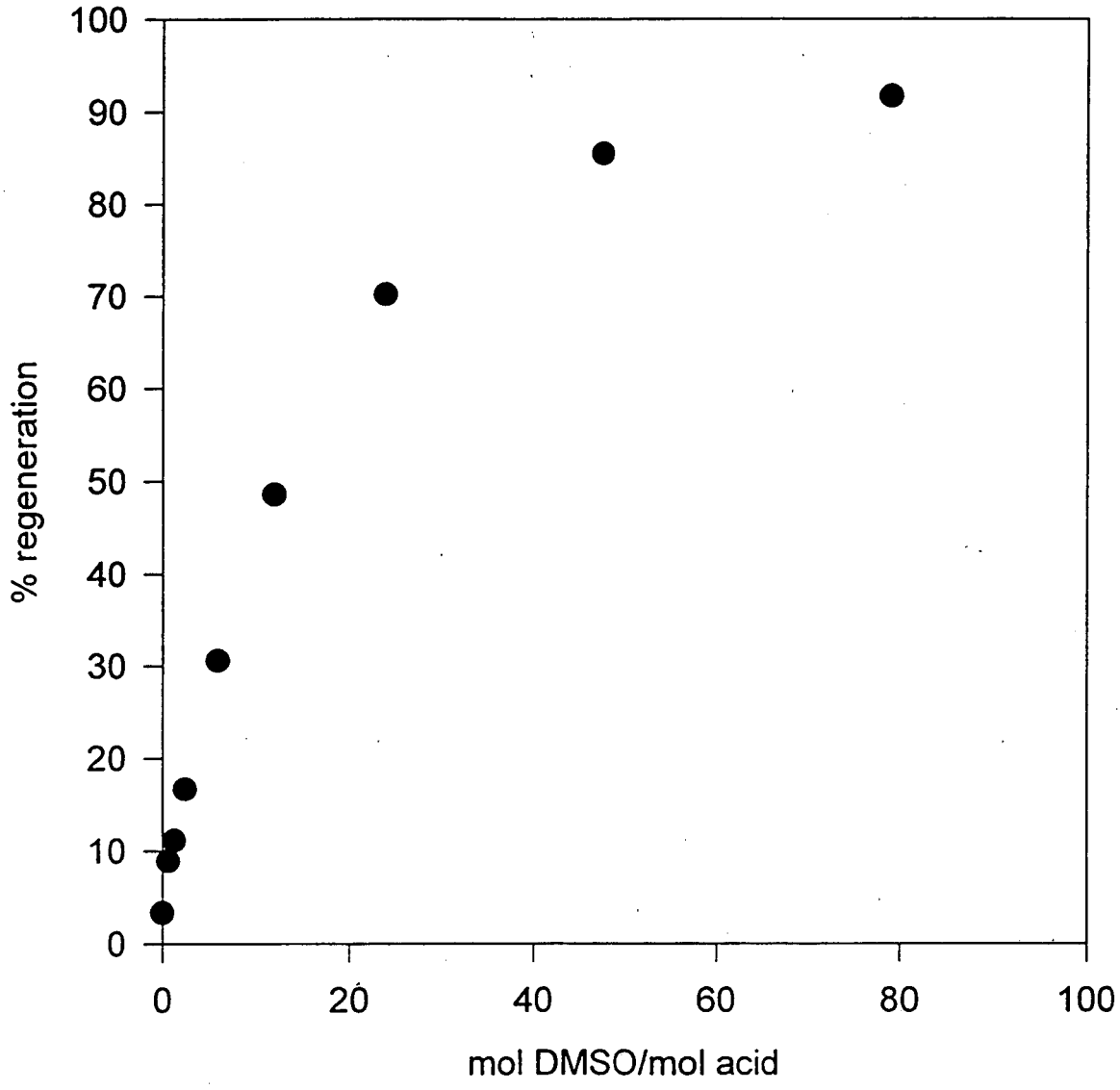


Figure 4.1-2. Leaching of lactic acid-laden Dowex MWA-1 by organic solutions of dimethyl sulfoxide in methyl ethyl ketone at 25°C.

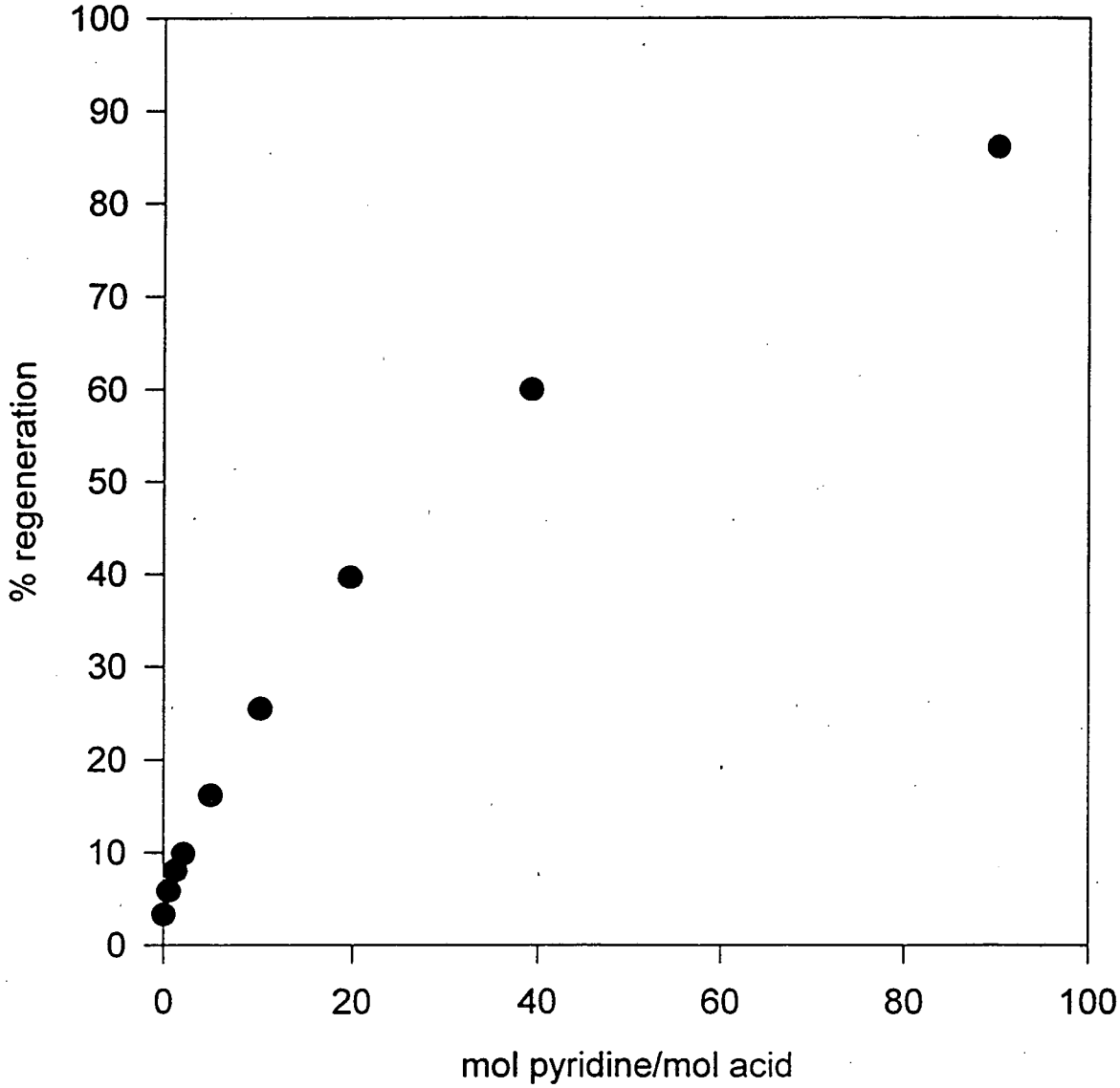


Figure 4.1-3. Leaching of lactic acid-laden Dowex MWA-1 by organic solutions of pyridine in methyl ethyl ketone at 25°C.

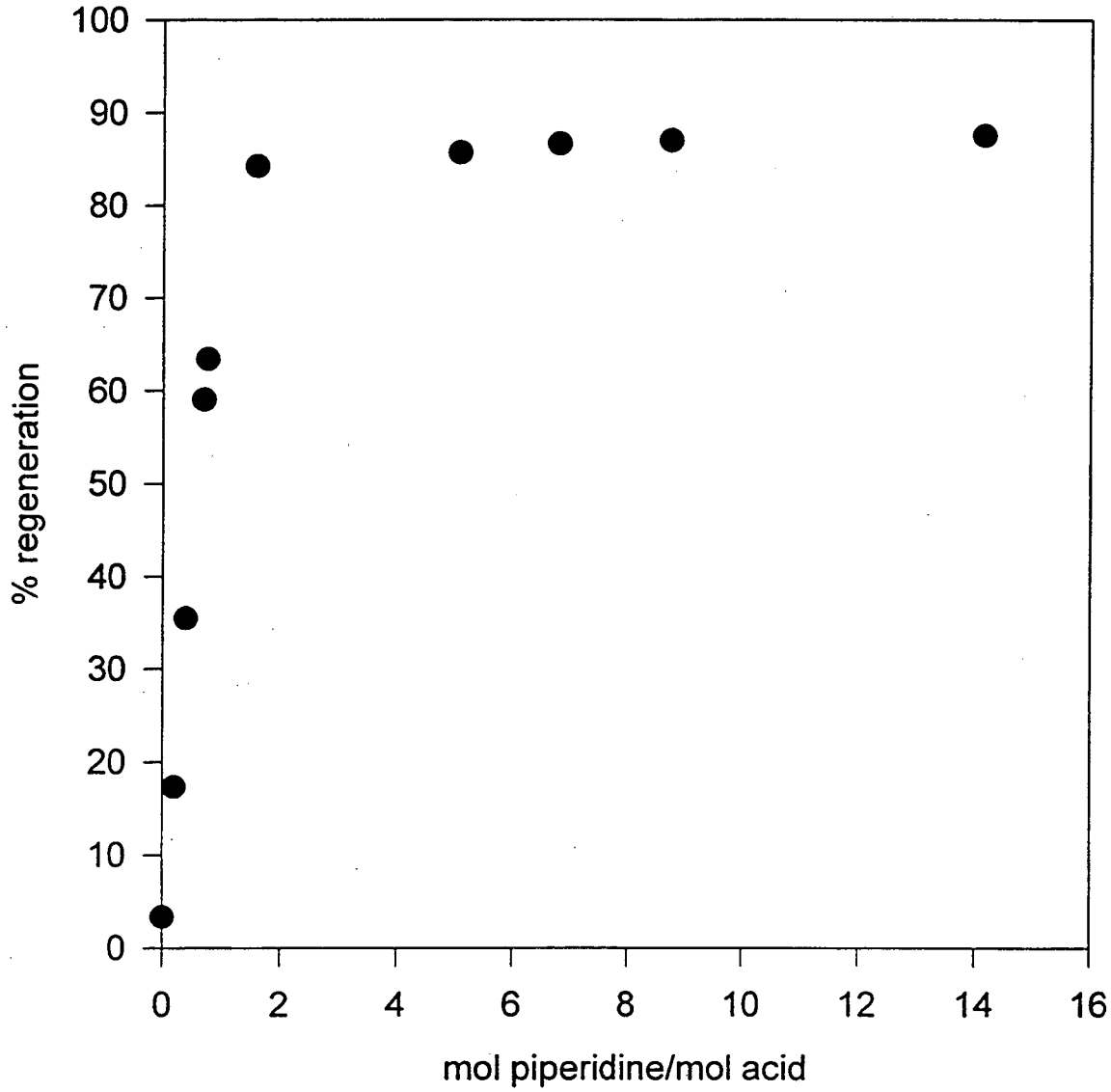


Figure 4.1-4. Leaching of lactic acid-laden Dowex MWA-1 by organic solutions of piperidine in methyl ethyl ketone at 25°C.

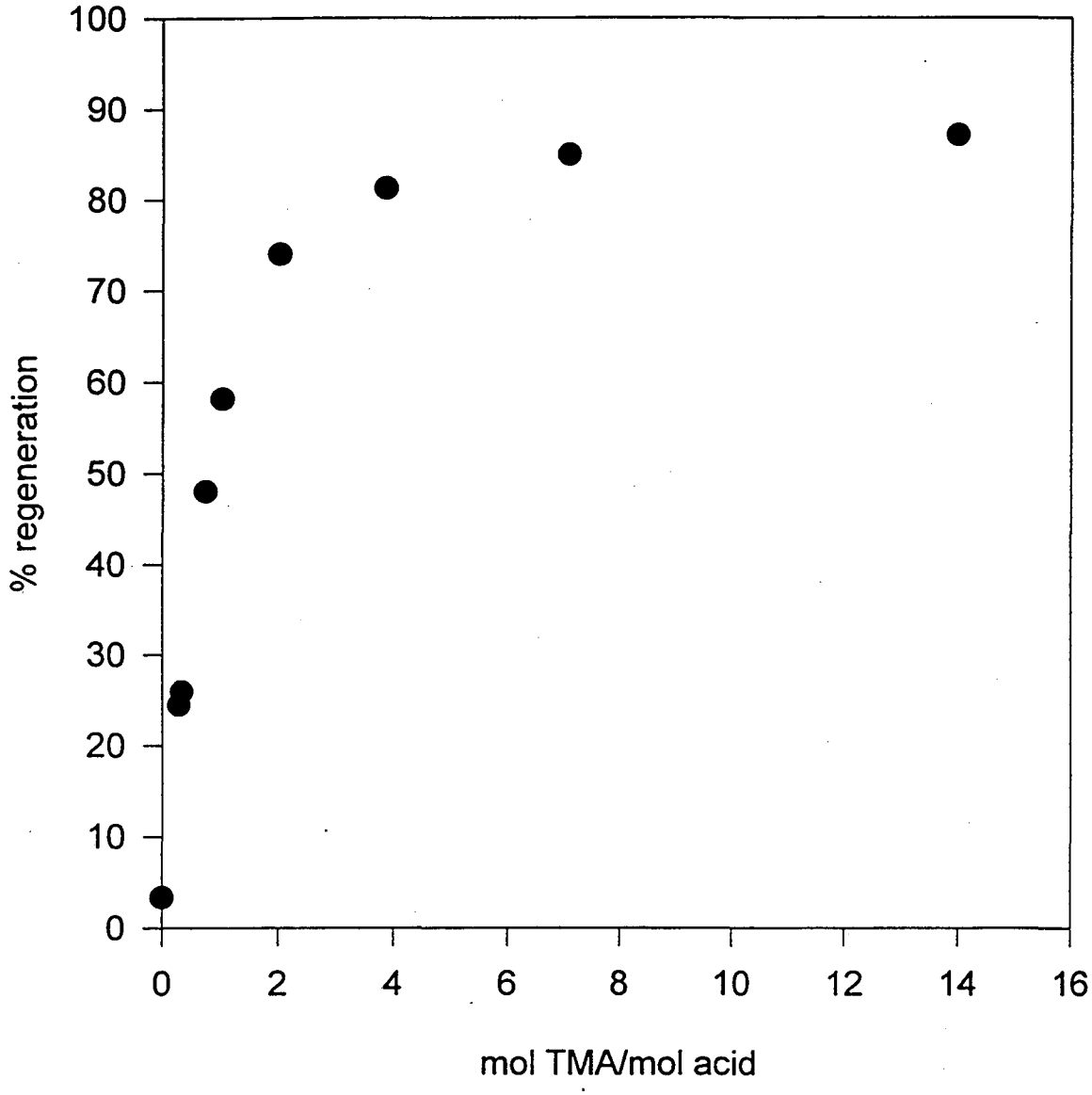


Figure 4.1-5. Leaching of lactic acid-laden Dowex MWA-1 by organic solutions of trimethylamine in methyl ethyl ketone at 25°C.

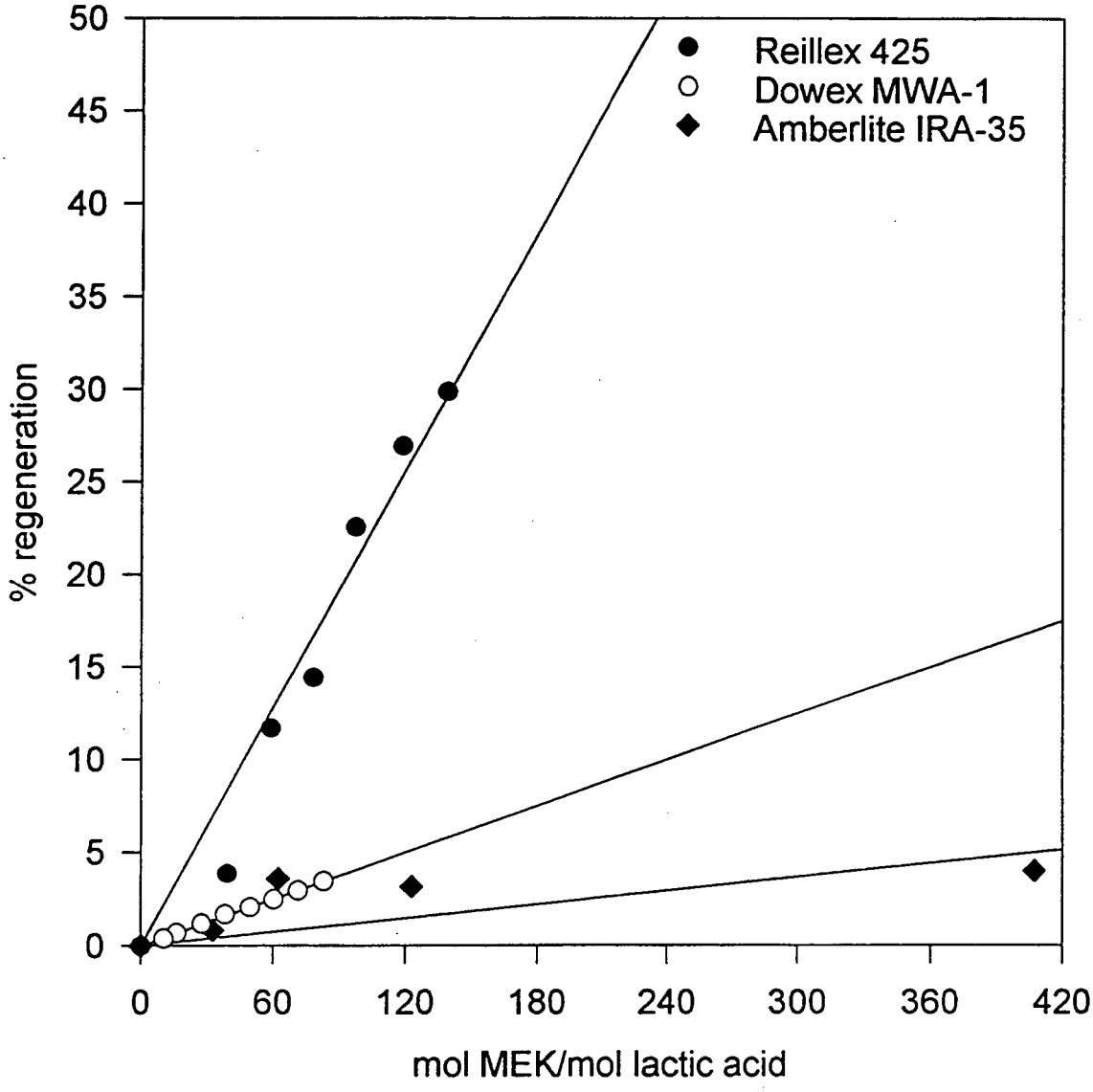


Figure 4.1-6. Leaching of lactic acid-laden polymeric sorbents by methyl ethyl ketone at 25°C.

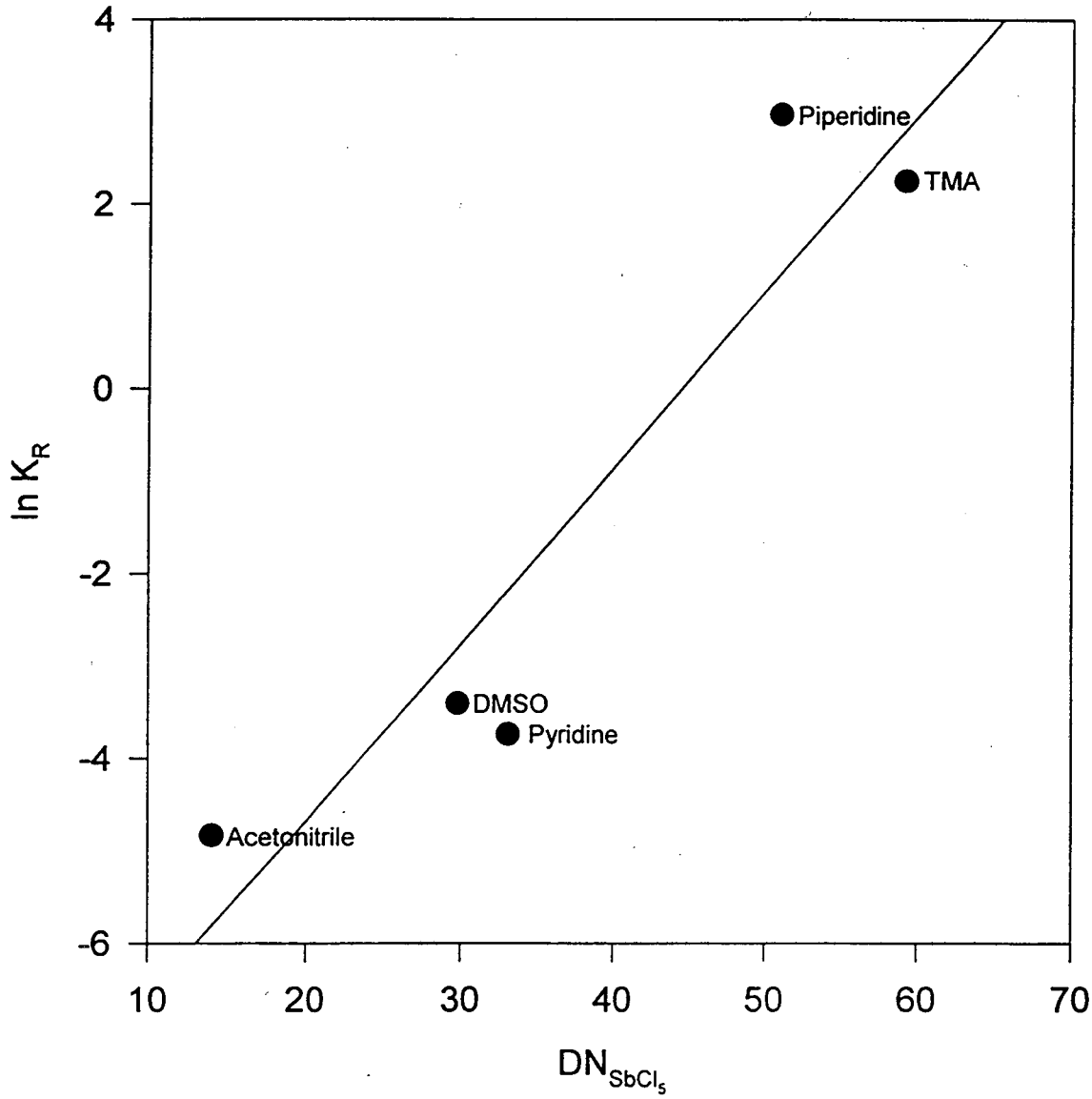


Figure 4.1-7 LFER to correlate equilibrium constant for regeneration of lactic acid-laden Dowex MWA-1 by organic bases of differing Lewis basicity as measured by the Gutmann donicity scale with donor number.

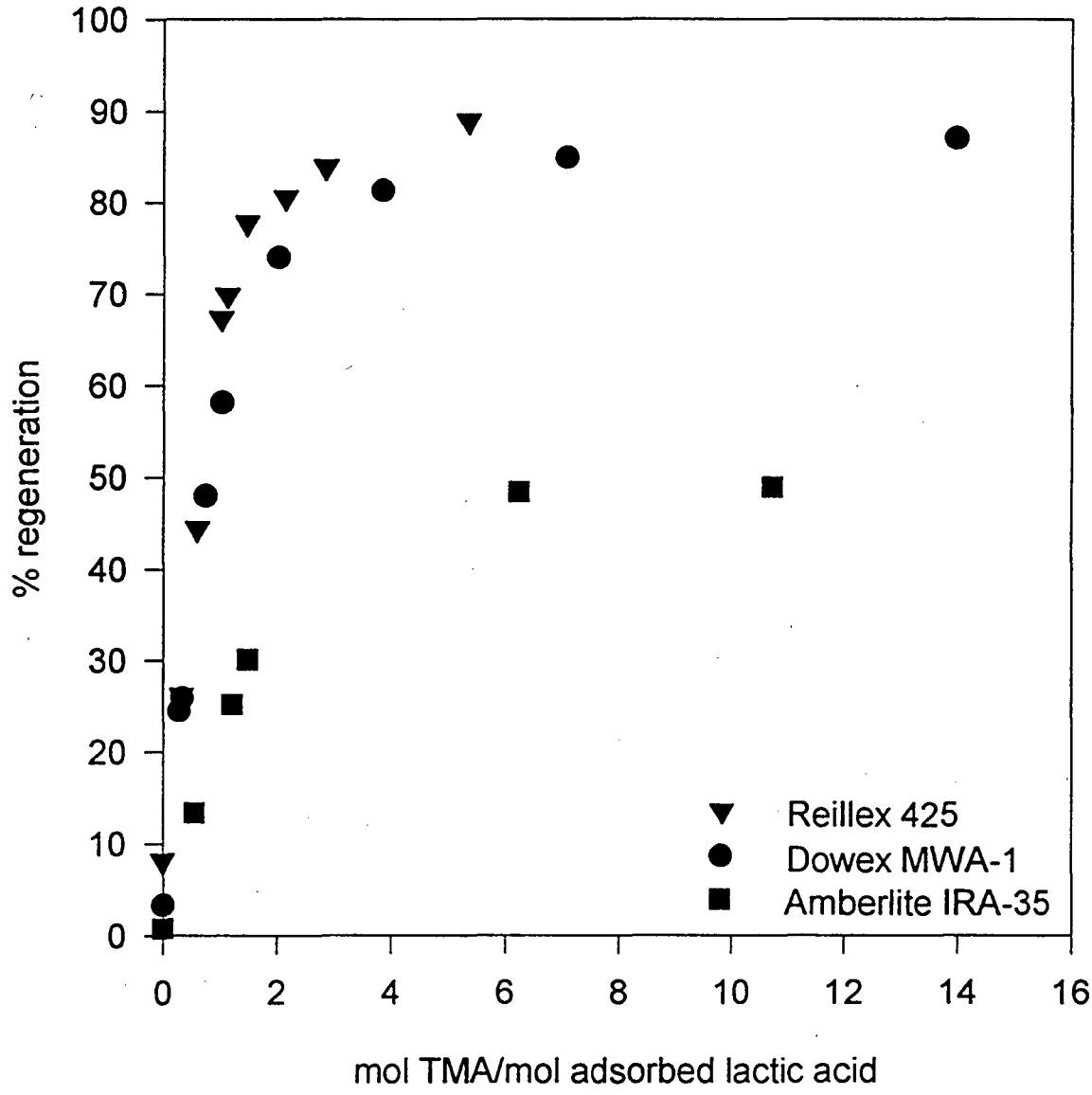


Figure 4.1-8. Leaching of lactic acid-laden polymeric sorbents by organic solutions of trimethylamine in methyl ethyl ketone at 25°C.

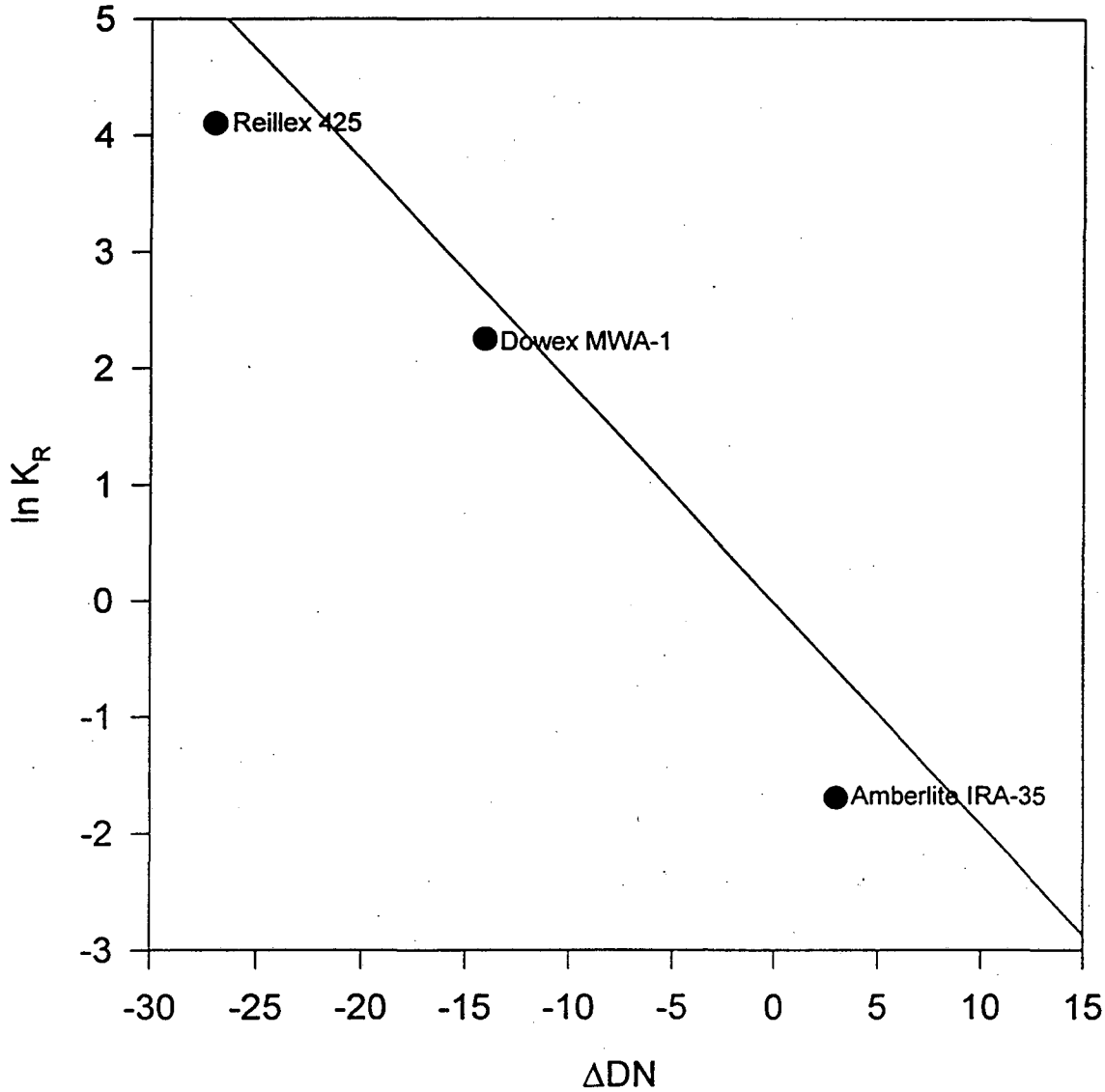


Figure 4.1-9. LFER to correlate equilibrium constant for regeneration of various lactic acid-laden polymeric sorbents by organic solutions of trimethylamine in methyl ethyl ketone at 25°C with difference in donor number between the sorbent and trimethylamine.

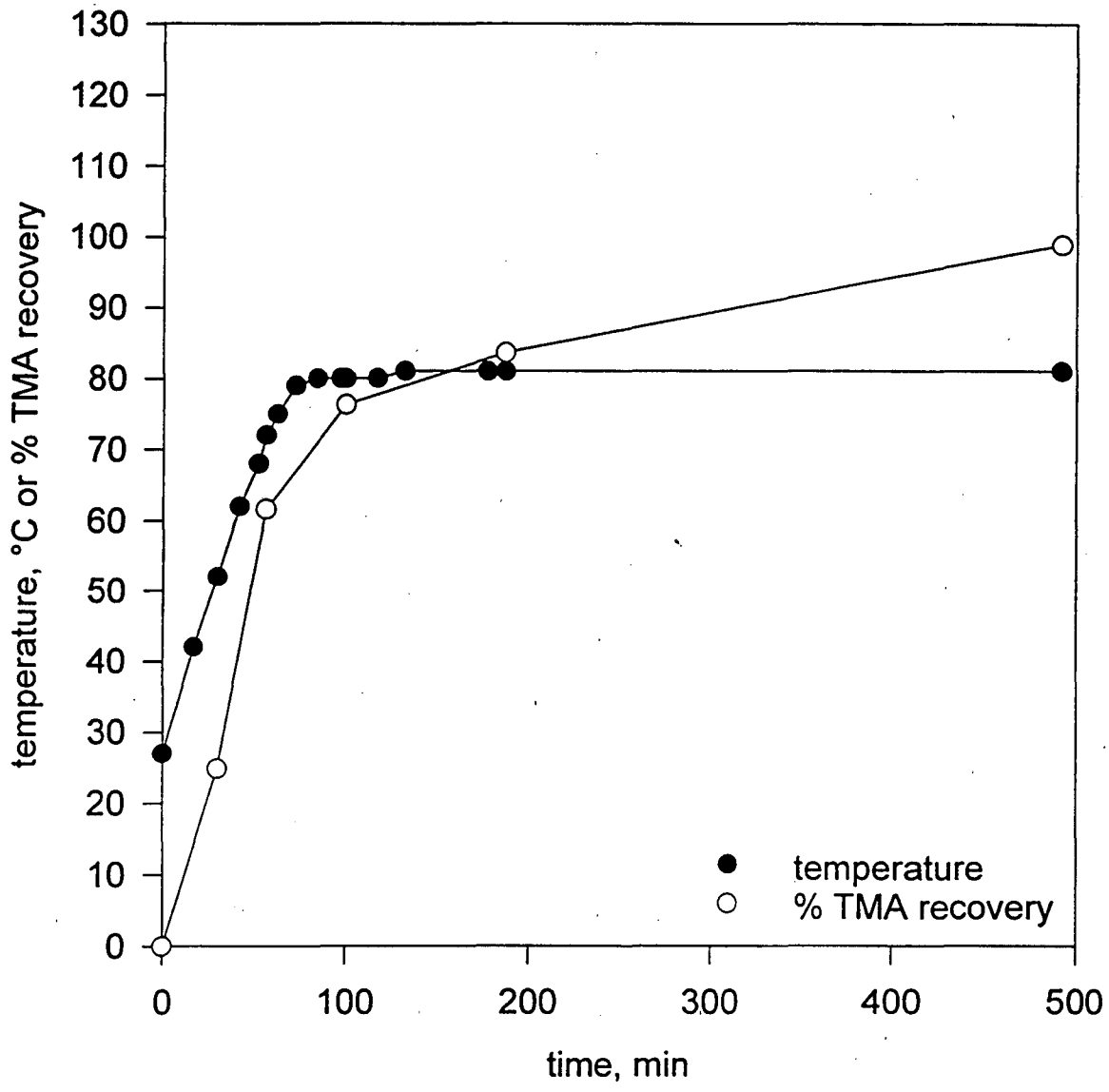


Figure 4.1-10. Rate of vaporization of trimethylamine during thermal cracking of trimethylamine-lactic acid in methyl ethyl ketone.

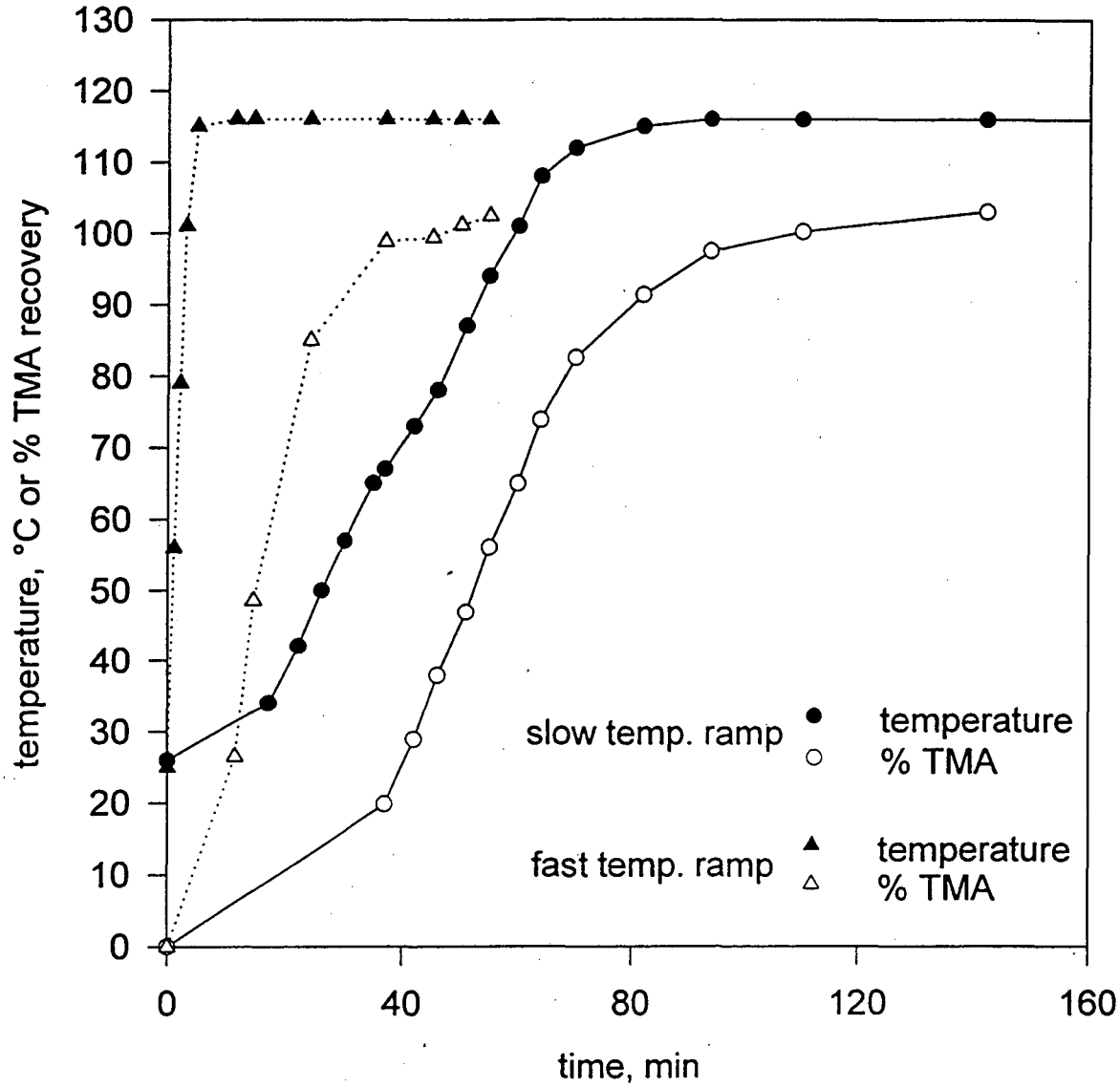
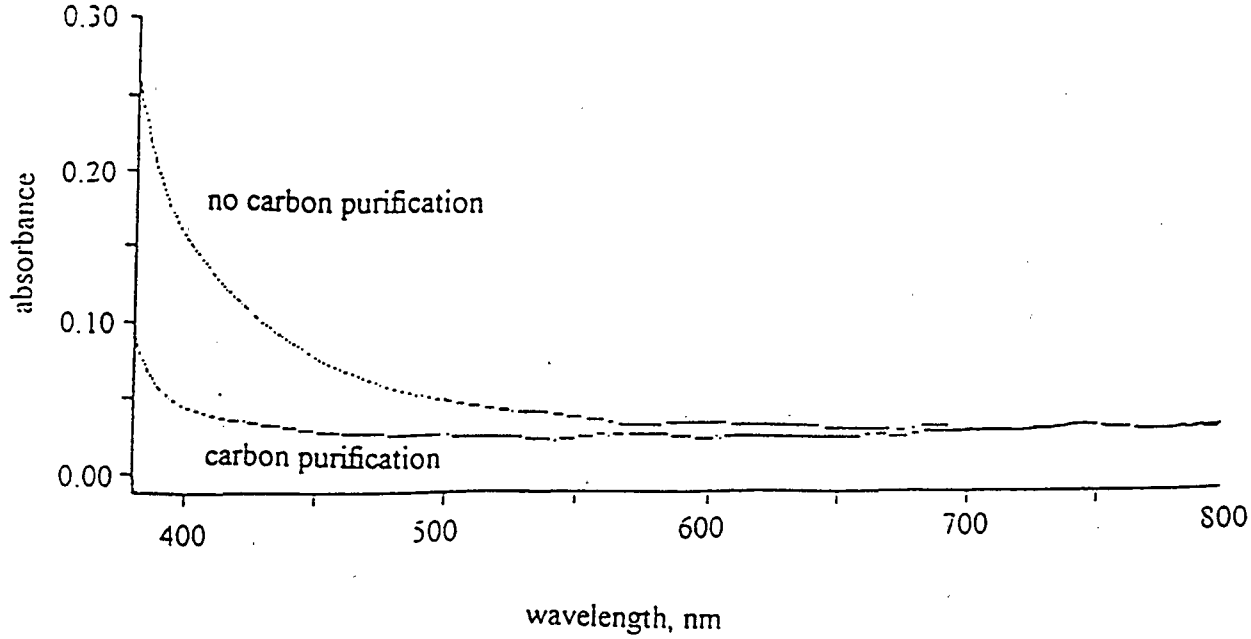
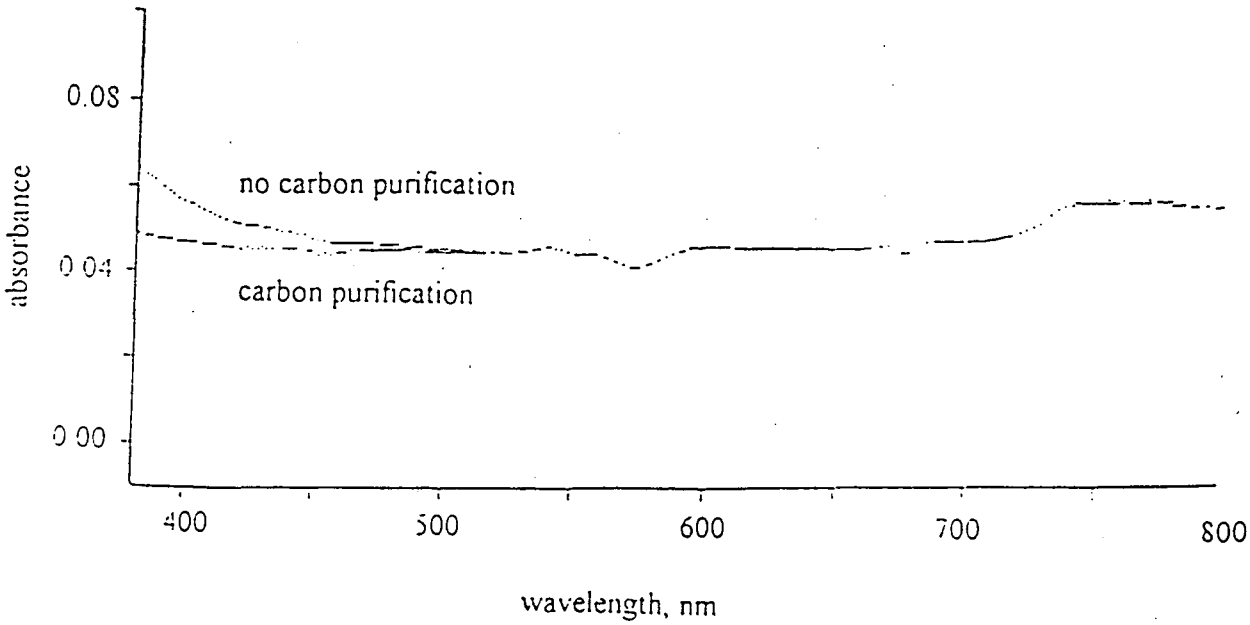


Figure 4.1-11. Rate of vaporization of trimethylamine during thermal cracking of trimethylamine-lactic acid in methyl isobutyl ketone. Effect of initial solution heating rate.



(a)



(b)

Figure 4.1-12. Visible light absorbance spectra for lactic acid solutions following thermal cracking of TMA-lactic acid complexes in MiBK. Spectra compare absorbance of carbon purified and non-purified samples: (a) lactic acid in MiBK, (b) lactic acid in water.

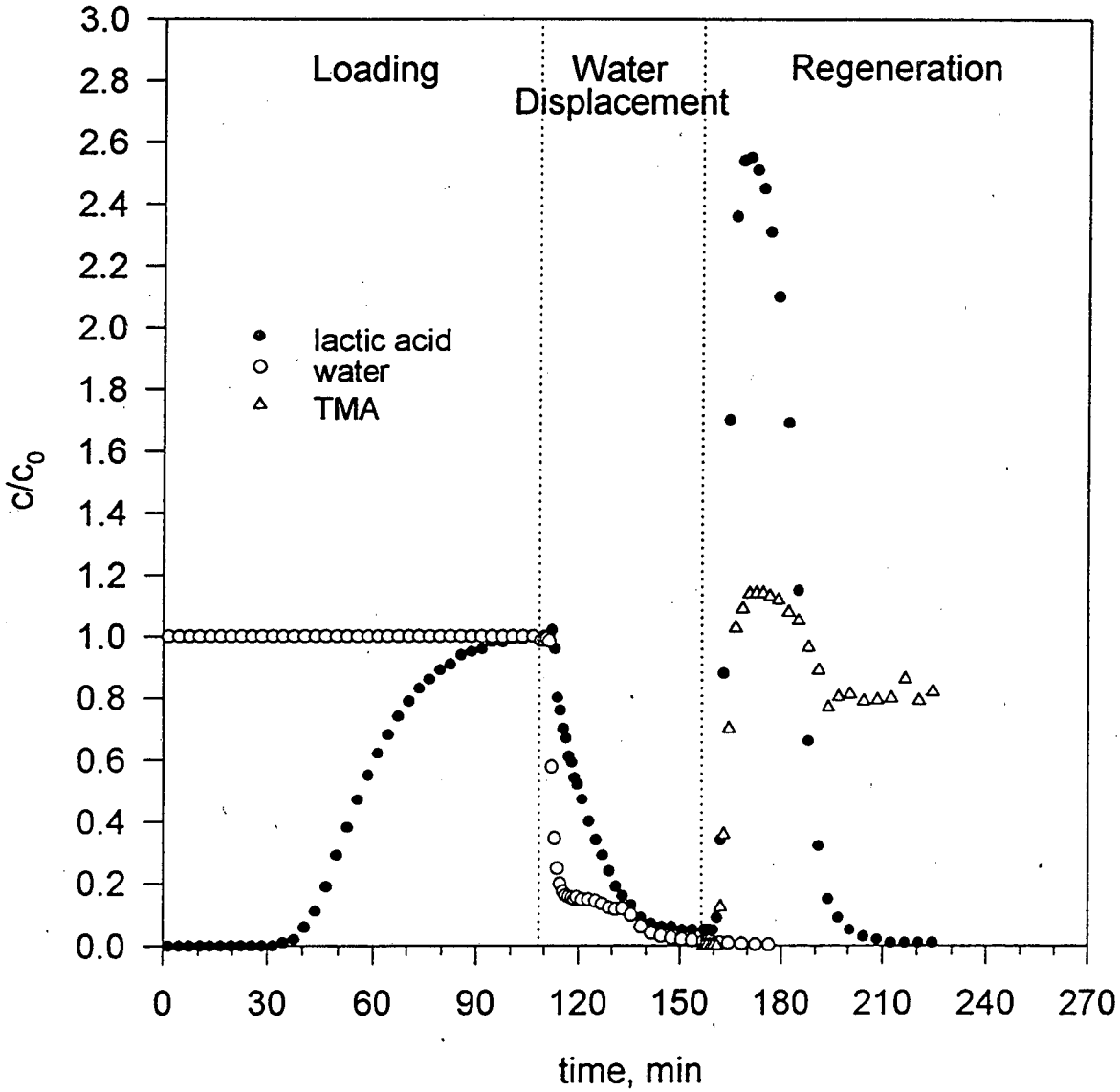


Figure 4.1-13. Concentration profiles for lactic acid, water and trimethylamine during a fixed-bed experiment examining a sequence of acid loading, water displacement by methyl ethyl ketone and sorbent regeneration by trimethylamine in methyl ethyl ketone for Dowex MWA-1 at 25°C.

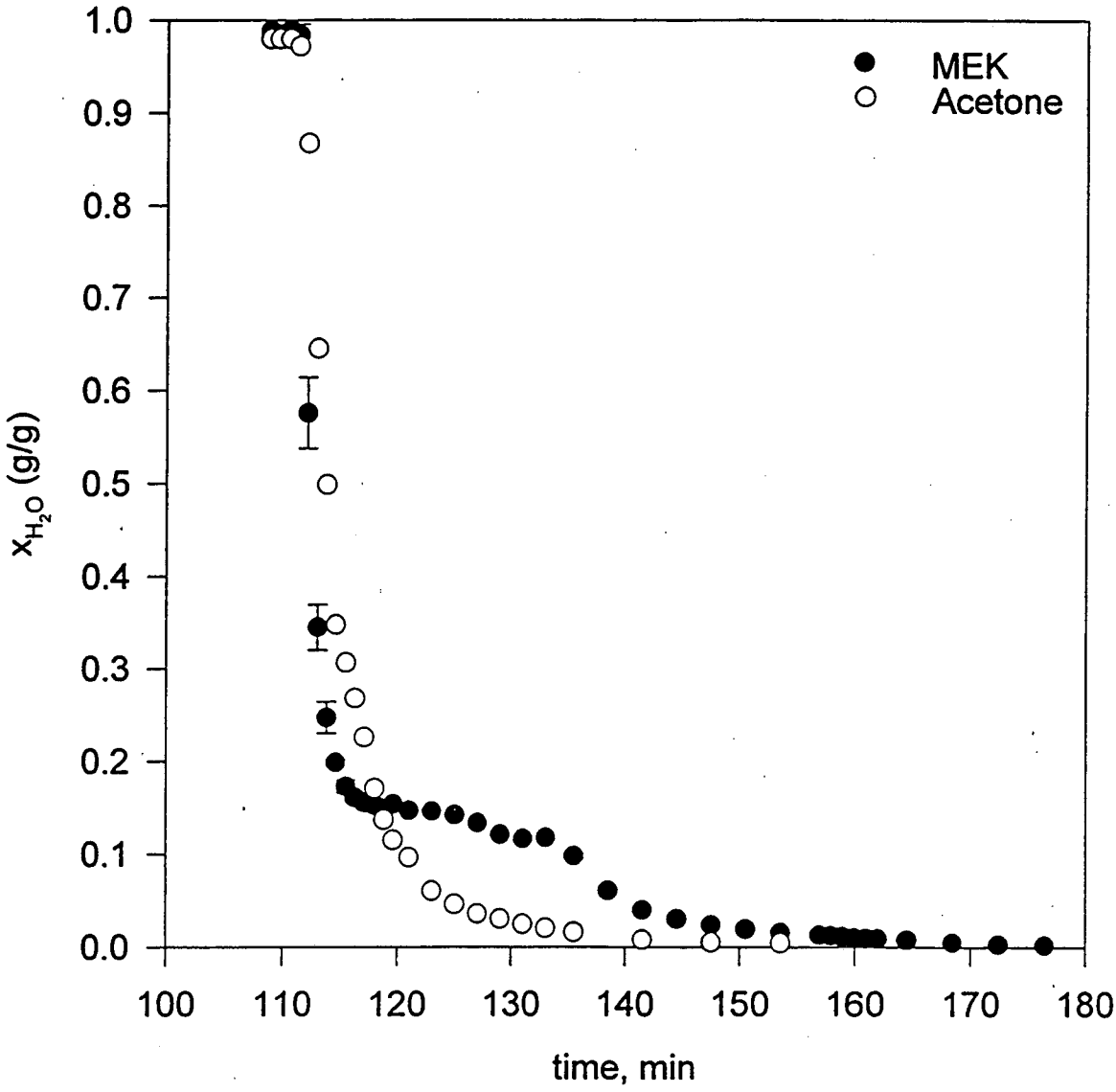


Figure 4.1-14. Water displacement from a fixed-bed of Dowex MWA-1 in equilibrium with a 2 wt.% lactic acid solution by acetone or methyl ethyl ketone. Miscible versus immiscible displacement.

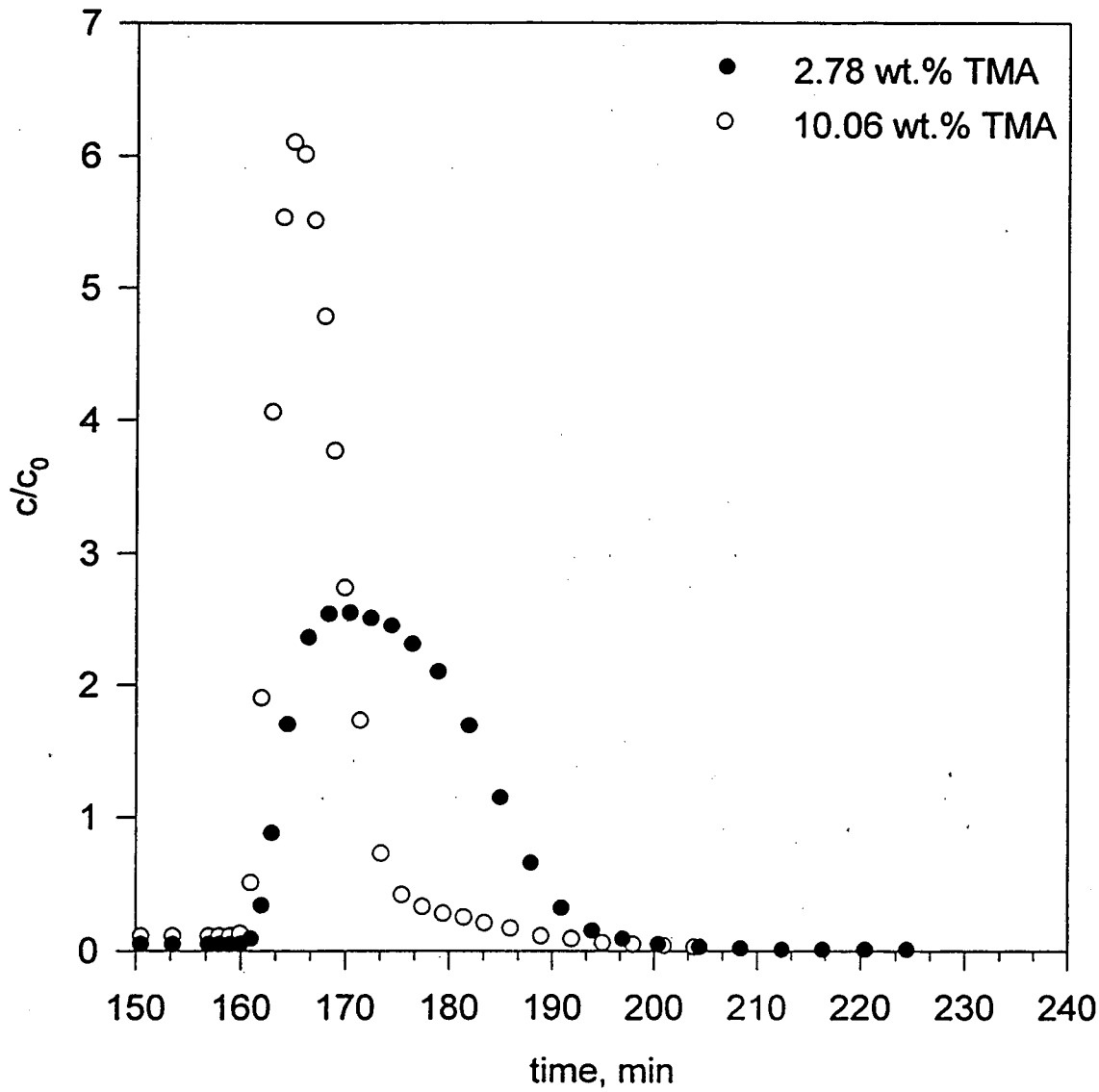


Figure 4.1-15. Effect of trimethylamine concentration on fixed-bed regeneration of lactic acid-laden Dowex MWA-1 at 25°C.

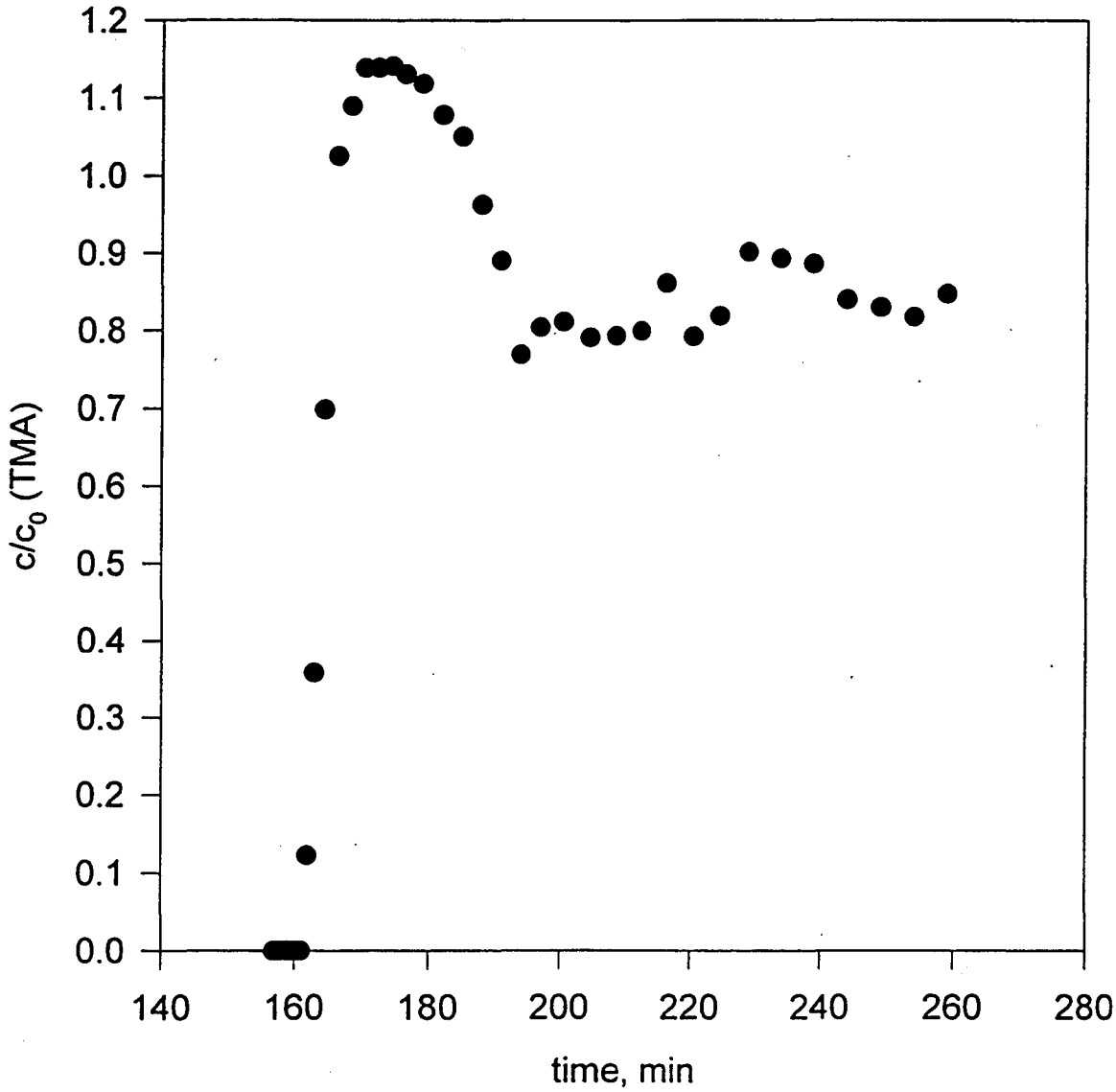


Figure 4.1-16. Typical trimethylamine concentration profile during fixed-bed regeneration of lactic acid-laden Dowex MWA-1 at 25°C.

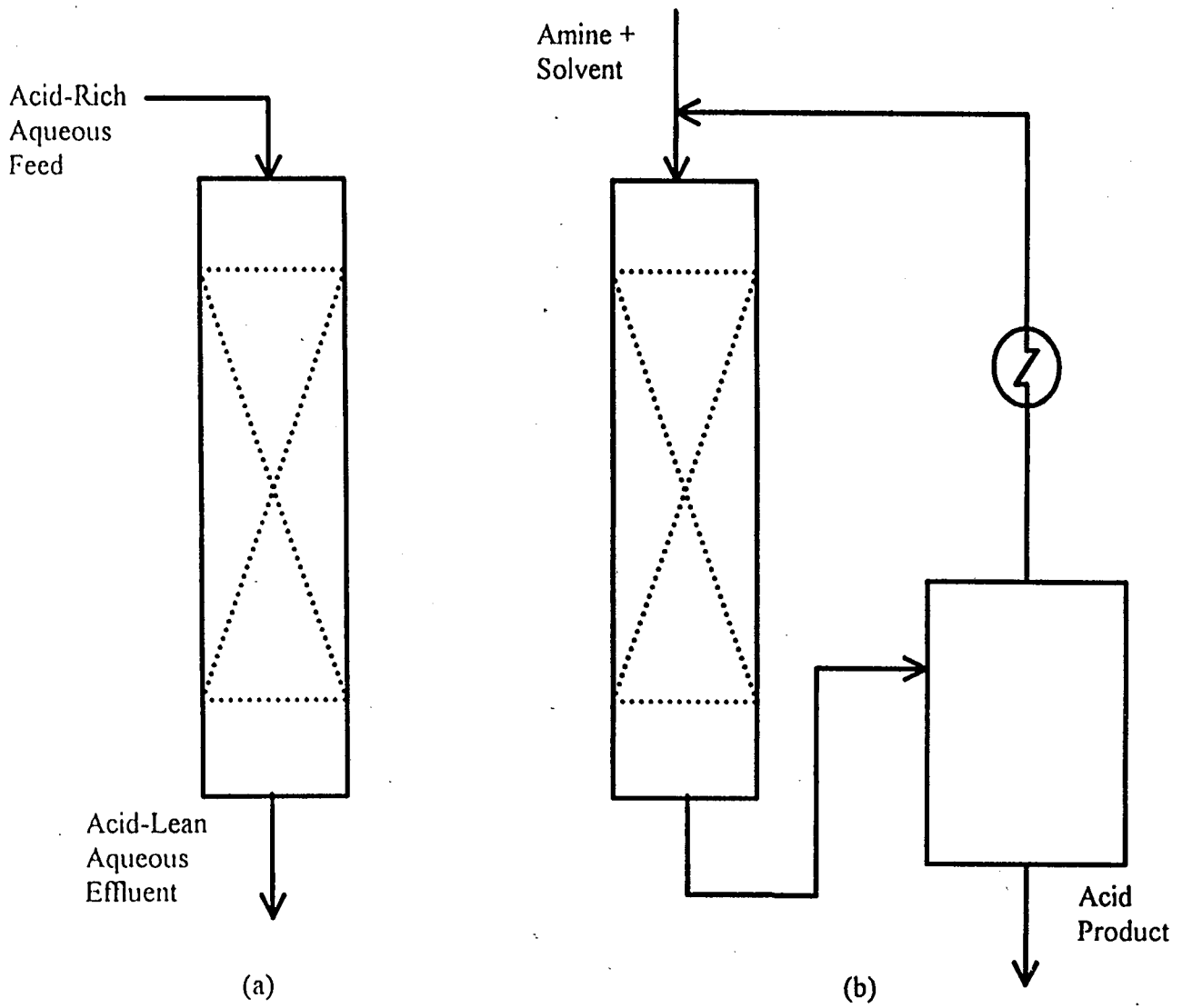


Figure 5.1-1. Carboxylic acid recovery process flow diagram: (a) on-stream for adsorption, (b) on-stream for regeneration and acid recovery.

Ernest Orlando Lawrence Berkeley National Laboratory
One Cyclotron Road ; Berkeley, California 94720

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