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# Equilibria and kinetics for reactive extraction of lactic acid using Alamine 336 in decanol

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**Abstract:** Lactic acid is an important commercial product and extracting this from aqueous solution is a growing requirement in fermentation-based industries. The design of an amine extraction process requires (i) equilibrium and (ii) kinetic data for the acid–amine (solvent) system used. The equilibrium complexation constants for ratios of (1:1) and (2:1) have been estimated. The kinetics of extraction of lactic acid by Alamine 336 in decanol has also been determined. The reaction between lactic acid and Alamine 336 in decanol in a stirred cell falls in Regime 3, ie extraction accompanied by a fast chemical reaction occurring in the diffusion film. The reaction has been found to be zero order in Alamine 336 and first order in lactic acid with a rate constant of  $0.21 \text{ s}^{-1}$ . These data will be useful in the design of extraction processes.

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**Keywords:** lactic acid; reactive extraction; Alamine 336; decanol; equilibria; kinetics

## NOTATION

$A_C$	Cross-sectional area of stirred cell ( $\text{m}^2$ )
[B]	Free Alamine concentration in the organic phase ( $\text{kmol m}^{-3}$ )
[BHL]	(1:1) Lactic acid–Alamine complex concentration in organic phase ( $\text{kmol m}^{-3}$ )
$D_A$	Diffusivity of solute A (lactic acid) in solvent (decanol) ( $\text{m}^2 \text{ s}^{-1}$ )
$K_{E1}$	(1:1) Lactic acid–Alamine equilibrium complexation constant ( $\text{m}^3 \text{ kmol}^{-1}$ )
$K_{E2}$	(2:1) Lactic acid–Alamine equilibrium complexation constant ( $(\text{m}^3 \text{ kmol}^{-1})^2$ )
$K_{E3}$	(3:1) Lactic acid–Alamine equilibrium complexation constant ( $(\text{m}^3 \text{ kmol}^{-1})^3$ )
[HL]	Lactic acid concentration ( $\text{kmol m}^{-3}$ )
$k_1$	First order rate constant ( $\text{s}^{-1}$ )
$k_L$	Mass transfer coefficient ( $\text{m s}^{-1}$ )
$k_{mn}$	Rate constant for a reaction that is $m$ th order in species A and $n$ th order in species B
$K_D$	Distribution coefficient (dimensionless)
$N$	Speed of agitation ( $\text{rev s}^{-1}$ )
$R_A$	Specific rate of extraction of lactic acid ( $\text{kmol m}^{-2} \text{ s}^{-1}$ )
$t$	Time of extraction (s)
$V$	Phase volume ( $\text{m}^3$ )
$z$	Loading ratio ( $\text{kmol lactic acid kmol amine}^{-1}$ )

## Subscripts

aq Aqueous phase

org Organic phase  
T Total

## Superscript

\* Equilibrium

## 1 INTRODUCTION

Lactic acid is a commodity chemical utilized in the food, chemical and pharmaceutical industries. Lactic acid is an important chemical, which can be converted to ethanol, propylene glycol, acrylic polymers and polyesters. In particular, an increasingly interesting application is the use of lactic acid as a monomer for the synthesis of biodegradable homopolymers and copolymers.<sup>1,2</sup> Lactic acid is the raw material for the production of biodegradable polylactic acid. A growing demand for biodegradable polymers, both as substitutes for conventional plastic materials and for new materials for specific uses such as controlled drug delivery or artificial prostheses, draws attention to the need to improve conventional processes for lactic acid production.<sup>3</sup>

Lactic acid can be produced by the fermentation of biomass. However, the fermentation broth has a low concentration (<10%) of lactic acid due to product inhibition during the biological process. The traditional recovery process of lactic acid from fermentation broth is quite complicated. In conventional

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processes, lactic acid has been recovered from the fermentation broth by precipitation of calcium lactate with calcium hydroxide. In this, the separation and final purification stages account for up to 50% of the production costs.<sup>4,5</sup> Thus, this method of recovery is expensive<sup>6,7</sup> and unfriendly to the environment as it consumes lime and sulfuric acid and also produces a large quantity of calcium sulfate sludge as solid waste.<sup>6</sup> Allowing accumulation of lactic acid product in fermentation broth inhibits further product formation. Reactor productivities are low and the products are obtained in a dilute form. The effects of end product inhibition can be reduced by *in-situ* removal of lactic acid from fermentation broth by several methods.

A number of processes for lactic acid recovery from fermentation broth without precipitation have been studied: solvent extraction,<sup>8–15</sup> membrane bioreactor,<sup>16,17</sup> liquid surfactant membrane extraction,<sup>18,19</sup> adsorption,<sup>20</sup> direct distillation,<sup>21</sup> electrodialysis,<sup>22–24</sup> chromatographic methods,<sup>15</sup> ultrafiltration,<sup>15</sup> reverse osmosis,<sup>15,25</sup> drying,<sup>15</sup> etc.

Reactive extraction with a specified extractant giving a higher distribution coefficient has been proposed as a promising technique for the recovery of carboxylic and hydroxycarboxylic acids.<sup>8,26</sup> Solvent extraction with tertiary amines has been widely used to recover/fractionate metals such as uranium, iron, cobalt, etc from aqueous solutions.<sup>27</sup> Long chain tertiary amines were used commercially for recovery of ethanoic acid from dilute aqueous streams.<sup>14,28</sup> Tertiary amines offer advantages over other extractants, on the grounds of lower cost and generally higher equilibrium distribution coefficients ( $K_D$ ).<sup>29</sup> Tertiary amines were found to be effective for extracting lactic acid, and alcohols were among the best diluents, with the additional advantage that a lactic acid ester could be produced after the extraction process was completed.<sup>30,31</sup> Alamine 336 (mixture of C<sub>8</sub>, C<sub>9</sub> and C<sub>10</sub> tertiary amines) yields a good combination of high  $K_D$ , low solubility in water and good regenerability.

The design of an amine extraction process requires (i) equilibrium and (ii) kinetic data for the acid–amine (solvent) system used. However, little information on the equilibria and no information pertaining to kinetics are available. In view of this it was thought desirable to obtain the equilibria and kinetics for the extraction of lactic acid by Alamine 336 (a tertiary amine, with aliphatic chains of 8–10 carbon groups) dissolved in decanol, as diluent.

## 2 MATERIALS AND METHODS

### 2.1 Materials

All the chemicals used (lactic acid, decanol, sodium hydroxide) were of reagent grade and were used without pretreatment. All solutions of lactic acid were prepared by dissolving lactic acid of analytical purity in distilled water. In practical situations of acid recovery from fermentation broths, the acid concentrations are not expected to be high. Hence, a low concentration

range (0.005–1.5 kmol m<sup>-3</sup>) of lactic acid concentration was used.

The reactive component was Alamine 336 (straight chain tertiary amine containing C<sub>8</sub>–C<sub>10</sub> alkyl groups (Henkel Corp, USA)) with decanol as diluent. Alamine was used as supplied.

## 2.2 Methods

### 2.2.1 Equilibria

All experiments were carried out at room temperature of 25 °C. Known volumes of aqueous (different concentrations of lactic acid) and organic phases (30 cm<sup>3</sup> each) (both pure decanol and decanol containing different concentrations of Alamine 336) of known concentrations were equilibrated in a temperature-controlled shaker bath for 24 h. The two phases were allowed to settle for at least 30 min, which was sufficient time for a complete phase separation.<sup>32</sup> To determine the concentration of lactic acid, the aqueous phase was titrated with NaOH using phenolphthalein as indicator. The acid concentrations in the organic phase were calculated by mass balance.

### 2.2.2 Kinetics

A stirred cell (Fig 1) of 0.07 m in diameter and 0.1 m height, with a flat bottom was used for the kinetic studies.<sup>33</sup> A 100 cm<sup>3</sup> sample of an aqueous solution of lactic acid of known concentration was first placed in the vessel. The position of the four-blade paddle (0.058 m in diameter and 0.01 m in width) double stirrer was adjusted to 0.01 m below and above the interface. A fixed volume (100 cm<sup>3</sup>) of the organic extractant mixture was then added, and the mixture was stirred. Using acid–base titration with NaOH and phenolphthalein as indicator, the acid concentration in the aqueous phase was determined periodically. The concentration of lactic acid in the organic phase was determined by mass balance.

The reproducibility was checked by carrying out

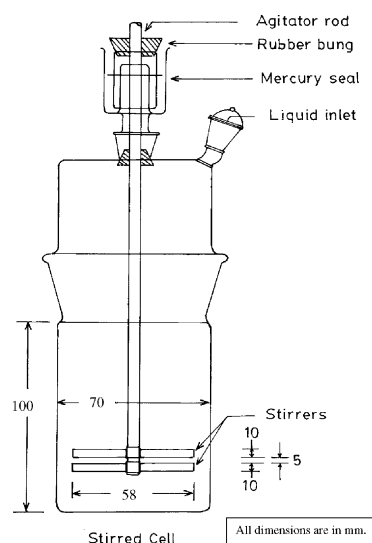


Figure 1. Stirred cell used for kinetic study.

**Table 1.** Procedure for discerning reaction mechanism: stirred cell

Regime	Effect on the specific rate of absorption ( $\text{kmol m}^{-2} \text{s}^{-1}$ )			Volume of liquid (B phase)
	$[A^*]$	$[B_o]$	Speed of agitation	
1	$\alpha [A^*]^m$	$\alpha [B_o]^n$	None	$\alpha$ volume
2	$\alpha [A^*]$	None	Increases with increase in the speed of stirring	None
3	$\alpha [A^*]^{(m+1)/2}$	$\alpha [B_o]^{n/2}$	None	None
4	None <sup>a</sup>	$\alpha [B_o]$	Increases with increase in the speed of stirring in the same manner as in Regime 2	None

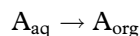
<sup>a</sup> Provided that  $[B_o] \gg z[A^*]$ .

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duplicate experiments in some selected cases. The results were found to be reproducible within  $\pm 5\%$ .

### 2.3 Theory of extraction accompanied by a chemical reaction

Doraiswamy and Sharma (1984) have given an exhaustive discussion on the theory of extraction accompanied by a chemical reaction.<sup>33</sup> Four regimes of extraction accompanied by reaction have been identified depending upon the physico-chemical and hydrodynamic parameters. When the reaction is reversible the solute has a finite equilibrium concentration in the bulk and the driving force needs to be modified by incorporating the same. The extraction involves the partitioning of the solute available in the aqueous phase to the organic phase:



Solute A present in the aqueous phase combines with the organic reactant (amine) B according to

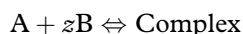


Table 1 gives the guidelines for discerning the mechanism. The hydrodynamic factors (as signified by the speed of agitation in a stirred cell) are unimportant in Regimes 1 and 3 whereas they do affect the rate of extraction in Regimes 2 and 4. The expressions for the rate of extraction for various regimes are given by Doraiswamy and Sharma.<sup>33</sup> The expression for Regime 3, extraction accompanied by a fast general order chemical reaction occurring in the diffusion film, is

$$R_A = [A^*] \sqrt{\frac{2}{m+1} D_A k_{mn} [A^*]^{m-1} [B_o]^n} \quad (1)$$

## 3 RESULTS AND DISCUSSION

### 3.1 Extraction equilibria

Experiments were carried out to describe the physical and chemical equilibria for lactic acid. The pH changes with the progress of extraction of lactic acid. The range of pH used for extraction experiments was 1.8–3.4. Equilibrium pH is always higher than initial pH and its value depends on the extent of lactic acid

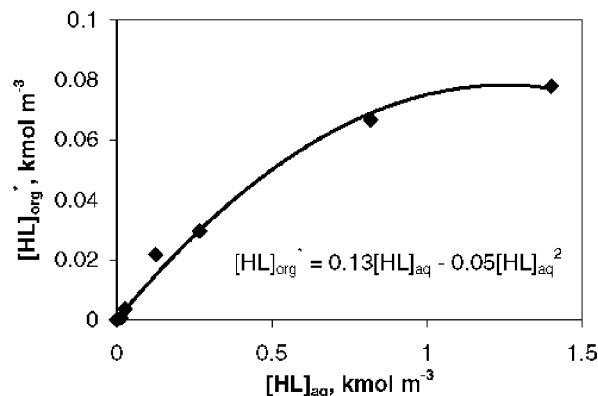
extraction. The pH was measured for various concentrations of lactic acid and the following correlation has been obtained for the above range of pH values:

$$\text{pH} = 1.9 - 0.26 \ln[\text{HL}]$$

The physical equilibrium distribution isotherm was measured at 25 °C in decanol. The results are shown in Fig 2. The regression equation for physical equilibria obtained by a statistical analysis of the equilibrium data is:

$$[\text{HL}]_{\text{org}}^* = 0.13[\text{HL}]_{\text{aq}} - 0.05[\text{HL}]_{\text{aq}}^2 \quad (2)$$

For a low range of lactic acid concentration there is a linear relationship between lactic acid concentration in the two phases, and a parabolic relationship for higher concentrations. It may be argued that for low concentrations of lactic acid a Henry's law type isotherm is valid, whereas at higher concentrations non-ideal behavior can prevail, causing the deviation from Henry's law. The chemical equilibrium distribution isotherms were measured at 25 °C for Alamine 336 concentrations of 20%, 30% and 40% (v/v) in decanol. The chemical equilibrium isotherms are shown in Fig 3. It was observed that equilibrium concentration in the organic phase increased with increases in Alamine 336 concentration. This shows that the extraction efficiency increases with increasing lactic acid concentrations. San-Martin *et al* 1992, have



**Figure 2.** Physical equilibria for extraction of lactic acid with decanol.

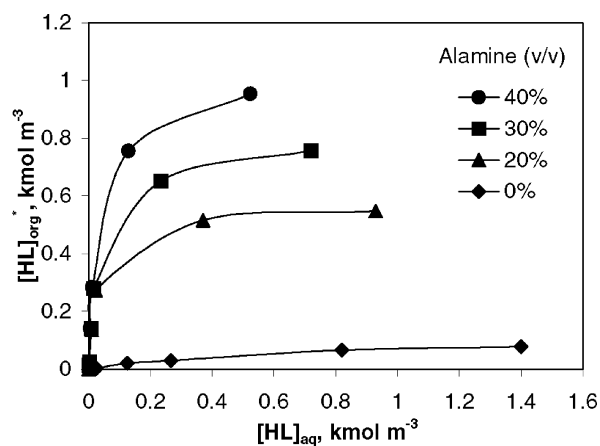


Figure 3. Chemical equilibrium isotherms for reactive extraction of lactic acid with various concentrations of Alamine 336 in decanol.

reported that the equilibrium concentration increased up to a concentration of 40% (v/v) of the Alamine 336 and then remained constant.<sup>32,34</sup>

The reactive liquid–liquid extraction of lactic acid (HL) with the tertiary amine Alamine 336 (B) gives a reaction complex (BHL) which remains in the organic phase and may be represented by:



The distribution coefficient,  $K_D$ , is defined by:

$$K_D = [\text{HL}]_{\text{org}} / [\text{HL}]_{\text{aq}} \quad (4)$$

The regression equations for chemical equilibria of lactic acid at low concentration for various Alamine 336 concentrations in decanol obtained by a statistical analysis of the equilibrium data as shown in Fig 4 are:

$$20\% \text{ Alamine, } [\text{HL}]_{\text{org}}^* = 12.57[\text{HL}]_{\text{aq}} \quad (5)$$

$$30\% \text{ Alamine, } [\text{HL}]_{\text{org}}^* = 16.44[\text{HL}]_{\text{aq}} \quad (6)$$

$$40\% \text{ Alamine, } [\text{HL}]_{\text{org}}^* = 23.37[\text{HL}]_{\text{aq}} \quad (7)$$

Distribution coefficients of lactic acid for low con-

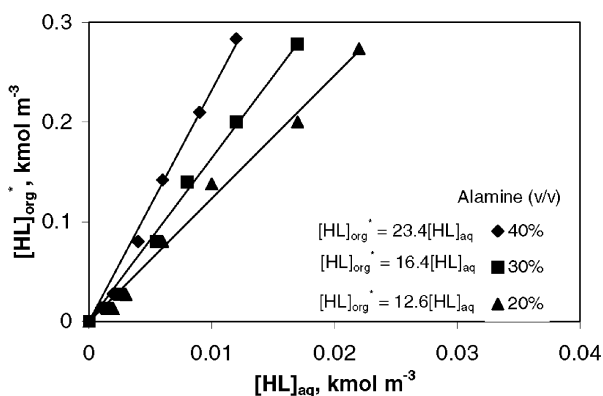


Figure 4. Equilibrium relationships (Distribution coefficients) for reactive extraction of low concentrations of lactic acid with various concentrations of Alamine 336 in decanol.

Table 2. Distribution coefficient for lactic acid extraction with various concentrations of Alamine 336 in decanol

% Alamine 336	Distribution coefficient, $K_D$
0	0.13
20	12.57
30	16.44
40	23.37

centration in Alamine concentration in decanol for various Alamine concentrations are given in Table 2.

A quantitative interpretation of the equilibrium for the acid–amine extraction may be made by defining an equilibrium complexation constant,  $K_E$ , as:

$$K_E = [\text{BHL}]_{\text{org}} / [\text{HL}]_{\text{aq}} [\text{B}]_{\text{org}} \quad (8)$$

The concentration of free amine in the organic phase would be:

$$[\text{B}]_{\text{org}} = [\text{B}]_{\text{T}} - [\text{BHL}]_{\text{org}} \quad (9)$$

If 1:1 lactic acid – Alamine 336 complex is formed then  $[\text{HL}]_{\text{org}} = [\text{BHL}]_{\text{org}}$ ; and

$$\text{hence, } \log K_D = \log K_E + \log [\text{B}]_{\text{org}} \quad (10)$$

If the former assumption is valid, a plot of  $\log K_D$  versus  $\log [\text{B}]_{\text{org}}$  should yield a straight line with a slope of unity. As shown in Fig 5 the slope is less than unity (0.54), which implies that the organic phase extracts more acid than would be expected on the basis of a 1:1 complex. Hence, the extraction equilibrium of the lactic acid is not adequately represented by eqn (3).

Generally, the simple stoichiometric reaction (eqn (3)) is not suitable for describing the formation of a complex of acid and amine molecules. Distribution data can be interpreted by a set of equilibria involving the formation of complexes with  $n$  acid molecules and

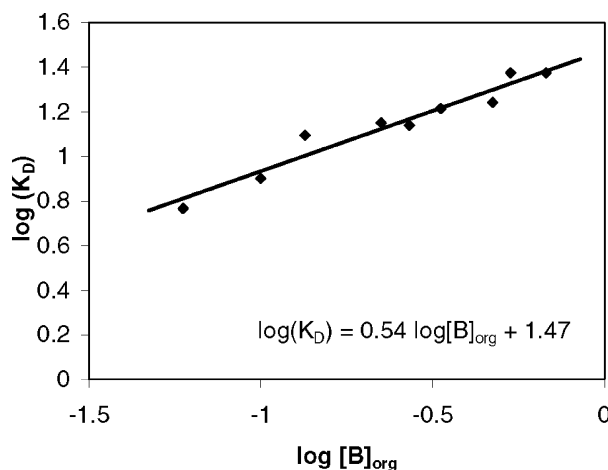
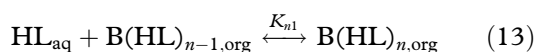
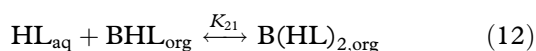


Figure 5. Distribution coefficient of lactic acid in Alamine dissolved in decanol as a function of free amine concentration in organic phase.

one amine molecule:<sup>11,12</sup>



The equilibrium complexation constant for the reaction represented by eqn (13) is:

$$K_{En} = \frac{[\text{BHL(HL)}_n]_{\text{org}}}{[\text{BHL}]_{\text{org}}[\text{HL}]_{\text{aq}}^n} \quad (14)$$

The extent to which the organic phase (Alamine 336 + decanol) can be loaded with lactic acid is expressed as the loading ratio,<sup>34</sup>  $z$ :

$$z = \frac{[\text{HL}]_{\text{org}}}{[\text{B}]_{\text{T}}} \quad (15)$$

The value of  $z$  depends on the extractability of the acid (strength of the acid–base interaction) and its aqueous concentration, and is independent of the amine content in an inert diluent.<sup>10–12</sup>

The stoichiometry of the overall extraction reaction depends on the loading ratio in the organic phase,  $z$ . If the organic phase is not highly concentrated i.e. at very low loading ratios ( $z < 0.5$ ), the (1:1) complex is formed and a plot of  $z/(1-z)$  versus  $[\text{HL}]_{\text{aq}}$  is a straight line whose slope gives the complexation constant  $K_{E1}$  in eqn (8) and  $K_{E1}$  in eqn (14).

$$\frac{z}{1-z} = K_{E1}[\text{HL}]_{\text{aq}} \quad (16)$$

A straight line of plot of eqn (16) with a slope of 45.21 is shown in Fig 6. Hence, the equilibrium complexation constant for a (1:1) lactic acid – Alamine 336 complex in decanol at 25°C for low concentrations of lactic acid in the organic phase is:

$$K_{E1} = 45.21 \text{ m}^3 \text{ kmol}^{-1}$$

For higher loading ratios, the (2:1) complex is

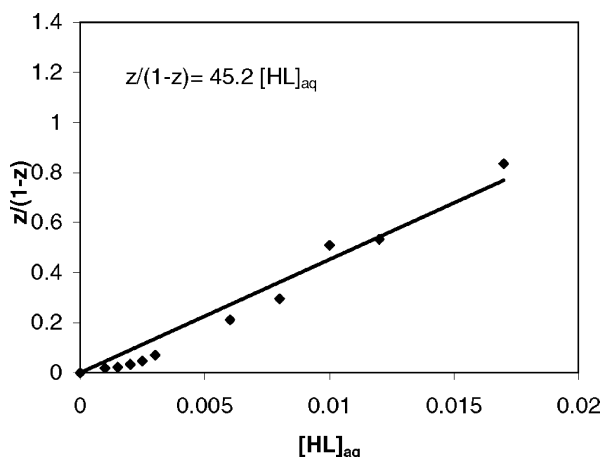


Figure 6. Plot of  $z/(1-z)$  versus  $[\text{HL}]_{\text{aq}}$  for the estimation of (1:1) lactic acid – Alamine 336 equilibrium complexation constant in decanol.

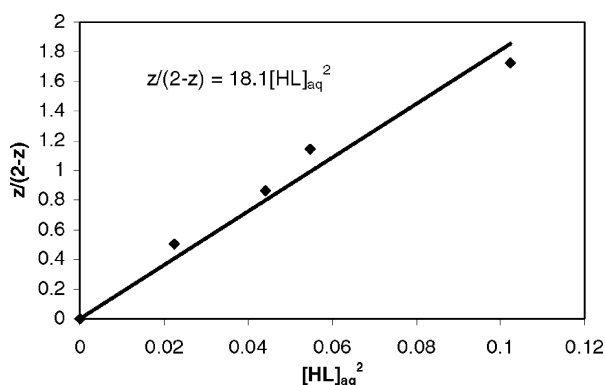


Figure 7. Plot of  $z/(2-z)$  versus  $[\text{HL}]_{\text{aq}}^2$  for the estimation of (2:1) lactic acid – Alamine 336 equilibrium complexation constant in decanol.

formed, and a plot of  $z/(2-z)$  versus  $[\text{HL}]_{\text{aq}}^2$  should yield a straight line, whose slope gives the complexation constant for the (2:1) complex,  $K_{E2}$ , in eqn (14).

$$\frac{z}{2-z} = K_{E2}[\text{HL}]_{\text{aq}}^2 \quad (17)$$

A straight line of plot of eqn (17) with a slope of 18.11 is shown in Fig 7. Hence, the equilibrium complexation constant for the (2:1) lactic acid–Alamine 336 complex in decanol at 25°C is:

$$K_{E2} = 18.11 \text{ (m}^3 \text{ kmol}^{-1})^2$$

If the lactic acid concentration is high enough, the (3:1) complex may be formed and a plot of  $z/(3-z)$  versus  $[\text{HL}]_{\text{aq}}^3$  should yield a straight line, whose slope gives the complexation constant for the (1:3) complex,  $K_{E3}$ , in eqn (14).

$$\frac{z}{3-z} = K_{E3}[\text{HL}]_{\text{aq}}^3 \quad (18)$$

A plot of eqn (18) is shown in Fig 8, which indicates that a straight line cannot be fitted. Hence, in the range of lactic acid concentration employed in this work, the (3:1) complex is not formed because the concentration

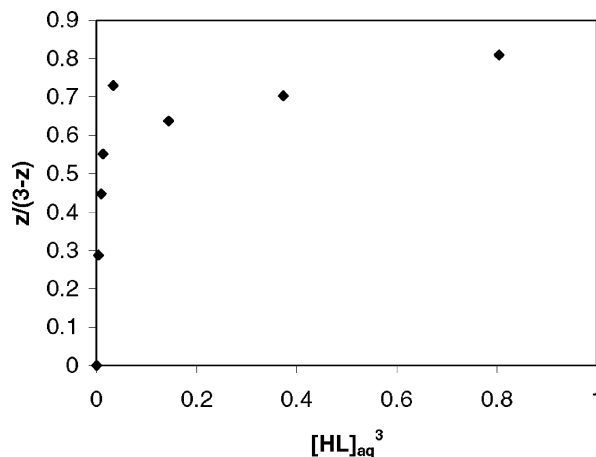


Figure 8. Plot of  $z/(3-z)$  versus  $[\text{HL}]_{\text{aq}}^3$  for the estimation of (3:1) lactic acid – Alamine 336 equilibrium complexation constant in decanol.

**Table 3.** Concentration range of lactic acid in the aqueous phase at which one of the complexes formed in the organic phase in equilibrium

Complex	Complexation constant	Concentration range ( $\text{kmol m}^{-3}$ )
(1:1)	$45.2 \text{ m}^3 \text{ kmol}^{-1}$	<0.02
(2:1)	$18.1 (\text{m}^3 \text{ kmol}^{-1})^2$	0.02–0.3

of lactic acid is not high enough. This situation is frequently encountered in fermentation processes for production of lactic acid.

Figures 6 and 7 allow the determination of the concentration range of lactic acid in the aqueous phase at which one of the reactants is present in a higher proportion. The results are shown in Table 3.

When the lactic acid concentration in the aqueous phase is within the range indicated in Table 3, the equilibrium concentration in the organic phase is high enough to form either the (1:1) or the (2:1) complexes. For the experimental conditions used in this work the lactic acid concentration is not high enough to allow formation of the (3:1) complex.

## 3.2 Kinetics

### 3.2.1 Physical Mass Transfer Coefficient

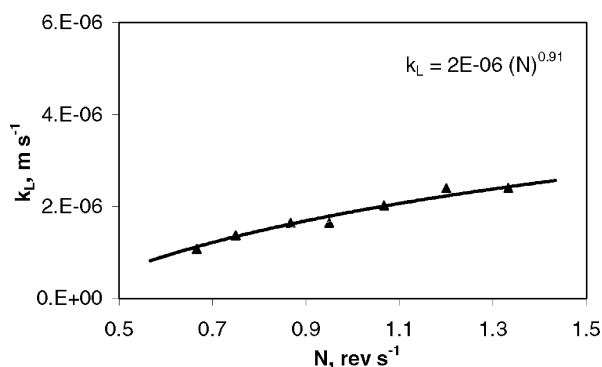
The value of the physical mass transfer coefficient,  $k_L$ , is required for confirming the regime of extraction. This was obtained by conducting physical extraction (diluent only) of lactic acid from water. For a batch process a differential mass balance yields the eqn (19):

$$V_{\text{aq}} \frac{d[\text{HL}]_{\text{org}}}{dt} = k_L A_C ([\text{HL}]_{\text{org}}^* - [\text{HL}]_{\text{org}}) \quad (19)$$

Here,  $[\text{HL}]_{\text{org}}^*$  is the equilibrium concentration in the diluent only. Integration of this equation yields:

$$k_L = \frac{V_{\text{aq}}}{A_C t} \int_0^{[\text{HL}]_{\text{org}}} \frac{d[\text{HL}]_{\text{org}}}{([\text{HL}]_{\text{org}}^* - [\text{HL}]_{\text{org}})} \quad (20)$$

The values of  $k_L$  evaluated using eqn (20) for different speeds of agitation are plotted in Fig 9. The regression relationship between mass transfer coefficient and

**Figure 9.** Effect of speed of agitation on physical mass transfer coefficient for the extraction of lactic acid with decanol (initial lactic acid concentration =  $0.76 \text{ kmol m}^{-3}$ ).

speed of agitation obtained by a statistical analysis data is given in eqn (21).

$$k_L = 1.86 \times 10^{-6} N^{1.84} \quad (21)$$

### 3.2.2 Reaction regime

The reaction between lactic acid and Alamine 336 is reversible, particularly under conditions of high loading in the organic phase. To avoid problems due to this reversibility only initial rates were considered for evaluation of the kinetics. The theory of mass transfer accompanied by chemical reaction was used to find the controlling regime.<sup>34</sup>

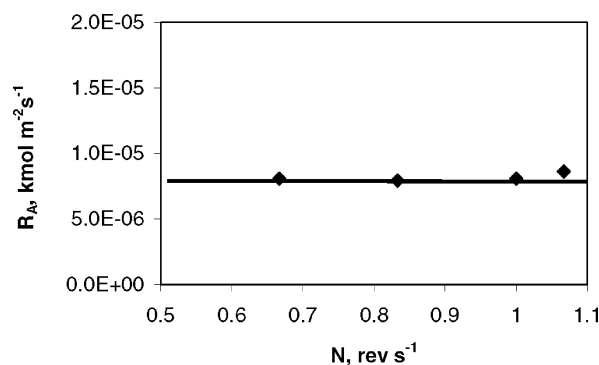
**3.2.2.1 Effect of speed of agitation.** The speed of agitation was varied from  $0.6 \text{ rev s}^{-1}$  to  $1.4 \text{ rev s}^{-1}$ . In this range the liquid–liquid interface was flat and the interfacial area for extraction was equal to the geometric area. Figure 10 indicates that there was no effect of speed of agitation on the specific rate of extraction,  $R_A$  ( $\text{kmol m}^{-2} \text{ s}^{-1}$ ). This situation is possible if either Regime 1 or Regime 3 is valid.

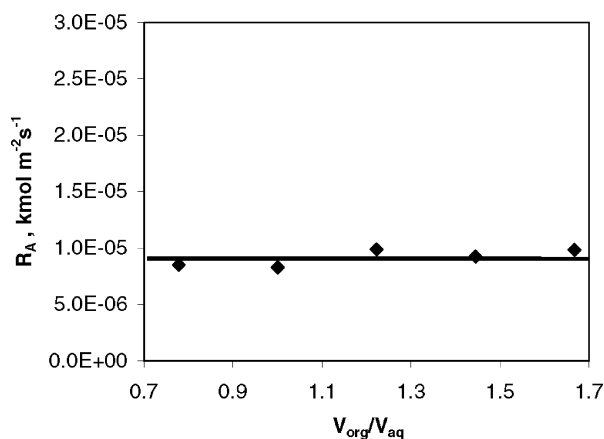
**3.2.2.2 Effect of phase volume.** To differentiate between Regimes 1 and 3, the effect of the organic phase volume on the specific rate of extraction was studied. Figure 11 shows the plot of  $R_A$  versus phase volume ratio (volume of organic phase/volume of aqueous phase) at a constant speed of agitation. Evidently, there is no dependence on phase volume ratio.

From the above experimental results it can be concluded that the reaction between lactic acid and Alamine 336 in decanol in a stirred cell falls in Regime 3, extraction accompanied by a fast chemical reaction occurring in the diffusion film.

### 3.2.3 Order of reaction

**3.2.3.1 Order with respect to lactic acid.** The aqueous phase lactic acid concentration was varied from  $0.1 \text{ kmol m}^{-3}$  to  $0.25 \text{ kmol m}^{-3}$ . Figure 12 shows the effect of organic phase lactic acid concentration on

**Figure 10.** Effect of speed of agitation on specific rate of extraction of lactic acid with Alamine 336 in decanol (initial lactic acid concentration =  $0.65 \text{ kmol m}^{-3}$ ; Alamine concentration in organic phase =  $0.41 \text{ kmol m}^{-3}$ ).



**Figure 11.** Effect of phase ratio on the specific rate of extraction of lactic acid with Alamine 336 in decanol (initial lactic acid concentration =  $0.53 \text{ kmol m}^{-3}$ ; Alamine concentration in organic phase =  $0.41 \text{ kmol m}^{-3}$ ; speed of agitation =  $1.07 \text{ rev s}^{-1}$ ).

specific rate of extraction,  $R_A$ . A regression analysis of the data yielded  $m = 1$  (as per eqn (1)). Thus, the reaction is first order with respect to lactic acid.

**3.2.3.2 Order with respect to Alamine 336.** Figure 13 shows a plot of the specific rate of extraction of lactic acid against initial Alamine 336 concentration in the organic phase. Evidently there is no effect of Alamine 336 concentration on the rate of extraction, indicating that the reaction is zero order in Alamine 336 ( $n = 0$  in eqn (1)).

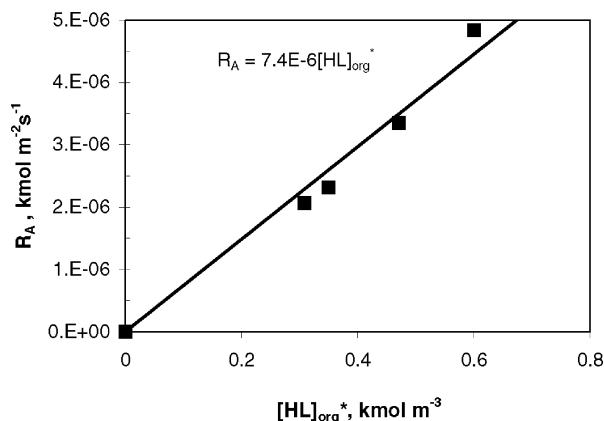
#### 3.2.4 Rate constant

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

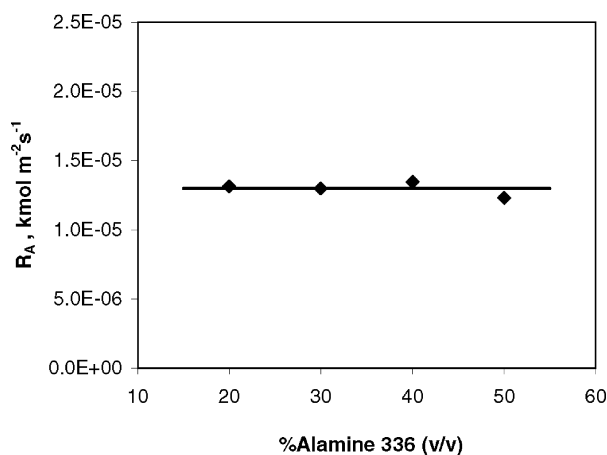
$$R_A = [\text{HL}]_{\text{org}}^* \sqrt{D_A k_1} \quad (22)$$

The data were fitted to eqn (22) to obtain the value of the first order rate constant,  $k_1$ , as  $0.21 \text{ s}^{-1}$

To confirm that Regime 3 holds, the value of the parameter  $\sqrt{D_A k_1}/k_L$  was evaluated.<sup>34</sup> It was found



**Figure 12.** Effect of initial lactic acid concentration on specific rate of extraction of lactic acid with Alamine 336 in decanol (Alamine concentration in organic phase =  $0.41 \text{ kmol m}^{-3}$ ; speed of agitation =  $1.07 \text{ rev s}^{-1}$ ).



**Figure 13.** Effect of initial Alamine 336 concentration on specific rate of extraction of lactic acid with Alamine 336 in decanol (initial lactic acid concentration =  $0.54 \text{ kmol m}^{-3}$ ; speed of agitation =  $1.07 \text{ rev s}^{-1}$ ).

that for the range of  $k_L$  values (Fig 9)  $\sqrt{D_A k_1}/k_L \cong 8$  or greater than 3 which is the condition for the validity of Regime 3. Thus, the above mentioned results reflect the intrinsic kinetics of the extraction process.

Further, Alamine 336 is a surface active solvent. Hence, Alamine molecules may concentrate at the interface, with nitrogen lone pairs pointing towards the water. Lactic acid would be distributed evenly throughout the aqueous phase and would diffuse through that phase on a first order basis. Therefore, there is possibility of a reaction at the interface that is zero order with respect to Alamine and first order with respect to lactic acid.

However, in the present case the solubility of lactic acid in the organic phase is higher than that in water. On the other hand the organic amine has practically negligible solubility ( $< 5 \text{ ppm}$ )<sup>35</sup> in the aqueous phase.<sup>30</sup> Thus, there is reason to believe that the reaction takes place in the organic phase where ionized species do not exist. This argument further supports the finite kinetics observed in the stirred cell experiments.

## 4 CONCLUSION

Physical and chemical equilibria for lactic acid extraction by Alamine 336 in decanol as a diluent have been determined. The extent to which the organic phase (amine + decanol) may be loaded with lactic acid is expressed as a loading ratio,  $z = [\text{HL}]_{\text{aq}}/[\text{B}]_{\text{org}}$ . Calculations based on the stoichiometry of the reactive extraction and the equilibria involved indicated that more lactic acid is transferred to the organic phase than would be expected from a 1:1 stoichiometry of the reaction. The extraction equilibrium was interpreted as a result of consecutive formation of two acid-amine species with stoichiometries of 1:1 and 2:1. The equilibrium complexation constants for (1:1) and (2:1) lactic acid-Alamine 336 complexes in decanol have been estimated.



The theory of extraction accompanied by chemical reaction has been used to obtain the kinetics of extraction of lactic acid by Alamine 336 in decanol. The reaction between lactic acid and Alamine 336 in decanol 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 Alamine 336 and first order in lactic acid with a rate constant of  $0.21\text{ s}^{-1}$ . These data will be useful in the design of extraction processes.

## REFERENCES

- Buchta K, Lactic acid. *Biotechnology* 3:409–412 (1983).
- Datta R, Tsai SP, Bonsignore P, Moon SH and Frank JR, Technology and economic potential of poly(lactic acid) and lactic acid derivatives. *FEMS Microbio Rev* 16:221–231 (1995).
- Lipinsky ES and Sinclair S, Is lactic acid a commodity chemical? *Chem Eng Prog* 82:26–32 (1986).
- Chaudhuri JB and Pyle DL, Emulsion liquid membrane extraction of organic acids. 1. A theoretical model for lactic acid extraction with emulsion swelling. *Chem Eng Sci* 47(1):41–48 (1992).
- Eyal AM and Bressler E, Mini-review industrial separation of carboxylic acid and amino acids by liquid membranes: applicability, process considerations and potential advantages. *Biotechnol Bioeng* 41:287–295 (1993).
- Shreve RN and Brink JA, *Chemical Process Industries*, 4th edn, McGraw-Hill, New York. pp 542 (1977).
- Nomura Y, Iwahara M and Hongo M, Lactic acid production by electro dialysis fermentation using immobilized growing cells. *Biotech Bioeng* 30:788–793 (1987).
- Wardell JM and King CJ, Solvent equilibria for extraction of carboxylic acids from water. *J Chem Eng Data* 23:144–148 (1978).
- Baniel AM, Blumbrerg R and Hadju K, Recovery of acids from aqueous solutions, US Patent 4,275,234 (1981).
- Kertes AS and King CJ, Extraction chemistry of fermentation product carboxylic acids. *Biotech Bioeng* 28:269–282 (1986).
- Tamada JA, Kertes AS and King CJ, Extraction of carboxylic acids with amine extractants. 1. Equilibria and law of mass action modeling. *Ind Eng Chem Res* 29:1319–1326 (1990).
- Tamada JA, Kertes AS and King CJ, Extraction of carboxylic acids with amine extractants. 2. Chemical interactions and interpretation of data. *Ind Eng Chem Res* 29:1327–1333 (1990).
- Yabannavar VM and Wang DIC, Extractive fermentation for lactic acid production. *Biotech Bioeng* 37:1095–1100 (1991).
- King CJ, Amine-based systems for carboxylic acid recovery. *Chemtech* 5:285–291 (1992).
- Hauer E and Marr R, Liquid extraction in biotechnology. *Int Chem Eng* 34(2):178–187 (1994).
- Moueddeb H, Sanchez J, Bardot C and Fick M, Membrane bioreactor for lactic acid production. *J Membrane Sci* 114:59–71 (1996).
- Jaung R and Huang R, Kinetic studies on lactic acid extraction with amine using a microporous membrane-based stirred cell. *J Membrane Sci* 129:185–196 (1997).
- Baniel AM, Process for the extraction of organic acids from aqueous solution, EP 0 049 429 (1982).
- Sirman T, Pyle DL and Grandison AS, Extraction of organic acids using a supported liquid membrane. *Biochem Soc Trans* 19(3):274–279 (1991).
- Kaufman EN, Cooper SP and Davison BH, Screening of resins for use in a biparticle fluidized-bed bioreactor for the continuous fermentation and separation of lactic acid. *Appl Biochem Biotech* 45–46:545–554 (1994).
- Cockrem MCM and Johnson PD, Recovery of lactate and lactic acid from fermentation broth, USP 5 210296 (1991).
- Hongo M, Nomura Y and Iwahara M, Novel method lactic acid production by electro dialysis fermentation. *Appl Environ Microbiol* 52(2):314–319 (1986).
- Heriban V, Skara J, Sturdik E and Ilavsky J, Isolation of the lactic acid using electro dialysis. *Biotech Tech* 7(1):63–68 (1987).
- Lee EG, Moon S, Chang YK, Yoo I and Chang HN, Lactic acid recovery using two-stage electro dialysis and its modelling. *J Membrane Sci* 145:53–66 (1998).
- Timmer JKM, Kromkamp J and Robbertsen T, Lactic acid separation from fermentation broth by reverse osmosis and nanofiltration. *J Membrane Sci* 92:185–197 (1994).
- Wennersten R, Extraction of carboxylic acid from fermentation broth using solution of tertiary amine. *J Chem Technol Biotechnol* 33B:85–94 (1983).
- Ricker NL, Michaels JN and King CJ, Solvent properties of organic bases for extraction of acetic acid from water. *J Separ Proc Technol* 1:36–41 (1979).
- Poposka FA, Nikolovski K and Tomovska R, Kinetics, mechanism and mathematical modeling of extraction of citric acid with isodecanol/*n*-paraffins solutions of trioctylamine. *Chem Engg Sci* 53(18):3227–3237 (1998).
- Ricker NL, Pittman EF and King CJ, Solvent extraction with amines for recovery of acetic acid from dilute aqueous industrial streams. *J Separ Proc Technol* 1(2):23–30 (1980).
- Ratchford WP, Harris EH, Fisher CH and Willits CD, Extraction of lactic acid from water solution. *Ind Eng Chem* 43:778–781 (1951).
- King CJ, in *Handbook of Solvent Extraction*, Ed by Lo TC, Baird MH and Hanson C, New York, Wiley-Interscience. pp 567–573 (1983).
- San-Martin M, Pazos C and Coca J, Reactive extraction of lactic acid with alamine 336 in the presence of salts and lactose. *J Chem Technol Biotechnol* 54:1–6 (1992).
- Doraiswamy LK and Sharma MM, *Heterogeneous Reaction: Analysis, Examples, and Reactor Design*, Vol 2: *Fluid-Fluid-Solid-Reactions*, 1st Ed, John Wiley & Sons, New York. pp 17–41 (1984).
- San-Martin M, Pazos C and Coca J, Reactive extraction of lactic acid with alamine 336. *J Chem Technol Biotechnol* 65:281–285 (1996).
- Henkel/MID Extraction Technology, Tucson, AZ, USA, BLUELINE Bulletin on Alamine 336 (Tricaprylyl Amine).