Intensification of conversion of glucose to lactic acid: equilibria and kinetics for back extraction of lactic acid using trimethylamine

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Abstract

Alamine 336 is an effective extractant for the recovery of lactic acid from aqueous solutions. An approach for regeneration and product recovery from such extracts is to back extract lactic acid with a water soluble, volatile tertiary amine such as trimethyl amine. Equilibrium data are presented that show near stoichiometric recovery of lactic acid from amine extract. Kinetics of back extraction of lactic acid from Alamine 336 in octanol into aqueous trimethyl amine (TMA) has been presented. Back extraction reaction in a stirred cell falls in Regime 3, extraction accompanied by a fast chemical reaction. The reaction has been found to be zero order in TMA and first order in lactic acid with a rate constant equal to 16.67 s−1. The data reported in this work will be useful in designing the lactic acid recovery system. In thermal regeneration of TMA, 99% of TMA was removed at 200 mmHg from trimethylammonium lactate aqueous solution.

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1. Introduction

Carboxylic acids are important commercial products, and extracting these acids out of aqueous solutions is a growing requirement of fermentation based industries. For volatile carboxylic acids, such as acetic acid, distillation and azeotropic or extractive distillation are alternatives, along with solvent extraction and adsorption (King, 1983; Kertes and King, 1986; Kuo et al., 1987). For low and nonvolatile acids distillation is not useful. Conventional process (Calcium hydroxide precipitation) is expensive as separation and final purification stages account for up to 50% of the production costs (Chaudhuri and Pyle, 1992; Eyal and Bressler, 1993) and unfriendly to the environment as it produces a large quantity of calcium sulphate sludge as solid waste (Shreve and Brink, 1977). Allowing accumulation of carboxylic acid product in fermentation broth inhibits further product formation. The effects of end product inhibition can be reduced by in situ removal of this acid from fermentation broth.

Reactive extraction with extractant giving a higher distribution coefficient has been proposed as a promising technique for the recovery of carboxylic (Wardell and King, 1978; Wennersten, 1983). Reactive extraction has the advantage that acid can be removed easily from the fermentation broth, preventing the lowering of pH. Further, carboxylic acid can be re-extracted and the extractant recycled to the fermentation process. Tertiary amines are found to be effective extractant (Ratchford et al., 1951; King, 1983). Alamine 336 (mixture of C8, C9 and C10 tertiary amines) yields a good combination of high $K_D$, very low solubility in water and good regenerability.

The acid examined in the present work is lactic acid because it is nonvolatile and has strong potential for being produced commercially by fermentation (Lipinsky and Sinclair, 1986; Lockwood, 1979). Lactic acid is utilized in the food, chemical and pharmaceutical fields, especially for synthesis of biodegradable polymers (Buchta, 1983; Datta et al., 1995). A growing demand for biodegradable polymers, call for attention in improvement of conventional processes for lactic acid production. Previously, equilibrium and kinetic study of lactic acid using Alamine-336 in various diluents (methylisobutylketone, decanol and octanol) were carried out by Wasewar et al. (2002a,b, 2003). It was found that...
octanol is better solvent than the other two solvents on equi-
librium and kinetics consideration. Wasewar et al. (2003) 
have suggested a more efficient method for lactic acid re-
covery. Lactic acid extracted in the organic phase can be 
back extracted with a stronger volatile amine like trimethyl-
lamine (TMA) in aqueous phase. TMA can be stripped and 
recovered by absorption in water and recycled to obtain a 
closed loop system. This process is a sustainable process as 
it does not consume extra reagents and also does not pro-
duce a large waste stream as in the conventional process.

In the present work, equilibrium and kinetic data for the 
back extraction of lactic acid from organic phase have been 
presented. The organic phase, Alamine 336 in octanol was 
chosen because of favourable equilibria, substantial equilib-
rium data, and interpretation thereof for forward extraction 
of lactic acid (Wasewar et al., 2003). The regeneration data 
of TMA have been presented.

2. Materials and methods

2.1. Reagents

The reagents used and their sources are given in Table 1. Distilled water was used to dilute the lactic acid, sulfuric 
acid, sodium hydroxide and trimethylamine when necessary.

2.2. Forward extraction

All experiments were carried out at room temperature at 
30°C. Equal volumes of an aqueous solution of lactic acid 
of known concentration were contacted with organic phase 
(20% Alamine 336 in octanol) in a temperature-controlled 
shaker bath for 24 h. The two phases were allowed to settle 
for 24 h in a separating vessel. To determine the concen-
tration of lactic acid, the aqueous phase was titrated with 
0.1 N NaOH and phenolphthalein as an indicator. The acid 
concentrations in the organic phase were calculated by mass 
balance.

2.3. Back extraction

2.3.1. Equilibrium

All experiments were carried out at room temperature at 
30°C. Known volumes (50 ml each) of aqueous phase 
(different concentrations of TMA) and lactic acid loaded or-
ganic phase of known lactic acid concentrations were equi-
librated in a temperature-controlled shaker bath for 24 h. 
The two phases were allowed to settle for 24 h in separating 
vessel for complete phase separation.

2.3.2. Kinetics

The theory of extraction accompanied by a chemical 
reaction was used to discern the kinetics in a stirred cell 
(Doraiswamy and Sharma, 1984). Four regimes of extrac-
tion accompanied by reaction (very slow, slow, fast and 
instantaneous) have been identified depending upon the 
physico-chemical and hydrodynamic parameters. The ex-
pression for regime 3, extraction accompanied by a fast 
general order chemical reaction occurring in the diffusion 
film is

\[ R_d = \left[ A^* \right] \frac{2}{m + 1} D_A k_{\text{mix}} [A^*]^{m-1} [B_0]^n. \]  

A stirred cell of 0.07 m diameter and 0.1 m height 
(Wasewar et al., 2002b), with a flat bottom was used for ki-
netic studies. Aqueous solution of TMA (100 ml) of known 
concentration was first placed in the vessel. A fixed volume 
of the lactic acid loaded organic phase (100 ml) was then 
added, and stirring was started. A sample of aqueous phase 
was taken out periodically.

The concentration of lactic acid in aqueous phase in both 
equilibrium and kinetics experiments was measured by a 
high-performance liquid chromatography (HPLC) system 
(Knauer Instruments, Germany) that consisted of a K-501 
HPLC pump and K-2501 UV Detector. The sample was 
eluted by 0.25 mol/l aqueous ammonium dihydrogen phos-
phate solution (Hironaka et al., 2001) adjusted to pH 2.2 by 
an aqueous phosphoric acid solution and flowing at a rate 
of 0.5 ml/min in a reverse phase C-18 column (4 mm i.d. × 
150 mm in length). Lactic acid was detected at 210 nm and 
the data were integrated by the Oracle Integrator.

2.4. Thermal regeneration of TMA

The aqueous solution (50 ml) of trimethylammonium lact-
tate was placed in a three neck, round bottom flask operated 
under vacuum. Water and TMA driven off from the solution 
was absorbed in a flask containing water which was im-
mersed in ice-salt mixture. The amount of TMA recovered

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Sources and description of chemicals used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>Supplier</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>s. d. fine chemicals Ltd. Mumbai, India</td>
</tr>
<tr>
<td>Octanol</td>
<td>s. d. fine chemicals Ltd. Mumbai, India</td>
</tr>
<tr>
<td>Alamine 336</td>
<td>Henkel Corporation, USA</td>
</tr>
<tr>
<td>TMA</td>
<td>Alkyl Amines Ltd. Mumbai, India</td>
</tr>
<tr>
<td>(\text{H}_2\text{SO}_4)</td>
<td>s. d. fine chemicals Ltd. Mumbai, India</td>
</tr>
</tbody>
</table>
in the absorber was estimated using the procedure given by Poole and King (1991).

The experiments were randomly replicated (30% of the total) and the results obtained were found to be within ±5%.

3. Results and discussion

3.1. Equilibria

During the back-extraction experiments, the concentration of acid in the extract was held constant while the TMA concentration was varied. Results are shown as data points in Fig. 1. Essentially 100% of lactic acid was back extracted into the aqueous phase at conditions in which there was at least 1 mol of TMA for every equivalent weight of lactic acid. This is a sign that the basicity of aqueous TMA is much stronger than that of the organic amine, as would be expected (Poole and King, 1991).

The complexation of lactic acid with Alamine 336 in octanol at 30°C is described as follows (Wasewar et al., 2003):

\[ \text{HL}_{\text{aq}} + \text{B}_{\text{org}} \rightleftharpoons \text{HLB}_{\text{org}}, \]

\[ 2\text{HL}_{\text{aq}} + \text{B}_{\text{org}} \rightleftharpoons (\text{HL})_2\text{B}_{\text{org}}, \]

\[ K_{11} = 73.55 \text{ (kmol/m}^3\text{)}^{-1}, \quad K_{21} = 10.95 \text{ (kmol/m}^3\text{)}^{-2}, \]

where HL denotes the unionized acid, B denotes the extractant (Alamine 336) and \( K_{pq} \) values are the equilibrium constants for complex formation.

Partition coefficient of lactic acid between water and octanol is given by (Wasewar et al., 2003)

\[ P = \frac{[\text{HL}]_{\text{org}}}{[\text{HL}]_{\text{aq}}} = 0.31. \]

![Fig. 1. Back extraction of lactic acid from 20% Alamine 336 in octanol into aqueous solution of varying TMA concentration: correlation coefficient, \( R^2 = 0.90 \).](image)

The equilibria in the aqueous phase are described as follows (Poole and King, 1991):

\[ \text{HL} \rightleftharpoons \text{H}^+ + \text{L}^-; \quad K_a = 1.41 \times 10^{-4} \text{ kmol/m}^3, \]

\[ \text{R}_3\text{NH}^+ \rightleftharpoons \text{R}_3\text{N} + \text{H}^+; \quad K_a = 1.585 \times 10^{-10} \text{ kmol/m}^3, \]

\[ [\text{H}^+]_{\text{aq}} + [\text{R}_3\text{NH}^+]_{\text{aq}} = [\text{L}^-]_{\text{aq}} + [\text{OH}^-]_{\text{aq}}, \]

where \( \text{R}_3\text{N} \) denotes TMA.

The concentration of unionized acid in the aqueous phase can be expressed as

\[ [\text{HL}]_{\text{aq}} = z[\text{HL}]_{\text{aq},T}, \]

where

\[ z = \frac{1}{1 + \frac{K_a}{[\text{H}^+]_{\text{aq}}}}. \]

Mass balance for lactic acid can be written as follows:

Total acid in system = Acid in organic phase + Acid in aqueous phase

\[ [\text{HL}]_T = K_{11}[\text{B}]_{\text{org}}[\text{HL}]_{\text{aq}} + 2K_{21}[\text{B}]_{\text{org}}[\text{HL}]_{\text{aq}}^2 \]

\[ + \phi P[\text{HL}]_{\text{aq}} + R[\text{HL}]_{\text{aq}}/z, \]

where \( \text{B}_{\text{org}} \) is uncomplexed Alamine 336 in organic phase, \( \phi \) is the volume fraction of diluent (octanol) in organic phase and \( R \) is the ratio of aqueous phase to organic phase used for back extraction.

Mass balance for Alamine 336 essentially present in the organic phase can be written as follows:

\[ [\text{B}]_{\text{org},T} = [\text{B}]_{\text{org}} + K_{11}[\text{B}]_{\text{org}}[\text{HL}]_{\text{aq}} + 2K_{21}[\text{B}]_{\text{org}}[\text{HL}]_{\text{aq}}^2; \]

Substituting Eq. (11) into Eq. (10) gives a mass balance equation for lactic acid in terms of only two unknown values, the pH (\( \text{H}^+ \) concentration) of aqueous raffinate phase. This equation can be solved for [HL]\(_{\text{aq}}\) at the set values of pH. For each pH values, the recovery of the acid into the aqueous phase can be calculated as

\[ \text{Recovery} = \frac{R[\text{HL}]_{\text{aq}}/z}{[\text{HL}]_{\text{org},\text{init}}}. \]

The ratio of moles of TMA to moles of acid originally present in the organic phase can be calculated as

\[ [\text{R}_3\text{N}]_{\text{aq},T} = [\text{R}_3\text{N}]_{\text{aq}} + [\text{R}_3\text{NH}^+]_{\text{aq}} = [\text{R}_3\text{NH}^+]_{\text{aq}}/\beta, \]

where

\[ \beta = \frac{1}{1 + \frac{K_a}{[\text{R}_3\text{NH}^+]_{\text{aq}}}}. \]

The curve shown in Fig. 1 depicts the above complexation model, which includes chemical-equilibrium and mass-balance equations that describe the system.
The back-extraction equilibrium data compare well with the prediction of the model.

3.2. Kinetics

3.2.1. Reaction regime

Effect of speed of agitation: The speed of agitation was varied from 0.6 to 1.4 rev/s. In this range the liquid–liquid interface was flat and the interfacial area for extraction was equal to the geometric area. Fig. 2 indicates that there is no effect of speed of agitation on the specific rate of back extraction of lactic acid, $R_A$ (kmol/m$^2$/s). This situation is possible if either regime 1 or 3 is valid.

Effect of phase volume ratio: To differentiate between regimes 1 and 3, the effect of phase volume ratio on the specific rate of back extraction of lactic acid was studied. Fig. 3 shows a plot of $R_A$ vs. phase volume ratio (volume of organic phase/volume of aqueous phase) at a constant speed of agitation. Evidently, there is no effect of phase volume ratio.

From the above experimental results it can be concluded that the reaction between lactic acid and TMA in a stirred cell falls in regime 3, extraction accompanied by a fast chemical reaction occurring in the diffusion film.

3.2.2. Order of reaction

Order with respect to lactic acid: Fig. 4 shows the effect of organic phase lactic acid concentration on specific rate of back extraction, $R_A$. A regression analysis of the data yielded $m = 1$ (as per Eq. (1)). Thus, the reaction is first order with respect to lactic acid.

Order with respect to TMA: Fig. 5 shows a plot of the specific rate of back extraction of lactic acid against initial TMA concentration in the aqueous phase. Evidently there is no effect of TMA concentration on the rate of extraction indicating that the reaction is zero order in TMA ($n = 0$ in Eq. (1)).

3.2.3. Rate constant

For $m = 1$ and $n = 0$, Eq. (1), the rate expression for the initial part of the extraction is reduced to

$$R_A = [HL]_{aq} \sqrt{D_A k_1}. \quad (15)$$

The data were fitted to the above equation to obtain the value of the first-order rate constant (Fig. 4), $k_1$ as $16.67$/s$^1$. The value of $D_A$ was estimated using Wilke and Chang (1955) equation as $3.26 \times 10^{-10}$ m$^2$/s.

To confirm the validity regime 3, the value of the parameter $\sqrt{(D_A k_1)}/k_L$ should be greater than 3 (Doraiswamy and Sharma, 1984).
The range of $k_L$ is $0.8 \times 10^{-5}$ to $1.2 \times 10^{-5}$ m/s and value of $\sqrt{D_L k_L}$ from Fig. 4 is $7.5 \times 10^{-5}$ m/s. Hence the range of value of $\sqrt{(D_L k_L)} / k_L$ is 6.25 to 9.4. Thus the condition for the validity of regime 3 is satisfied. Therefore, the above-mentioned results reflect the intrinsic kinetics of the extraction process.

### 3.3. Thermal regeneration and absorption of TMA

Thermal regeneration experiments were carried out to remove TMA from the trimethylammonium lactate solution. As an aqueous solution of lactic acid is concentrated the acid does not precipitate due to the high solubility and the viscosity of the solution increases steadily as self-association of the acid occurs. As described by Poole and King (1991) thermal regeneration of TMA loaded with lactic acid was performed in the total pressure range of 350–380 mmHg. It was found that essentially all the TMA (> 99%) could be removed by heating under the above total pressure range. The lower pressure requirement is mainly due to a lowering of the volatility of TMA as the lactic acid concentration increases (Poole and King, 1991). When 50 ml of 0.25 N lactic acid and 0.25 N TMA in water was heated at 100–120°C and total pressure of 300, 250, 200 mmHg, 85%, 94% and 99% of the TMA present in the initial aqueous solution was removed, respectively, leaving behind a viscous aqueous solution.

In an actual industrial unit as shown in the flowsheet (Wasewar et al., 2003) the thermal regeneration of gases containing water vapour and TMA can be first cooled in a falling film type of condenser where most of the TMA will be absorbed by the condensing water vapour. It is well known that when the direction of heat and mass transfer is the same (such as in this case) relatively high mass transfer coefficient are realized (Bennett and Myers, 1962). Thus a falling film condenser cum absorber can yield good recovery of TMA-water vapours. Final polishing of the exhaust can be done in an additional falling film absorber in order to maintain a low pressure drop. TMA being highly soluble in water under proper operating conditions and a well designed absorber, negligible quantities of TMA are expected to escape.

### 4. Conclusion

Lactic acid extracted in the organic phase can be back extracted with a stronger volatile amine like TMA in aqueous phase. The TMA can be stripped and recovered by absorption in water, and recycled to obtain a closed loop system. Equilibria for back extraction of lactic acid from organic phase (Alamine 336 + octanol) into aqueous TMA have been determined. Essentially 100% of lactic acid was back extracted into the aqueous phase at conditions such that at least 1 mol of TMA for every equivalent weight of acid is present in the aqueous phase. This clearly indicates that the basicity of aqueous TMA is much stronger than that of Alamine 336.

The theory of extraction accompanied by chemical reaction has been used to obtain the kinetics of back extraction of lactic acid by aqueous TMA. The reaction between lactic acid and TMA in a stirred cell falls in regime 3, extraction accompanied by a fast chemical reaction occurring in the diffusion film. The reaction has been found to be zero order in TMA and first order in lactic acid with a rate constant of $16.67/s^1$. The data reported in this work will be useful in designing the lactic acid recovery system. In thermal regeneration of TMA, 99% of TMA was removed at 200 mmHg from trimethylammonium lactate aqueous solution. This recovered TMA can be recycled back for back extraction of lactic acid form loaded organic phase.

### Notation

- $[A^+]$: equilibrium concentration in aqueous phase, kmol/m³
- $[B]_0$: concentration of extractant, kmol/m³
- $D_L$: molecular diffusivity of lactic acid in water, m²/s¹
- $[H][L]$: lactic acid concentration, kmol/m³
- $k_1$: first-order reaction rate constant for the reaction between lactic acid and TMA, s⁻¹
- $k_L$: physical mass transfer coefficient, m s¹
- $k_{me}$: rate constant for a reaction that is $m$th order in species $A$ and $n$th order in species $B$, (m³/kmol¹)⁺²⁺⁻⁺⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻myśl⁻¹
- $N$: speed of agitation, rev/s¹
- $R_A$: specific rate of back extraction of lactic acid, kmol/m³/s¹
- $V$: phase volume, m³
Subscripts

aq  aqueous phase

org  organic phase

Superscript

*  equilibrium

References


