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Equilibrium studies on reactive extraction of lactic acid with an amine extractant

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Abstract

Equilibrium studies on the extraction of lactic acid from aqueous solutions with tri-*n*-octylamine (TOA) in xylene were made in the temperature range 293–323 K. The formulation of the extracted species in the organic phase and the corresponding equilibrium constants were numerically determined at different temperatures. Also, the apparent thermodynamic functions were calculated. Finally, the effect of a water-insoluble organic acid, di(2-ethylhexyl)phosphoric acid (D2EHPA), on this extraction was investigated. Synergistic and antagonistic effects were observed in the presence of D2EHPA, mainly depending on the concentration ratio of D2EHPA to TOA.

Keywords: Reactive extraction; Equilibrium; Lactic acid; Tri-*n*-octylamine; Di(2-ethylhexyl)phosphoric acid; Synergistic effect

1. Introduction

The possibility of recovery of carboxylic acids from aqueous streams such as fermentation broths and wastewaters by solvent extraction has received increasing attention [1,2]. The traditional solvents such as ketones, alcohols, ethers, and esters give rather low distribution ratios, making the extraction inefficient especially when applied to dilute acid solutions. In this respect, a solvent giving a higher distribution ratio is needed. This leads to the use of specific extractants through reversible chemical complexation [1].

When phosphorus-based oxygen-containing extractants are used for recovering citric acid from a fermentation medium, a stable emulsion exists which is difficult to break up [2]. Amine extractants are consequently suggested to be particularly suitable for the recovery of aliphatic carboxylic acids [2–24]. According to whether solution pH is less or greater than the pK_a of the acid, tertiary and quaternary amines have been found to be probably better choices than primary and secondary amines, since the latter two amines can react irreversibly when heated (in distillation or in back-extraction processes) with the acids to form amides [3–5].

The use of tertiary amines including tri-*n*-octylamine (TOA), triisooctylamine, and Alamine 336 for the extraction of lactic acid from aqueous streams has been often reported [14–24]. Although the stoichiometry of lactic acid–amine extraction systems has been studied, there is no general agreement. The formation of a (1, 1) acid–amine complex has been commonly suggested [16–19]. In addition to this, (p, 1) complexes with $p = 2$–3, depending on the nature of the diluents, were proposed to fit the distribution data [19]. Prochazka et al. [16] have recently indicated the formation of (1, 1), (2, 1) and (2, 2) complexes for the extraction of lactic acid by trialkylamine in mixtures of 1-octanol–*n*-hexane. Moreover, many problems in this subject appear to be unclear, for example the quantitative description of the effect of amine and acid concentrations on the change in complex composition.

In this paper, the compositions of lactic acid–TOA complexes were numerically determined by a modified LETAGROP-DISTR program [25–27], and the effect of amine and acid concentrations on complex formation was quantitatively studied. The effect of temperature on the extraction of lactic acid with TOA was also examined. In the pioneer work of Baniel [15], moreover, carboxylic acids such as citric and lactic acids were extracted with mixtures of tertiary amine and a water-immiscible organic acid. The role of such hydrophobic acids was not clarified in his patent. As mentioned above, a high distribution ratio is a prerequisite for economical recovery by solvent extraction; the effect of a water-insoluble organic acid, di(2-ethylhexyl)phosphoric acid (D2EHPA), on the extraction of lactic acid with TOA was therefore investigated.

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2. Experimental details

2.1. Reagents and solutions

Deionized water produced by a Millipore Milli-Q Water System was used in this work. TOA and D2EHPA were the products of Tokyo Chemical Industry Co. Ltd., Japan, and Merck Co. respectively. They both had a purity of about 98.5% and were used as received. Lactic acid, xylene, and other inorganic chemicals were supplied by Sigma Chemical Co., as analytical reagent grade, and all were used without further purification. Lactic acid, a concentrated aqueous solution, was diluted to 15 wt.% and depolymerized by boiling under reflux condenser for 10 h [16,19]. The aqueous solution was prepared by diluting such acid solution in deionized water without pH adjustment. The organic solution was prepared by diluting TOA and/or D2EHPA in xylene.

2.2. Experimental procedure

For measuring the distribution ratio of lactic acid, equal volumes (40 cm^3) of the organic and aqueous solutions were mixed in glass flasks by a magnetic stirrer for at least 12 h. The two phases were separated after they had been allowed to settle for 1 h. Experiments were performed in the temperature range 293–323 K. After phase separation, the concentration of lactic acid in the aqueous phase was determined by potentiometric titration with a known NaOH using a Radiometer autotitrator model RTS82. The concentration of lactic acid in the organic phase was similarly determined but with an isopropyl alcohol solution of NaOH. Each experiment was duplicated under identical conditions. The distribution ratio of the acid was calculated as the ratio of the molarity of the acid in the organic phase to that in the aqueous phase. In some cases the mass balance of the acid does not involve organic and aqueous phase titrations; in such instances the data are based on only the aqueous phase titration values. In such cases the errors do not exceed 5%.

3. Results and discussion

3.1. Extraction of lactic acid with pure xylene

It is known that most carboxylic acids mainly exist as dimers in the organic phase owing to the strong intermolecular hydrogen bonding, especially in non-polar or slightly polar solvents such as xylene [1]. In the aqueous phase, on the contrary, they exist mainly as monomers because the intermolecular hydrogen bonding between the acids is destroyed owing to their preferential hydrogen bonding with water molecules.

As the aqueous pH is far less than the dissociation constant of lactic acid ($pK_a = 3.86$), we have the following reactions:

$$\mathrm{HA} \rightleftharpoons \overline{\mathrm{HA}};\ K_d \tag{1}$$

$$2\overline{\mathrm{HA}} \rightleftharpoons \overline{(\mathrm{HA})_2};\ K_2 \tag{2}$$

$$\mathrm{HA} \rightleftharpoons \mathrm{H}^+ + \mathrm{A}^-;\ K_a \tag{3}$$

where the overbar refers to the organic phase.

The total concentrations $[\overline{\mathrm{HA}}]_t$ and $[\mathrm{HA}]_t$ of lactic acid at equilibrium in the organic and aqueous phases are obtained as follows:

$$[\overline{\mathrm{HA}}]_t = [\overline{\mathrm{HA}}] + 2[\overline{(\mathrm{HA})_2}] \tag{4}$$

$$[\mathrm{HA}]_t = [\mathrm{HA}] + [\mathrm{A}^-] \tag{5}$$

Thus, the distribution ratio D_0 of lactic acid in the absence of TOA and D2EHPA (i.e. physical extraction) is given by

$$\begin{aligned} D_0 &= [\overline{\mathrm{HA}}]_t/[\mathrm{HA}]_t \\ &= (K_d + 2K_d^2K_2[\mathrm{HA}])/(1 + K_a/[\mathrm{H}^+]) \end{aligned} \tag{6}$$

Here, the concentration [HA] of the undissociated acid in the aqueous phase can be obtained from Eq. (5) and the measured equilibrium pH, that is $[\mathrm{A}^-] = [\mathrm{H}^+]$.

The lowest data points in Fig. 1 shows the measured results. Evidently, K_2 and K_d can be determined from the slope and intercept of the plot of D_0 vs. [HA], and in this way they are found to be 2.55×10^2 dm^3 mol^{-1} and 1.97×10^{-3} respectively. As expected, the value of K_d obtained here is significantly smaller than those in oxygen-containing diluents (active diluents) such as alcohols, ethers, and ketones [1].

3.2. Extraction of lactic acid with tri-n-octylamine

Fig. 1 also shows the distribution ratio of elastic acid extracted with TOA as a function of initial acid and TOA

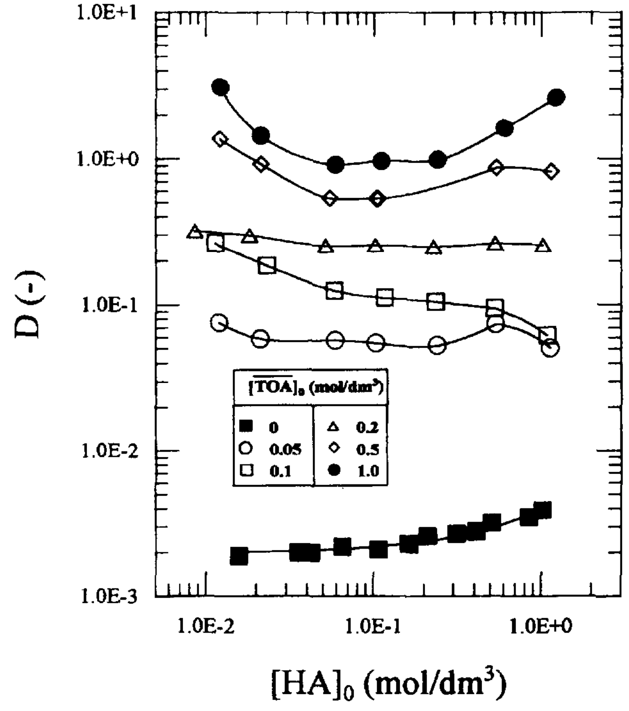

Fig. 1. Extraction of lactic acid with TOA at 293 K.

concentrations. It is found that the distribution ratio increased with TOA concentration. Nevertheless, at a fixed TOA concentration the distribution ratio has no certain dependence with respect to initial acid concentration, although the acid concentration in the organic phase still increases.

It has been shown that tertiary amines (e.g. Alamine 336) extract only the undissociated molecules of carboxylic acids [4]. Therefore, the extraction of lactic acid with TOA at $\mathrm{pH} < \mathrm{p}K_a$ can be expressed by the following stoichiometric relation:

$$p\mathrm{HA} + q\overline{\mathrm{TOA}} \rightleftharpoons \overline{(\mathrm{HA})_p(\mathrm{TOA})_q};\ K_{pq} \tag{7}$$

For amine extraction of carboxylic acids, it was reported that there exists a different extent of water coextraction in the organic phase and this strongly depends on the types of diluents and the nature of the acids used [6–8,21]. As often done previously [5,10,12–14,16–19], such an effect is not considered here for simplicity. In this instance, the extraction equilibrium constant, K_{pq} of Eq. (7) is given by

$$K_{pq} = [\overline{(\mathrm{HA})_p(\mathrm{TOA})_q}]/[\mathrm{HA}]^p[\overline{\mathrm{TOA}}]^q \tag{8}$$

The total concentration of lactic acid in the organic phase satisfies

$$\begin{aligned}[\overline{\mathrm{HA}}]_t &= [\overline{\mathrm{HA}}] + 2[\overline{(\mathrm{HA})_2}] + \sum_p\sum_q p[\overline{(\mathrm{HA})_p(\mathrm{TOA})_q}] \\ &= K_d[\mathrm{HA}] + 2K_2K_d^2[\mathrm{HA}]^2 \\ &\quad + \sum_p\sum_q pK_{pq}[\mathrm{HA}]^p[\overline{\mathrm{TOA}}]^q \end{aligned} \tag{9}$$

Eq. (9) means that the amount of lactic acid complexed with TOA is corrected by subtracting that physically extracted by pure diluent from the measured $[\overline{\mathrm{HA}}]_t$. The term $[\overline{\mathrm{TOA}}]$ in Eqs. (8) and (9) is calculated from the following mass balance equation since the solubility of TOA in acidic aqueous solution is negligibly small [2]:

$$\begin{aligned}[\overline{\mathrm{TOA}}]_0 &= [\overline{\mathrm{TOA}}] + \sum_p\sum_q q[\overline{(\mathrm{HA})_p(\mathrm{TOA})_q}] \\ &= [\overline{\mathrm{TOA}}] + \sum_p\sum_q qK_{pq}[\mathrm{HA}]^p[\overline{\mathrm{TOA}}]^q \end{aligned} \tag{10}$$

The LETAGROP-DISTR computer program was originally developed to analyse the distribution data of a component between two phases using the least-squares error method [25]. The "best" equilibrium constants for the formation of a set of complexes with up to four components can be calculated. This program was extended to five-component systems and was successfully applied to treat the distribution data for the extraction of metals with organophosphoric acids [26,27]. Now, we further modify it by eliminating one system variable to analyse the equilibrium data for the extraction of carboxylic acids with amines, since here the extraction reaction involves three reactive species (Eq. (7)), rather than four in the case of metal extraction with extractants [26,27].

In this calculation, the computer searches for the best set of equilibrium constants for a given model that would minimize the error squares sum defined by

$$U = \sum(\log D_{\mathrm{expt}} - \log D_{\mathrm{calc}})^2 \tag{11}$$

where D_{expt} is the measured distribution ratio of acid and D_{calc} is the distribution ratio calculated by the program considering the above mass balance equations (Eqs. (9) and (10)). This program also calculates the standard deviation $\sigma(\log D)$ defined by

$$\sigma(\log D) = (U/N_p)^{1/2} \tag{12}$$

where N_p is the number of degrees of freedom, that is the difference between total number of data points and total number of equilibrium constants calculated.

The values tried in this study are $p = 1$–4 and $q = 1$–2, which are inferred from the literature results [16,19]. The calculated results at 293 K are listed in Table 1. It is observed that simultaneous formation of (1, 1), (1, 2) and (3, 1) complexes can fit the distribution data best. The equilibrium constants calculated are $K_{11} = 1.31\ \mathrm{dm^3\ mol^{-1}}$, $K_{12} = 8.08 \times 10^{-2}\ (\mathrm{dm^3\ mol^{-1}})^2$, and $K_{31} = 0.95\ (\mathrm{dm^3\ mol^{-1}})^3$ at 293 K. It is evident that overloading, i.e. complexes with more than one acid per amine, occurs. Although some researchers [17,18] indicated that lactic acid forms only the (1, 1) complex with tertiary amines, the present results are somewhat similar to those obtained for Alamine 336 in chloroform and methyl isobutyl ketone [19] and for trialkylamine in 1-octanol–*n*-hexane [16], in which the formation of (2, 1) and/or (3, 1) complexes is suggested.

The overloaded complex (3, 1) rather than (2, 1) obtained here may be understood from the findings of Chaikhorskii et al. [9] for the extraction of acetic acid by tridecylamine in carbon tetrachloride. They studied the IR spectra of the complexes and proposed that an additional acid is hydrogen bonded to the (2, 1) complex to form a cyclic arrangement around the amine nitrogen atom, with the proton associated with the two oxygen atoms near it. This would lead to a more stable (3, 1) complex, in comparison with (2, 1) complex.

In addition to (1, 1) and (3, 1) stoichiometries observed, a multiamine complex (1, 2) is obtained in this study. This is possibly due to the effect of the hydroxyl group of lactic acid. It is reported that an octanol diluent allows for significant (1, 2) complex formation with succinic acid and Alamine 336 [19]. In addition, Gusakova et al. [11] showed that the malonic acid and triethylamine in methanol form a (1, 2) complex, whereas in dioxane and chloroform they do not. This is explained by the fact that the alcohol hydroxyl group interferes with the intramolecular hydrogen bond of malonic acid, thus facilitating the formation of multiamine complexes [19].

Figs. 2 and 3 show the mole fraction of species present in the organic phase as a function of initial acid concentration. These results are obtained by solving Eqs. (9) and (10), coupled with the measured distribution ratios. At low TOA concentration (Fig. 2), the mole fraction of (1, 1) complex

Table 1
Results of the numerical calculation obtained at 293 K for various model species $\overline{(\mathrm{HA})_p(\mathrm{TOA})_q}$

Model	Species (p, q)	$\log K_{pq}$ [a,b]	10.554	$\sigma(\log D)$	Rejected [c]
I	(1, 1)	0.174 ± 0.154	1.554	0.240	
II	(1, 2)	1.464 (maximum 1.762)	10.31	0.618	
III	(2, 1)	0.688 (maximum 1.012)	9.662	0.598	
IV	(3, 1)	3.301 (maximum 3.682)	23.90	0.941	
V	(4, 1)	5.315 (maximum 5.692)	36.50	1.163	
VI	(1, 1)	0.134 ± 0.162	1.344	0.227	
	(1, 2)	0.023 (maximum 0.402)			
VII	(1, 1)	0.124 ± 0.173	1.347	0.228	
	(2, 1)	−0.122 (maximum 0.231)			
VIII	(1, 1)	0.140 ± 0.170	1.273	0.221	
	(3, 1)	−0.032 (maximum 0.401)			
IX	(1, 1)	0.148 ± 0.154	1.310	0.224	
	(4, 1)	−0.158 (maximum 0.209)			
X	(1, 1)	0.093 ± 0.251	1.334	0.231	
	(1, 2)	−1.034 (maximum −0.224)			
	(2, 1)	−0.080 (maximum 0.385)			
XI	(1, 1)	0.118 ± 0.154	1.266	0.225	
	(1, 2)	−1.093 (maximum −0.328)			
	(3, 1)	−0.023 (maximum 0.321)			
XII	(1, 1)	0.137 ± 0.159	1.273	0.226	(2, 1)
	(2, 1)				
	(3, 1)	−0.038 (maximum 0.264)			
XIII	(1, 1), (2, 1), (4, 1)		1.303	0.228	
XIV	(1, 1), (3, 1), (4, 1)		1.273	0.226	(4, 1)
XV	(1, 1), (1, 2), (4, 1)		1.310	0.229	
XVI	(1, 1), (1, 2), (2, 1), (3, 1)		1.266	0.230	(2, 1)
XVII	(1, 1), (1, 2), (3, 1), (4, 1)		1.266	0.230	(4, 1)
XVIII	(1, 1), (2, 1), (3, 1), (4, 1)		1.273	0.231	

[a] The error given corresponds to $3\sigma(\log K)$.
[b] The maximum value given corresponds to $\log[K + 3\sigma(K)]$.
[c] The species were rejected by the program since the equilibrium constants were set equal to zero.

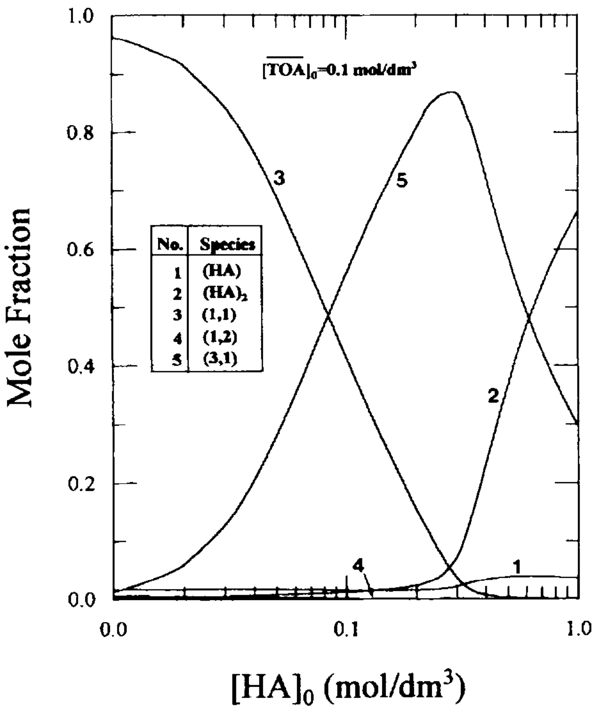

Fig. 2. Mole fraction of each species present in the organic phase at 293 K.

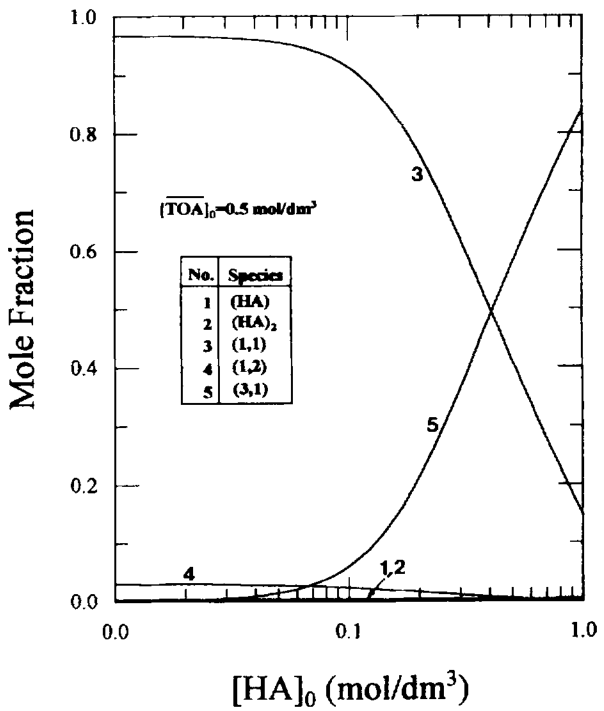

Fig. 3. Mole fraction of each species present in the organic phase at 293 K.

continuously decreases when $[HA]_0$ is increased, whereas that of (3, 1) complex initially increases and then reaches a maximum for acid concentration up to 1.0 mol dm^{-3}. At high TOA concentration (Fig. 3), it is also found that the dominant complex is (1, 1) at low $[HA]_0$ and becomes (3, 1) at higher $[HA]_0$. Furthermore, the preferential formation of (3, 1) complex over (1, 1) occurs at $[HA]_0 = 0.08$ mol dm^{-3} and 0.40 mol dm^{-3} in the cases of $[\overline{TOA}]_0 = 0.1$ mol dm^{-3} and 0.5 mol dm^{-3} respectively. Such a behaviour probably results from an accompanying close organic loading, defined as the total acid concentration in the organic phase divided by initial TOA concentration [19]. It is worth noting that the contributions of the multiamine complex (1, 2), as well as of the uncomplexed lactic acid monomer, are negligibly small in the ranges studied. Similar results were mentioned by Prochazka et al. [16] for the extraction of lactic acid by trialkylamine in 1-octanol–*n*-hexane. They found that ignorance of the (2, 2) complex has no effect on the model accuracy although the three complexes (1, 1), (2, 1), and (2, 2) were suggested.

3.3. *Effect of temperature on acid extraction with tri-n-octylamine*

The effect of temperature on the extraction of lactic acid is shown in Fig. 4. As indicated earlier [21], the complexation reactions of acid and amine in the organic phase involve proton transfer or hydrogen bond formation and are therefore expected to be exothermic. Also, formation of a complex makes the system more ordered and therefore decreases the entropy. Thus, as the temperature is increased, the amount of acetic acid extracted decreases.

Similar computer calculations were performed to treat the data obtained at different temperatures. The temperature corrections of K_d, K_2, and K_a are not considered here [21], and thus those values obtained at 293 K were used. It is observed that the best-fit formulation of the complexes is unchanged with temperature. Fig. 5 illustrates the temperature dependence of the equilibrium constants K_{pq}. It is surprising to find that the value of K_{12} is abnormally small at 293 K. This may imply that the contribution of (1, 2) complex is greater as the temperature is raised. The cause leading to such behaviour remains unclear. If we ignore this data point, the apparent enthalpies and entropies for the formation of complexes can be calculated as described earlier [13,21] and are listed in Table 2. It is found that the formation of (1, 2) complex is nearly unaffected by temperature. Also, 1:1 complexation is much more exothermic and involves a much greater loss of entropy than the formation of (3, 1) complex. Critical comment on such differences is rather difficult to give since K_{pq} obtained here is only an overall constant. However, it is understood that 1:1 complexation involves either hydrogen bonding (carbonyl complex) or ion pair formation (carboxylate complex), but the higher complex (3:1) involves hydrogen bonding only [21].

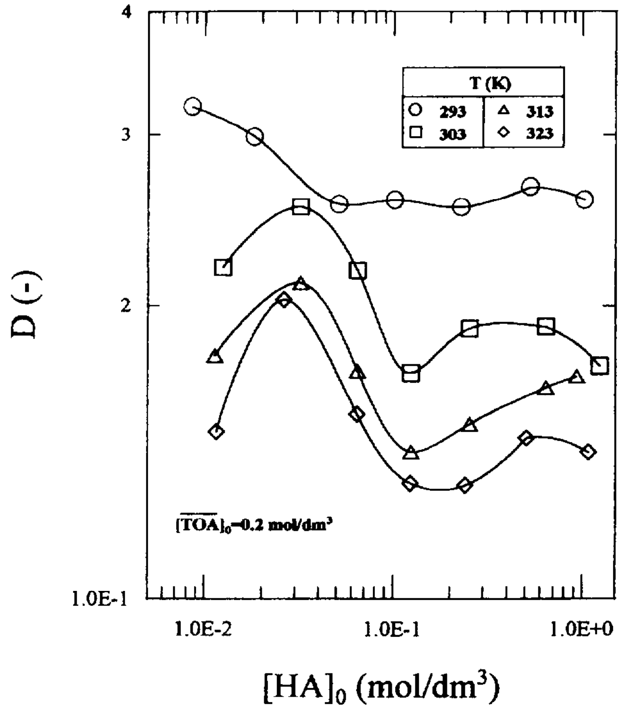

Fig. 4. Effect of temperature on the extraction of lactic acid with TOA.

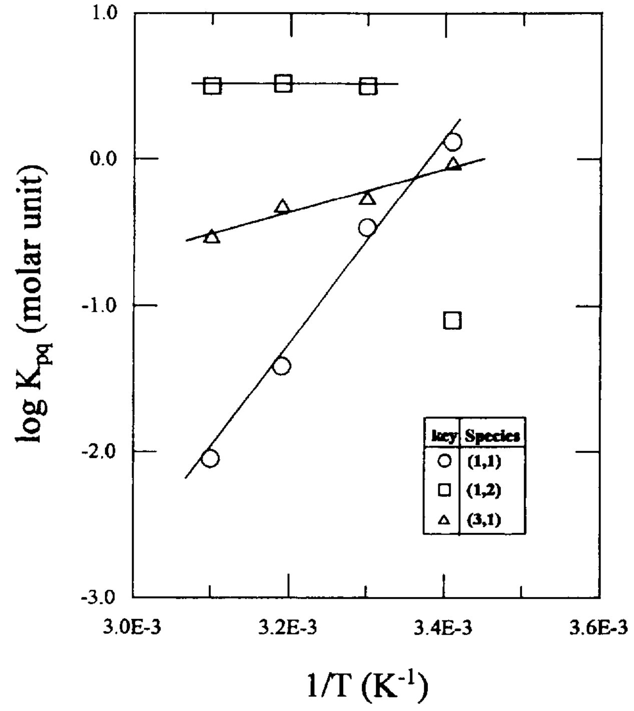

Fig. 5. Temperature dependence of the equilibrium constants K_{pq}.

Table 2
Apparent enthalpies and entropies for the formation of the complex $(HA)_p(\overline{TOA})_q$ in the temperature range 293–323 K

(p, q)	(1, 1)	(1, 2)	(3, 1)
ΔH (kJ mol^{-1})	−137.0	−0.3	−28.7
ΔS (J mol^{-1} K^{-1})	−201.2 ± 8.5	3.8 ± 0.1	−42.9 ± 3.8

3.4. Extraction of lactic acid with tri-n-octylamine and di(2-ethylhexyl)phosphoric acid

The extraction of lactic acid at different concentration ratios β of D2EHPA and TOA is shown in Fig. 6. At this TOA concentration, a synergistic effect, that is $D_s/D>1$, exists when $[\mathrm{HA}]_0>0.02$ mol dm^{-3} and $\beta=0.05$–3, and reaches a maximum at $\beta=1$. In addition, a relatively high value of D_s/D is obtained when $[\mathrm{HA}]_0$ is not far from $[\overline{\mathrm{TOA}}]_0$. The present observations are similar to those obtained for the extraction of citric acid, a tricarboxylic acid, by TOA and D2EHPA in xylene [13].

Attempts were also made to determine the complex formulation for the extraction of lactic acid with TOA and D2EHPA by numerical calculation. Unfortunately, this attempt fails because the complex compositions are rather complicated (up to three types) in the absence of D2EHPA and the interactions among D2EHPA with TOA and the complexes remain unclear. More information, including determination of equilibrium concentrations of free TOA and free D2EHPA in the organic phase and the molecular IR spectra of the complexes, is needed to clarify the reaction stoichiometry.

D2EHPA is a monoacidic organophosphoric extractant that has been widely used for the extraction of metals and is a moderately effective surfactant [13,26,27]. It tends to adsorb at the aqueous–organic interface and then dissociates to hydrogen ions and phosphoryl anions. When D2EHPA (HR) is added in the organic phase, it may react with TOA molecules and/or their acid complexes according to the following equations [13,28]:

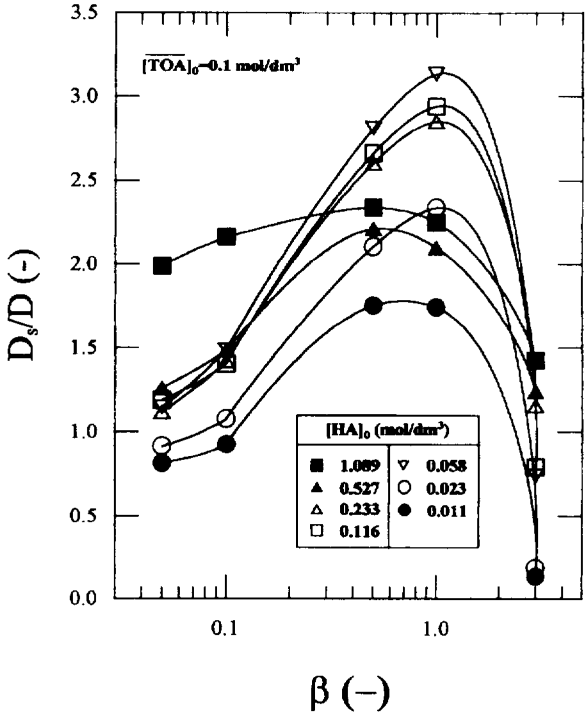

Fig. 6. Extraction of lactic acid with a mixture of TOA and D2EHPA.

$$\overline{(\mathrm{HR})_2}+\overline{\mathrm{TOA}} \rightleftharpoons \overline{(\mathrm{HR})(\mathrm{TOA})}+\mathrm{H}^++\mathrm{R}^- \quad (13)$$

$$\overline{(\mathrm{HA})(\mathrm{TOA})}+(1/2)\overline{(\mathrm{HR})_2} \rightleftharpoons \overline{(\mathrm{HR})(\mathrm{TOA})}+\mathrm{H}^++\mathrm{A}^- \quad (14)$$

where $\overline{(\mathrm{HR})_2}$ denote D2EHPA molecules because they mainly exist as dimers owing to strong intermolecular hydrogen bonding in non-polar diluents.

It is experimentally found that lactic acid is not extractable by D2EHPA alone (not shown) because of the cation exchange nature of D2EHPA. The possible explanation of an antagonistic effect when $\beta>3$ is that D2EHPA would react with TOA according to Eq. (13), thus decreasing the effective TOA concentration for lactic acid extraction. This inference was also confirmed experimentally by the fact that the aqueous pH after extraction is less than that before extraction in these cases.

The above-mentioned effect is also caused when $\beta<3$. However, at low lactic acid concentrations the depolymerization ability of TOA aggregates may be highly improved when a small amount of D2EHPA is added [13,28,29]. It is deduced that the latter effect is comparatively pronounced in the present systems, thereby increasing the extractability. Since organophosphorus compounds such as tributylphosphate and tri-*n*-octylphosphine oxide are frequently used as phase modifiers in solvent extraction systems [30], a small amount of D2EHPA may also enhance the solubility of the lactic acid–TOA complexes in the organic phase, thus increasing the distribution ratio.

4. Conclusions

The reactive extraction of lactic acid from aqueous solutions with TOA and/or D2EHPA in xylene has been studied based on the law of mass action. Simultaneous formation of lactic acid–TOA complexes (1, 1), (1, 2), and (3, 1) is proposed in the organic phase when TOA is used as extractant alone. It is shown that the dominant complex is (1, 1) at low $[\mathrm{HA}]_0$ and becomes (3, 1) at higher $[\mathrm{HA}]_0$. Also, the preferential formation of (3, 1) over (1, 1) occurs at lower $[\mathrm{HA}]_0$ in the case of lower $[\overline{\mathrm{TOA}}]_0$, which may be effected by reaching a close organic loading. The apparent thermodynamic functions for the formation of complexes are listed in Table 2. In the presence of D2EHPA, for the described conditions ($[\overline{\mathrm{TOA}}]_0=0.1$ mol dm^{-3}) a synergistic effect is present at $[\mathrm{HA}]_0>0.02$ mol dm^{-3} and $\beta=0.05$–3, and reaches a maximum at $\beta=1$. Higher D_s/D is obtained when $[\mathrm{HA}]_0$ is not far from $[\overline{\mathrm{TOA}}]_0$.

Acknowledgment

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Appendix A: Nomenclature

D	distribution ratio of lactic acid by TOA (dimensionless)
D_0	distribution ratio of lactic acid by pure diluent (dimensionless)
D_s	distribution ratio of lactic acid by TOA and D2EHPA, (dimensionless)
ΔH	apparent enthalpy change ($\mathrm{kJ\ mol^{-1}}$)
K_2	dimerization constant of lactic acid in the organic phase ($\mathrm{dm^3\ mol^{-1}}$)
K_a	dissociation constant of lactic acid in the aqueous phase ($\mathrm{mol\ dm^{-3}}$)
K_d	distribution constant of the monomeric acid defined in Eq. (1) (dimensionless)
K_{pq}	overall equilibrium constant defined in Eq. (8) ($(\mathrm{mol\ dm^{-3}})^{1-p-q}$)
p	number of lactic acid molecules involved in the complex
q	number of TOA molecules involved in the complex
ΔS	apparent entropy change ($\mathrm{J\ mol^{-1}\ K^{-1}}$)
T	temperature (K)
U	error squares sum defined in Eq. (11)
[ ]	molar concentration of species in the brackets ($\mathrm{mol\ dm^{-3}}$)

Greek letters

β	$[\overline{\mathrm{HR}}]_0/[\overline{\mathrm{TOA}}]_0$, initial concentration ratio of D2EHPA to TOA
σ	standard deviation defined in Eq. (12)

Superscript

—	species in the organic phase

Subscripts

0	initial
min	minimum

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