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### Publication Date

1995-07-01



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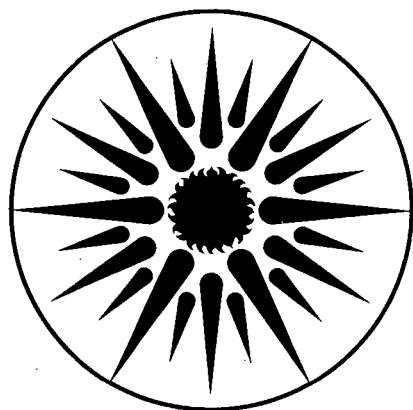
UNIVERSITY OF CALIFORNIA

## ENERGY & ENVIRONMENT DIVISION

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Y. Dai and C.J. King

July 1995



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LBL-37486

UC - 1400

**Approaches for Regeneration of Amine-Carboxylic Acid Extracts**

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**July 1995**

**This work was supported by the Assistant Secretary for the Office of Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Concepts Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.**

## **Approaches for Regeneration of Amine-Carboxylic Acid Extracts**

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### **ABSTRACT**

Extraction processes based on reversible chemical complexation can be useful for separation of polar organics from dilute solution. Tertiary amines are effective extractants for the recovery of carboxylic acids from aqueous solution. The regeneration of amine-carboxylic acid extracts is an important step which strongly influences the economic viability of the separation process. Several regeneration methods are critically reviewed, and the factors that affect swing regeneration processes, including temperature-swing, diluent composition-swing and pH-swing with a volatile base, are discussed.

## INTRODUCTION

The need to recover polar organic solutes, such as carboxylic acids, from dilute aqueous solutions arises in many industrial processes. Removing these solutes from aqueous solutions is necessary in petrochemical and fermentation manufacture, and is desirable for recovery from waste streams.

Distillation is the conventional separation method for the more volatile components, such as alcohols. Acetic acid is less volatile than, and forms a close-boiling solution with, water. Commercially, acetic acid is separated from water by solvent extraction integrated with azeotropic distillation for dilute feeds, and by azeotropic distillation for more concentrated feeds [1]. For low-volatility carboxylic acids, e.g., dicarboxylic acids and hydroxycarboxylic acids, conventional distillation is not favorable. For acids present at low concentration, there would be a high energy cost due to the need to vaporize large quantities of water. Furthermore, there would be no separation of the product acid from other high-boiling impurities.

Separation of polar organic solutes from dilute aqueous solutions by extraction with conventional solvents can be difficult because

the aqueous-phase activity coefficient of the solute is lowered by hydrophilicity or even ionic character.

In recent years there has been renewed interest in large-volume production of fermentation chemicals. Carboxylic acids are readily made by fermentation and are among the most attractive substances that can be manufactured from biomass [2,3]. Recovery of coproducts offers potential for improving the economics of fermentation production [4]. However the current economic impact of fermentation chemicals is still limited, in large part because of difficulties of product recovery.

For nonvolatile carboxylic acids, such as citric and lactic acids, the classical approach for recovery from a fermentation broth is to add calcium hydroxide to form the calcium salt of the carboxylic acid, followed by addition of sulfuric acid to liberate the product acid while precipitating calcium sulfate [5]. The aqueous solution containing the free organic acid is then purified by techniques such as carbon adsorption and ion exchange. This method consumes lime and sulfuric acid and produces large quantities of calcium sulfate sludge waste. It is therefore desirable to improve the existing recovery technology substantially and/or to develop novel recovery technology.

Extraction processes based on reversible chemical complexation can

give high capacities for separation of polar organics from water [6]. In these extraction processes, a liquid-phase complexing agent (extractant) pulls the solute into the solvent phase by forming a complex with a functional group of the solute. Thus the distribution of solute into the solvent phase is substantially increased over conventional solvent extraction. The extractant is usually dissolved in a diluent. Diluents which have functional groups can interact with the complex and affect the distribution ratio of the solute between the aqueous and organic phase.

Long-chain, aliphatic amines are strongly basic. Alamine 336, a commercially available tertiary amine, with aliphatic chains that are 8-10 carbons in length, is an effective extractant for separation of carboxylic acids from dilute aqueous solutions [7,8]. Many factors affect the equilibrium characteristics for extraction of carboxylic acids with amines. Three important variables are the nature of the acid extracted, the concentration of amine extractant and the type of diluent.

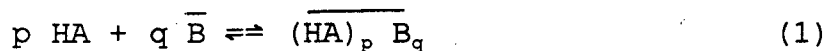
Generally, extraction processes based on reversible chemical complexation are carried out step by step. At first the solvent containing complexing agent extracts the solute into the organic phase. A second step or series of steps is needed to recover the solute in product form and regenerate the solvent phase so that it can be recycled back to the extractor.



It is necessary to emphasize that the cost of the regeneration step, which is tied to the energy and chemical consumption, is an important, if not the most important, factor in determining the economic viability of a separation process utilizing chemical complexation. In this article we compare and evaluate existing and novel regenerated extraction processes. We also discuss the factors affecting these regenerated processes.

#### EQUILIBRIUM RELATIONSHIPS AND REGENERATION PROCESSES

In general, regeneration methods for solvent extraction processes are based on shifts in the extraction equilibrium, except for distillation or precipitation directly from the extract. Extraction of a carboxylic acid by reversible chemical complexation can be described by the following reaction, in which  $p$  unionized acid, HA, molecules and  $q$  amine, B, molecules interact to form various  $(p, q)$  complexes:



where the organic species are marked with an overbar.

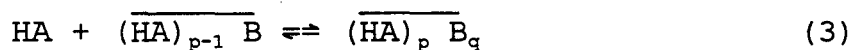
If we assume that the differences in partition coefficient (e.g.

hydrophobicity) among the various acids are incorporated into the equilibrium constant, the apparent equilibrium constant for the overall reaction,  $\beta_{pq}$ , can be written as

$$\beta_{pq} = \frac{[(\text{HA})_p \text{B}_q]}{[\text{HA}]^p [\bar{\text{B}}]^q} \quad (2)$$

where species concentrations are denoted by square brackets and expressed in molar terms.

In cases where there is a single amine per complex, as in (p,1) stoichiometries, it is convenient to recast the complexation constant for the overall reaction into the constants for the stepwise reactions:



and

$$K_{pq} = \frac{[\overline{(\text{HA})_p \text{B}_q}]}{[\text{HA}] [\overline{(\text{HA})_{p-1} \text{B}}]} \quad (4)$$

The association constant for the stepwise reaction,  $K_{p1}$ , is the ratio of the association constants for the overall reactions,  $\beta_{p1}/\beta_{p-1,1}$ , and  $K_{11}$  is equal to  $\beta_{11}$ .

In extraction-based reversible chemical complexation the solvent is composed of the extractant (e.g. amine) and diluent. One must take into account the transfer of carboxylic acid from water into the

amine-free diluent with which the acid does not interact to form specific solvates. Ignoring dimerization of the acid in the organic phase, the partition coefficient,  $P$ , can be written as:

$$P = \frac{[\overline{\text{HA}}]}{[\text{HA}]} \quad (5)$$

where both concentrations have units of moles per liter.

Carboxylic acid is present in the organic extract solution as a result of two interactions, acid-diluent and acid-amine. We assume that the acid concentration resulting from the acid-diluent interaction is equal to the product of the partition coefficient, the concentration of unionized acid in aqueous phase, and a correction factor,  $\phi$ , which is the volume fraction diluent in the solvent mixture. We also assume that various  $(p,1)$  complexes are formed. Then the equilibrium acid concentration in the solvent phase can be obtained as

$$\begin{aligned} [\text{HA}]_{(o)} &= [\overline{\text{HA}}] + \sum p \beta_{p1} [\text{HA}]^p [\overline{\text{B}}] \\ &= \phi P [\text{HA}] + \frac{B_0 \sum p \beta_{p1} [\text{HA}]^p}{1 + \sum \beta_{p1} [\text{HA}]^p} \end{aligned} \quad (6)$$

where  $B_0$  is the initial concentration of amine extractant.

The equilibrium distribution ratio can be written as:

$$D = [\text{HA}]_{(o)} / [\text{HA}] \quad (7)$$

## REGENERATION ALTERNATIVES

There have been a number of regeneration alternatives proposed for recovery of polar organic solute. These methods can be classified into three categories.

### Distillation Regeneration Process

For a volatile organic solute, such as acetic acid, an amine extract can be regenerated by distilling the organic solute overhead. Ricker et al [7] performed detailed experiments and an economic assessment of an acetic acid recovery process utilizing extraction by Alamine 336 in diisobutylketone (DIBK) and subsequent distillation of the extract. The results show that the relative volatility between the acid and the diluent governs the distillation, and the diluent should have sufficiently low volatility so that the acid is the more volatile component. Use of a tertiary amine would prevent formation of amides during distillation, and exclusion of oxygen should avoid any oxidation of the amine.

Economic analysis [7] indicates that even seemingly small losses of extractant can be important. Here amine extractants derive a benefit from being less expensive than tri-n-octyl phosphine (TOPO) and related compounds.

However, most carboxylic acids of commercial interest are nonvolatile. Distillation regeneration of extracts is not suitable for less volatile acids because neither they nor a typical amine extractant can be distilled overhead.

### **Swing Processes**

One general approach for regeneration is called the "swing" process, in which factors are altered so as to promote back-extraction of the organic solute from the solvent phase into an aqueous phase.

If the flow rates of the two phases are constant in a back-extraction regeneration process, the operating curve on a plot of solute concentration in the organic phase vs. that in aqueous phase is a straight line with a slope equal to the W/S flow ratio (W = Aqueous phase flow rate, S = Solvent phase flow rate). During the extraction step, the equilibrium curve must lie above the operating line. Thus for the solute to become more concentrated in the extract a large W/S flow ratio (>1) should be used, and, in order

to achieve a large recovery fraction, the equilibrium distribution coefficient  $D$  should be large enough to make  $DS/W > 1$ . Conversely, for the regeneration stage the equilibrium curve must lie below the operating line. For the solute to be concentrated in the aqueous product a small  $W/S$  flow ratio ( $<1$ ) should be used, and, in order to achieve a high recovery fraction, the equilibrium distribution coefficient  $D$  should be small enough so that  $DS/W < 1$ .

Obviously, for a back-extractive regeneration to be an efficient process, there must be a downward shift in the equilibrium relationship between the extraction and regeneration. There is another approach that can be used, namely to remove diluent from extract by evaporation or other means. This method can reduce the flow rate of the solvent phase, promoting high  $W/S$  in the back-extraction. This can also reduce distribution ratio  $D$ . The results would be to make  $DS/W < 1$  for regeneration. Generally, factors which can be altered to bring about an efficient extraction-regeneration process include pH, temperature and diluent composition.

### **Other Methods**

Solubilities of carboxylic acids in certain solvents increase markedly in the presence of co-extracted water. Removal of the

water from the solvent phase by evaporation or stripping lessens the solubility and causes the acid to precipitate. This approach to regeneration has been explored experimentally [9,10] and has been shown to be effective for extraction of several kinds of carboxylic acids from ketone extracts. Because there is not a marked solubility enhancement in amine extractants in the presence of water, the factor by which water enhances the solubility of the acid in a mixture of an amine extractant and a suitable diluent (e.g. a ketone) is less than that for the ketone alone.

Other possibilities for solvent regeneration include precipitation of the solute from the extract by means of temperature change, adsorption or ion exchange onto a solid, and reextraction into yet another, immiscible solvent. But in the latter two cases another separation step is required for final recovery of the product in isolated form.

Several regeneration processes - pH swing, pH swing with a volatile base, temperature swing, and swings of diluent composition and/or concentration - will be discussed in more detail.

## **pH SWING REGENERATION PROCESS**

The equilibria shown in Eqs. (1), (4) and (6) involve the concentration of unionized acid in the aqueous solution. Altering the value of pH can bring about a substantial shift in the equilibrium. Regeneration of amine-carboxylic acid extracts can be achieved by back-extraction with an aqueous base, such as NaOH. However, this approach results in a salt rather than product acid. The salt could be acidified to produce the free acid form, but this would bring about additional chemical consumption and a waste salt stream, which would require disposal. Ricker et al [7] discussed back extraction of the extract with an aqueous base, and concluded that development of a regeneration method which recycles all reagents is important for an economic process.

A typical example of a pH-swing regeneration process is treatment of phenolic waste water from salicylic acid manufacture. In the synthesis of salicylic acid phenol is needed as a raw material, and phenol usually is transformed into sodium phenolate to take part in the reaction. In China, phenolic waste water has been treated by extraction with a mixed solvent containing an amine extractant [11]. The waste feed concentration is 3500 ppm or more, and the raffinate phenol concentration is less than 0.5 ppm. The loaded



solvent is back-extracted by aqueous NaOH solution, and the resultant phenolate solution is recycled to the synthesis reaction.

#### TEMPERATURE SWING REGENERATION PROCESS

Another way of altering the equilibrium distribution ratio can be through a change in temperature. It has been found that the association equilibrium constants of amine extractants with carboxylic acids  $K_{pq}$  decrease with an increase in temperature [12-15]. Therefore the forward extraction takes place at a low temperature and the back-extraction at a high temperature. The end product is an aqueous solution which can be sent to an evaporative crystallizer. The typical flow diagram of temperature-swing process is shown in Fig 1.

Baniel et al [13] have developed a process for citric acid recovery based on the shift of equilibrium with temperature. The extraction of citric acid is carried out with a mixed solvent containing a long-chain tertiary amine as extractant, a hydrocarbon as diluent, and a higher alcohol, such as decanol, as "modifier". The citric acid is removed from the extract by back-extraction into water at a higher temperature.

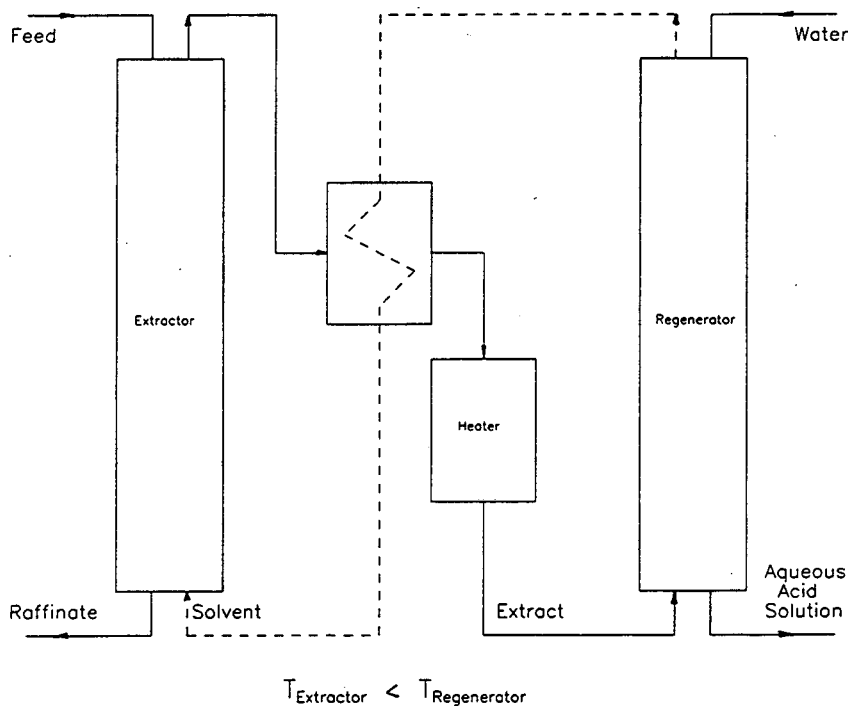


Figure 1. Temperature-Swing Process Flow Diagram

### Feasibility of Temperature Swing Processes

There are several factors that affect the practicability of temperature-swing processes.

#### (1) Apparent Enthalpy and Entropy of Complexation

Generally speaking, complexation reactions in the organic phase involve proton transfer or hydrogen-bond formation and are exothermic [16]. Formation of a complex makes the system more

ordered and decreases the entropy. If the enthalpy and entropy of reaction are assumed to be constant over the temperature range, then:

$$\ln K_{pq} = - \Delta H_{pq}/RT + \Delta S_{pq}/R \quad (8)$$

where  $\Delta H_{pq}$  and  $\Delta S_{pq}$  represent the apparent enthalpy and apparent entropy, respectively, of stepwise complex formation for the (p,q) complex.

In a similar way, the effect of temperature on the partition coefficients, P, for extraction by the diluent alone may be expressed through

$$\ln P = - \Delta H_{trans}/RT + \Delta S_{trans}/R \quad (9)$$

where  $\Delta H_{trans}$  and  $\Delta S_{trans}$  are the enthalpy of transfer and entropy of transfer, respectively, from the aqueous phase to the organic phase.

Tables 1 and 2 show values for the apparent  $\Delta H$  and  $\Delta S$  and values for  $\Delta H_{trans}$  and  $\Delta S_{trans}$  obtained by Tamada and King [12] from a linear least-squares fit of the experimental data. A sufficiently large enthalpy change is needed for temperature-swing regeneration to be attractive.

Table 1. Apparent Enthalpies of Complex Formation  
with 0.29M Alamine 336 in Different Diluents\*

System	$\Delta H$ kcal/mol			$\Delta H_{trans}$
	(1,1)	(2,1)	(3,1)	
		Lactic acid		
MIBK	-5.6 ± 0.4	-0.4 ± 0.9	-0.4 ± 1.1	+1.1 ± 0.1
chloroform	-12.1 ± 0.2	+1.9 ± 0.3		
		Succinic acid		
MIBK	-9.2 ± 0.4	-4.4 ± 1.0		-1.7 ± 0.3
chloroform	-16.5 ± 0.4			

\* ± means values are standard error of estimate

Table 2. Apparent Entropies of Complex Formation  
with 0.29M Alamine 336 in Different Diluents\*

System	$\Delta S$ cal/(mol K)			$\Delta S_{trans}$
	(1,1)	(2,1)	(3,1)	
		Lactic acid		
MIBK	-12.6 ± 0.4	-0.9 ± 0.5	-2.09 ± 0.7	-0.7 ± 0.1
chloroform	-29.0 ± 0.1	+4.2 ± 0.1		
		Succinic acid		
MIBK	-24.6 ± 0.2	-11.9 ± 0.6		-8.7 ± 0.2
chloroform	-44.2 ± 0.2			

\* ± means values are standard error of estimate

(2) Operating temperature range

For operations at atmospheric pressure, there is a limit to the

range of operating temperatures. The boiling point of the diluent, azeotropy and/or the boiling point of water restrict the swing in temperature. For example the boiling point of chloroform is 63 °C, and the azeotrope temperature of MIBK with water is 87.9 °C [17]. Increasing the operating temperature over these limits requires equipment to operate under a higher pressure.

### (3) Shape of equilibrium curve and pinch point

For a usual extraction system using chemical complexation the equilibrium curve has a concave downward shape. The extraction equilibrium curve is well above the extraction operating line. However, for back-extractive regeneration the same equilibrium curve can produce an internal pinch point in the system, and a high degree of regeneration with simple back-extraction is difficult to achieve.

It is therefore necessary to weigh the advantage of stronger complexation and curvature of equilibrium relationship for extraction against the disadvantage for back-extraction regeneration. One source of flexibility is to use a less active diluent or to mix some active diluent with an inert diluent so as to lower the magnitudes of the distribution ratios. This approach may be used not only to bring the extraction equilibria into the appropriate range of distribution ratios but also to decrease the equilibrium curve at higher temperatures enough for practical back-

extraction. For example, relatively inert diluents, such as petroleum fractions with alcohol modifiers, were found to give appropriate equilibrium distribution ratios for extraction and regeneration of citric acid [13].

Besides the operating diagram method, a mathematical modeling method can be used to estimate the feasibility of the temperature-swing process. In order to calculate the maximum recovery and overall concentration factor, infinite stages are assumed for both the extractor and regenerator. The solute concentration in the extract,  $Y_{LS}$ , which is also the concentration of solute in the solvent feed to the regenerator,  $Y'_{LS}$ , is calculated as the solute concentration in the organic phase at equilibrium with the solute concentration in the aqueous feed  $X_f$  at the lower temperature. The raffinate concentration,  $X_R$ , is calculated as the solute concentration in the aqueous phase at equilibrium at the lower temperature with the concentration in the solvent feed to the extractor,  $Y_{RS}$ , which is also the concentration of solute in the solvent leaving the regenerator,  $Y'_{RS}$ . It is assumed that there is no solute in the inlet aqueous phase to the regeneration step. A typical operating diagram of the extraction-regeneration process is shown in Fig. 2, where there is assumed to be no internal pinch at the higher temperature, despite the curvature of the equilibrium relationship. The following relationship should be satisfied if

there is to be maximum removal of the solute:

$$(dY'/dX)_{X=X_p} = (Y'_{LS} - Y'_{RS})/X_p \quad (10)$$

where  $X_p$  is product concentration in the aqueous phase from back-extraction, which is calculated as that in equilibrium with loaded solvent,  $Y'_{LS}$ , at the higher temperature. This condition corresponds the maximum recovery fraction for the solute under conditions where there is no internal tangent pinch. If the solute concentration in the feed stream is  $X_F$ , the overall concentration factor of in the extraction-regeneration process,  $CF$ , and recovery fraction available  $RY$  are then obtained as:

$$CF = X_p/X_F = D_1(X_F)/D_2(X_p) \quad (11)$$

$$RY = 1 - X_R/X_F \quad (12)$$

where  $D_1$  and  $D_2$  represent distribution ratio at the lower and higher operating temperatures, respectively, at solvent-phase composition  $Y_{LS}$ .

For back-extractive regeneration the effect of an internal pinch point on concentration factor is considerable. For example, a much

higher recovery fraction (e.g. 95% recovery) is assumed in the system used. A typical operating diagram of the extraction-regeneration process is shown in Fig. 3, where  $(X_i, Y_i)$  is an internal pinch point on the equilibrium curve at the higher temperature. The concentration factor available,  $CF_{95}$ , can be obtained as:

$$(dY'/dX)_{X=X_i} = (Y'_{LS} - Y'_{RS})/X_P \quad (13)$$

$$X_i D_2(X_i) = X_i (Y'_{LS} - Y'_{RS})/X_P + Y'_{RS} \quad (14)$$

$$CF_{95} = X_P/X_F \quad (15)$$

where the raffinate concentration,  $X_R$ , is calculated from the value of the concentration of solute in the feed stream and the assumption of recovery fraction (e.g., 95% recovery). The concentration in the solvent feed to the extractor,  $Y_{RS}$ , which is also the concentration of solute in the solvent leaving the regenerator,  $Y'_{RS}$ , is calculated as solute concentration at equilibrium at the lower temperature with the raffinate concentration.



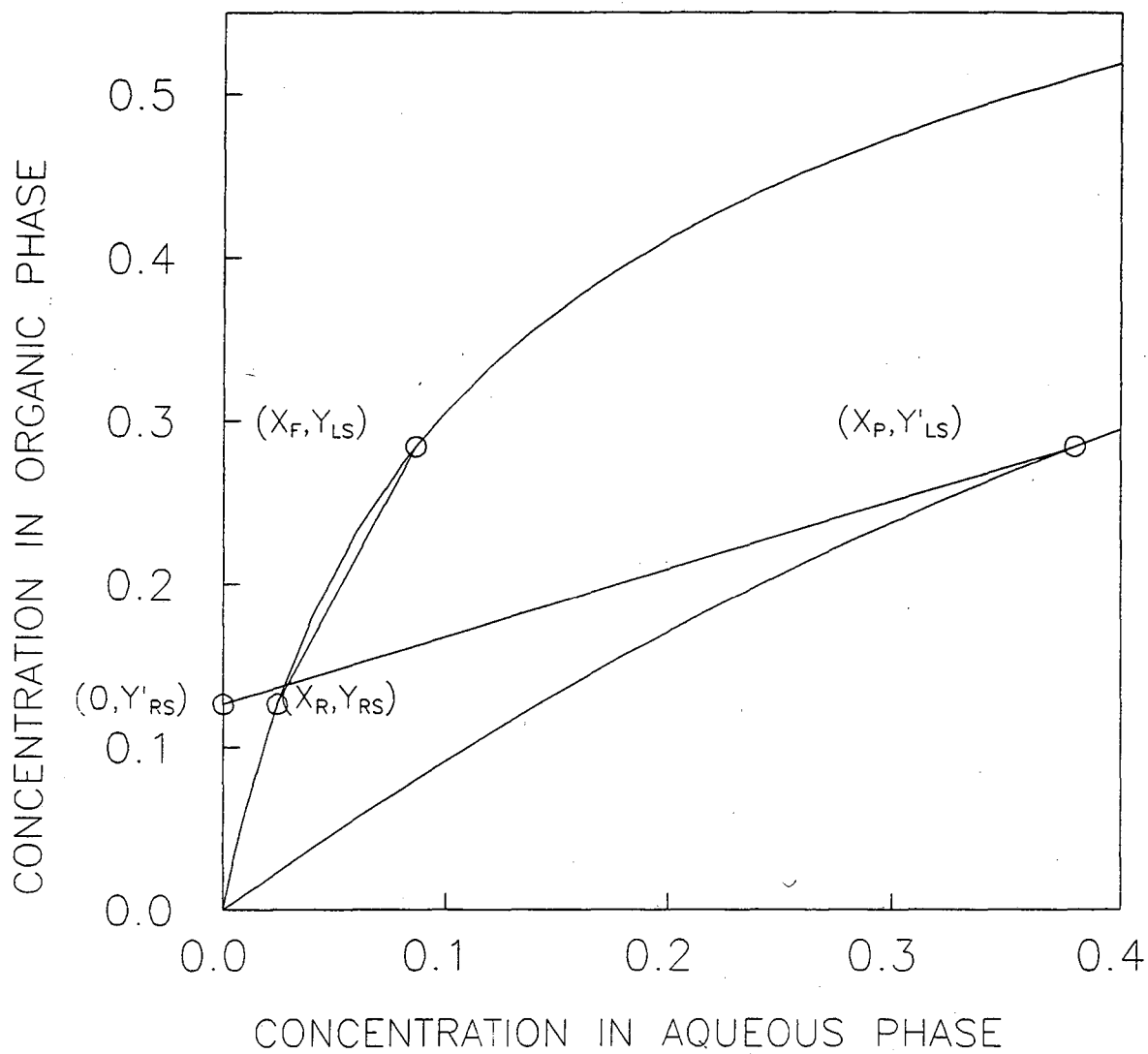


Figure 2. Maximum Concentration Factor and Recovery for a Temperature-Swing Process

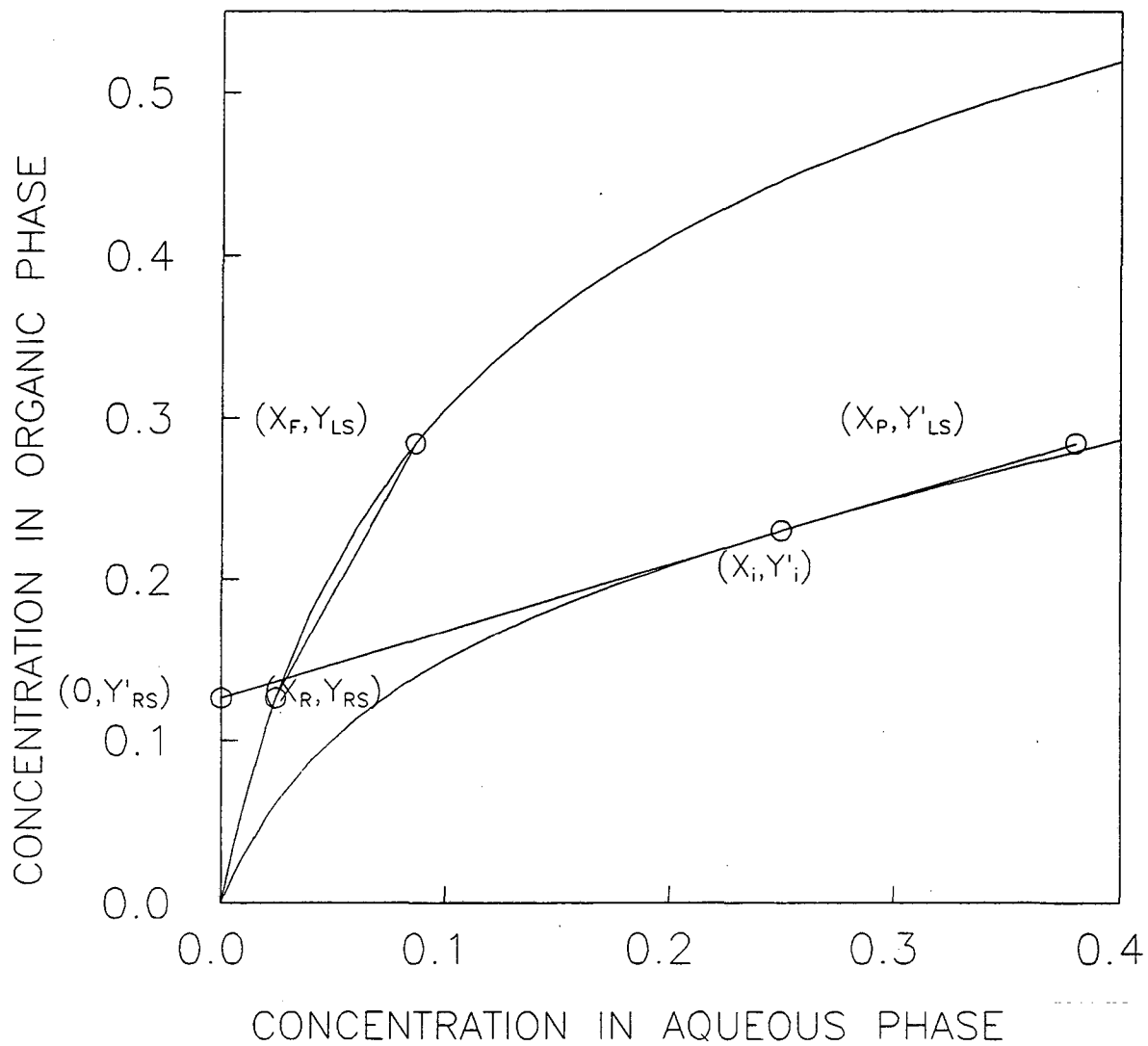


Figure 3. Effect of the Internal Pinch on Concentration Factor for a Temperature-Swing Process

Given the solute concentration in the feed stream,  $X_F$ , the maximum concentration factor  $CF$ , recovery fraction  $RY$  and the W/S (water/solvent) flow ratio at the degree of maximum concentration can be calculated from Equations (6), (8), (9), (10), (11) and (12). Assuming 95% recovery, the available concentration factor,  $CF_{95}$ , can be calculated from Equations (13), (14) and (15). Calculation results for the systems listed in Tables 1 and 2 are shown in Table 3.

These results show that MIBK has desirable properties for use as a diluent in temperature-swing regeneration for recovery of succinic acid. A substantial concentration factor and a high recovery can be obtained. Although the concentration factor is even greater due to a large temperature effect, chloroform is probably not as good a diluent choice for temperature-swing regeneration of succinic acid. The substantial curvature of the equilibrium relationship requires much higher recycle solvent flow, and a lower recovery fraction  $CF_{95}$  would be obtained. Another possibility is to use a split-flow configuration [18] to move the operating curve around the pinch point. Because of the lower enthalpy change and consequent less change in equilibrium as temperature changes, temperature-swing regeneration is less effective for lactic acid.

Table 3. Concentration Factors and Recovery Fractions  
for the Temperature-Swing Processes

Solvent	Temperature (°C)	$X_F$ (mol/L)	CF	RY (%)	W/S (L/h:L/h)	$CF_{95}$
----- Lactic acid						
0.29M Alamine 336 (in MIBK)	25 - 85	0.05	3.02	88.8	3.12	2.94
		0.10	2.35	89.1	2.08	2.27
		0.15	1.99	89.6	1.56	1.91
		0.20	1.76	89.9	1.11	1.70
0.29M Alamine 336 (in chloroform)	25 - 55	0.05	3.20	76.6	1.19	1.71
		0.10	2.10	84.3	0.53	1.41
		0.15	1.64	87.5	0.35	1.27
		0.20	1.40	89.1	0.26	1.17
Succinic acid						
0.29M Alamine 336 (in MIBK)	25 - 85	0.05	6.80	93.1	4.00	6.78
		0.10	5.39	88.4	2.70	5.27
		0.15	4.61	86.6	2.00	4.41
		0.20	4.09	85.8	1.56	3.86
0.29M Alamine 336 (in chloroform)	25 - 55	0.05	12.79	51.7	0.70	3.73
		0.10	12.79	50.9	0.19	3.14
		0.15	12.79	50.6	0.09	2.92
		0.20	12.79	50.4	0.05	2.80

### Energy Consumption of Temperature Swing Process

For a temperature-swing extraction-regeneration process the minimum energy consumption is given by the sensible heat required to raise the temperature of the aqueous regeneration stream to the regenerator temperature and that of the extract from the extractor temperature to the regenerator temperature. Most extraction

operations are carried out at a ambient temperature. Ignoring the offsetting effect of using a heat exchanger between the regenerated solvent and loaded solvent, this energy consumption is expressed approximately as:

$$E = W_R C_{p,w} (T_R - T_E) + S C_{p,s} (T_R - T_E) \quad (16)$$

where  $W_R$  is the water flow rate entering the regenerator (L/h),  $S$  is the solvent flow rate (L/h),  $T_E$  and  $T_R$  represent the temperatures of the extractor and the regenerator, respectively, and  $C_{p,w}$  and  $C_{p,s}$  are the heat capacities of water and solvent, respectively (kcal/L K).

In Table 4 several performances of temperature-swing processes for extraction of succinic acid by 0.29M Alamine 336 in MIBK at 25 and 85 °C are compared. In the calculations the acid concentration in the feed is assumed to be 0.1 mol/L, the feed flow rate is 1 L/h, the aqueous raffinate concentration is 0.01 mol/L (90% recovery), the acid concentration in the recycle solvent is 0.02 mol/L, and the aqueous product concentration from the back extraction is 0.3 mol/L (threefold overall concentration factor). The heat capacity of water is 1.0 kcal/L K. The heat capacity of the solvent is taken to be 0.424 kcal/L K [19]. Different aqueous/solvent flow ratios and consequent equilibrium stages are compared.

Table 4. Several Performances of Temperature-Swing Processes for Extraction of Succinic Acid by 0.29M Alamine 336 (in MIBK) at 25 and 85 °C

Acid Conc. (Extract) mol/L	W/S (Extractor) L/h : L/h	Equilibrium Stages (Extractor)	W/S (Regenerator) L/h : L/h	Equilibrium Stages (Regenerator)	Energy Consumption (kcal/h)
0.200	2.0	2.6	0.60	12.1	30.71
0.225	2.28	2.9	0.68	7.3	29.16
0.250	2.56	3.6	0.77	5.7	27.94
0.275	2.83	4.4	0.85	4.9	26.97

For the same concentration factor and acid recovery, to increase slope of operating line for extraction as far as possible could decrease the recycle amount of solvent and the energy consumption to some extent. The equipment investment of the regenerator where the high operating temperature is needed could be decreased because of decreasing the number of equilibrium stages. To weigh the decrease of energy consumption of process against the increase in the number of equilibrium stages in the extractor, an optimum water/solvent flow ratio can be sought.

Generally, limits on the amount of temperature change and/or the effect of the curvature of equilibrium relationship reduce the effectiveness of temperature-swing process. Temperature-swing can at best obtain a purified solute in the aqueous back-extract at somewhat greater concentration [20].

## DILUENT COMPOSITION AND/OR CONCENTRATION SWING REGENERATION PROCESS

To change the composition of the diluent is yet another approach for regeneration. On the hand, to remove part of diluent from extract can reduce the flow rate of the solvent phase, promoting low S/W in the back-extraction (concentration swing). On the other hand, change of diluent composition can also reduce the distribution ratio  $D$ , because the nature and the concentration of the diluent strongly affect the equilibrium distribution of the solute [8]. This approach for regeneration is called diluent composition and/or concentration swing. One form of diluent-composition-swing regeneration is shown in Fig. 4. The forward extraction is performed with high active diluent content in the solvent, so as to promote a large distribution ratio. The regeneration is carried out with low active diluent content and relatively high inert diluent content in the solvent, so as to facilitate back-extraction of the solute into the aqueous phase. The composition of the diluent is altered between the extractor and the regenerator by use of a distillation column. In this case the active diluent must be more volatile than the inert diluent. Because of removal of active diluent in the distillation, this is also a diluent-concentration-swing process.

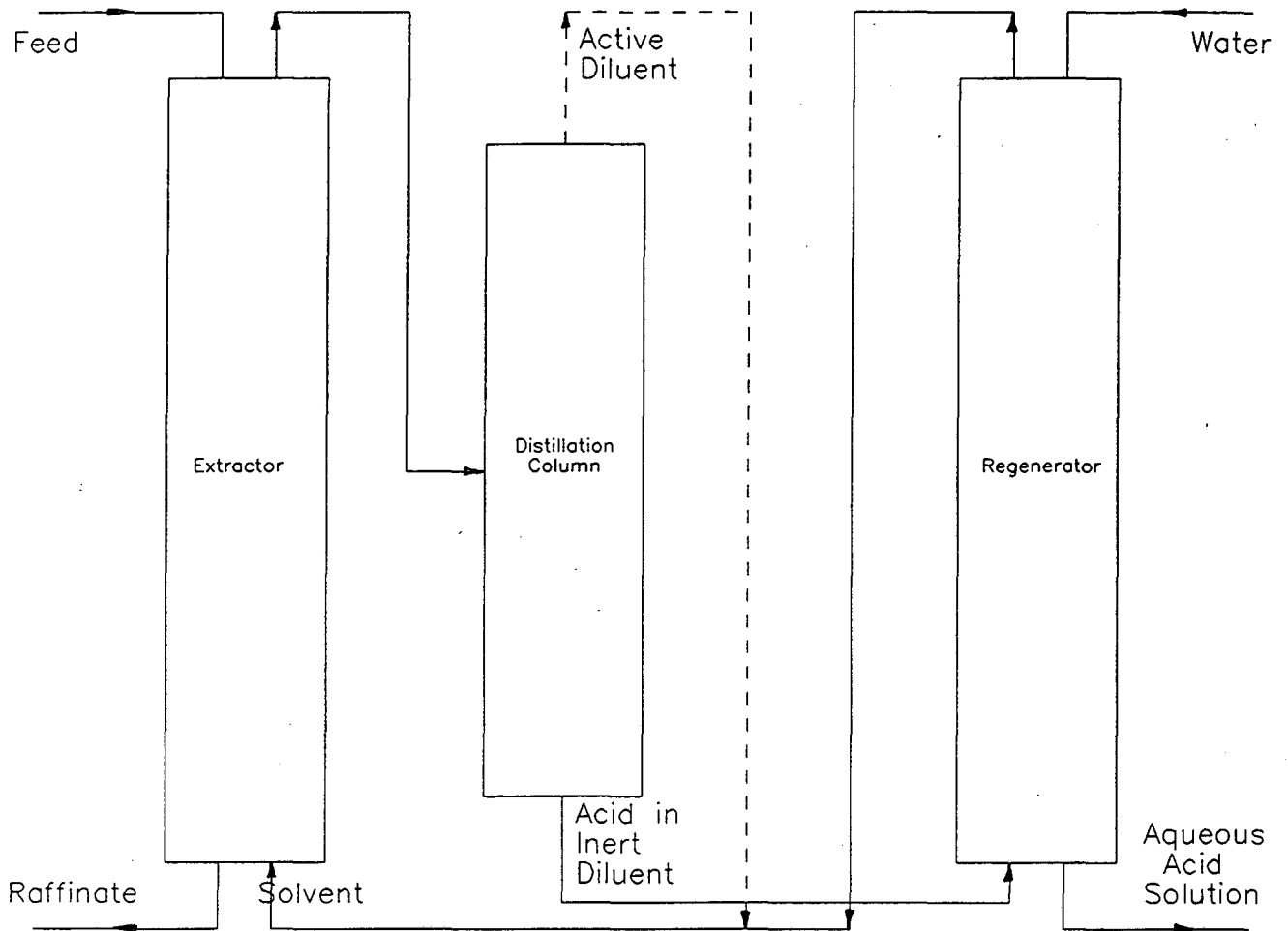


Figure 4. Diluent-Composition-Swing Process

### Feasibility of Diluent Composition Swing Processes

Unlike the temperature-swing process, an appropriate diluent composition change can, in effect, avoid an internal pinch point for regeneration, because of the strong effect of the nature of the diluent on the shape of the equilibrium curve. Figure 5 [12] shows



that lower proportions of chloroform (the active diluent) in a chloroform-heptane diluent greatly decrease the equilibrium extraction of succinic acid in the forward direction. Therefore a regeneration process can be carried out with a lower active diluent content. As another example, the acid-base complexation constant for lactic acid changes by a factor of 50 to 100 between a diluent containing 5% dodecane and 95% 1-octanol, and one containing 95% dodecane and 5% 1-octanol [21].

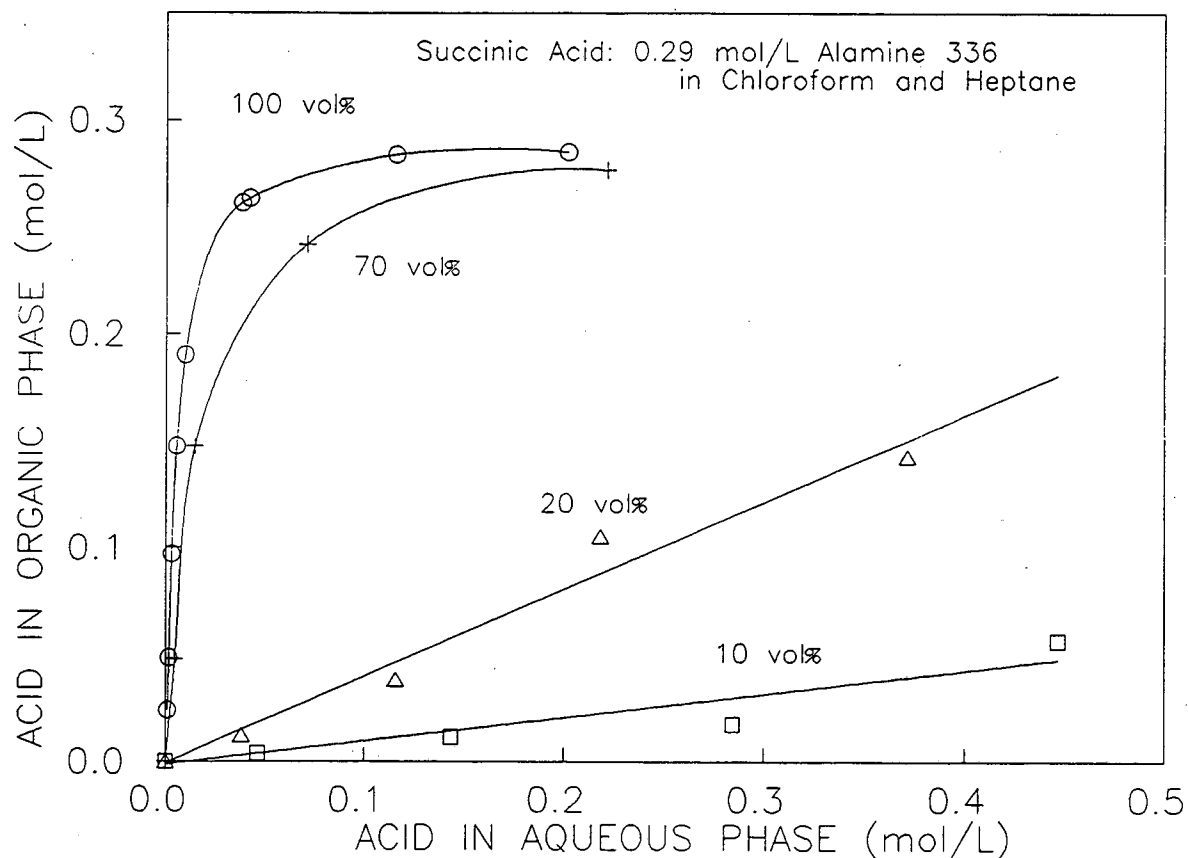


Figure 5. Effect of Proportions of Chloroform in a Chloroform-Heptane Mixed Diluent on Equilibrium Relationship<sup>[12]</sup>

Using a modeling method similar to that mentioned above, the performance of a diluent-composition-swing process can be estimated. A typical operating diagram is shown in Figure 6, where there is assumed to be no internal pinch at the regeneration. In contrast to the temperature-swing process, the solute concentration in the extract that enters the regenerator considerably increases because a part of the active diluent has been removed by distillation. Therefore, the following relationships should be satisfied:

$$(dY'/dX)_{X=X_P} = (Y'_{LS} - Y'_{RS}) / X_P \quad (17)$$

and

$$Y'_{LS} = C_S Y_{LS} ; \quad Y'_{RS} = C_S Y_{RS} \quad (18)$$

where  $Y_{LS}$  and  $Y'_{LS}$  represent the solute concentration in the extract and that in the solvent feed to the regenerator,  $Y_{RS}$  and  $Y'_{RS}$  represent the concentration in the solvent feed to the extractor and that in the regenerated solvent,  $C_S$  is the factor by which the volume of the extract stream is diminished by removal of the active

diluent by distillation.

The maximum concentration factor of this swing process, CF, and recovery fraction available, RY, can be obtained as

$$CF = X_P/X_F = C_S D_1(X_F)/D_2(X_P) \quad (19)$$

$$RY = 1 - X_R/X_F \quad (12)$$

where  $D_1$  is the distribution ratio at extraction and  $D_2$  is that at back-extractive regeneration.

A typical operating diagram showing the effect of an internal pinch point on concentration factor is shown in Fig. 7, where  $(X_1, Y_1)$  is the internal pinch point.

Given the solute concentration in the feed stream,  $X_F$ , the maximum concentration factor CF, the recovery fraction RY and the W/S (water/solvent) flow ratio at the degree of maximum concentration can be calculated. Assuming 95% recovery, the corresponding concentration factor available,  $CF_{95}$ , can also be obtained.

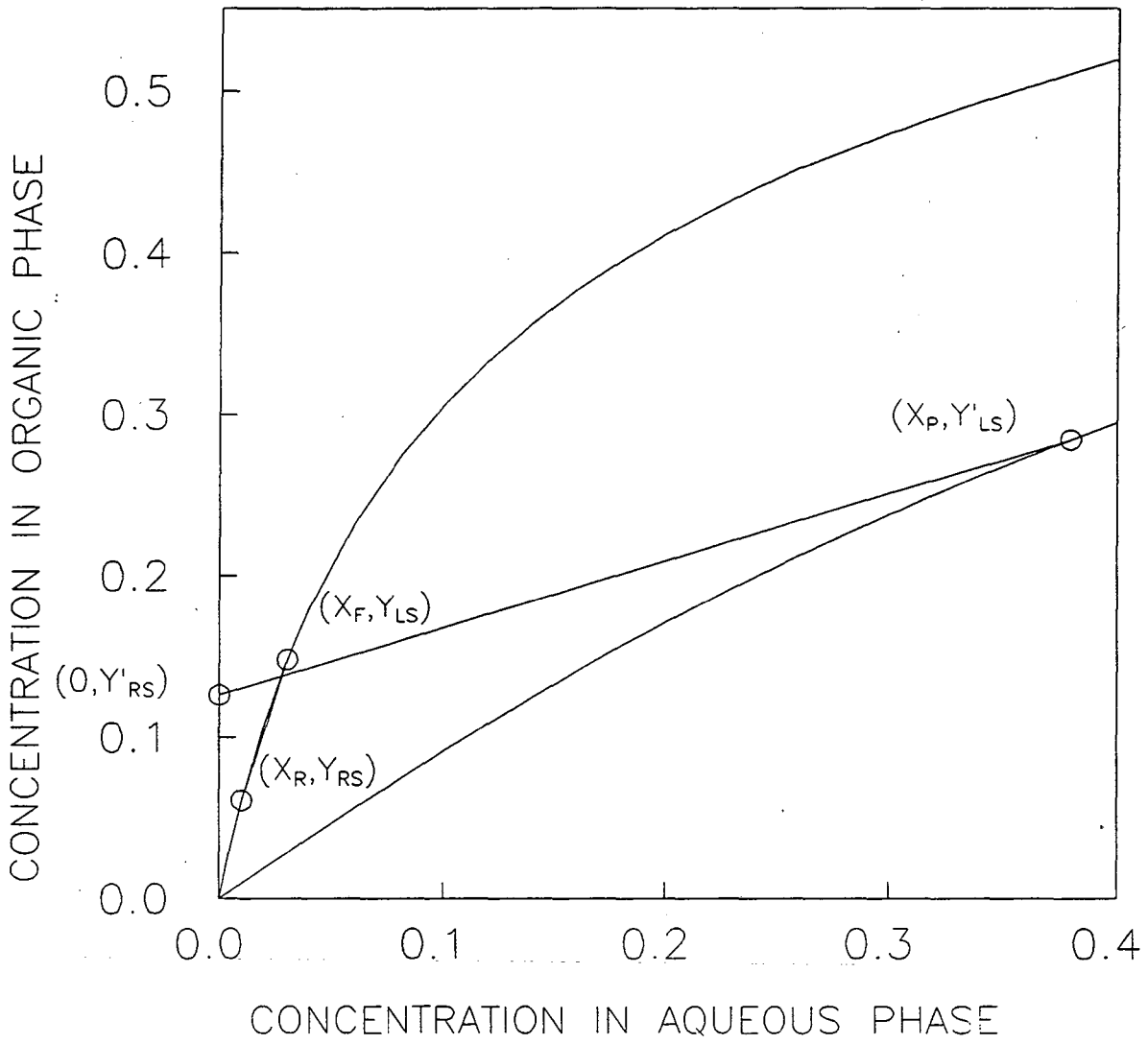


Figure 6. Maximum Concentration Factor and Recovery Fraction for a Diluent-Composition-Swing Process

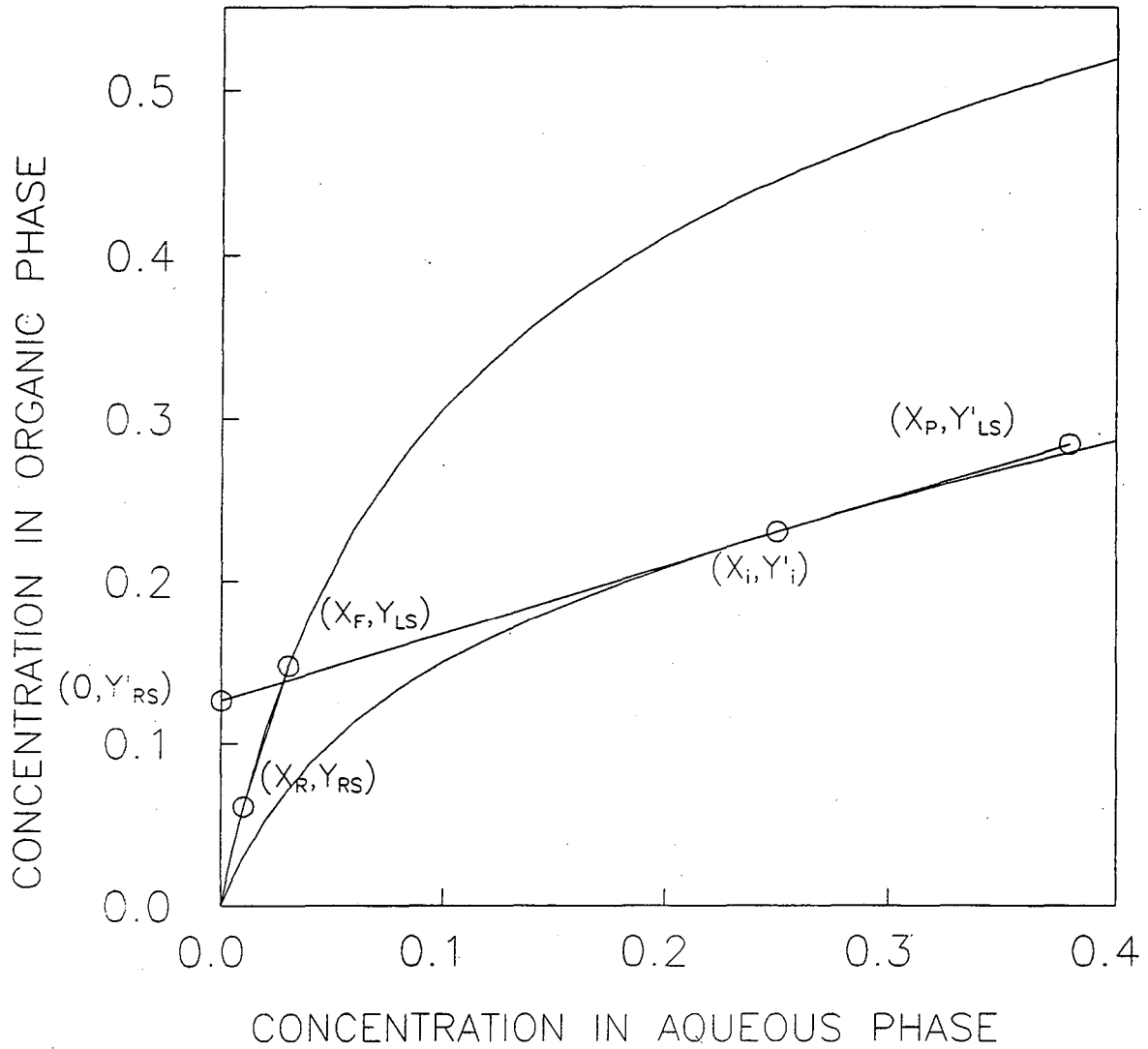


Figure 7. Effect of the Internal Pinch on Concentration Factor for a Diluent-Composition-Swing Process

Consider the extraction of succinic acid by Alamine 336 in chloroform and heptane, with half of the solvent volume being removed before the regenerator. The solvent composition in the extractor is taken to be 53.5% (v/v) chloroform + 31.5% (v/v) heptane + 15% (v/v) Alamine 336 (0.29 mol/L). It is assumed that all of the solvent removed in the distillation is the more volatile component, chloroform (b.p. 63°C). Thus the solvent composition in the regenerator is 7% (v/v) chloroform + 63% (v/v) heptane + 30% (v/v) Alamine 336 (0.58 mol/L). By ignoring the transfer of succinic acid from aqueous solution to diluent alone (i.e. assuming that  $P=0$ ),  $\log K_{11}$  can be obtained from fit of experimental data for this system [22]. The calculation results are shown in Table 5.

Table 5. Concentration Factors and Recovery Fractions of Succinic Acid for Diluent-Composition-Swing Processes

Solvent	$\log K_{11}$ (Extractor)	$\log K_{11}$ (Regenerator)	$X_F$ (mol/L)	CF	RY (%)	W/S (L/h:L/h)	$CF_{95}$
Alamine 336 in chloroform and heptane	1.720	-0.128	0.05	70.5	58.0	2.00	37.6
			0.10	70.5	54.4	0.76	28.7
			0.15	70.5	53.0	0.36	24.7
			0.20	70.5	52.3	0.22	22.4

These results show that the diluent-composition-swing process provides a much better overall degree of concentration. Comparing with the temperature-swing process, the concentration factor at 95% recovery,  $CF_{95}$ , is much higher.

### Energy Consumption of Diluent Composition Swing Processes

In comparison with the temperature-swing process, the energy consumption of a diluent-composition-swing process is larger, because both the sensible heat to raise the temperature of the solvent and the heat of vaporization of the active diluent are needed.

The minimum energy consumption for a diluent-swing extraction-regeneration process with an ideal distillation column, in which complete separation and minimum reflux are assumed, is given by the heat required to create the necessary vapor flow in the reboiler plus the sensible heat of raising the solvent temperature. Again neglecting the use of heat exchangers, it is given by

$$E = SC_{p,s1}(T_C - T_F) + S_R C_{p,s2}(T_R - T_C) + \Delta H_{vap}(S_D + L_{min}) \quad (20)$$

where  $\Delta H_{vap}$  is heat of vaporization of the active diluent;  $C_{p,s1}$  and  $C_{p,s2}$  represent the specific heat of solvent feed and that of the solvent entering the regenerator;  $S$ ,  $S_R$  and  $S_D$  represent the solvent feed flow rate to the distillation column, the column bottoms flow rate into the regenerator and the flow rate of the active diluent flow rate leaving the top of the column, respectively, i.e.,  $S = S_R + S_D$ ;  $T_F$ ,  $T_R$  and  $T_C$  represent temperature of the solvent feed,

temperature of the reboiler and that of the condenser respectively; and  $L_{\min}$  is minimum reflux for the distillation.

For an ideal distillation column (i.e., one with complete separation) the minimum reflux of distillation can be calculated as [23]:

$$L_{\min} = S / (\alpha - 1) \quad (21)$$

and

$$\ln \alpha = \Delta H_{\text{vap}} (1/T_C - 1/T_R) / R \quad (22)$$

where  $R$  is the gas constant.

In the calculation of the minimum energy consumption for a diluent-composition-swing process it is assumed that the specific heat of the mixed solvent is equal to the linear sum of the product of the specific heat of components of the solvent,  $C_{pi}$ , weighted by the volume fractions in the solvent,  $V_i$ :

$$C_{p,s} = \sum V_i C_{pi} \quad (23)$$

Other assumptions are that temperature of the reboiler and temperature of the condenser are equal to the boiling point of the inert diluent component and that of active diluent component, respectively.



Analyzing equations (15) and (16), three main factors affecting the energy consumption for a diluent-composition-swing process can be identified.

(1) The solvent recycle flow rate,  $S$ , affects energy consumption directly. If the solvent flow rate is low, the energy requirement is reduced.

(2) The minimum reflux required in the distillation column is another important factor. Higher reflux ratios lead to higher energy consumptions. The reflux requirement is related to the difference between the boiling points of active and inert diluents.

(3) The boiling point of the active diluent is yet another factor. A lower boiling point of the active diluent results in smaller energy consumption because of the sensible heat needed to raise the solvent to distillation temperatures.

Several performances of diluent-composition-swing processes are compared. The parameters used in calculation are listed in Table 6. Calculation results for extraction of succinic acid by Alamine 336 in chloroform + heptane are listed in Table 7. In the calculations the acid concentration in the feed is 0.1 mol/L, the feed flow rate is 1 L/h, the aqueous raffinate concentration is 0.005 mol/L (95% overall recovery fraction), the acid concentration of recycle

solvent is 0.0075 mol/L, and the aqueous product concentration is 0.5 mol/L (fivefold concentration factor). The solvent composition entering the extractor is 15% (v/v) Alamine 336 + 53.5% (v/v) chloroform + 31.5 (v/v) heptane, and the extractor temperature is 25°C. Half of the solvent volume, all of it chloroform, is removed before the regenerator. In Table 8 the energy consumptions of two different solvent systems for diluent composition swing processes are compared.

Table 6. The Parameters Used for Minimum Energy Consumption of Diluent-Composition-Swing Process<sup>[17]</sup>

Component	bp (°C)	C <sub>p</sub> (kCal/L K)	ΔH <sub>vap</sub> (kCal/L)
chloroform	61.7	0.196	88.78
Heptane	98.4	0.368	
1-octanol	195.2	0.493	71.15
dodecane	216.3	0.396	
Alamine 336	365-7	0.403 <sup>[19]</sup>	

Table 7. Performances of Diluent-Composition-Swing Processes for Succinic Acid by Alamine 336 (in chloroform and heptane)

Acid Conc. (Extract) mol/L	W/S (Extractor) L/h : L/h	Equilibrium Stages (Extractor)	W/S (Regenerator) L/h : L/h	Equilibrium Stages (Regenerator)	Energy Consumption (kcal/h)
0.150	1.50	1.9	0.57	4.7	72.7
0.175	1.76	2.0	0.67	4.0	62.0
0.200	2.03	2.4	0.77	3.7	53.7
0.225	2.29	2.9	0.87	3.4	47.6

Table 8. The Comparison of Minimum Energy Consumptions for Two Different Solvent Systems

Solvent (Feed of Distillation)	Solvent (Entering Regenerator)	S (L/h)	E (kcal/h)
15%(v/v) Alamine 336 +53.5%(v/v) chloroform +31.5%(v/v) heptane	30%(v/v) Alamine 336 +7.0%(v/v) chloroform +63.0%(v/v) heptane	0.67 0.44	72.7 47.6
15%(v/v) Alamine 336 +53.5%(v/v) 1-octanol +31.5%(v/v) dodecane	30%(v/v) Alamine 336 +7.0%(v/v) 1-octanol +63.0%(v/v) dodecane	0.67 0.44	147.2 96.4

It is obvious from the simulation results in Table 7 that, for the same concentration factor and acid recovery, increased slope of operating line for extraction decreases the recycle flow rate of solvent. The optimum water/solvent flow ratio would be chosen to correspond to a low energy consumption without excessive equilibrium stages in the extraction or the regeneration.

The results in Table 8 show that, because of higher reflux and higher boiling points of the diluent components, the energy consumption of the system Alamine 336 in 1-octanol and dodecane is higher.

In general, a diluent-composition-swing process can bring about greater concentration factor, but the energy consumption is higher than for a temperature-swing process. In addition, the diluent-composition-swing regeneration process requires capital costs for the distillation column.

Combining diluent composition change with temperature change can achieve a greater swing and hence greater CF and RY than that attainable with either approach alone.

#### **pH SWING REGENERATION PROCESS WITH A VOLATILE BASE**

An aqueous solution of a volatile base can be used for back extraction. Unlike back-extraction with NaOH aqueous solution, regeneration with a volatile base solution can avoid consuming chemicals and forming a waste salt [24]. For example, the carboxylic acid extract can be back-extracted into an aqueous trimethylamine solution, as is shown in Fig. 8, which corresponds to the extraction of an acid that will crystallize. The aqueous solution of the trimethylamine salt is then heated to drive off water and trimethylamine, forming product carboxylic acid. The trimethylamine can be recycled.

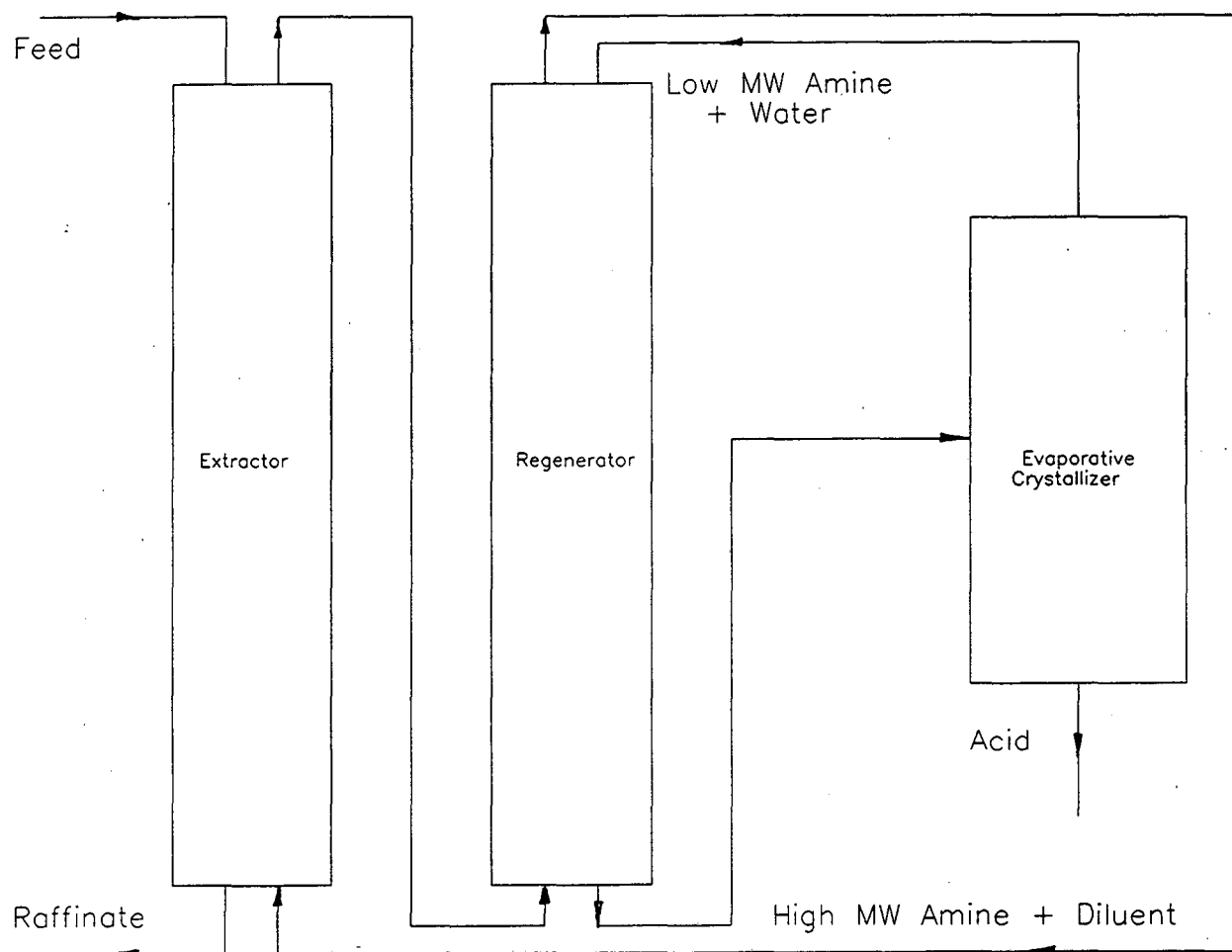


Figure 8. pH Swing Process with a Volatile Base<sup>[24]</sup>

### **Selection of the Volatile Base**

For a pH-swing process using a volatile base, the selection of the volatile base is very important. The general requirements for the base are as follows:

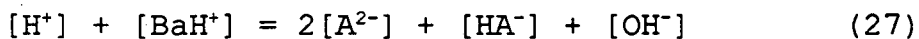
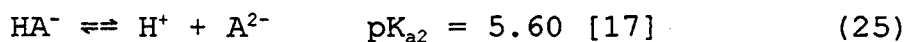
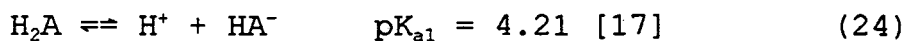
- (1) The base must have sufficient basic strength to compete effectively with the organic extractant (e.g. Alamine 336) for the solute.
- (2) The base must be water-soluble.
- (3) The base must have a substantially higher volatility than that of the solute.
- (4) The base should not form a thermodynamically irreversible bond with the solute.
- (5) The base should be thermally stable at whatever temperature is required to crack the salt. Also there should not be side product (e.g. amides).
- (6) The base must be non-toxic.

Ammonia is a relatively strong, water-soluble, volatile base. However, heating a solution of ammonia and a carboxylic acid results in amide formation [25]. Primary and secondary amines would also react with carboxylic acids to form amides under the anticipated conditions of the regeneration process [26]. Tertiary

amines cannot form amides with carboxylic acids. Poole and King [24] have explored experimentally the feasibility of regenerating carboxylic acid extracts with aqueous trimethylamine.

Evaluation of the basic strength of a molecular species is complicated by the fact that the basicity can depend upon the molecular environment. In general,  $pK_a$  values and donor number [27,28] can be used as guides for selection of the volatile base. Here it is assumed that the regeneration used for back-extraction is in aqueous solution. Therefore, the  $pK_a$  value of the volatile base can guide selection.

For simulation of back-extraction with a volatile aqueous base a batch operation is considered. The equilibria in the aqueous phase are:



where Ba denotes a volatile base, equation (27) describes the charge balance in the aqueous phase.

For succinic acid, the distribution coefficient  $D$  between aqueous solution and 0.29 M Alamine 336 in MIBK at 25 °C can be obtained from equations (6) and (7).

The mass balance for the succinic acid can be written as:

$$[H_2A]_{init} - D S/W [H_2A] - [H_2A]_w = 0 \quad (28)$$

$$[H_2A]_w = [H_2A] + [HA^-] + [A^{2-}] \quad (29)$$

where  $[H_2A]_{init}$  is the initial concentration of succinic acid in the system,  $[H_2A]_w$  is the total acid concentration in aqueous phase.  $S/W$  is the volume ratio of solvent phase to solution phase.

It is assumed that 99% succinic acid is recovered at equilibrium between the organic phase and the aqueous phase, giving

$$0.01 [H_2A]_{init} = D S/W [H_2A] \quad (30)$$

If the solvent/aqueous volume ratio,  $S/W$ , and the total acid concentration in the system are specified, the pH at equilibrium, the equilibrium  $BaH^+$  concentration and initial base concentration,  $[Ba]_0$ , can be obtained from equations (24)-(30). Simulation results under different operating conditions with several volatile bases are shown in Tables 9 and 10.



Table 9. Back-Extraction of Succinic Acid Extract  
by Several Volatile Bases

Pyridine ( $pK_a = 5.17$ ) [17]							
$[H_2A]_{init}$ (mol/L)	0.05	0.10	0.15	0.20	0.25	0.30	
$[H_2A]_w$ (mol/L)	0.0495	0.0990	0.1485	0.1980	0.2475	0.2970	
pH	6.539	6.539	6.539	6.539	6.539	6.539	
$[Ba]_0$ (mol/L)	2.290	4.580	6.868	9.156	11.443	13.729	
$[Ba]_0/[H_2A]_w$	46.268	46.260	46.252	46.242	46.234	46.225	
Acetonitrile ( $pK_a = 6.70$ ) [17]							
$[H_2A]_{init}$ (mol/L)	0.05	0.10	0.15	0.20	0.25	0.30	
$[H_2A]_w$ (mol/L)	0.0495	0.0990	0.1485	0.1980	0.2475	0.2970	
pH	6.539	6.539	6.539	6.539	6.539	6.539	
$[Ba]_0$ (mol/L)	0.1578	0.3173	0.4759	0.6345	0.7931	0.9516	
$[Ba]_0/[H_2A]_w$	3.205	3.205	3.205	3.205	3.204	3.204	
2,4,6-Trimethyl pyridine ( $pK_a = 7.43$ ) [17]							
$[H_2A]_{init}$ (mol/L)	0.05	0.10	0.15	0.20	0.25	0.30	
$[H_2A]_w$ (mol/L)	0.0495	0.0990	0.1485	0.1980	0.2475	0.2970	
pH	6.539	6.539	6.539	6.539	6.539	6.539	
$[Ba]_0$ (mol/L)	0.1059	0.2118	0.3177	0.4236	0.5295	0.6354	
$[Ba]_0/[H_2A]_w$	2.140	2.140	2.140	2.140	2.140	2.139	
Trimethylamine ( $pK_a = 9.80$ ) [17]							
$[H_2A]_{init}$ (mol/L)	0.05	0.10	0.15	0.20	0.25	0.30	
$[H_2A]_w$ (mol/L)	0.0495	0.0990	0.1485	0.1980	0.2475	0.2970	
pH	6.539	6.539	6.539	6.539	6.539	6.539	
$[Ba]_0$ (mol/L)	0.0939	0.1878	0.2817	0.3756	0.4695	0.5634	
$[Ba]_0/[H_2A]_w$	1.897	1.897	1.897	1.897	1.897	1.897	
Piperidine ( $pK_a = 11.12$ ) [17]							
$[H_2A]_{init}$ (mol/L)	0.05	0.10	0.15	0.20	0.25	0.30	
$[H_2A]_w$ (mol/L)	0.0495	0.0990	0.1485	0.1980	0.2475	0.2970	
pH	6.539	6.539	6.539	6.539	6.539	6.539	
$[Ba]_0$ (mol/L)	0.0939	0.1877	0.2815	0.3754	0.4692	0.5631	
$[Ba]_0/[H_2A]_w$	1.896	1.896	1.896	1.896	1.896	1.896	

the simulation results in Table 9 show that essentially complete

removal of the succinic acid from the organic phase is achieved when a volatile base having a higher  $pK_a$  has been used and two moles of the base are present for every mole of succinic acid. Obviously, the value of  $pK_a$  is an important parameter for selection of the volatile base. If a volatile base having a lower  $pK_a$  is used the mole ratio of the base to the acid to be removed is increased.

Table 10. Back-Extraction of Succinic Acid Extract by a Volatile Base with Different Values of S/W

Trimethylamine ( $pK_a = 9.80$ ), $[H_2A]_{init} = 0.2$ mol/L						
S/W	(L/L)	1.0	3.0	5.0	10.0	15.0
$[H_2A]_w$	(mol/L)	0.1980	0.1980	0.1980	0.1980	0.1980
pH		6.282	6.539	6.655	6.811	6.902
$[Ba]_0$	(mol/L)	0.3615	0.3756	0.3801	0.3849	0.3870
$[Ba]_0/[H_2A]_w$		1.826	1.897	1.920	1.944	1.955
2,4,6-trimethyl pyridine ( $pK_a = 7.43$ ), $[H_2A]_{init} = 0.2$ mol/L						
S/W	(L/L)	1.0	3.0	5.0	10.0	15.0
$[H_2A]_w$	(mol/L)	0.1980	0.1980	0.1980	0.1980	0.1980
pH		6.282	6.539	6.655	6.811	6.902
$[Ba]_0$	(mol/L)	0.3877	0.4236	0.4437	0.4770	0.5011
$[Ba]_0/[H_2A]_w$		1.955	2.140	2.241	2.409	2.531

The results in Table 10 show that the volume ratio of solvent phase to aqueous phase, S/W, can affect the size of the mole ratio of the base to the acid. Back-extraction operating at a larger S/W should need a little higher mole ratio. For a volatile base having a little lower  $pK_a$ , this change is more considerable.

### Degree of Concentration of the Solute and Energy Consumption

The economic feasibility of the solute recovery process depends in part on the degree of concentration of the solute that can be achieved during the forward and back extraction steps. For a pH-swing process with a volatile base, if a recycle stream is to be used in the back-extractor the maximum degree of concentration depends only on the solubility of the volatile base in water at the temperature and pressure of operation.

For example, suppose that the commercially available 3.95 M aqueous trimethylamine solution [29] is used as the aqueous phase for back-extraction of succinic acid extract. Suppose also that the acid concentration in the final aqueous phase after back-extraction is half the initial trimethylamine concentration or 1.97 M. If the succinic acid concentration of feed solution is 0.25 M, the maximum overall concentration factor (the ratio of acid concentration in the aqueous back-extract to the acid concentration in the feed solution) would be  $3.95 / (2 \times 0.25) = 7.9$ .

The energy consumption during the back-extraction step itself would be lower for pH-swing regeneration with a volatile base than the energy required for the temperature-swing and diluent-composition-swing regenerations. In the pH-swing process with a volatile base,

energy is not required to raise the temperature of the inlet stream to the back-extractor or to alter the diluent composition by distillation.

However, after the back-extraction step there is a concentration and heating step, during which water and volatile base are removed to generate the solute in product form, in all regeneration processes, including the temperature-swing process, the diluent-composition-swing process and pH-swing process with a volatile base. The greater degree of concentration achieved during the pH-swing process with a volatile base results in lower energy consumption during this step. But we may have to raise the aqueous phase to a higher temperature to decompose the carboxylate.

For pH-swing process with a volatile base, a final purification step is needed to remove residual volatile base from the solute product. This step is not needed for the temperature-swing or diluent composition-swing methods. This step could involve dissolution in a solvent, and evaporative crystallization followed by heating (possibly under vacuum) to drive off the solvent, residual volatile base and water. The energy consumption for this step is given by the sum of sensible heat required to raise the temperature of the mixture of solvent and solute, and the latent heat required to vaporize the solvent and the water. Additional purification steps may also be needed.

**ACKNOWLEDGMENT**

This research was supported by the Biological and Chemical Technology Research Program, Advanced Industrial Concepts Division, Office of Industrial Technologies, U.S. Department of Energy.

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