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GAS ANTISOLVENT-INDUCED REGENERATION OF LACTIC ACID-LADEN EXTRACTANTS

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ABSTRACT

Extraction equilibria are presented for reversible chemical complexation of lactic acid by the liquid tertiary amine extractant, tri-n-octylamine, in mixed diluents composed of 1-octanol and the gas antisolvent, propane. Experimental data were collected that show that the effect of increasing propane partial pressure during extraction is to decrease the acid loading of tri-n-octylamine. This result is discussed. A simple complexation model was employed to predict and to fit the experimental results. The model uses the Law of Mass Action to describe reaction equilibria and Wohl's expansion to estimate the solubility of propane in the organic-phase mixture. Finally, estimated energy requirements are presented for a gas antisolvent-induced regeneration process for acid-laden basic extractants; results are compared with those for a conventional diluent-swing regeneration process.

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INTRODUCTION

Separation technologies based on reversible chemical complexation are well suited to separations involving high dilution and complex solutions of chemically similar solutes. An example of where these issues pertain is product recovery in the manufacture of carboxylic acids from biomass by fermentation. Many of the present separation techniques described for removal and recovery of carboxylic acids from aqueous solution are energy-intensive and therefore expensive. Recovery technology using reversible complexation with agents such as liquid extractants with amine functionalities can reduce energy consumption substantially.

A number of researchers [1-12] have employed extraction and adsorption by reversible chemical complexation to recover carboxylic acids from dilute aqueous solutions. In extraction, the amine extractant recovers the acid by reacting with it to form an acid-amine complex that is solubilized into the extractant phase. A second step, referred to as regeneration, reverses this reaction to recover the acid into a product phase and the acid-free extractant, available for recycle.

Typically, the amine extractants are employed as organic solutions in a suitable organic solvent (referred to as the diluent) that controls physical properties such as density, viscosity, interfacial tension, water uptake, and boiling point of the extractant phase. Additionally, the diluent can dramatically affect the extraction equilibria. There is increased extraction power with a diluent that stabilizes the acid-amine complex effectively. Such diluents are referred to as ‘active’ diluents. Relatively nonpolar aprotic diluents provide no such stabilization of the acid-amine complex. Such diluents are referred to as ‘inert’ diluents.

A process has been described [5,10,13] known as diluent-swing regeneration that uses these results to advantage. Diluent-swing regeneration is based on a shift of the equilibrium distribution of acid from the aqueous phase to the organic phase between forward and back extraction caused by a change in the composition of the diluent with which the extractant is mixed. This diluent composition swing facilitates back extraction of the acid into an aqueous product phase. Baniel et al. [13] summarized some of the methods that may be applied to accomplish this change in diluent composition.

In a diluent-swing process to recover carboxylic acids, the acid is extracted from the aqueous feed into an organic solvent containing the amine extractant. The composition of the organic phase is chosen to promote acid distribution into the organic phase. For example, the diluent would contain a high percentage ($>$ 70%) of active diluent and a low percentage ($<$ 30%) of inert diluent. In a subsequent step, the composition of the acid-laden organic phase is changed (e.g., by distillation or dilution) to produce an organic phase that promotes acid distribution into the aqueous phase. This situation corresponds to an organic phase rich in the inert diluent. The acid-laden organic phase is then contacted with an aqueous product phase to produce an aqueous acid solution and an acid-lean organic phase, available for recycle.

To date, diluent systems have been composed of organic solvents that are liquids at room temperature. A drawback to such systems is that changes in extractant-phase composition generally involve a distillation step to separate the active and inert diluents. To avoid this energy expense, a new process is proposed that will replace the inert liquid diluent with a gas antisolvent. Here, antisolvent is used to connote a substance that has a low capacity to solubilize the extracted acid. In this process, the diluent composition change will be effected by pressurizing it with a gas antisolvent (e.g., propane). For carboxylic acids that exist as solids at room temperature, this composition change might induce precipitation of the acid product from the extractant phase. Alternatively, for acids that are not solids at room temperature, this composition change will be carried out while the extractant is in contact with an aqueous product phase. Here, the antisolvent will shift the equilibrium distribution of the acid to favor the aqueous product phase.

The idea for this process stems from previous work [10] on extraction of carboxylic acids with amine extractants that indicated that the chain length of *liquid-phase* aliphatic hydrocarbon diluents (C_7-C_{12}) has little effect on extractant loading. This result is not surprising, since such diluents provide essentially no stabilization of the acid-amine complex. It is therefore expected that gaseous aliphatic hydrocarbons (e.g., propane) will behave similarly as inert diluents. Acid extraction power is expected to decrease with increasing concentrations (i.e., higher partial pressures) of propane in the organic extractant phase. Thus, a diluent-swing regeneration process will be devised whereby changes in extractant composition will be effected by pressurizing the system with propane gas. A benefit of this process over conventional recovery techniques is that the diluent components can be easily separated (e.g., by a flash operation) without involving a distillation step.

EXPERIMENTAL MATERIALS AND METHODS

Materials

Chemical Reagents

1-Octanol (Sigma, 99+%, HPLC grade), tri-n-octylamine (TOA; Aldrich, 98%), and propane (Matheson, 99.95%) were used as received. All aqueous solutions were prepared from distilled water that had been passed through a Milli-Q water purification system (Millipore Corp.). A 85+ wt.% lactic acid solution (Aldrich, A.C.S. reagent) was diluted with water to approximately 15 wt.% and boiled under constant reflux for at least 12 hours to hydrolyze any lactic acid polymers. Complete hydrolysis of the esters was confirmed by high-performance liquid chromatography (HPLC).

Methods

The equilibrium cell used in all of the regeneration experiments was a 500 mL stainless steel cylinder. The cell was maintained at 25 °C in a constant-temperature, reciprocating shaker bath operating at 90 RPM.

Known weights of extractant (typically 32-34 g) and acid solution (typically 40-42 g) were contacted in the cell. To purge the system of air, propane was introduced to one end of the cell from a pressurized propane gas cylinder. Air and propane exited the cell through the opposite end of the column, which was connected to a bubble flow meter that served to measure the volumetric flow rate of propane into the cell. To ensure that essentially all of the air was removed from the vapor space, high purge volume-to-vapor volume ratios (> 5) were employed during this step.

When the system had been purged of air, the outlet to the bubble flow meter was closed, and the system was pressurized with propane to the desired working pressure (0-100 kPa gauge). Working pressures were measured with a Bourdon-tube type, Heise gauge (Model CM) that had been calibrated against a Budenberg dead-weight gauge (Model 380 H).

After 24 hours, the concentration of lactic acid in the aqueous solution was measured by HPLC, and the amount of lactic acid removed by extraction was calculated by mass balance. Additional measurements showed that equilibrium was reached within the experimental error in the batch equilibration experiments within 5 hours. 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 maintained at 60 °C, a 0.01 N H_2SO_4 mobile phase, and an ultraviolet detector operating at 210 nm.

DESCRIBING AND MODELING THE EXTRACTION SYSTEM

The system comprises three phases and five species. Therefore, a rigorous mathematical description of this system would be quite cumbersome. A more manageable description results with a few simplifying assumptions. Those species present in negligible amounts in a particular phase are neglected. Lactic acid, TOA, and 1-octanol have low volatilities at 25 °C relative to water and propane. Therefore, the vapor phase consists primarily of propane and water. Propane, TOA, and 1-octanol have low solubilities in water at 25 °C over the pressure range employed. The aqueous phase thereby consists primarily of water and lactic acid. Water uptake into the organic phase was neglected, recognizing that some water will be present in this phase. The organic phase comprises propane, 1-octanol, TOA, and lactic acid.

The equations needed to describe the system include phase equilibria, reaction equilibria, and mass balances.

Phase Equilibria

Vapor-Liquid Equilibria

By definition, the condition for vapor-liquid equilibrium is the equality of vapor- and liquid-phase fugacities for each species. For propane, this condition can be written in terms of species mole fractions using Henry's law:

$$y_p \overline{\phi}_P^V P = x_P^{org} H_{P,mix}^{org} \tag{1}$$

where y_p and x_P^{org} represent the mole fractions of propane in the vapor and organic phases, $\overline{\phi}_P^V$ represents the fugacity coefficient of propane in the vapor phase, and $H_{P,mix}^{org}$ represents the Henry's constant for propane in the organic-phase mixture.

For water, the condition for vapor-liquid equilibrium can be written as

$$y_w \overline{\phi}_w^V P = x_w^{aq} P_w^s \tag{2}$$

where x_w^{aq} represents the mole fraction of water in the aqueous phase and is the saturation pressure for water at the system temperature; it is 0.0317 bar at 25 °C [17].

Values of the vapor-phase fugacity coefficients for propane and water were calculated using the volume-explicit form of the virial equation:

$$\ln \overline{\phi}_i^V = \left[2 \cdot \sum_j y_j B_{ij} - B_{mix} \right] \cdot \frac{P}{RT} \tag{3}$$

$$B_{mix} = \sum_i \sum_j y_i y_j B_{ij} \tag{4}$$

Values of the second virial coefficient for propane and water were estimated to be –396 cm^3/mol and –1239 cm^3/mol using corresponding-states correlations [24,25]. The value of the cross coefficient was estimated to be –700 cm^3/mol.

To estimate the Henry's constant for propane in the organic phase, the organic phase was treated as a binary mixture of 1-octanol and TOA. The procedure for making this estimate is discussed by O'Connell and Prausnitz [26], and is based on the simplest form of Wohl's expansion. Using this expansion, the Henry's constant for propane in the organic phase mixture is given as

$$\ln H_{P,mix}^{org} = x_{oct} \cdot \ln H_{P,oct} + x_{TOA} \cdot \ln H_{P,TOA} - a_{oct,TOA} \cdot x_{oct} \cdot x_{TOA} \quad (5)$$

where x_{oct} and x_{TOA} represent the mole fractions of 1-octanol and TOA in the organic phase on a solute-free basis, $H_{P,oct}$ and $H_{P,TOA}$ represent the Henry's constants for propane in pure 1-octanol and pure TOA, and $a_{oct,TOA}$ is a constant characteristic of the 1-octanol/TOA binary pair. If 1-octanol/TOA form an ideal mixture, then this constant will equal zero. Values of $H_{P,oct}$ and $H_{P,TOA}$ were estimated using UNIFAC (Dortmund); they are 7.6 bar and 5.4 bar, respectively, at 25 °C.

Liquid-Liquid and Reaction Equilibria

If specific, "chemical" interactions between the acid and extractant molecules are strong relative to "physical" interactions, the Law of Mass Action can be a useful tool for describing extraction equilibria [18]. Using a mass-action-law description of equilibrium, modeling of acid extraction is possible by postulating the formation of one or more stoichiometric complexes of acid and amine. An equilibrium description of the system consists of a set of reactions of p acid, HA, molecules and q amine, B, molecules to form the corresponding set of (p, q) complexes along with overall equilibrium constants, $K_{pq,true}$:

$$K_{pq,true} = \frac{\gamma(HA_p - B_q)}{\gamma_{HA}^{p}\,\gamma_{B}^{q}} \frac{[HA_p - B_q]}{[HA]^p\,[B]^q} \quad (6)$$

Brackets represent molar concentrations. For dilute liquid solutions, the ratio of activity coefficients in Equation 6 can be assumed to be constant over the experimental concentration range [19]. With this assumption, the ratio of activity coefficients can be incorporated into an apparent equilibrium constant, K_{pq}. Loading of the extractant, defined as the concentration of acid in all forms in the organic phase, divided by the concentration of extractant in all forms in the organic phase, is then given as

$$Z = \frac{\sum_p \sum_q p\, K_{pq}\, [HA]^p\, [B]^{(q-1)}}{1 + \sum_p \sum_q q\, K_{pq}\, [HA]^p\, [B]^{(q-1)}} \quad (7)$$

Factors that influence the values of the equilibrium constants, and therefore the extractant loading, include the natures of the acid, amine, and diluent. Tamada and King [19] present a rather comprehensive summary of mass-action-law modeling results for carboxylic acid-tertiary amine systems.

In addition to specific, "chemical" extraction of the acid by the amine extractant, there is "physical" extraction of the acid by the amine extractant and the diluent(s). Allowing for acid partitioning between the aqueous and organic phases and for acid dimerization within the organic phase, the distribution of acid from the aqueous phase to the organic phase follows (Kertes and King, 1986):

$$\frac{[C_{a,org}]}{C_{a,aq}} = P + 2\,P^2\,K_D\,[c_{a,aq}] \tag{8}$$

where P is the acid partition coefficient, and K_D is the organic-phase dimerization constant. For low aqueous-phase acid concentrations and/or low K_D values, the second term on the right hand side of Equation 8 is negligible. Additionally, for inert diluents, such as aliphatic hydrocarbons, the partition coefficients for low-molecular-weight carboxylic acids are sufficiently low so that one can neglect physical extraction by such diluents in amine-containing systems (Kertes and King, 1986). Furthermore, physical extraction is negligible for the long-chain amine extractant itself.

A correction to the calculated extractant loading was made for "physical" extraction of the acid by the diluent. This correction was made by subtracting out the amount of acid extracted by the diluent alone, calculated as the multiplication product of the aqueous acid concentration, the experimentally determined partition coefficient ($P = 0.162$) for lactic acid monomer into the active diluent, 1-octanol, and the initial mole fraction of 1-octanol. This correction assumes that the organic-phase acid concentration is the sum of two binary interactions, acid-extractant and acid-diluent, on a mole fraction basis.

Estimation of the Equilibrium Constant for Extraction

Previous work [8,10] on extraction of lactic acid by tertiary amines in 1-octanol has shown that uptake can be described well by assuming the existence of only (1:1) complexes. With this assumption, Equation 6 becomes

$$Z = \frac{x_L^{org}}{x_{toa}^{org}} = \frac{K_{11}\,[HA]}{1 + K_{11}\,[HA]} \tag{9-10}$$

The value of the apparent equilibrium constant K_{11} depends on the volume percentage of active diluent (i.e., 1-octantol) in the extractant phase [10]. Figure 1 shows the relationship between K_{11} (L/mol) and the volume fraction of active diluent, 1-octanol, in the extractant phase on an extractant-free basis. This relationship can be expressed mathematically as

$$\ln K_{11} = -0.48 + 8.82 \cdot X_{oct} - 3.19 \cdot X_{oct}^2 \tag{11}$$

where X_{oct} is the volume fraction of 1-octanol in the extractant phase on an extractant-free basis. When comparing experimental loading data with model predictions, the amount of acid extracted by physical extraction must be subtracted from the total amount of acid extracted, as previously described.

Mass Balance

Acid Mass-Balance

Because loading depends on the aqueous-phase lactic acid concentration, a mass balance is needed to account for transfer of acid into the organic phase. Lactic acid exists in the aqueous phase and in the organic phase:

$$n_L = x_L^{aq} \cdot n_T^{aq} + x_L^{org} \cdot n_T^{org} \tag{12}$$

where n_L represents the number of moles of lactic acid in the system and subscript $_T$ represents the total number of moles in a particular phase.

No mass balance was needed for water. Two assumptions were made: The mass of water in the vapor phase was negligible compared to the total mass of water in the aqueous phase. No water distributed into the organic phase. This second assumption is in error; however, this same assumption was used by previous researchers in the development of Equation 11.

The final equations are given by the definition of mole fractions:

$$\sum_i x_i^{org} = 1, \quad \sum_i x_i^{aq} = 1, \quad \sum_j y_i = 1 \tag{13-15}$$

The extraction system consists of 12 unknown quantities, described by 11 equations. This set of equations was solved by specifying the system pressure.

RESULTS AND DISCUSSION

In Fig. 1, increasing values of K are related to decreasing values of the acid-amine activity coefficients associated with increasing solvating power of the diluent [20]. There are two contributions to the apparent equilibrium constant, as shown in Equation 6. $K_{pq,true}$ is the true thermodynamic equilibrium constant describing the reaction of the acid with the amine to form the acid-amine complex; it is independent of the diluent and is truly a constant. Hence, changes in K_{pq} must be related to changes in the ratio of activity coefficients. Increased interaction between a diluent and the complex will decrease $\gamma_{HA\text{-}B}$, and thereby increase K_{pq}.

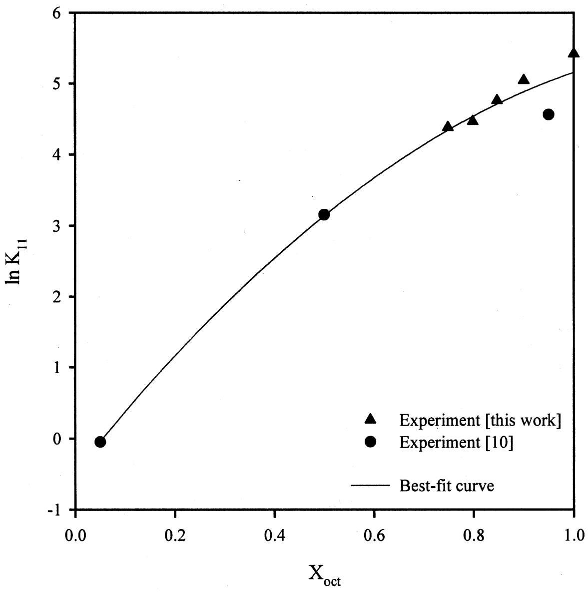

Figure 1. Effect of active diluent composition on the equilibrium constant for (1:1) complexation of lactic acid by Alamine 336 at 25 °C. X_{oct} represents the volume fraction of 1-octanol on an extractant-free basis.

Tamada and King [19] presented a linear free-energy relation to describe how the apparent equilibrium constant for (1,1) complexation is influenced by the nature of the acid, the amine and the diluent:

$$\log K_{11} = pK_B - pK_A - pK_P \tag{16}$$

where K_B is related to the basicity of the amine, K_A is related to the acidity of the acid, and K_P is governed by acid-diluent and base-diluent interactions. Because the amine and acid are identical for the systems studied here, the diluent composition is likely the most important parameter affecting differences in the (1,1) apparent equilibrium constants values.

Figure 2 shows the equilibrium loading data for extraction of lactic acid from a 0.45 M aqueous solution into 0.3 M TOA in 1-octanol/propane at 25 °C and five propane partial pressures. Experimental data are represented by symbols. The curves represent the mathematical model to describe loading equilibria for this system. The solid curve was generated using the model with no fitted parameters; all input parameters were obtained from independent measurements made by Husson and King [10] or by parameter estimation methods. In this model, formation of only (1,1) acid-amine complexes were postulated. Values of the appar-

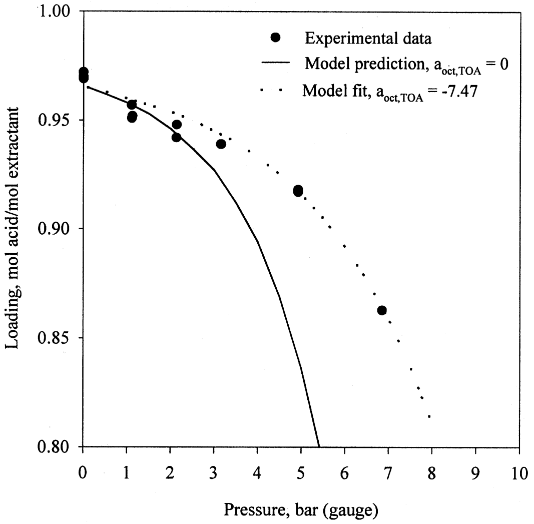

Figure 2. Experimental and predicted loading data for extraction of lactic acid by TOA in a mixed diluent composed of 1-octanol and propane. Symbols represent experimental data; the curves represents the model predictions and model fit.

ent equilibrium constants K_{11} were obtained as a function of active diluent composition from the data of Husson and King [10]. The dotted curve used the model to fit the experimental data. The adjustable parameter was $a_{oct,TOA}$ in Equation 5. A value of $a_{oct,TOA} = -7.47$ provided the best-fit dotted curve. The negative value for this constant indicates that the binary mixture of 1-octanol/TOA exhibits negative deviations from Raoult's law. Such deviations are likely due to hydrogen bonding between the two types of molecules.

With increasing inert diluent concentration, the extractant loading decreased. This result suggests that 1-octanol provides better solvation of the acid-amine complex than does propane. It has been previously reported that 1-octanol may stabilize the acid-amine complex by hydrogen bonding with the carbonyl oxygen of the complexed acid [19]. The model fit well the experimental results.

While inclusion of only (1,1) acid-amine complexes was used in the model to predict and to fit the experimental results, the absence of (2,1) acid-amine complexes cannot be confirmed. The presence of such complexes for acetic acid and triethylamine in the active diluent, chloroform, has previously been inferred from infrared spectroscopic data by Barrow and Yerger [21]. However, for extraction of acetic acid by Alamine 336 in the protic diluent, 2-ethyl-1-hexanol [22], and by TOA in the protic diluent, chloroform [23], formation of (1,1) complexes dominate formation of higher order complexes.

PROCESS CONSIDERATIONS

Diluent composition changes can be effected by removal of an active diluent from the acid-laden extractant phase or by addition of a volatile inert diluent to the acid-laden extractant phase prior to back extraction (i.e., regeneration). Figures 3 and 4 present schematic representations of these two diluent-swing processes. In the first scheme, the diluent composition change is effected by removal of an active diluent component from the acid-laden extractant phase by distillation. In the second scheme, the diluent composition change is effected by addition of a volatile inert diluent component to the acid-laden extractant phase. Following regeneration, this inert diluent is removed by a flash operation from the acid-lean extractant to produce an active diluent-rich extractant for reuse in forward extraction. Energy requirements for both processes will be compared for recovery of lactic acid by reversible complexation with amine extractants.

Scheme 1. Batch equilibrium data [10] were used for extraction of lactic acid by the liquid tertiary amine extractant Alamine 336 (67% C_8/33% C_{10} chains) in a mixed diluent composed of 1-octanol and dodecane to estimate the energy requirements for lactic acid recovery using a diluent-swing process that involves removal of the active diluent by distillation. Specifically, the reboiler duty was estimated for the distillation unit operation in the process shown schematically in Fig. 3.

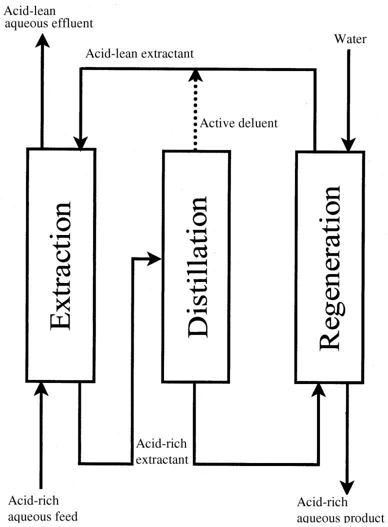

Figure 3. Schematic representation of a diluent-swing process that employs distillation to modify the diluent composition between forward and back extraction.

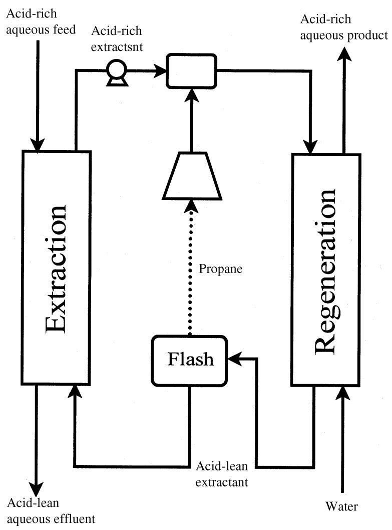

Figure 4. Schematic representation of a diluent-swing process that employs pressurization with a gas antisolvent to modify the diluent composition between forward and back extraction.

With the assumption that this system does obey a simple (1,1) stoichiometry, it is possible to extrapolate extractant loading data obtained at one amine concentration to predict loading at a different amine concentration. Therefore, it is possible to construct equilibrium curves for extraction by extractants of varying composition using only the data obtained from the batch experiments.

Table 1 summarizes the operating conditions used in the energy requirement calculations for Scheme 1. The distillation unit operation was treated as a binary separation of 1-octanol and n-dodecane. The feed to the distillation column was assumed to be saturated liquid, and the sensible heat required to achieve this condition was not taken into account.

In order to construct the equilibrium curves for forward extraction and regeneration, values for the apparent equilibrium constants had to be determined for the organic-phase compositions employed. The value of K_{11} for the 0.30 M Alamine 336/95 vol% 1-octanol/5 vol% n-dodecane extractant was interpolated from the data in Fig. 1 to be 151.4 L/mol. The value of K_{11} for the 1.26 M Alamine 336/50 vol% 1-octanol/50 vol% n-dodecane was interpolated from the data in Fig. 1 to be 22.9 L/mol. Note that a 1.26 M Alamine 336 concentration results following removal of 1-octanol to produce a diluent mixture composed of 50 vol% 1-octanol/50 vol% dodecane.

Figure 5 shows the equilibrium curves for forward extraction and regeneration; concentrations are presented as mole fractions of acid in each phase. From

Table 1. Operating Conditions Used in the Energy Requirement Calculations for Scheme 1

Feed acid concentration	1.00–4.00 wt.%
Extractant composition for forward extraction	0.30 M Alamine 336 95 vol.% 1-octanol/5 vol.% n-dodecane (extractant-free basis)
Extractant composition for regeneration (calculated based on an assumption that only 1-octanol was removed by distillation)	1.26 M Alamine 336 50 vol.% 1-octanol/50 vol.% n-dodecane (extractant-free, acid-free basis)
Percent removal of acid from feed during forward extraction	95 %
Percent removal of acid from acid-laden extractant during regeneration	95 %
Stage requirements	∞ stages in all contactors
Reflux conditions for distillation	Minimum reflux

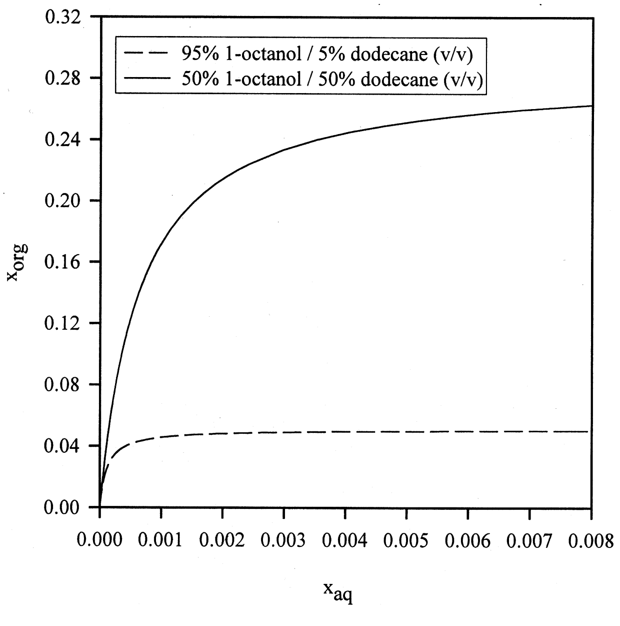

Figure 5. Equilibrium curves for forward and back extraction of lactic acid by Alamine 336 in a diluent composed of 1-octanol and dodecane at 25 °C. These curves were used in the energy requirements calculation for Scheme 1.

Equation 9, the concentration of the acid in the organic phase for a system that obeys (1,1) stoichiometry is given as

$$[\mathrm{HA}]_{\mathrm{org}} = \frac{[\mathrm{B}]\mathrm{K}_{11}\,[\mathrm{HA}]_{\mathrm{aq}}}{1 + \mathrm{K}_{11}\,[\mathrm{HA}]_{\mathrm{aq}}} \tag{17}$$

At low aqueous-phase acid concentrations, or low values of K_{11}, the organic-phase acid concentration will increase linearly with aqueous-phase acid concentration. At high aqueous-phase concentrations, the organic-phase acid concentration will saturate at a value equal to the amine concentration. The aqueous-phase acid concentration at which saturation occurs will be higher for a system with a lower value of K_{11}. Equation 17 suggests that the equilibrium curve for forward extraction of lactic acid by Alamine 336 will saturate at a lower aqueous-phase acid concentration than that for regeneration, based on the higher value of K_{11} during forward extraction. Additionally, Equation 17 suggests that the higher amine concentration in the organic phase following distillation will increase the value of the organic-phase acid saturation concentration during regeneration.

Figure 6 shows the reboiler duty as a function of initial feed concentration. The reboiler duty, D, was calculated as the heat required to create the necessary vapor flow rate in the reboiler of an ideal distillation column:

$$\mathrm{E} = (\mathrm{D} + \mathrm{R}_{\min})\,(\Delta h_{o}^{vap}\, y_{o} + \Delta h_{d}^{vap}\, y_{d}) \tag{18}$$

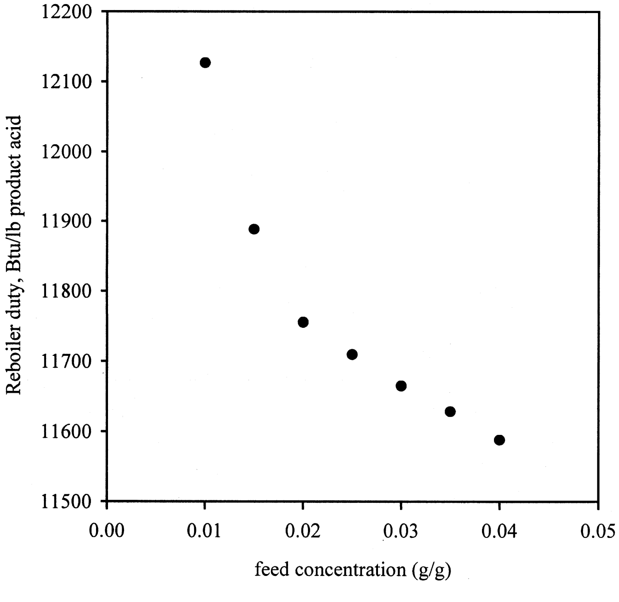

Figure 6. Estimated energy requirements for the diluent-swing process involving distillation (Scheme 1).

where D is the molar flow rate of the distillate stream, R_{min} is the minimum reflux, Δh_i^{vap} is the molar heat of vaporization of component *i*, and y_i is the vapor-phase mole fraction of component *i* exiting the top of the column. The sensible heat of raising the solvent temperature was not included in this calculation. The decrease in reboiler duty with increasing feed concentration is related to the higher extractant loadings with increasing feed concentration. Increased extractant loadings mean lower extractant flow rates to achieve the same percentage removal of acid from the aqueous feed. At all feed concentrations, the energy requirements to accomplish regeneration (assuming no heat integration) are extraordinarily high. This fact results from the need to supply the heat of vaporization for a large percentage (~78 vol.%) of the feed to the distillation column.

Scheme 2. Data were used from our model predictions of extraction of lactic acid by TOA in a mixed diluent composed of 1-octanol and propane to estimate the energy requirements for lactic acid recovery using a diluent-swing process that involves dilution of the extractant phase by pressurization with propane and subsequent removal of the propane by a flash operation. Specifically, the pump and compressor work were estimated for the flash operation in the process shown schematically in Fig. 4. Table 2 summarizes the operating conditions used in the energy requirement calculations.

The assumption of (1,1) stoichiometry was used to construct equilibrium curves for forward extraction and regeneration, as previously described for Scheme 1. Figure 7 shows these equilibrium curves. Unlike Scheme 1, the regeneration curve lies below the forward extraction curve at all values of aqueous-phase concentration. This difference can be attributed to the fact that pressurization with propane effects a decrease in the molar concentration of amine in the

Table 2. Operating Conditions Used in the Energy Requirement Calculations for Scheme 2

Feed acid concentration	0.75–4.20 wt.%
Extractant composition for forward extraction (equilibrium values at 1 bar absolute pressure)	0.30 M Alamine 336 99.6 vol.% 1-octanol/0.4 vol.% propane (extractant-free basis)
Extractant composition for regeneration (equilibrium values calculated from model at 7.3 bar absolute pressure)	0.17 M Alamine 336 53.6 vol.% 1-octanol/46.4 vol.% propane (extractant-free, acid-free basis)
Percent removal of acid from feed during forward extraction	95 %
Percent removal of acid from acid-laden extractant during regeneration	95 %
Stage requirements	∞ stages in all contactors
Reflux conditions for distillation	Minimum reflux

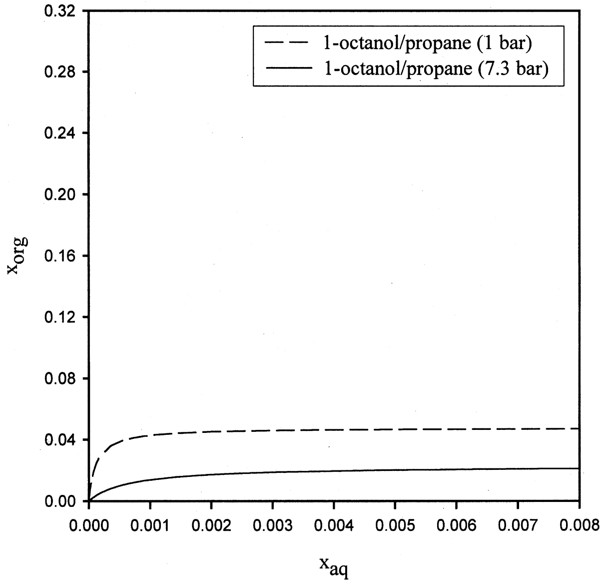

Figure 7. Equilibrium curves for forward and back extraction of lactic acid by TOA in a diluent composed of 1-octanol and propane at 25 °C. These curves were used in the energy requirements calculation for Scheme 2.

extractant phase by dilution prior to regeneration, whereas distillation effects an increase by concentration.

Figure 8 shows the required work per lb of acid product as a function of initial feed concentration. The work comprises shaft work W_s required to pump the acid-rich extractant from 1 bar to 7.3 bar, plus PV work W_{pv} required to compress the propane gas from 1 bar to 7.3 bar:

$$W_s = \int v \cdot dP \tag{19}$$

$$W_{pv} = -\int P \cdot dv \tag{20}$$

Equation 19 was solved assuming a constant molar volume for the acid-rich liquid solution. Equation 20 was solved using the Peng-Robinson equation-of-state for P. The decrease in work requirements with increasing feed concentration is related again to the higher extractant loadings with increasing feed concentration, as previously described. Unlike the energy requirements for Scheme 1, the energy requirements are feasible for this gas-antisolvent-regeneration scheme.

Finally, the abilities of the two diluent-swing processes to concentrate the acid feed were compared. Figure 9 compares the maximum concentration factors, defined as the product-to-feed concentration ratios, for both processes as a function of feed concentration. Scheme 1 recovers the acid at significantly higher

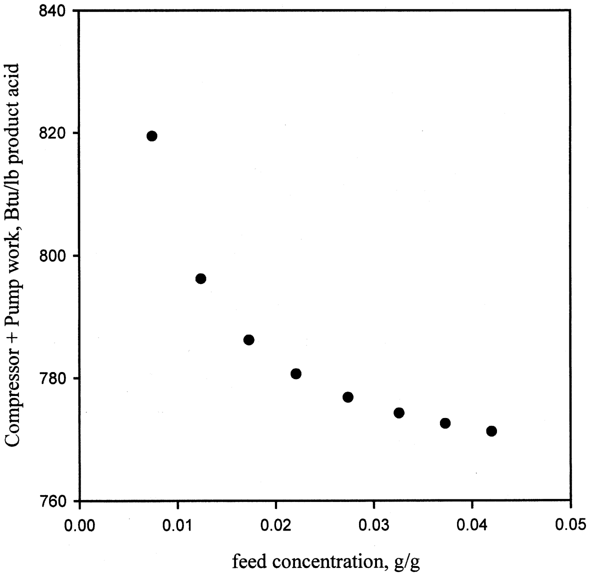

Figure 8. Estimated energy requirements for the diluent-swing process involving gas antisolvent pressurization with propane (Scheme 2).

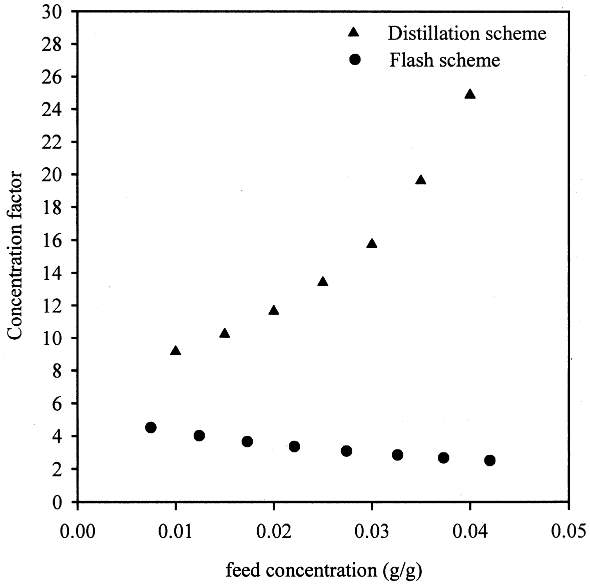

Figure 9. Comparison of the concentration factors for the diluent-swing processes that involve diluent composition changes by distillation and by gas antisolvent pressurization with propane.

product concentrations than Scheme 2. This result is consistent with the differences in the diluent-swing processes for these two schemes. Diluent swing is accomplished by concentration of the acid-laden extractant prior to back extraction in Scheme 1, whereas Scheme 2 involves dilution of the acid-laden extractant prior to back extraction.

CONCLUSIONS

Regeneration of lactic acid-laden amine extractants by addition of a gas antisolvent appears to have economic advantages over more traditional diluent swing methods. Addition of the inert gas diluent, propane, to the extractant phase decreases the equilibrium loading of lactic acid on TOA by decreasing the overall solvating power of the diluent. Both experimental and model predicted loading values show this result.

Estimated energy requirements (per lb. of product) for a diluent-swing process involving the gaseous diluent, propane, were lower by at least a factor of 14 than those for a diluent-swing process involving the inert liquid diluent, dodecane, for the conditions studied. This difference is due primarily to the need to carry out a distillation step in the latter process. For a given percentage removal of acid from the feed, higher feed concentrations resulted in lower energy consumptions per unit of product acid for both processes. This result is related to the higher extractant loadings with increasing feed concentration.

A potential secondary benefit of regeneration by gas antisolvents might be the ability to fractionate a mixture of carboxylic acids. While many conventional processes have focused on separation during forward extraction, regeneration with a gas antisolvent may allow fractionation of acids during regeneration of an extractant loaded with multiple acids. Here, precipitation of individual acids might occur, for example, at different partial pressures of gas antisolvent. Studies are under way to investigate this possibility.

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