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Mariam G. Sadaka; Antonio A. Garcia

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The Effect of Temperature on Forward/Back Extraction Using an Amine Extractant for the Recovery of Cyclic Hydroxy Carboxylic Acids

MARIAM G. SADAKA
SEMICONDUCTOR PRODUCTS SECTOR
MOTOROLA
2100 EAST ELLIOT ROAD, TEMPE, ARIZONA 85284, USA

ANTONIO A. GARCIA*
DEPARTMENT OF CHEMICAL BIO & MATERIALS ENGINEERING
ARIZONA STATE UNIVERSITY
TEMPE, ARIZONA 85287-6006, USA

ABSTRACT

Forward extraction of shikimic and quinic acids with tridodecylamine (TDA)/1-heptanol is favored at low temperature. In back extraction, higher temperatures and the addition of oleic acid as a competitive displacer provided 80% recovery for shikimic acid and 70% recovery for quinic acid. Higher recoveries are possible since these values are limited by the forward extraction step. The effect of temperature swing on carboxylic acid extraction by amines is primarily due to the change in amine basicity with temperature. The addition of a displacer lowers the energy cost by lowering the temperature required in back extraction.

Key Words Shikimic acid; Quinic acid; Tridodecylamine; 1-Heptanol; Oleic acid; Extraction

INTRODUCTION

Previous studies have investigated the effect of temperature on the extraction of carboxylic acids by amine extractants (1–3). These studies showed

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* To whom correspondence should be addressed.

that complex formation is strongly dependent on temperature. Because of our interest in the extraction of shikimic acid (SAH) and derivatives, we decided to explore process conditions under which the extraction system 1-heptanol/tridodecylamine (TDA) could be used to recover the cyclic hydroxy carboxylic acids of interest (4). Using a tertiary amine, tridodecylamine, as an extractant and a primary alcohol, 1-heptanol, as a diluent proved to be very effective for the forward extraction step, especially at low temperature where the transfer favors the organic phase.

Back extraction involves reversing the complexation between the acid and the extractant, and recovering the acid in water at a higher concentration and purity. This is done by adding a displacer, oleic acid (OAH), which is another carboxylic acid of lower water solubility (4). Competitive back extraction proved to be a promising solution, especially at high temperature where the distribution favors the aqueous phase.

Forward Extraction

In forward extraction the acid gets transferred from the aqueous to the organic phase. This transfer is not only due to the complexation reaction that takes place between the acid and the tertiary amine, but it is also due to the solvating ability of the diluent. The equilibria describing the forward extraction step is considered to be a two-part process described by the following equilibria (5):

$$\text{Acid}_{\text{aq}} + \text{Extractant}_{\text{org}} \overset{K_{a_1}}{\Longleftrightarrow} \text{Acid–Extractant}_{\text{org}}$$

$$\text{Acid–Extractant}_{\text{org}} + m\ \text{Diluent}_{\text{org}} \overset{K_{a_2}}{\Longleftrightarrow} \text{Acid–Extractant–Diluent}_{m_{\text{org}}}$$

Assuming that the acid-base complexation is only due to the formation of a (1,1) acid–amine complex and that the diluent is a good solvating medium, the system can be described by a simple mass-action model (6). The distribution coefficient of the forward extraction process, K_d, can be expressed in terms of the equilibrium constants of the acid, the extractant (base), and the complexation reaction;

$$K_d = \frac{\{\text{Acid}\}_{\text{org}}}{\{\text{Acid}\}_{\text{aq}}} = K_{a_1}\{\text{Extractant}\} + K_{a_1}K_{a_2}\{\text{Extractant}\}\{\text{Diluent}\}^m$$

where the braces represent the activity of the species.

Stoichiometric ratios other than 1:1 could also be considered to define K_{a_1}. However, there is no reason to suspect that more than one base will complex with these monacids. Also, K_{a_2} has the biggest effect since the solvated complex, (Acid–Extractant–Diluent$_m$), is more likely to form than the unsolvated complex, (Acid–Extractant), and the diluent concentration is higher than the solute and extractant concentrations. Therefore, $K_{a_2} \gg K_{a_1}$ and only terms containing K_{a_2} should be considered.

1. At low extractant activity, $\{\text{Diluent}\}^m \gg \{\text{Extractant}\}$ and is a constant:

$$K_d = \frac{K_{\text{acid}}}{K_{\text{Extractant}}} K_{a_2}[\text{Extractant}]\gamma_{\text{Extractant}}(\text{constant}) \qquad (1)$$

where the brackets represent the concentration of the species and K_{acid} and $K_{\text{Extractant}}$ are the aqueous proton dissociation constants of the solute (acid) and the extractant (base).

2. At high extractant activity, $\{\text{Diluent}\}^m = (\text{constant})/\{\text{Extractant}\}^m$:

$$K_d = \frac{K_{\text{acid}}}{K_{\text{Extractant}}} K_{a_2}\left(\frac{\text{constant}}{[\text{Extractant}]^{m-1}\gamma_{\text{Extractant}}^{m-1}}\right) \qquad (2)$$

Thus, this model predicts a maximum in the plot of extractant concentration with K_d because high extractant concentration impedes the effect of the active diluent in solubilizing the complex in the organic phase.

Back Extraction

Back extraction is done by reversing the complexation and allowing for recovery of the acid in a pure water phase. Reversing the reaction is a complicating step due to the fact that chemical complexation should be a strong interaction in order to affect forward extraction. However, controlling temperature swing combined with displacing the acid using another carboxylic acid of lower water solubility is a promising solution for back extraction (4).

When the displacer is added to the organic phase extract, oleic acid displaces the acid and complexes with the extractant to form an oleic acid–amine complex. At this point the acid goes back to the aqueous phase where it is recovered at a higher concentration and purity. Hence, reversing the reaction in the back extraction process is due to competitive displacement by oleic acid. The equilibrium describing the back extraction step is the following (5):

$$\text{Acid–Extractant}_{\text{org}} + \text{Displacer}_{\text{org}} \xleftrightarrow{K_{a_3}} \text{Displacer–Extractant}_{\text{org}} + \text{Acid}_{\text{aq}}$$

The distribution coefficient of the back extraction process, K_{be}, can be expressed in terms of the equilibrium constants of the acid, the extractant (base), and the displacer (OAH):

$$K_{\mathrm{be}} = \frac{\{\mathrm{Acid}\}_{\mathrm{aq}}}{\{\mathrm{Acid}\}_{\mathrm{org}}} = \frac{K_{\mathrm{Extractant}}}{\{\mathrm{Extractant}\}K_{\mathrm{acid}}} = \frac{K_{\mathrm{displacer}}}{K_{\mathrm{acid}}}\,\frac{\{\mathrm{Displacer}\}}{\{\mathrm{Displacer{-}Extractant}\}} \tag{3}$$

EXPERIMENTAL

All forward and back extraction experiments were performed in test tubes using a wrist action shaker. Parafilm was used to hold cork stoppers firmly in place and to provide a more effective liquid barrier. The initial volume ratio of organic to aqueous phases for all of the forward and back extractions was 1 : 1. For low temperature experiments the shaker was placed in a refrigerator. Higher temperature experiments were conducted using a thermostat bath.

Shikimic and quinic acids were analyzed by HPLC using a 25-cm Microsorb-MV reverse phase column. Aqueous and organic phases were individually diluted in a mobile phase to a concentration of <0.04 M and then applied to the column. The mobile phase consists of 0.013 M tetrabutylammonium hydroxide, 0.0087 M trizma base, 0.09 M acetonitrile, and approximately 0.0045 M acetic acid. The exact amount of glacial acetic acid was determined by titrating with the acid. Elution with the mobile phase was carried out isocratically at 1.0 mL/min. HPLC traces were acquired at 254 nm for shikimic acid and 218 nm for quinic acid. Concentrations were determined by comparing the shikimic acid peak area for each sample with standard peak areas. In addition, a material balance was calculated for all samples to check if the sum of the amounts of shikimic and quinic acids determined in each phase was approximately equal to the known amount of acid added.

RESULTS AND DISCUSSION

Effect of Temperature Swing on the Extraction Process

Based on previous extraction experiments performed on shikimic acid (4) and a more extensive series of experiments on shikimic and quinic acids, increasing the temperature decreases the distribution coefficient of the forward extraction process and increases the distribution coefficient of the back extraction process (Figs. 1–4). This has been observed by previous research on other systems, (2, 3, 7), but there has never been a comprehensive explanation of this behavior. This paper investigates the effect of temperature swing on the forward/back extraction process. Interesting conclusions are drawn regarding the important effect of temperature on the forward extraction of cyclic hydroxy carboxylic acids by amine extractants, and back extraction by addition of a displacer.

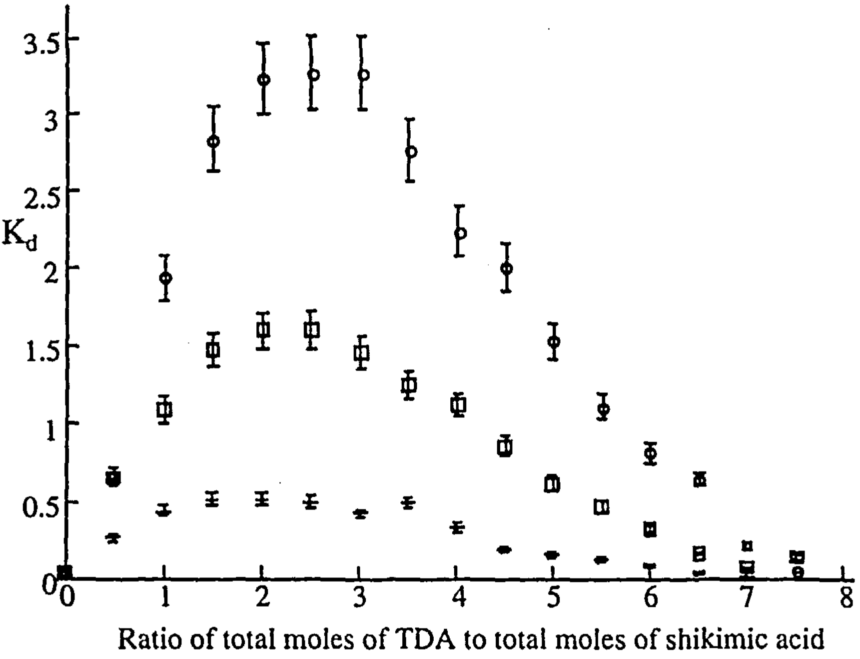

FIG. 1 Effect of temperature on the forward extraction of shikimic acid. (○) K_d at 5°C, (□) K_d at 25°C, (–) K_d at 60°C.

Effect of Temperature Swing on the Distribution Coefficient of the Forward Extraction Process

The decrease in the value of K_d with temperature increase could be due to many factors including: 1) a decrease in extractant basicity, 2) an increase in acid water solubility, 3) a decrease in the acid acidity, and 4) a change in the activity coefficient of the extractant.

The effect of temperature on the distribution coefficient of the forward extraction process can be obtained from taking the logarithm of both sides of the expressions describing K_d and differentiating with respect to the logarithm of temperature. Perrin, Dempsey, and Serjeant showed that the acid dissociation constants of carboxylic acids are virtually unaffected by temperature for the temperature range discussed here (9). At low extractant activity (Eq. 1), the concentration of the extractant and K_{acid} are not functions of temperature. It is also assumed that K_{a_2} is not a function of temperature based on the fact that the complex solubility in both the water and organic phases likely increases with increasing temperature and decreases with decreasing

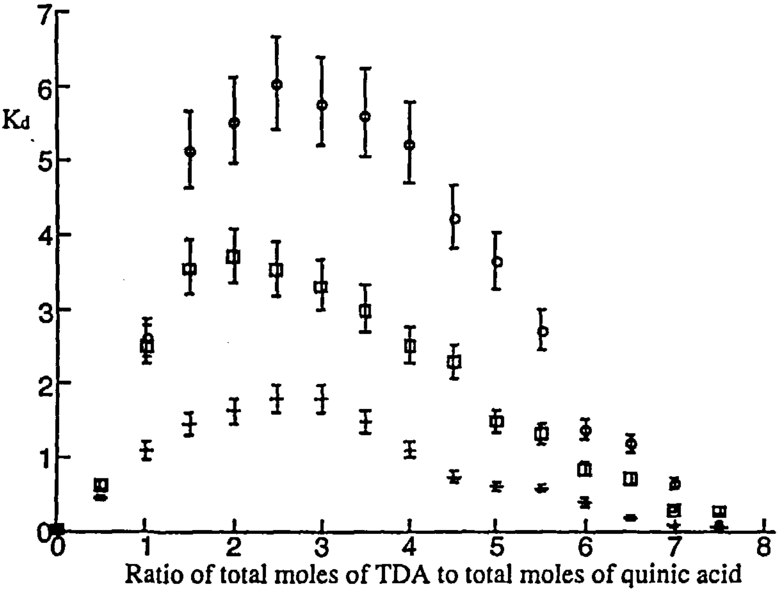

FIG. 2 Effect of temperature on the forward extraction of quinic acid. (○) K_d at 5°C, (□) K_d at 25°C, (–) K_d at 60°C.

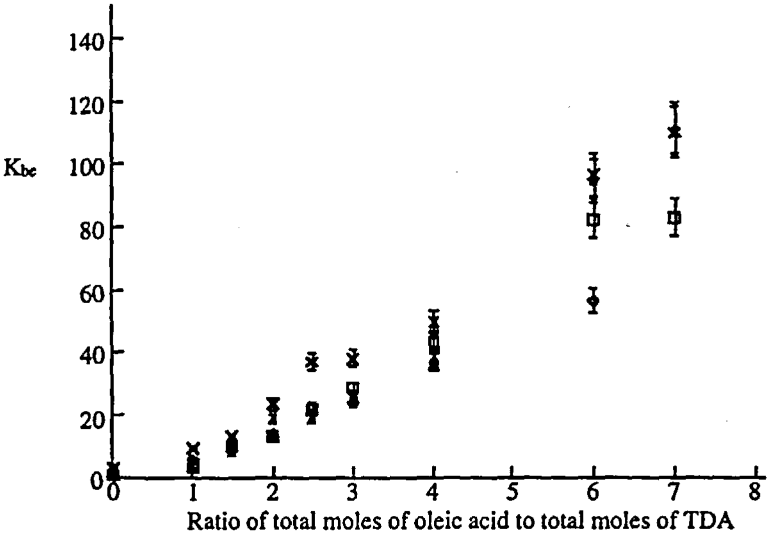

FIG. 3 Effect of temperature on the back extraction of shikimic acid. (▲) K_{be} at 5°C, (□) K_{be} at 22°C, (◇) K_{be} at 48°C, (×) K_{be} at 75°C.

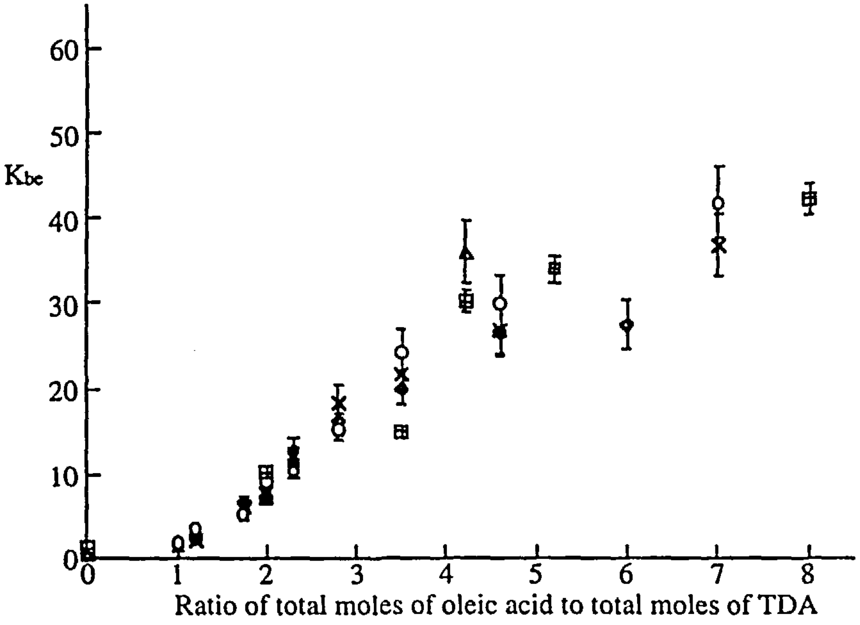

FIG. 4 Effect of temperature on the back extraction of quinic acid. (×) K_{be} at 5°C, (◇) K_{be} at 22°C, (○) K_{be} at 48°C, (⊞) K_{be} at 75°C, (△) K_{be} at 95°C.

temperature. Thus, the net effect of temperature on complex transport to one phase or the other is negligible. Therefore:

$$\frac{d \log K_d}{d \log T} = \frac{dpK_{a_{\text{Extractant}}}}{d \log T} + \frac{d \log \gamma_{\text{Extractant}}}{d \log T}$$

At this point we can hypothesize that the decrease in the distribution coefficient with increasing temperature is not only due to the change in basicity of TDA, but also due to the change in the activity coefficient of TDA with temperature.

For TDA in 1-heptanol, the effect of varying temperature on the activity coefficient is not large. This was concluded from comparing our system (tridodecylamine in 1-heptanol) to triethylamine in 1-propanol at 20°C (8). Using the three-suffix Margules equation with empirical constants $A = 0.0172$ and $B = 0.248$ at $x_{\text{Diluent}} = 1$, we find that the derivative, $(d \log \gamma_{\text{Extractant}})/(d \log T)$, is a very small number, at most equal to -1×10^{-4}. Accordingly, this shows that the change in the activity coefficient of TDA with respect to temperature has a negligible effect on the distribution coefficient. Thus the decrease in the distribution coefficient with increasing temperature is suggested to be due to the change in the basicity of the amine.

In order to understand the change in the amine basicity with increasing temperature, a relationship between temperature and pK_a of the amine is employed (9):

$$-\frac{dpK_a}{dT} = \frac{(pK_a - 0.9)}{T} \tag{4}$$

The pK_a for TDA at 25°C was determined using a correlation given by Perrin, Dempsey, and Serjeant for tertiary amines (9):

$$pK_a = (10.5 \pm 0.2) - (n \times 0.2) \tag{5}$$

where n is the number of methyl groups bound to the basic nitrogen atom, and in the case of TDA, $n = 0$. Hence the pK_a of tridodecylamine is 10.5.

From Eq. (4), the value of $(dpK_{a_{\text{Extractant}}})/(d \log T)$ equals -9.6. This shows that increasing the temperature decreases the basicity of the amine, thus decreasing the affinity of the amine for the acid. Consequently, this causes a decrease in the value of the distribution coefficient of the forward extraction process.

We reach the same conclusion at high amine activity from Eq. (2):

$$\frac{d \log K_d}{d \log T} = \frac{dpK_{a_{\text{Extractant}}}}{d \log T} + (1 - m)\frac{d \log \gamma_{\text{Extractant}}}{d \log T}$$

where $m > 1$.

Likewise, applying the three-suffix Margules equation in this case leads to the same result: namely, that the change in the activity coefficient of TDA with respect to temperature is negligible and has no effect on the distribution coefficient of the process for all reasonable values of m.

In conclusion, it is suggested that the effect of temperature on the distribution coefficient of the forward extraction process is more likely to be due to a decrease in the basicity of the amine with increasing temperature at both high and low amine activity. Hence, for our system where TDA is used as an extractant:

$$\frac{d \log K_d}{d \log T} = \frac{dpK_{a_{\text{Extractant}}}}{d \log T} = -9.6$$

Plotting $\log K_d$ vs $\log T$, and applying a best-fit results in values for $(dpK_{a_{\text{Extractant}}})/(d \log T)$. If values of $(dpK_{a_{\text{Extractant}}})/(d \log T)$ are approximately equal to -9.6, then what we have concluded from our model is consistent with our experimental results. In other words, this will prove that the drop in the distribution coefficient with increasing temperature is primarily attributed to the de-

TABLE 1
Average Slope Value of the Linear Fit for the Forward Extraction of Shikimic Acid

TDA:SAH	Maximum SAH slope	Minimum SAH slope	Average SAH slope
1	−9.1	−7.1	−8.1
1.5	−10.4	−8.1	−9.3
2	−11.2	−8.8	−10.0
2.5	−11.6	−8.9	−10.2
3	−12.4	−9.8	−11.1
3.5	−10.4	−8.1	−9.2
4	−11.6	−9.2	−10.4
4.5	−14.3	−11.5	−12.9
5	−14.0	−10.9	−12.5
5.5	−13.9	−10.2	−12.0
6	−15.1	−10.5	−12.8

Average SAH slope = −10.8 ± 1.6

crease in amine basicity. A linear regression was performed to find the maximum and minimum slope values (5). In Tables 1 and 2 we average the maximum and minimum values, resulting in a slope of −10.8 ± 1.6 for shikimic acid, and −8.3 ± 2.3 for quinic acid. Both values of the slope are close to −9.6. Thus, for our system the decrease in K_d with increasing temperature is most likely due to the decrease in the basicity of TDA.

TABLE 2
Average Slope Value of the Linear Fit for the Forward Extraction of Quinic Acid

TDA:QAH	Maximum QAH slope	Minimum QAH slope	Average QAH slope
2	−8.7	−4.2	−6.4
2.5	−8.5	−3.8	−6.2
3	−8.3	−3.7	−6.0
3.5	−9.0	−4.6	−6.8
4	−10.0	−6.2	−8.1
4.5	−11.2	−7.9	−9.6
5	−11.0	−8.0	−9.5
5.5	−9.6	−6.9	−8.2
6	−8.0	−5.6	−6.8
6.5	−12.3	−9.4	−10.9
7	−16.1	−10.2	−13.2

Average QAH slope = −8.3 ± 2.3

Effect of Temperature Swing on the Distribution Coefficient of the Back Extraction Process

The effect of temperature on the distribution coefficient of the back extraction process can be obtained from taking the logarithm of both sides of the expression describing K_{be} (Eq. 3) and differentiating with respect to the logarithm of temperature. The concentration of the extractant, K_{acid}, and K_{a_2} are essentially not functions of temperature. Therefore:

$$\frac{d \log K_{be}}{d \log T} = -\left(\frac{dpK_{a_{Extractant}}}{d \log T} + \frac{d \log \gamma_{Extractant}}{d \log T}\right)$$

From the three-suffix Margules equation, we find that for the system TDA in 1-heptanol, the effect of varying the temperature on the activity coefficient is negligible. Therefore, an increase in the distribution coefficient of the back extraction process with increasing temperature is essentially due to the decrease in amine basicity. For our system where tridodecylamine is used as an extractant:

$$\frac{d \log K_{be}}{d \log T} = -\frac{dpK_{a_{Extractant}}}{d \log T} = 9.6$$

Plotting log K_{be} vs log T at different oleic acid:TDA ratios and applying a best-fit results in values for $-(dpK_{a_{Extractant}})/(d \log T)$. If values of $-(dpK_{a_{Extractant}})/(d \log T)$ are approximately equal to 9.6, then the model is consistent with experimental results. A linear regression was performed to find the slope for shikimic acid and quinic acid systems (5). The slope was 10.9 for shikimic acid, but 9.6 for quinic acid only at an oleic acid:TDA ratio of zero (Table 3). This implies that when no oleic acid was added to the system the slope was close to the predicted value of 9.6, but upon the addition of oleic acid the value of the slope changed greatly. Therefore, for back extraction performed with no oleic acid added, the increase in the distribution coefficient is more likely to be due to the decrease in the basicity of the amine. However, upon the addition of oleic acid, the system becomes less sensitive to temperature effects and more sensitive to the amount of oleic acid added.

Plotting percent recovery versus the oleic acid:TDA ratio at different temperatures helps in understanding the overall picture of the combined effect of temperature and displacer concentration on back extraction. Percent recovery is defined by the following equation:

$$\% \text{ Recovery} = \frac{\text{Mass of acid in aqueous phase after back extraction}}{\text{Mass of acid initially in the aqueous phase}} \times 100$$

Applying competitive back extraction by adding oleic acid and increasing the temperature greatly improved percent recovery of the overall process. For the shikimic acid and quinic acid systems (Figs. 5 and 6); increasing the temperature by 65°C increased the percent recovery by about 20 for shikimic

TABLE 3
Average Slope Value of the Linear Fit for the Back Extraction of Shikimic and Quinic Acids at Different Oleic Acid to TDA Molar Ratios

OA:TDA	Shikimic acid slope	Quinic acid slope
0	10.9	9.6
1	6.2	2.2
1.5	1.9	3.3
2	1.2	1.4
2.5	2.8	0.4
3	1.3	−1.1
4	0.9	−1.3
6	−0.4	−1.2

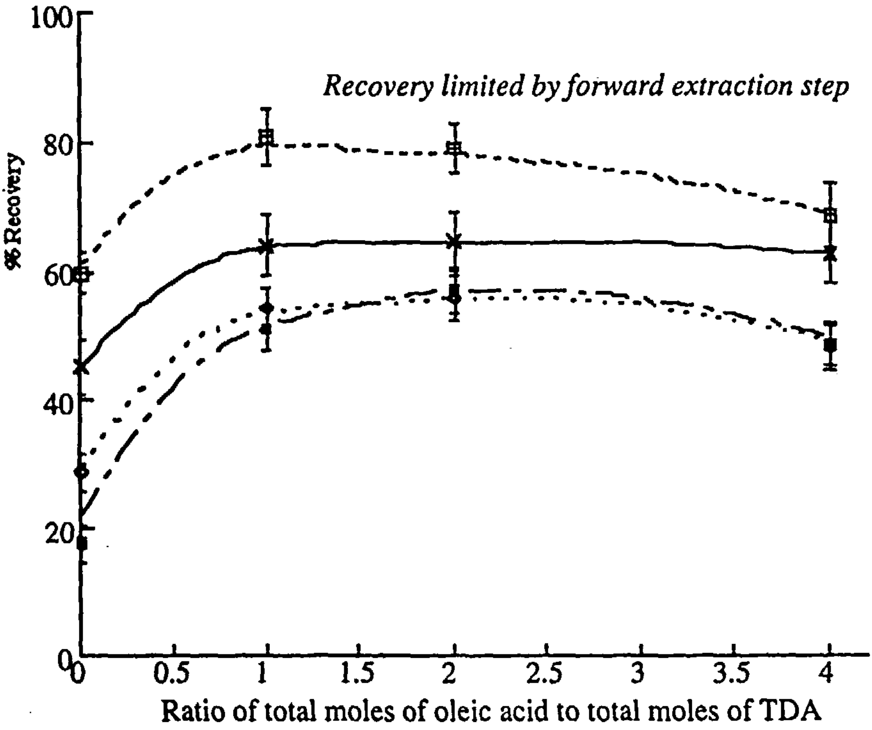

FIG. 5 % Recovery of shikimic acid vs oleic acid:TDA molar ratio. (■) % recovery at 5°C, (◇) % recovery at 25°C, (×) % recovery at 50°C, (⊞) % recovery at 70°C.

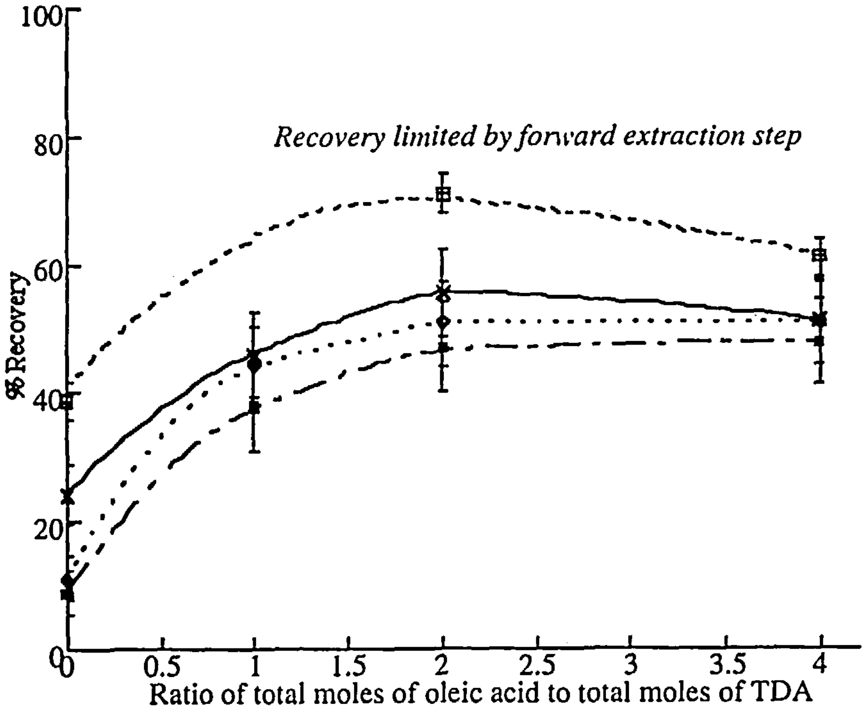

FIG. 6 % Recovery of quinic acid vs oleic acid:TDA molar ratio. (■) % recovery at 5°C, (◇) % recovery at 25°C, (×) % recovery at 50°C, (⊞) % recovery at 70°C.

acid and 25 for quinic acid at OAH:TDA = 2. Likewise, increasing the temperature resulted in higher recovery even when no oleic acid was added (Fig. 7). However, this is not as great as the increase in recovery brought about by increasing the molar ratio of oleic acid to TDA with temperature. From Table 4, increasing the mole to mole ratio of oleic acid to TDA from 0 to 2 at room temperature resulted in an increase in the percent recovery to 25 for shikimic acid and 40 for quinic acid. At 70°C and the same oleic acid to TDA ratio, the increase in percent recovery is 20 for shikimic acid and 30 for quinic acid. Hence, this increase in percent recovery is smaller than the increase brought about at the lower temperature. This suggests that competitive displacement is more effective at smaller temperature swings.

For the shikimic acid system at OAH:TDA = 0, recovery is 60% at 70°C; this is the same as the percent recovery at 25°C and OAH:TDA = 1. For the quinic acid system at OAH:TDA = 1, recovery is 60% at 70°C; this is

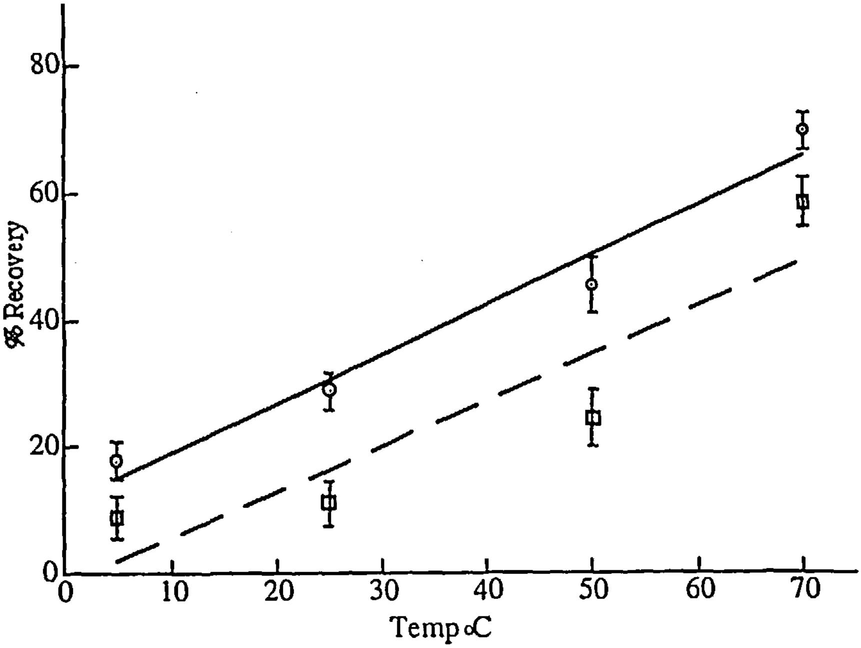

FIG. 7 % Recovery vs temperature with no oleic acid added. (⊙) % recovery of SAH, (☐) % recovery of QAH.

TABLE 4
Increase in Percent Recovery (at OAH:TDA = 2:1) with Increasing Temperature

Temperature (°C)	Increase in % recovery upon adding oleic acid to the ratio of OAH:TDA = 2:1	
	Shikimic acid	Quinic acid
5	35	40
25	25	40
50	20	30
70	20	30

also about the same as the recovery at 25°C and OAH:TDA = 2. Consequently, adding oleic acid in higher amounts at room temperature leads to achieving the same recovery as adding oleic acid in smaller amounts at a higher temperature. Therefore, the cost of temperature swing decreases with the introduction of oleic acid, resulting in high product concentration with low energy cost. In conclusion, for an economic recovery of cyclic hydroxy carboxylic acids, consideration should be given to the cost of heating versus the oleic acid added to achieve maximum yield.

CONCLUSION

For the forward extraction step, using a tertiary amine as an effective extractant coupled with decreasing temperature drove the complexation reaction toward the products, resulting in a higher distribution coefficient. For the back extraction process, increasing the temperature with the addition of oleic acid as a displacer resulted in substantially concentrating the product acid in the water phase. Also, back extraction with competitive displacement was more effective at smaller temperature swings. Thus, the cost of temperature swing decreases by introducing oleic acid, resulting in high product concentration with low energy cost. In conclusion, for an economic recovery of cyclic hydroxy carboxylic acids, consideration should be given to the cost of heating versus the amount of oleic acid added at the maximum achievable percent recovery.

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