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Modeling of Ion-Pairing Extraction with Quaternary Amines

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ABSTRACT

The objective of this work is to present a general methodology and to describe the modeling of ion-pairing extraction of organic acids, including amino acids, with quaternary amines, allowing for the prediction of equilibrium concentrations with different operating conditions. The model takes into account the hydration of the organic phase, thus making it also valid for any organic phase used. A rational design of the operating conditions to be used to optimize extraction and stripping is then possible from simulation studies. The model developed is tested by comparing predictions of equilibrium concentrations with experimental studies using lactate extraction with different amine concentrations. Validation is extended to the stripping process using chloride as the counterion; the model thus obtained adequately describes the extraction and stripping of lactate.

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Key Words. Extraction; Modeling; Ion pairing; Organic acids; Quaternary amines

INTRODUCTION

Recovery of organic acids and amino acids from dilute aqueous solutions, such as fermentation broths and wastewaters, with concentrations lower than 10% (w/w) have high separation and purification costs due to complex and energy intensive recovery technology (1). Liquid extraction using reversible chemical complexation for reactive extraction has been tried as an alternative to the conventional process (2–4).

The chemistry of acid extraction has been investigated recently (5–7). Three different extraction categories were distinguished (5):

1. Acid extraction by solvation with carbon-bonded oxygen-bearing (CBO) extractants.
2. Acid extraction by solvation with phosphorus-bonded oxygen-bearing (PBO) extractants.
3. Acid extraction by proton transfer or by ion-pair (IP) formation, with high molecular weight aliphatic amine extractants.

The first two categories involve solvation of the acid by donor bonds. The strength of the solvation bonds and the specificity of the solvation distinguishes them. Solvation with alcohols, ethers, and ketones, which are typical CBO extractants, is not specific, while the more significant basic donor properties of the PBO extractants cause a specific solvation process (8). PBO extractants contain a phosphoryl group which is a strong Lewis base. The undissociated acid is extracted according to the following stoichiometry:

$$HA + nE \rightleftharpoons HAE_n$$

When using amine extractants, proton transfer occurs during the extraction, and the acid prevails in the organic phase as an amine–acid ion pair. Formation of an ion-pair complex in an acid/base-type reaction can be described as follows:

$$H^+ + A^- + E \rightleftharpoons HAE$$

In some cases the amine base can take up acid in excess, and thus different stochiometries for reactions are involved (9). Long-chain tertiary amines proved to be effective extractants for carboxylic acids. The strong interaction between the acid and the amine facilitates the formation of acid–amine complexes, thereby providing for high equilibrium distribution rates (5).

The use of phosphorus-bonded and amine extractants is limited to acid solutions. Therefore, extraction with phosphorus-based extractants and amines is only possible for a pH lower than the acid pK_a values. At neutral pH, which is the most adequate pH range for most organic acid fermentation processes, only anion exchangers are able to extract the dissociated form of the organic acid. Most work on the separation of amino acids has also been performed using quaternary ammonium salts as extractants (10, 11).

The dissociated acid form is removed from the aqueous phase by ion exchange with the counterion of the positively charged amine, which is dissolved in the organic phase. Counter transport of anions is required to maintain electroneutrality:

$$A^- + R^+X^- \rightleftharpoons R^+A^- + X^-$$

This ion-pairing mechanism presents some important advantages: 1) extraction and fermentation can be carried out at the same pH, eliminating pH adjustment which requires an external loop; 2) coupled transport allows for simultaneous organic acid extraction and concentration if adequate concentrations of the counterion and phase ratio (feed phase volume/organic phase volume/stripping phase volume) are used (12).

The aim of this work is to characterize organic acid extraction using quaternary ammonium salts and to develop a general mathematical model of equilibrium which can be used to predict equilibrium concentrations for any chosen operating conditions.

The outline of the paper is as follows: A model of ion-pairing extraction with quaternary amines is presented. The model parameter is the equilibrium constant, K_e, of the ion-exchange reaction between the dissociated organic acid and the quaternary amine. The model is tested for extraction and stripping of lactate used as an organic acid extraction case study.

The equilibrium constant, K_e, is evaluated from simple equilibrium experiments. Then, using this constant, a significant number of simulation studies is performed in order to optimize the extraction and stripping processes.

The developed model is experimentally validated for extraction using three different amine concentrations and for stripping using a sodium chloride solution.

MODELING EXTRACTION EQUILIBRIUM OF LACTATE WITH QUATERNARY AMINES

Extraction

Aliquat 336 is a quaternary ammonium salt that can exchange its chloride anion with the aqueous phase anions (Fig. 1a). The following reversi-

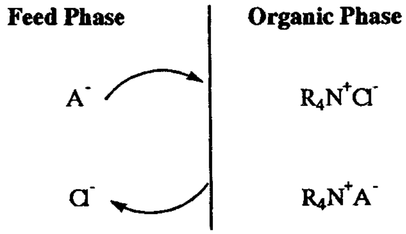

FIG. 1a Ion-pairing transport mechanism—extraction.

ble reaction describes the transport of anion A^- by this ion-pairing mechanism:

$$A^- + \overline{RCl} \xrightleftharpoons{K_e} \overline{RA} + Cl^- \tag{1}$$

with the equilibrium constant

$$K_e = \frac{[\overline{RA}][Cl^-]}{[A^-][\overline{RCl}]} \tag{2}$$

The organic acid dissociation in the aqueous phase is described by the following reaction:

$$HA \xrightleftharpoons{K_a} H^+ + A^- \tag{3}$$

and the dissociated acid concentration present in the aqueous solution is related to the pH and acid pK_a according to the Hasselbach–Henderson equation:

$$[A^-] = [HA]_t\left[1 - \left(\frac{1}{1 + 10^{pH-pK_a}}\right)\right] \tag{4}$$

where $[HA]_t = [A^-] + [HA]$. At $pH - pK_a = 2$, A^- represents 99% of the total acid present (dissociated plus undissociated forms). At neutral pH the transport of OH^- can be considered negligible compared with A^- transport. As the diluent used, an aromatic hydrocarbon mixture (Shellsol A), is practically insoluble in the aqueous phase and the anionic solute is also insoluble in the diluent, it is assumed that there is no physical extraction (this was experimentally confirmed for lactate extraction). As a consequence of the insolubility of both phases, the ion-exchange reaction takes place at the interface, and solute transport is assumed to be exclusively accomplished by an ion-pairing mechanism.

Consequently, the model proposed here is based on the following assumptions:

1. The organic acid is assumed to be totally dissociated (anion form), as the undissociated form of the acid represents only 1% of the total acid present, at $\mathrm{pH} - \mathrm{p}K_a = 2$.
2. The transport of OH^- is negligible compared with anion transport at neutral pH.
3. There is no physical extraction because the ions are insoluble in the diluent.
4. The ion-exchange reaction between the anion and the quaternary ammonium salt occurs at the interface.
5. Transport of the dissociated form of the organic acid is accomplished exclusively by an ion-pairing mechanism.

The water concentration in the organic phase has to be analyzed during the extraction process in order to evaluate the significance of hydration of the organic phase on the ion-pairing mechanism of A^- transport. For the particular case of the organic phase used, the ratio of water concentration/amine concentration, designated by w_0 (moles water/moles amine), was found to be $w_0 = 5$ at equilibrium for different amine concentrations. The use of the hydration ratio, w_0, allows the application of the model to any organic phase.

For different volumes of aqueous and organic phases, v_a and v_{org}, the material balances for amine, anion, and chloride can be expressed as

$$v_{org}[\overline{RCl}]_0 = v_{org}[\overline{RCl}] + v_{org}[\overline{RA}] \tag{5}$$

$$v_a[A^-]_0 = v_{a_e}[A^-] + v_{org}[\overline{RA}] \tag{6}$$

$$v_{org}[\overline{RCl}]_0 = v_{org}[\overline{RCl}] + v_{a_e}[Cl^-] \tag{7}$$

where v_a and v_{a_e} are the initial and final aqueous volumes, respectively, and $[RCl]_0$ and $[A^-]_0$ are the initial concentrations of Aliquat 336 and solute anion, respectively. The final aqueous volume is determined by subtracting from the initial aqueous volume, v_a, the volume of water present in the organic phase, and v_{org} is the intrinsic organic phase volume (without hydration).

By substituting Eqs. (5)–(7) in Eq. (2), the equilibrium constant can be evaluated:

$$K_e = \frac{\dfrac{v_{org}}{v_{a_e}}\left(\dfrac{v_a}{v_{org}}[A^-]_0 - \dfrac{v_{a_e}}{v_{org}}[A^-]\right)^2}{[A^-]\left([\overline{RCl}]_0 - \dfrac{v_a}{v_{org}}[A^-]_0 + \dfrac{v_{a_e}}{v_{org}}[A^-]\right)} \tag{8}$$

Rearranging the above equation, the equilibrium concentration can be obtained as

$$[\mathrm{A}^-] = \frac{b - \sqrt{b^2 - 4(1 - K_e)[\mathrm{A}^-]_0^2\left(\frac{v_a}{v_{org}}\right)^2}}{2\frac{v_{a_e}}{v_{org}}(1 - K_e)} \tag{9}$$

where

$$b = K_e[\overline{\mathrm{RCl}}]_0 + (2 - K_e)[\mathrm{A}^-]_0\frac{v_a}{v_{org}} \tag{10}$$

and v_{a_e}/v_{org} is related to w_0, v_a/v_{org}, and $[\mathrm{RCl}]_0$ by

$$\frac{v_{a_e}}{v_{org}} = \frac{v_a}{v_{org}} - 0.018[\overline{\mathrm{RCl}}]_0 w_0 \tag{11}$$

By nonlinear regression of Eqs. (9) (10), and (11), the equilibrium constant of the reaction, K_e, can be obtained by using the experimental values of initial and equilibrium anion concentrations, initial amine concentration and volume phase ratio, v_a/v_{org}, and the hydration of the organic phase, w_0. Then, with this K_e value, it is possible to predict equilibrium concentrations for any other extractant concentration, initial lactate concentration, volume phase ratio, or organic phase hydration ratio.

Usually, a measure of the affinity of the solute to the organic phase used in the extraction process is given by the distribution coefficient K_D, an empirical parameter defined as

$$K_D = [\overline{\mathrm{RA}}]/[\mathrm{A}^-] \tag{12}$$

A high value of the distribution coefficient indicates a high affinity of the solute for the organic phase and consequently a high degree of extraction. On the contrary, a low value of this parameter means that a high organic/aqueous phase volume ratio is needed in order to improve extraction.

As K_D is an empirical parameter, it can only be used for the tested conditions, i.e., the values obtained for the distribution coefficient are only valid for the specific amine concentration, initial anion concentration, and volume phase ratio used experimentally; thus, it is not possible to predict the value of the distribution coefficient for any other experimental conditions.

On the contrary, using the model previously described with the equilibrium constant, K_e, it is possible to predict equilibrium for different conditions from those experimentally performed. Moreover, the use of K_e permits generalization, allowing for comparison between different studies.

These two variables can be related and the distribution coefficient can always be determined whenever K_e is evaluated. For different volumes of aqueous and organic phases, K_D is expressed as

$$K_D = K_e \frac{[\mathrm{RCl}]}{[\mathrm{Cl}^-]} = K_e \frac{[\mathrm{RCl}]_0 - \dfrac{v_a}{v_{org}}[\mathrm{A}^-]_0 + \dfrac{v_{a_e}}{v_{org}}[\mathrm{A}^-]}{\dfrac{v_a}{v_{org}}[\mathrm{A}^-]_0 - \dfrac{v_{a_e}}{v_{org}}[\mathrm{A}^-]} \tag{13}$$

and $[\mathrm{A}^-]$ is given by Eqs. (9) (10), and (11).

Stripping

After contacting the organic phase with the feed phase, a stripping solution may be used to reextract the anion present in the organic phase (Fig. 1b). A sodium chloride solution was used for lactate stripping.

The same reaction as described in Eq. (1) takes place and the same equilibrium constant is valid for the stripping process if chloride is used as stripping agent. During the stripping process the water content of the organic phase (which had previously contacted the feed phase) was also monitored and remained constant, indicating that the organic phase was already water-saturated and, consequently, the volume of the stripping phase, v_s, remains constant. The material balances for amine, anion, and chloride are:

$$v_{org}[\overline{\mathrm{RCl}}]_e + v_{org}[\overline{\mathrm{RA}}]_e = v_{org}[\overline{\mathrm{RCl}}]_f + v_{org}[\overline{\mathrm{RA}}]_f \tag{14}$$

$$v_{org}[\overline{\mathrm{RA}}]_e = v_s[\mathrm{A}^-]_s + v_{org}[\overline{\mathrm{RA}}]_f \tag{15}$$

$$v_{org}[\overline{\mathrm{RCl}}]_e + v_s[\mathrm{Cl}^-]_0 = v_s[\mathrm{Cl}^-]_s + v_{org}[\overline{\mathrm{RCl}}]_f \tag{16}$$

where $[\mathrm{RA}]_e$ and $[\mathrm{RCl}]_e$ represent the concentrations of solute an-

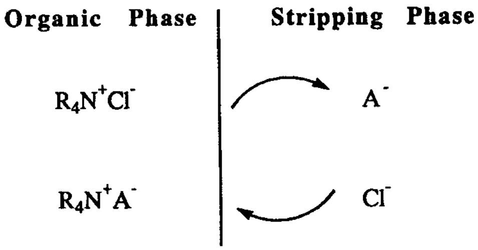

FIG. 1b Ion-pairing transport mechanism—stripping.

ion–amine and chloride–amine complexes at the beginning of the stripping process (extraction equilibrium concentrations), while $[\mathrm{RA}]_f$ and $[\mathrm{RCl}]_f$ are the concentrations of the complexes at stripping equilibrium. $[\mathrm{A}^-]_s$ and $[\mathrm{Cl}^-]_s$ represent the anion and chloride equilibrium concentrations in the stripping phase, respectively.

The equilibrium constant can be defined as

$$K_e = \frac{[\mathrm{RA}]_f[\mathrm{Cl}^-]_s}{[\mathrm{A}^-]_s[\mathrm{RCl}]_f} \tag{17}$$

By combining Eqs. (14)–(17) the anion concentration in the stripping phase can be predicted, using the same equilibrium constant.

$$[\mathrm{A}^-]_s = \frac{c - \sqrt{c^2 - 4d(1 - K_e)\left(\dfrac{v_s}{v_{\mathrm{org}}}\right)}}{2(1 - K_e)\dfrac{v_s}{v_{\mathrm{org}}}} \tag{18}$$

where

$$c = K_e[\overline{\mathrm{RCl}}]_0 + (1 - K_e)\left([\mathrm{A}^-]_0\frac{v_{a_0}}{v_{\mathrm{org}}} - [\mathrm{A}^-]\frac{v_a}{v_{\mathrm{org}}}\right) + \frac{v_s}{v_{\mathrm{org}}}[\mathrm{Cl}^-]_0 \tag{19}$$

$$d = \left([\mathrm{A}^-]_0\frac{v_{a_0}}{v_{\mathrm{org}}} - [\mathrm{A}^-]\frac{v_a}{v_{\mathrm{org}}}\right)[\mathrm{Cl}^-]_0 \tag{20}$$

and $[\mathrm{A}^-]$ is obtained from Eqs. (9), (10), and (11).

EXPERIMENTAL

Extraction System

The organic phase was composed of a quaternary ammonium salt Aliquat 336 (Fluka, Germany) and Shellsol A (Shell, UK), an aromatic hydrocarbon mixture.

The aqueous phase consisted of a lactate solution with a variable concentration from 6 to 700 mM, obtained by dilution of sodium lactate 60% (Sigma, USA). The pH of the solution was adjusted to 6.3 with a 0.1 M NaOH solution.

The stripping phase was a 1 M sodium chloride solution.

Equilibrium Constant Evaluation Experiments

Equal volumes of aqueous and organic phases (15 mL) were kept in contact for 20 hours in a thermostated shaker (100 rpm, $T = 40°C$). Then the phases were allowed to settle in separatory funnels for another 20 hours at the same temperature. The phases were separated, the volume of each phase was measured, and the pH of the aqueous solution was determined.

The phases were weighed before and after contact. Lactate concentration was determined in the initial and in the final aqueous solution; lactate in the organic phase was obtained by mass balance. The water content of the organic phase was determined.

Model Validation Experiments

A lactate solution (280 mM) was in contact with an equal volume of organic phase (15 mL), and the experimental procedure was analogous to that previously described. Three experiments with different organic phase compositions were carried out. The compositions of the organic phase were 10% (w/w), 30% (w/w), and 50% (w/w) Aliquat 336 in Shellsol A. After equilibrium, the lactate present in the organic phase was stripped using a 1 M sodium chloride solution and equal volumes of stripping and hydrated organic phases.

Analytical Methods

The lactate concentration was determined by HPLC. The column used was a Shodex SH 1011 (Showa Denko K.K., Japan) and the eluent was 0.01 N sulfuric acid. A refractive index detector (Merck Hitachi, Japan) was employed.

The water content of the organic phase was determined by Karl Fischer titration (AQUAPAL III, UK).

RESULTS AND DISCUSSION

This section is made up of three parts:

Equilibrium constant evaluation
Model simulations
Model validation experiments

In the first set of experiments the equilibrium constant K_e is evaluated for a specific carrier concentration and volume phase ratio.

The effect of different experimental conditions on extraction and stripping equilibrium is discussed using model simulations.

Finally, the model developed is tested by comparing predictions of equilibrium concentrations with experimental studies using different amine concentrations. Validation is extended to the stripping process, using chloride as the counterion.

Equilibrium Constant Evaluation

The equilibrium constant of the reaction, K_e, was evaluated by nonlinear regression (Marquardt algorithm) of the experimental values of the final and initial lactate concentrations using Eqs. (9) and (10). The organic phase was composed of 30% (w/w) Aliquat 336 in Shellsol A, corresponding to $[RCl]_0 = 0.654$ mol/L. The volumes of aqueous and organic phases were equal ($v_a = v_{org}$) and $v_{a_e}/v_{org} = 0.94$ (see Eq. 11 for $v_a = v_{org}$).

Figure 2 represents the fitting of the experimental values; the K_e value obtained expressed at the 95% confidence level was

$$K_e = 0.104 \pm 0.012$$

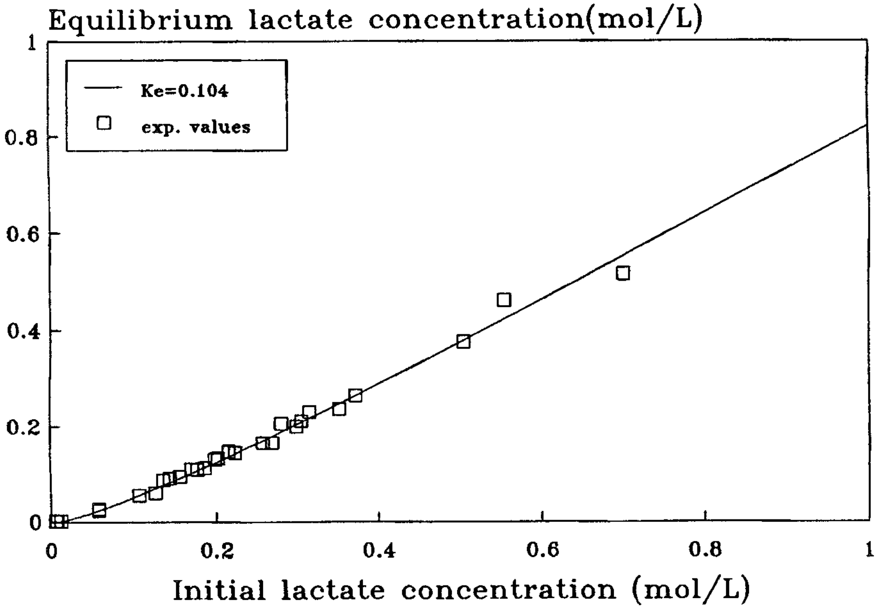

FIG. 2 Equilibrium constant evaluation (30% Aliquat 336 + 70% Shellsol A, $T = 40°C$).

The distribution coefficient evolution, K_D, estimated with K_e and given by Eq. (13), is represented in Fig. 3.

Model Simulations

The model previously developed can be used to evaluate how a defined set of operating conditions affects extraction and/or stripping equilibrium. This model simulation study enables a rational design of the conditions to be used in order to optimize the extraction and stripping process of lactate.

The model parameters selected to study the extraction process were the amine concentration, $[RCl]_0$, and the volume phase ratio (feed volume/organic volume), v_a/v_{org}. The effectiveness of the extraction process was determined by varying these parameters, and the results obtained are represented in Figs. 4a, 4b, and 4c.

As expected, the percentage of extraction, defined as $([A^-]_0 - [A^-] v_{a_e}/v_a)/[A^-]_0) \times 100$, increases with an increase in amine concentration and with decreasing v_a/v_{org}.

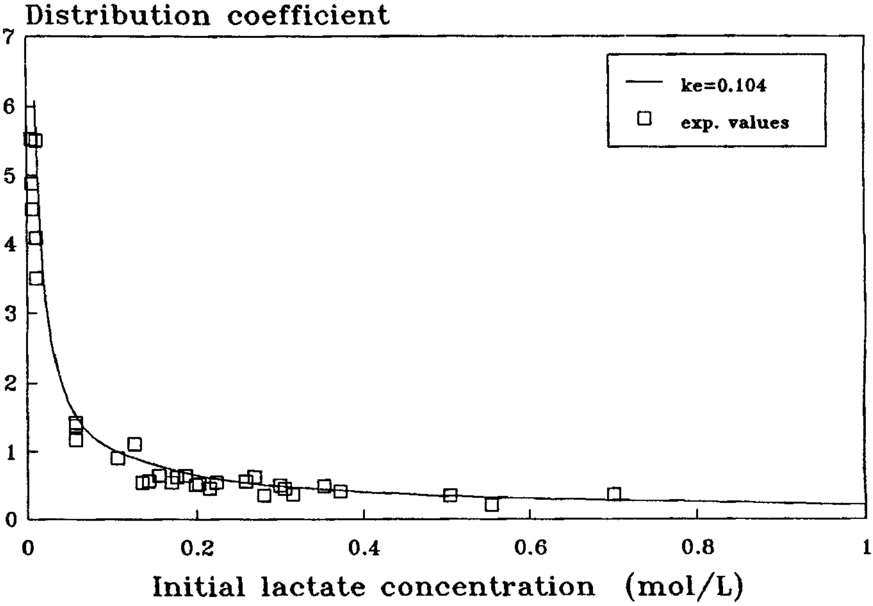

FIG. 3 Distribution coefficient prediction with $K_e = 0.104$ (30% Aliquat 336 + 70% Shellsol A, $T = 40°C$).

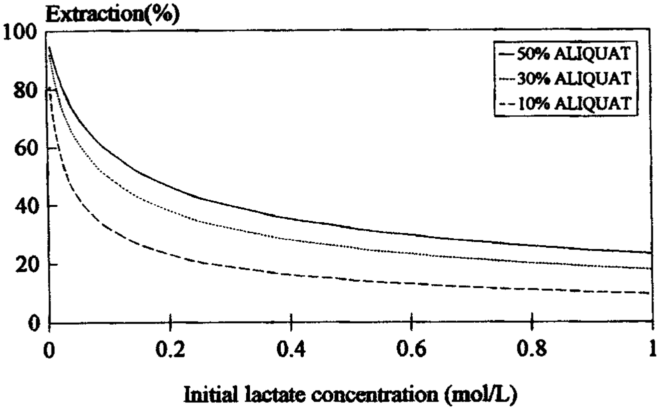

FIG. 4a Effect of amine concentration on extraction (K_e = 0.104 v_a/v_{org} = 1).

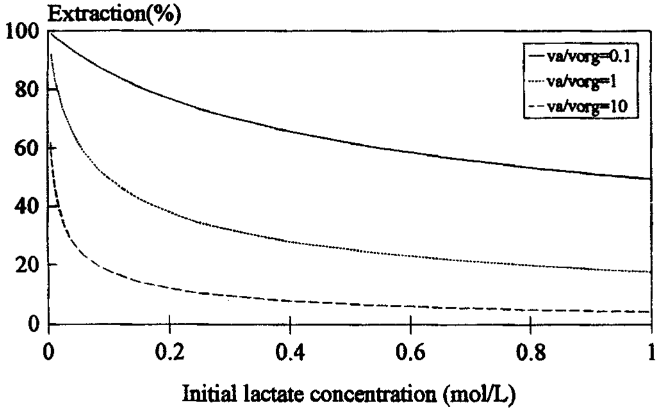

FIG. 4b Effect of the volume phase ratio v_a/v_{org} on extraction (K_e = 0.104, organic phase = 30% Aliquat 336 + 70% Shellsol A).

For the stripping process the parameters selected were the stripping agent concentration, $[Cl^-]_0$, and the volume phase ratio (stripping volume/organic volume), v_s/v_{org}. The efficiency of the reextraction process is defined as $([A^-]_s v_s/[A^-]_e v_{org}) \times 100$, where $[A^-]_e$ is the equilibrium

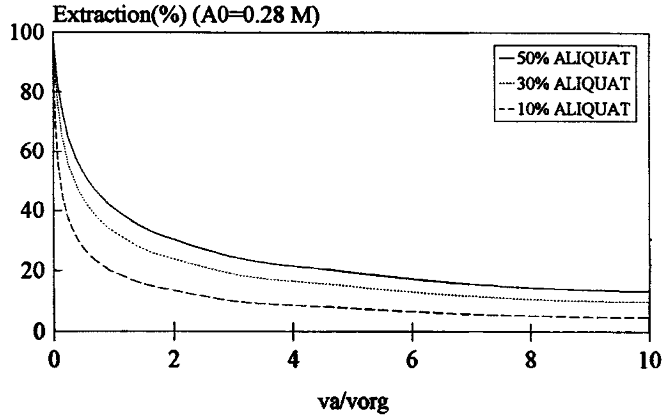

FIG. 4c Evolution of extraction with the volume phase ratio v_a/v_{org} for three different amine concentrations (K_e = 0.104, $[A^-]_0$ = 0.28 M).

lactate concentration present in the organic phase at the beginning of the stripping process, $[A^-]_e = ([A^-]_0 - [A^-]v_{a_e}/v_a) \times v_a/v_{org}$.

The efficiency of the reextraction process increases with increasing chloride concentration for equal v_s and v_{org}; however, a chloride concentration of 1 M is sufficient to achieve a high percentage of reextraction (95%). Using $[Cl^-]_0$ = 1 M, it is not necessary to increase the ratio v_s/v_{org} beyond 1 because the increase in the degree of reextraction is not significant for higher v_s/v_{org} ratios (Figs. 5a, 5b, and 5c).

With the parameters selected to study the extraction and the reextraction processes, it is possible to evaluate the efficiency of the overall process: extraction followed by stripping of lactate. This efficiency is defined as $[A^-]_s v_s/([A^-]_0 v_a) \times 100$ and depends on amine concentration, chloride concentration, and the volume phase ratios, v_a/v_{org} and v_s/v_{org}.

The model simulations performed are represented in Figs. 6a, 6b, 6c, and 6d. As the efficiency of the overall process is the product of the extraction and stripping efficiencies, the results are ruled by extraction when the parameters selected are the amine concentration and v_a/v_{org}. The results are similar to those obtained in the stripping process when the parameters selected are the chloride concentration and v_s/v_{org}.

The concentration effect is another important variable to be considered in separation processes. It is usually in opposition to the efficiency, so it

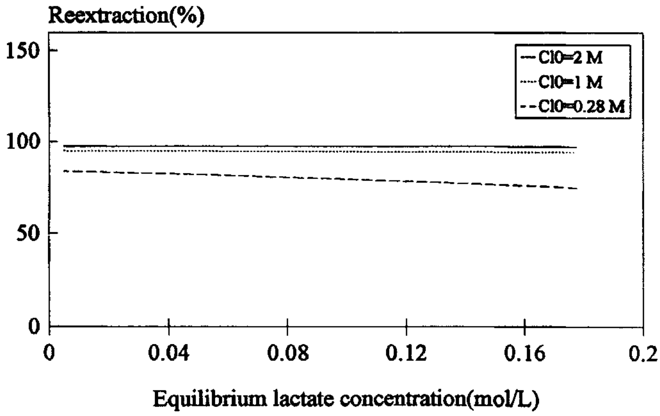

FIG. 5a Effect of chloride concentration on reextraction (K_e = 0.104, v_a/v_{org} = v_s/v_{org} = 1, organic phase: 30% Aliquat 336 + 70% Shellsol A).

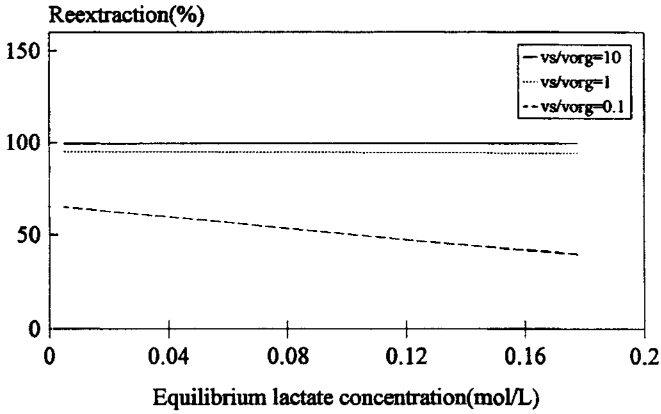

FIG. 5b Effect of the volume phase ratio v_s/v_{org} on reextraction (K_e = 0.104, v_a/v_{org} = 1, $[Cl^-]_0$ = 1 M, organic phase: 30% Aliquat 336 + 70% Shellsol A).

is infeasible to obtain both a high concentration effect and a high efficiency unless an extract recycle strategy is used.

Figures 7a, 7b, and 7c show how the concentration effect varies with the parameters $[Cl^-]_0$ and v_s/v_{org}. In order to have a high concentration

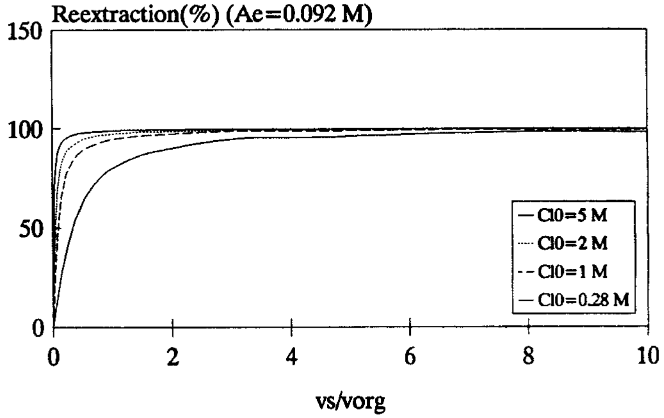

FIG. 5c Evolution of reextraction with the volume phase ratio v_s/v_{org} for different chloride concentrations (K_e = 0.104, $[A^-]_e$ = 0.092 M, v_a/v_{org} = 1, organic phase: 30% Aliquat 336 + 70% Shellsol A).

effect, the chloride concentration should be as high as possible and the volume phase ratio as low as possible.

Model Validation Experiments

Table 1 shows the experimental and predicted values of equilibrium lactate concentrations in aqueous and stripping phases. The initial lactate concentration, $[A^-]_0$, is 0.280 mol/L; the initial amine concentration, $[RCl]_0$, is 0.218, 0.654, and 1.09 mol/L, corresponding to 10% (w/w), 30% (w/w), and 50% (w/w) of Aliquat 336 in Shellsol A. The initial aqueous and organic phase volumes are equal, the organic phase hydration ratio, w_0, is 5, and the equilibrium constant used, K_e, is 0.1041. The ratio v_{a_e}/v_{org}, calculated by Eq. (11), gives the values 0.98, 0.94, and 0.91 for 10% (w/w), 30% (w/w), and 50% (w/w) of Aliquat 336 in Shellsol A, respectively.

The model predictions for the equilibrium lactate concentrations in the feed phase were obtained using Eqs. (9), (10), and (11).

The model predictions of lactate equilibrium concentrations in the stripping phase were obtained by Eqs. (18)–(20) using an initial chloride concentration $[Cl^-]_0$ = 1 M and equal volumes of the stripping and organic phases. Taking into account that for the stripping process the organic

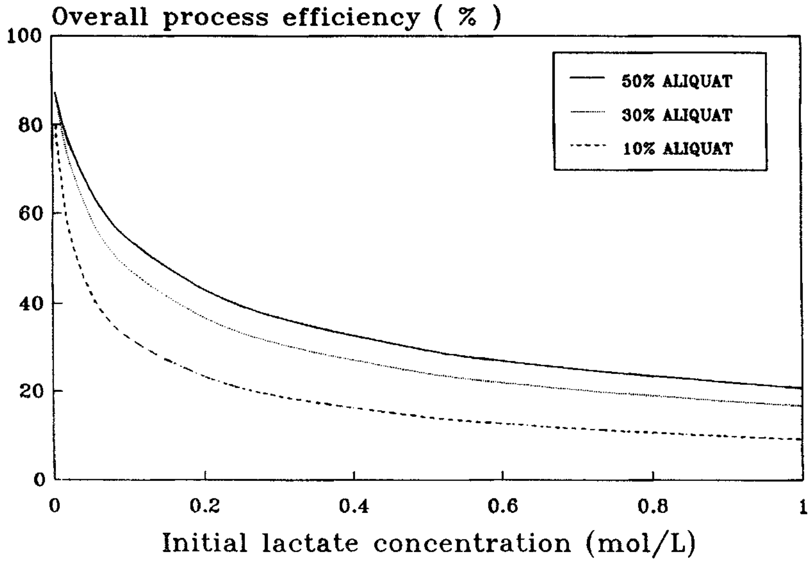

FIG. 6a Effect of amine concentration on the efficiency of the overall process ($K_e = 0.104$, $v_a/v_{org} = v_s/v_{org} = 1$, $[Cl^-]_0 = 1$ M).

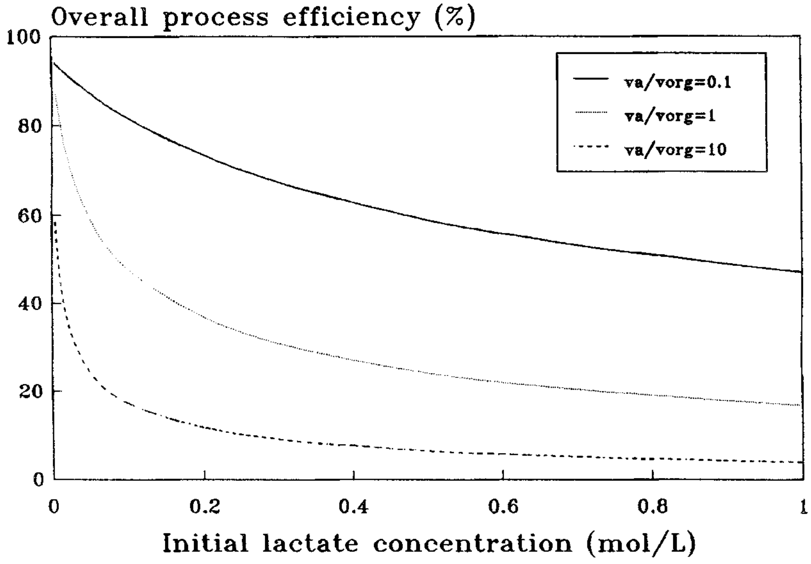

FIG. 6b Effect of volume phase ratio v_a/v_{org} on the efficiency of the overall process ($K_e = 0.104$, $v_s/v_{org} = 1$, $[Cl^-]_0 = 1$ M, organic phase: 30% Aliquat 336 + 70% Shellsol A).

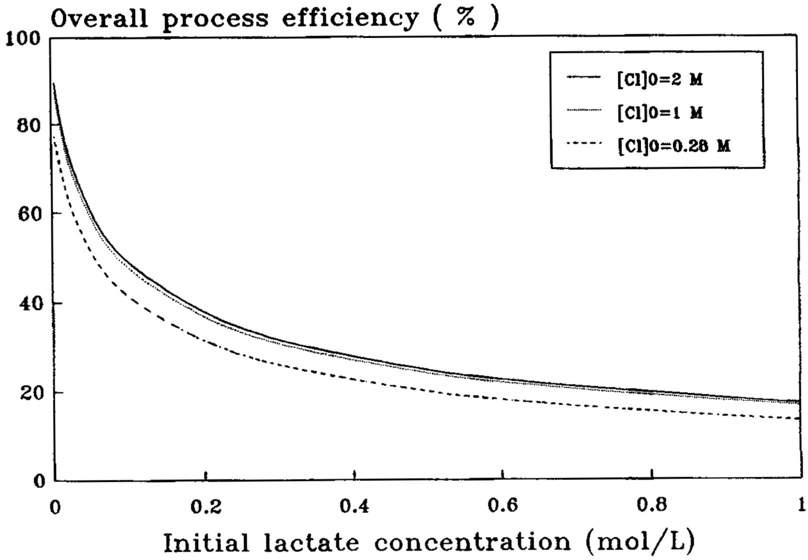

FIG. 6c Effect of chloride concentration on the efficiency of the overall process (K_e = 0.104, $v_a/v_{org} = v_s/v_{org} = 1$, organic phase: 30% Aliquat 336 + 70% Shellsol A).

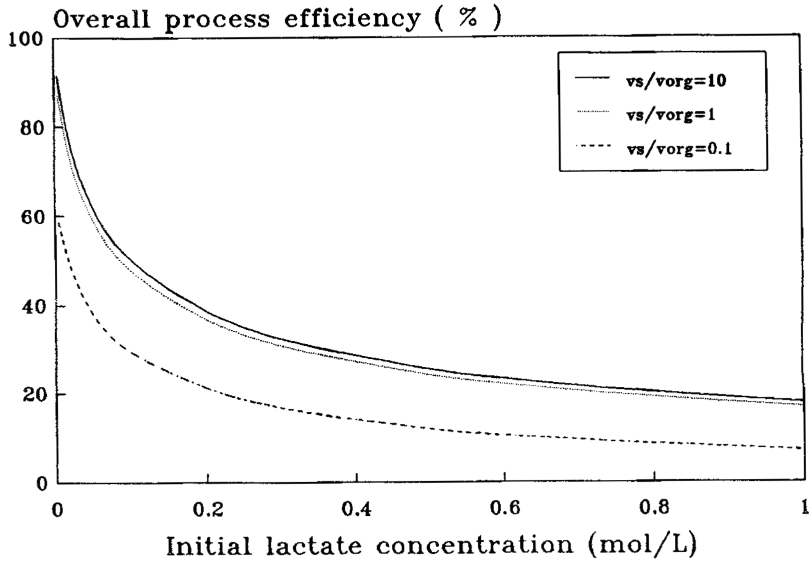

FIG. 6d Effect of volume phase ratio v_s/v_{org} on the efficiency of the overall process (K_e = 0.104, $v_a/v_{org} = 1$, $[Cl^-]_0 = 1$ M, organic phase: 30% Aliquat 336 + 70% Shellsol A).

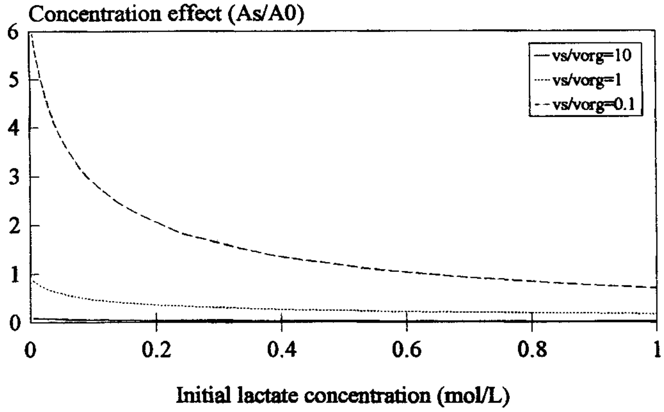

FIG. 7a Effect of volume phase ratio on the concentration of lactate (K_e = 0.104, v_a/v_{org} = 1, $[Cl^-]_0$ = 1 M, organic phase: 30% Aliquat 336 + 70% Shellsol A).

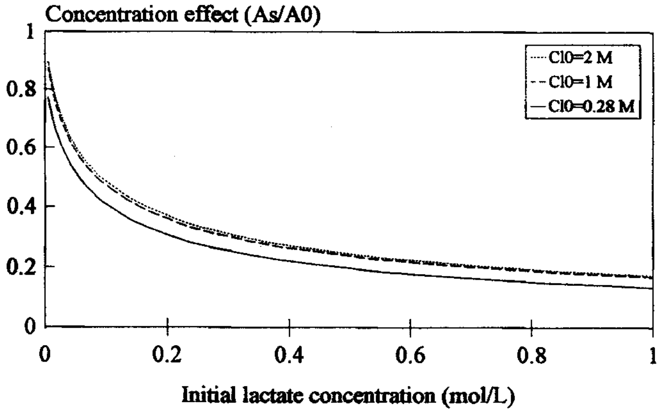

FIG. 7b Effect of chloride concentration on the concentration of lactate (K_e = 0.104, $v_a/v_{org} = v_s/v_{org}$ = 1, $[Cl^-]_0$ = 1 M, organic phase: 30% Aliquat 336 + 70% Shellsol A).

phase is already hydrated and that in the model v_{org} is the intrinsic organic phase volume, this implies that the ratio $v_s/v_{org} = 1 + v_a/v_{org} - v_{a_e}/v_{org}$. For 10% (w/w), 30% (w/w), and 50% (w/w) of Aliquat 336 in Shellsol A, v_s/v_{org} takes the values 1.02, 1.06, and 1.09, respectively.

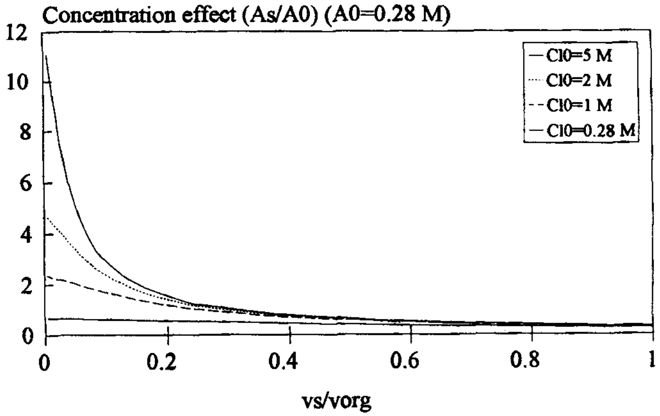

FIG. 7c Evolution of the concentration effect with the volume phase ratio v_s/v_{org} using different chloride concentrations (K_e = 0.104, v_a/v_{org} = 1, $[Cl^-]_0$ = 1 M, organic phase: 30% Aliquat 336 + 70% Shellsol A, $[A^-]_0$ = 0.28 M).

TABLE 1
Comparison of Experimental and Predicted Values of Equilibrium Lactate Concentrations in Aqueous and Stripping Phases

Extraction

Amine (%)	$[A^-]_0$ (M)	$[A^-]_{exp}$ (M)	$[A^-]_{model}$ (M) (K_e = 0.104)	Deviation (%)
10	0.282	0.220	0.225	−2
30	0.275	0.184	0.184	0
50	0.294	0.178	0.182	−2

Stripping

Amine (%)	$[A^-]_0$ (M)	$[A^-]_s$ exp (M)	$[A^-]_{s\ model}$ (M) (K_e = 0.104)	Deviation (%)
10	0.282	0.057	0.058	−2
30	0.275	0.086	0.089	−3
50	0.294	0.109	0.106	3

The agreement between experimental and model results is good, giving a percentage deviation relative to the experimental value of less than 3%, in the order of the analytical error for lactate detection.

CONCLUSIONS

A general model for dissociated organic acids extraction by an ion-pairing mechanism using a quaternary ammonium salt (Aliquat 336) is developed. The model parameter is the equilibrium constant of the ion-exchange reaction between the dissociated acid and the quaternary amine, K_e. It allows for general prediction of equilibrium concentrations of any dissociated organic acid, including amino acids (with charge $z = -1$) and for any organic phase used if the hydration ratio, w_0, is known.

The effect of different experimental conditions on extraction and stripping equilibrium is evaluated using model simulations, thus allowing a rational design of the operating conditions to be used for process optimization.

The model developed is validated for lactate extraction with experimental studies using different amine concentrations. Validation is extended to the stripping process, using chloride as counterion. The agreement between the experimental equilibrium lactate concentrations and model predictions was particularly good.

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SYMBOLS

$[A^-]$	solute anion concentration (mol/L)
$[Cl^-]$	chloride concentration (mol/L)
K_e	equilibrium constant (dimensionless)
K_D	distribution coefficient (dimensionless)
$[RA]$	solute anion–amine complex (mol/L)
$[RCl]$	chloride–amine complex (mol/L)
v_a	aqueous phase volume (L)
v_s	stripping phase volume (L)
v_{org}	organic phase volume (L)

w_0	ratio of water molar concentration/amine molar concentration (dimensionless)

Subscripts

0	initial
e	equilibrium in the organic phase for the extraction process
s	stripping phase
f	equilibrium in the organic phase for the stripping process

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Note Added in Proof

If the initial and final aqueous volumes are equal, $v_a = v_{a_e}$, then $K_e = 0.081 \pm 0.007$, which was the value used in the paper "Transport Mechanisms in Liquid Membranes with Ion Exchange Carriers" by I. M. Coelhoso, T. F. Moura, J. P. S. G. Crespo and M. J. T. Carrondo, accepted for publication in *Journal of Membrane Science*.