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Reactive Extraction of Lactic Acid with Trioctylamine/Methylene Chloride/*n*-Hexane

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ABSTRACT

The trioctylamine (TOA)/methylene chloride (MC)/*n*-hexane system was used as the extraction agent for the extraction of lactic acid. Curves of equilibrium and hydration were obtained at various temperatures and concentrations of TOA. A modified mass action model was proposed to interpret the equilibrium and the hydration curves. The reaction mechanism and the corresponding parameters which best represent the equilibrium data were estimated, and the concentration of water in the organic phase was predicted by inserting the parameters into the simple mathematical equation of the modified model. The concentration of MC and the change of temperature were important factors for the extraction and the stripping process. The stripping was performed by a simple distillation which was a combination of temperature-swing regeneration and diluent-swing regeneration. The type of inactive diluent has no influence on the stripping. The stripping efficiencies were about 70%.

INTRODUCTION

The recovery of carboxylic acids from a dilute aqueous solution, such as a fermentation broth or a wastewater stream which has acid concentrations lower than 10 wt%, has recently received increasing attention (1). Among carboxylic acids, lactic acid has been especially considered as a monomer of biodegradable and biocompatible materials. Lactic acid was mainly obtained from the fermentation and the hydration of lactonitrile

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synthesized from hydrogen cyanide and acetaldehyde. The fermentation process, due to various impurities of fermentation broth, needs an economic separation method to compete with the synthetic process (2). Reactive extraction using long-chain aliphatic amine has been studied as an effective and economical separation process of carboxylic acids (3–5). The basic factors affecting reactive extraction were studied, and the mass action model was applied to interpret the equilibrium data. Ratchford et al. (3) studied the effects of amine structure and the solvent properties. King (6) investigated the effects of temperature and composition of an active diluent on reactive extraction. Duyne et al. (7) showed that carboxylic acid exists in the form of a acid–water complex in an organic solvent. Starr et al. (8) studied the effect of water in the organic phase on the extraction of carboxylic acid. Tamada et al. (4) investigated the reaction mechanism of extraction by the mass action model. Bizek et al. (9) performed the extraction of citric acid and introduced the nonidealities of an organic phase into the mass action model. They predicted the concentration of water in the organic phase by assuming the hydration number. Prochazka et al. (10) extended Bizek's results to several carboxylic acids such as lactic, malic, and citric acid. In addition to the correction of nonidealities in the organic phase, they considered the effect of temperature and the dissociation of carboxylic acids in the aqueous phase.

In this study the reactive extraction of lactic acid using trioctylamine (TOA)/methylene chloride (MC)/*n*-hexane was investigated and a modified mass action model was proposed to describe the reactive extraction of lactic acid from fermentation. In addition to the study of the extraction process, various conditions for extraction and of the inactive diluent were also studied. The stripping was effectively performed by simple distillation.

EXPERIMENTAL

Materials

Trioctylamine (TOA), a C_8 straight-chain tertiary amine, was obtained from Janssen Co. and was used as an extractant without further purification. Methylene chloride, 1-octanol, and *n*-decanol were used as active diluents. Hexane, cyclohexane, isooctane, heptane, and chlorobenzene were used as inactive diluents. Lactic acid (20 wt%), obtained from Janssen, was diluted to various concentrations. All reagents were GR grade.

The initial concentration of lactic acid was varied from 0.1 to 2.22 M to obtain equilibrium data by considering the concentration of lactic acid obtained from fermentation. TOA was used at 0.4, 0.6, 0.8, and 1.2 M as the basis of methylene chloride and hexane (4:1 volume ratio) for extraction. The 0.6 M TOA/MC/*n*-hexane system was applied for the stripping of lactic acid.

Experimental Procedures

Lactic acid was extracted and stripped as follows. A 10-mL solution of lactic acid and a 10-mL TOA solution were transferred into a 25-mL vial. Phase mixing was carried out by stirring with a magnetic bar at 1000 rpm for 15 minutes. Two phases were centrifuged at 5000 rpm and 20°C for 15 minutes. In the stripping, extraction was first performed with 100 mL of both phases. The 100-mL extracted organic phase and the 100-mL stripping water (distilled water) were mixed and distilled at 50°C. The active diluent was obtained from the condenser, and the stripped lactic acid was recovered in the reboiler. The variation of temperature was limited to 20 and 35°C due to the low boiling point of methylene chloride.

The concentration of lactic acid was titrated by 0.1 N NaOH using phenolphthalein as indicator. The water concentration in the organic phase was analyzed by a Coulometric Karl-Fisher Titrimeter.

RESULTS AND DISCUSSION

Equilibrium of Reactive Extraction at Various Concentration of TOA

The influence of TOA concentration in the methylene chloride/*n*-hexane phase on equilibrium distribution is shown in Fig. 1. The distribution of lactic acid increases with the concentration of TOA. The 1.0 M solution of TOA was not used since the difference of density between the aqueous and organic phases was very small. As the concentration of TOA increases, the density of the organic phase decreases and phase inversion occurs near 1.0 M TOA/MC/*n*-hexane. The concentration of water in the organic phase was also measured at various concentrations of TOA. As can be seen from Fig. 2, the concentration of water in the organic phase increases with an increase in the concentration of TOA.

Fitting of Experimental Data by Modified Model

Various mass action models have been proposed to interpret the equilibrium data of reactive extraction. In these models, nonidealities in the organic phase were explained by introducing the activity coefficients. Recently, Bizek et al. (9) modified the mass action model to explain the nonidealities of the organic phase and to predict the concentration of water in the organic phase. In this study, instead of correcting the nonidealities by introducing activity coefficients, the mass action model was simply

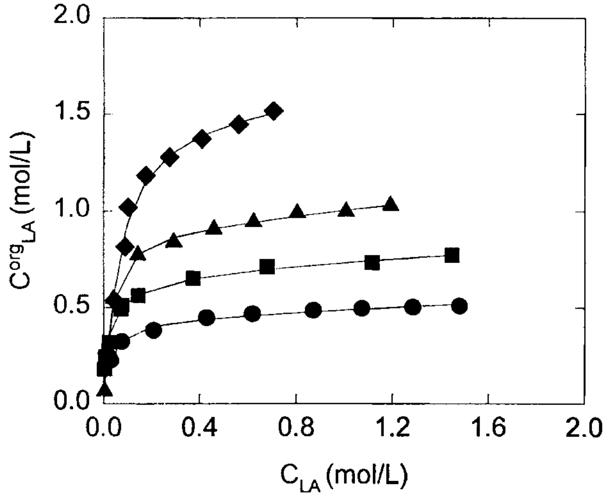

FIG. 1 Equilibrium curves of lactic acid at various concentrations of trioctylamine at 20°C: (●) $\overline{C}^0_{Am}$ = 0.4 mol/L, (■) $\overline{C}^0_{Am}$ = 0.6 mol/L, (▲) $\overline{C}^0_{Am}$ = 0.8 mol/L, (◆) $\overline{C}^0_{Am}$ = 1.2 mol/L. Solid lines: calculated value by modified model.

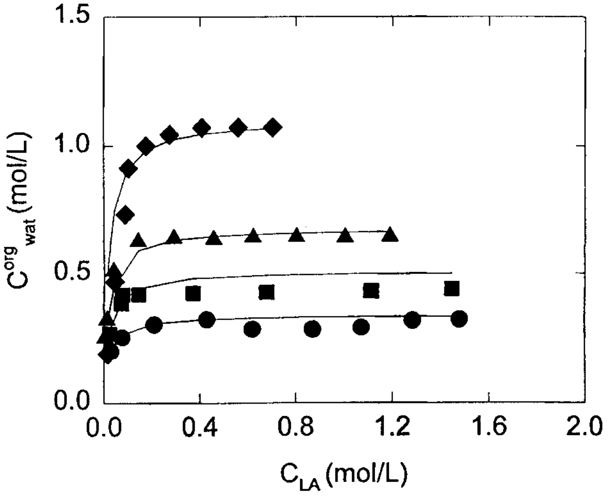

FIG. 2 Prediction of water concentration in the organic phase by parameters at 20°C: (●) $\overline{C}^0_{Am}$ = 0.4 mol/L, (■) $\overline{C}^0_{Am}$ = 0.6 mol/L, (▲) $\overline{C}^0_{Am}$ = 0.8 mol/L, (◆) $\overline{C}^0_{Am}$ = 1.2 mol/L. Solid lines: calculated value by modified model.

modified by adding water as the reaction species. The modified model has several assumptions as follows.

The amine–water–acid complex was assumed based on Duyne et al.'s study (7). This modified complex is obtained from the reaction of amine, water, and acid. The water extraction without lactic acid by amine was assumed based on the structural characteristics of long-chain aliphatic amines. As aliphatic long-chain amines have a similar structure with the surfactant, it acts as the emulsifier and extracts the water into the organic phase. The concentration of water was nearly constant in the aqueous phase because the concentration of extracted water was much smaller than that of raffinate water at equilibrium. However, the extracted water has a considerable effect in the organic phase. The symbols p and q were defined as the hydration numbers of assumed reactions. The moles of amine reacted assumed 1 mol per a moles of lactic acid because lactic acid is a monocarboxylic acid. The physical extraction by active diluent was simply described by a distribution of lactic acid between the aqueous and organic phases. It was assumed that both phases are ideal. Each reaction was analyzed in the equilibrium state. Extraction reactions of lactic acid by a long-chain aliphatic amine can be described as follows.

$$a\text{Lactic acid} + \overline{\text{Amine}} + p\text{H}_2\text{O} \leftrightarrow \overline{\text{Lactic acid}_a\cdot\text{Amine}\cdot(\text{H}_2\text{O})_p} \tag{1}$$

$$\overline{\text{Amine}} + q\text{H}_2\text{O} \leftrightarrow \overline{\text{Amine}\cdot(\text{H}_2\text{O})_q} \tag{2}$$

$$\text{Lactic acid} \leftrightarrow \overline{\text{Lactic acid}} \tag{3}$$

Equilibrium constants of reactions are defined by mass action law as follows.

$$K_1 = \frac{\overline{C}_{\text{L-A-W}}}{C_{\text{LA}}^{a}\overline{C}_{\text{Am}}C_{\text{W}}^{p}} \tag{4}$$

$$K_2 = \frac{\overline{C}_{\text{A-W}}}{\overline{C}_{\text{Am}}C_{\text{W}}^{q}} \tag{5}$$

$$K_3 = \frac{\overline{C}_{\text{LA}}^{\text{phy}}}{C_{\text{LA}}} \tag{6}$$

The concentration of free amine, which was not reacted with lactic acid, was obtained by a simple manipulation. The total concentration of amine is the sum of free amine and the amine of complexes formed by Reactions (1) and (2). By substituting Eqs. (4) and (5) for the concentration of the complexes, the concentration of free amine was obtained as Eq. (7):

$$\overline{C}_{\text{Am}} = \overline{C}_{\text{Am}}^{0} - \overline{C}_{\text{L-A-W}} - \overline{C}_{\text{A-W}} = \frac{\overline{C}_{\text{Am}}^{0}}{1 + K_1 C_{\text{W}}^{p} C_{\text{LA}}^{a} + K_2 C_{\text{W}}^{q}} \tag{7}$$

The concentration of lactic acid in the organic phase is the sum of the lactic acid extracted by Reaction (1) and by physical extraction. Equation (7) was substituted for the concentration of free amine to obtain Eq. (8), the concentration of lactic acid in the organic phase.

$$\overline{C}_{\mathrm{LA}} = a\overline{C}_{\mathrm{L\text{-}A\text{-}W}} + \overline{C}_{\mathrm{LA}}^{\mathrm{phy}} = \frac{aK_1C_{\mathrm{W}}^{p}C_{\mathrm{LA}}^{a}\overline{C}_{\mathrm{Am}}^{0}}{1 + K_1C_{\mathrm{W}}^{p}C_{\mathrm{LA}}^{a} + K_2C_{\mathrm{W}}^{q}} + K_3C_{\mathrm{LA}} \quad (8)$$

The hydration of water in the organic phase is also the sum of water extracted by Reactions (1) and (2). By substituting Eq. (7) for the concentration of free amine, the concentration of water in the organic phase was obtained as Eq. (9):

$$\overline{C}_{\mathrm{W}} = p\overline{C}_{\mathrm{L\text{-}A\text{-}W}} + q\overline{C}_{\mathrm{A\text{-}W}} = \frac{\overline{C}_{\mathrm{Am}}^{0}(pK_1C_{\mathrm{LA}}^{a}C_{\mathrm{W}}^{p} + qK_2C_{\mathrm{W}}^{q})}{1 + K_1C_{\mathrm{LA}}^{a}C_{\mathrm{W}}^{p} + K_2C_{\mathrm{W}}^{q}} \quad (9)$$

As can be seen in the above equations, the expressions are only a function of unreacted lactic acid because the concentration of water in the aqueous phase is nearly constant. The parameters K_1, K_2, K_3, a, p, and q are easily calculated by regressing the experimental equilibrium data. Then the concentration of water in the organic phase was calculated by inserting the parameters obtained from Eq. (8) into Eq. (9).

To verify the proposed model, experimental data were obtained at 20°C and fitted by Eq. (8). The parameters obtained were presented in Table 1. The concentration of water in the organic phase was calculated by inserting the estimated parameters into Eq. (9). Modified reactions were obtained by inserting parameters a, p, and q into Eqs. (1), (2), and (3) as follows.

$$1.122\text{Lactic acid} + \overline{\text{Amine}} + 0.841\mathrm{H_2O} \leftrightarrow \overline{\text{Lactic acid}_{1.122}\cdot\text{Amine}\cdot(\mathrm{H_2O})_{0.841}} \quad (10)$$

$$\overline{\text{Amine}} + 0.371\mathrm{H_2O} \leftrightarrow \overline{\text{Amine}\cdot(\mathrm{H_2O})_{0.371}} \quad (11)$$

$$\text{Lactic acid} \leftrightarrow \overline{\text{Lactic acid}} \quad (12)$$

TABLE 1
The Parameters of Modified Model at 20°C (0.4–1.2 mol/L trioctylamine (TOA)/methylene chloride (MC)/hexane)

Extractant	Volume ratio	K_1	K_2	K_3	a	p	q
TOA/MC/hexane	4(MC/hexane)	3.602	0.305	0.115	1.122	0.841	0.371

As can be seen from Fig. 1, equilibrium data fitted well. Figure 2 shows that the results of the organic water prediction are in good agreement with the experimental data at various concentrations of TOA.

Comparison of Conventional Model and Modified Model

The modified model was compared with the model of Prochazka et al. (10) for the extraction of lactic acid. Extraction data of lactic acid were obtained from Prochazka et al.'s results (10), and their data were fitted by the modified model. As can be seen from Figs. 3 and 4, the modified model gives better results at various concentrations of amine. Especially for the top and bottom lactic acid concentrations, the modified model shows good agreement with the experimental data. Tamada et al. (4) studied the extraction of lactic acid by 0.29 M Alamine 336 in chloroform and in methyl isobutyl ketone. They considered the extraction of lactic acid for a wide range of concentrations from 10^{-5} to 10 mol/L based on the concentration of unreacted lactic acid at equilibrium. As can be seen from Fig. 5, the mass action model of Tamada et al. (4) showed better results than the modified model in the case of chloroform as the diluent. This phenomenon resulted from the applicable concentration range of the

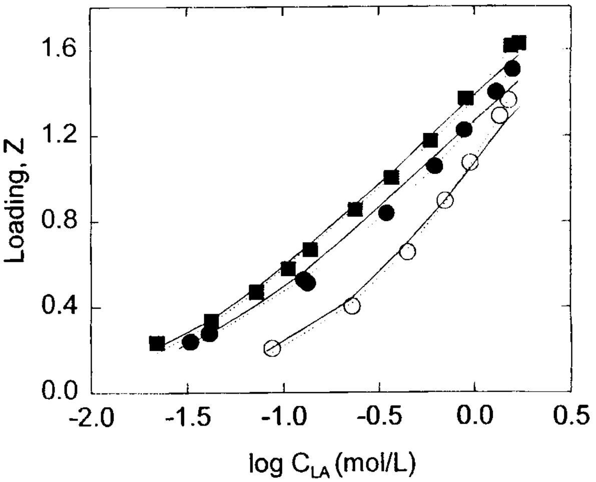

FIG. 3 Comparison of modified model and Prochazka's model at 25°C: (●) $\overline{C}^0_{\mathrm{Am}}$ = 1.130 mol/kg trialkylamine, x = 0.384; (○) $\overline{C}^0_{\mathrm{Am}}$ = 1.210 mol/kg trialkylamine, x = 0.189; (■) $\overline{C}^0_{\mathrm{Am}}$ = 1.910 mol/kg trialkylamine, x = 0.527. Solid lines: Prochazka's model. Dotted lines: Modified model.

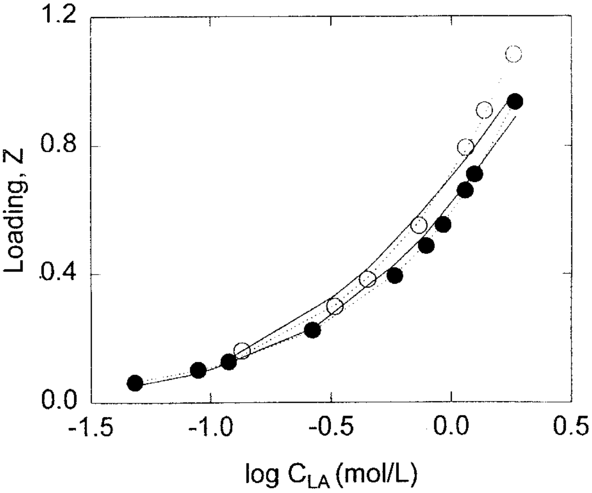

FIG. 4 The comparison of modified model and Prochazka's model at 75°C: (●) $\overline{C}^0_{\mathrm{Am}}$ = 1.040 mol/kg trialkylamine, x = 0.225; (○) $\overline{C}^0_{\mathrm{Am}}$ = 1.040 mol/kg trialkylamine, x = 0.284. Solid lines: Prochazka's model. Dotted lines: Modified model.

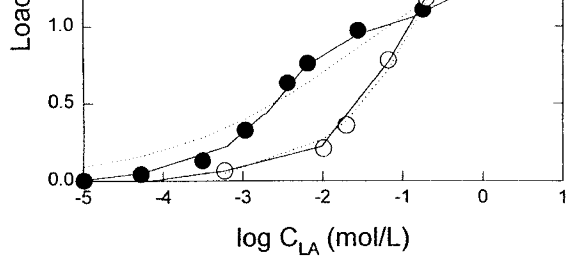

FIG. 5 Comparison of modified model and Tamada's model at 25°C: (●) 0.29 M Alamine 336 in chloroform, (○) 0.29 M Alamine 336 in methyl isobutyl ketone. Solid lines: Tamada's model. Dotted lines: Modified model.

model. However, in the extraction of lactic acid from fermentation, the nonidealities are not severe because of the low concentration (below 10 wt%, 1.11 M) of lactic acid produced by fermentation (1), and the modified model shows reasonable results in the low concentration range of lactic acid.

Effect of the Concentration of Active Diluent on the Extraction Efficiency

Methylene chloride was used in this study as an active diluent because of its low boiling point, excellent extractability, low toxicity, and low cost. Methylene chloride has a low boiling point, about 40°C at atmospheric pressure. The concentration of methylene chloride as an active diluent was varied to measure the stripping power by diluent-swing regeneration (DSR). As can be seen from Fig. 6, the extraction efficiencies sharply increased with an increase of methylene chloride. Therefore, the solubility of the reaction complex in the active diluent as well as the extractability of amine is an important factor in the extraction of lactic acid. The differences of solubilities according to the variation of composition were adequately large for the stripping of lactic acid. Variation of the inactive

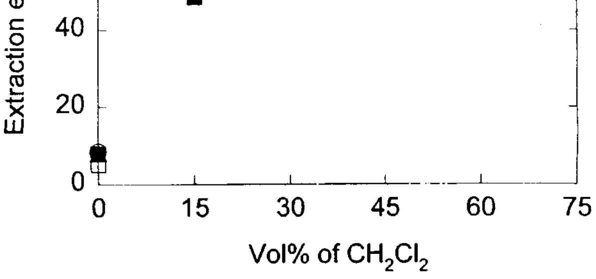

FIG. 6 The effect of concentration of methylene chloride on the extraction of lactic acid at 20°C. Extractant: 0.6 M Trioctylamine. (●) Chlorobenzene, (○) cyclohexane, (■) hexane, (□) heptane, (▲) isooctane.

diluent has little influence on the extraction efficiencies except for polar chlorobenzene.

Effect of Temperature on the Extraction Efficiency

The reaction of amine and acid is an exothermic reaction, so the extraction efficiency of lactic acid decreases with increasing temperature. Experiments were performed at 20 and 35°C because of the boiling point of the active solvent. As can be seen from Figs. 6 and 7, the effect of temperature is smaller than that of composition. In the 0.6 M TOA/1-decanol and 0.6 M TOA/1-octanol systems, the effect of temperature was not large in comparison with the effect of composition in spite of a large variation of temperature (Fig. 8). However, in stripping by simple distillation, temperature swing regeneration (TSR) and diluent swing regeneration (DSR) were both used because a change in the composition of the active diluent is related to an increase in temperature.

Stripping of Lactic Acid by Simple Distillation

The lactic acid extracted had to be stripped for the final production of lactic acid (6). The stripping of lactic acid was generally performed by

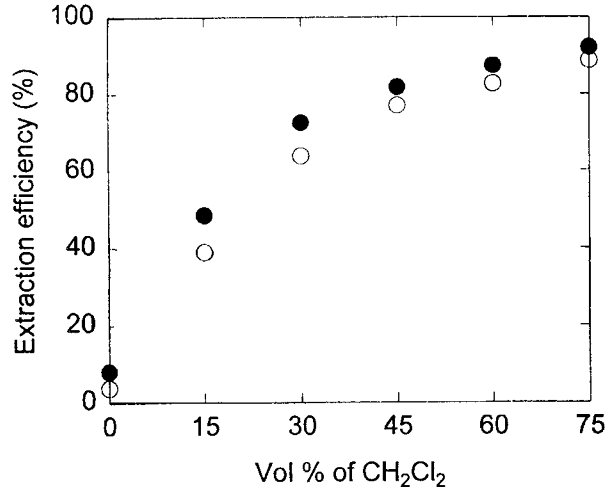

FIG. 7 The effect of temperature on the extraction of lactic acid. Extractant: 0.6 M Trioctylamine/methylene chloride/hexane. (●) 20°C, (○) 35°C.

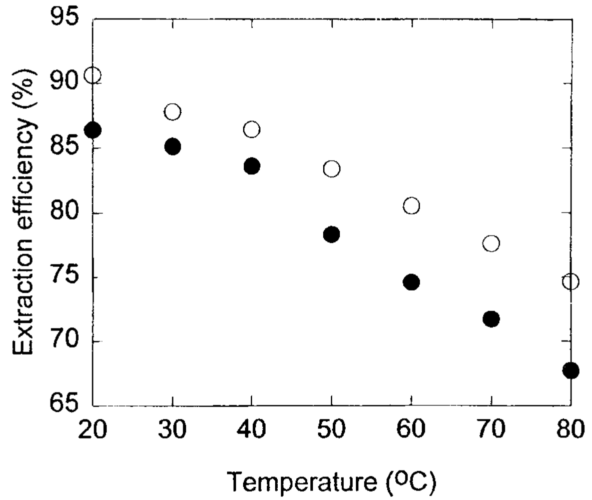

FIG. 8 The effect of temperature on the extraction of lactic acid (*n*-decanol, 1-octanol). Extractant: 0.6 M Trioctylamine. (●) *n*-Decanol, (○) 1-octanol.

TSR or DSR. As mentioned in the previous section, a combination of two processes was recommended for the economic stripping of lactic acid. In this study the lactic acid in the organic phase was stripped by a simple distillation process at 50°C. Lactic acid was stripped in the reboiler, and methylene chloride was condensed and recovered from the condenser for reuse. The stripped lactic acid was nearly pure. As can be seen from Table 2, the stripping efficiencies were about 70% and did not change with the variation of inactive diluent except for polar chlorobenzene.

TABLE 2

The Effect of Various Inactive Diluents on the Stripping Efficiencies. Extractant: 0.6 M Trioctylamine/Methylene Chloride

Inactive diluents	Hexane	Cyclohexane	Heptane	Isooctane	Chlorobenzene
Stripping efficiency (%)	71.23	68.7	68.16	71.06	16.67

ACKNOWLEDGMENT

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DEFINITIONS

$$\text{Loading } (Z) = \frac{\text{concentration of lactic acid in the organic phase}}{\text{initial concentration of amine}}$$

Extraction efficiency (%)

$$= \frac{\begin{array}{c}\text{(initial concentration of lactic acid}\\ -\text{ raffinate concentration of lactic acid)}\end{array}}{\text{initial concentration of lactic acid}} \times 100$$

Stripping efficiency (%)

$$= \frac{\text{stripped concentration of lactic acid}}{\begin{array}{c}\text{(initial concentration of lactic acid}\\ -\text{ raffinate concentration of lactic acid)}\end{array}} \times 100$$

SYMBOLS

C	concentration of materials (mol/L)
K	reaction equilibrium constant
a	moles of lactic acid
p	moles of hydration in Reaction (1)
q	moles of hydration in Reaction (2)
x	mass fraction of (1 − octanol) in diluent (1 − octanol + heptane) for Prochazka's model

Subscripts

L-A-W	complex of lactic acid, water, and amine
W	water
A-W	complex of amine and water
Am	amine
LA	lactic acid
1, 2, 3	number of reactions

Superscripts

0	initial concentration
$\overline{\text{(overbar)}}$	species in the organic phase

$\overline{C}$ concentration in the organic phase
phy lactic acid which was physically extracted

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