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Comparison of the Efficiencies of Amine Extractants on Lactic Acid with Different Organic Solvents

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ABSTRACT: The aim of this study is to compare different types of solvents and amines for extraction of carboxylic acids from fermentation broth and to find the most effective amine—solvent composition for the extraction. Studies have been made of the extraction of L-(+)-lactic acid and citric acids from fermentation broth by tridodecylamine (TDA), a long-chain tertiary amine, and Amberlite LA-2, a secondary amine mixture. These extractants dissolved in different solvents which have different chemical structures. The extraction of acids was carried out at 298 K. Comparison of the results was made using the distribution coefficients (K_d), loading factor (Z), and the percentage of extraction yield. 1-Octanol was found to be the most effective solvent with a maximum distribution value of 4.25 and 37.93 for TDA and Amberlite LA-2, respectively.

INTRODUCTION

Organic acids produced by fermentation, such as lactic acid and other carboxylic acids, have been used in many industrial fields as intermediate and starting materials, and their importance is still growing. The purification of organic acids is very important as they are used as starting materials for food additions, pharmaceuticals, biodegradable plastics, and other products because the purity of organic acids affects the quality of the final products.[1,2]

Lactic acid contains hydroxyl and carboxylic groups together. This property of the acids permits them to participate in many interesting and useful chemical reactions. Lactic acid has a wide range of applications in the food, pharmaceutical, leather, and textile industries. Lactic acid salts are very useful compounds which are used generally in the food industry as flavoring material.[3]

Because this acid is produced by fermentation, its solutions contain many impurities, such as microorganisms, other organic acids, and residual raw material compounds. Hence organic acid purification from fermentation broth is a very difficult procedure. The choice of purification methods is based on cost, environmental limitations, and facility.[3,4]

Lactic acid is conventionally purified by precipitation and acidification steps. In lactic acid purification, lime is added to a fermentation broth, and calcium lactate is precipitated and acidified with H_2SO_4. After these steps, lactic acid is purified. This method has a lot of disadvantages. It is a batch purification method. After the acidification step, it subsequently leads to generation of a large quantity of calcium sulfate, and also it contains retained organic impurities. The waste must be released to the environment. After the precipitation step, acid salts have some impurities. For reduction of these impurities, acid salts are washed by an excess of water. This causes loss of product. The advantage of this method is its cheaper unit cost than other methods.[3]

Alternatively, reactive extraction, adsorption, membrane separation, and electrodialysis can be used for removing organic acids from the fermentation broth continuously. Reactive extraction of organic acids by an amine extractant has been found to be a promising alternative to the conventional process. In reactive extraction, a reaction occurs between the amine extractant and the acid being extracted. In this reaction, acid—amine complex formation occurs. This complex is solubilized into the organic phase, and the organic acid is recovered from the organic phase by stripping. For economic recovery, the extractant should provide a high equilibrium distribution coefficient. For this purpose, the extractant selection is very important. The extractant should also have low water solubility. It has been reported that secondary and long chain tertiary amines are suitable for the extraction of organic acids from aqueous solution. Amine extractants are solubilized in organic solvents. Thus, extractant composition, viscosity, and density can be controlled.[3,5]

The recovery of carboxylic acids by reactive extraction has been studied by several researchers.[6−9]

In this study, comparison of extractability of lactic acid by TDA (tertiary amine) and Amberlite LA-2 (secondary amine) to investigate the effect of amine type was studied with respect to thermodynamic parameters (distribution coefficient, loading factors, and extraction efficiency).

THEORETICAL

The complex formation, during the extraction of hydroxycarboxylic acids by long-chain aliphatic amines, can be generally described by the following reactions.

$$p[\mathrm{A}] + q[\mathrm{B}]_{\mathrm{org}} \leftrightarrow [\mathrm{A}_p\mathrm{B}_q]_{\mathrm{org}} \qquad (1)$$

The complex formation is an equilibrium reaction. In this reaction, A is the acid molecule and B is the amine molecule. If

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Table 1. Results for Extraction of Lactic Acid by (a) TDA and (b) Amberlite La-2 with Individual Solvents at 298 K[a]

(a)	$C_{B,org}$	C_A	$C_{A,org}$						
diluent	$mol \cdot L^{-1}$	$mol \cdot L^{-1}$	$mol \cdot L^{-1}$	pH	K_d	Z_t	Z_s	S_f	$100E$
toluene	0.22	1.05	0.06	1.79	0.06	0.272	0.261	0.010	5.85
	0.52	0.71	0.39	2.00	0.56	0.750	0.740	0.099	36.04
	0.94	0.54	0.57	2.10	1.05	0.606	0.598	0.168	51.35
	1.57	0.44	0.67	2.13	1.52	0.426	0.420	0.203	60.36
	2.62	0.35	0.76	2.21	2.17	0.290	0.285	0.257	68.47
1-octanol	0.22	0.81	0.30	1.82	0.37	1.363	1.299	0.052	27.03
	0.52	0.61	0.50	1.91	0.84	0.961	0.906	0.102	45.05
	0.94	0.45	0.66	2.06	1.45	0.702	0.656	0.175	59.46
	1.57	0.32	0.79	2.13	2.50	0.503	0.467	0.230	71.17
	2.62	0.21	0.90	2.29	4.25	0.343	0.316	0.330	81.08
MIBK	0.22	0.83	0.28	1.96	0.34	1.272	1.246	0.067	25.23
	0.52	0.60	0.51	2.05	0.84	0.980	0.958	0.138	45.95
	0.94	0.45	0.66	2.08	1.49	0.702	0.683	0.182	59.46
	1.57	0.32	0.79	2.18	2.47	0.503	0.488	0.252	28.83
	2.62	0.28	0.83	2.32	2.94	0.316	0.305	0.328	74.77
2,2,4-trimethylpentane	0.22	0.96	0.15	1.80	0.16	0.681	0.659	0.025	13.51
	0.52	0.90	0.21	1.84	0.23	0.403	0.384	0.039	18.92
	0.94	0.71	0.40	1.91	0.56	0.425	0.409	0.083	36.04
	1.57	0.70	0.41	2.01	0.58	0.261	0.248	0.105	36.94
	2.62	0.51	0.60	2.09	1.18	0.229	0.219	0.172	54.05
cyclohexane	0.22	1.08	0.03	1.83	0.02	0.136	0.132	0.005	2.70
	0.52	1.05	0.06	1.85	0.06	0.115	0.112	0.011	5.41
	0.94	0.97	0.14	1.88	0.14	0.148	0.146	0.029	12.61
	1.57	0.83	0.28	1.94	0.33	0.178	0.176	0.064	25.23
	2.62	0.66	0.45	2.00	0.68	0.171	0.1701	0.112	40.54

(b)	$C_{B,org}$	C_A	$C_{A,org}$						
diluent	$mol \cdot L^{-1}$	$mol \cdot L^{-1}$	$mol \cdot L^{-1}$	pH	K_d	Z_t	Z_s	S_f	$100E$
toluene	0.32	0.72	0.37	2.30	0.53	1.156	1.148	0.172	33.94
	0.74	0.52	0.57	2.65	1.12	0.770	0.763	0.417	52.29
	1.33	0.25	0.84	3.10	3.41	0.631	0.625	0.748	77.06
	2.22	0.09	0.99	3.56	10.25	0.445	0.441	0.910	91.10
	3.70	0.06	1.03	4.03	17.86	0.278	0.274	0.968	94.86
1-octanol	0.32	0.64	0.45	2.24	0.72	1.406	1.362	0.180	41.28
	0.74	0.39	0.70	2.60	1.80	0.945	0.907	0.439	64.22
	1.33	0.21	0.88	3.04	4.36	0.661	0.629	0.731	80.73
	2.22	0.05	1.04	4.00	21.25	0.468	0.442	0.967	95.41
	3.70	0.03	1.06	4.57	37.93	0.286	0.267	0.991	97.43
MIBK	0.32	0.68	0.41	2.34	0.60	1.281	1.263	0.201	37.62
	0.74	0.42	0.67	2.76	1.63	0.905	0.889	0.520	61.47
	1.33	0.22	0.87	3.22	4.10	0.654	0.640	0.802	79.82
	2.22	0.06	1.03	3.89	18.22	0.463	0.453	0.957	94.50
	3.70	0.03	1.06	4.32	34.36	0.286	0.278	0.984	97.16
2,2,4-trimethylpentane	0.32	0.76	0.33	2.33	0.45	1.031	1.015	0.165	30.30
	0.74	0.51	0.58	2.66	1.18	0.783	0.770	0.427	53.21
	1.33	0.29	0.80	3.03	2.76	0.601	0.590	0.707	73.40
	2.22	0.12	0.97	3.59	8.29	0.436	0.427	0.914	88.99
	3.70	0.08	1.01	3.95	12.11	0.272	0.266	0.962	92.30
cyclohexane	0.32	0.84	0.25	2.28	0.31	0.781	0.778	0.118	22.94
	0.74	0.58	0.51	2.62	0.88	0.689	0.686	0.374	46.78
	1.33	0.33	0.76	2.96	2.30	0.571	0.569	0.661	69.72
	2.22	0.16	0.93	3.36	5.80	0.418	0.417	0.857	85.32
	3.70	0.09	1.00	3.82	11.15	0.270	0.269	0.949	91.74

[a] $C_{B,org}$ is the amine concentration of the organic phase; C_A is the acid concentration in the aqueous phase; $C_{A,org}$ is the acid concentration in the organic phase; K_d is the distribution coefficient; Z_t is the loading factor; Z_s is the stoichiometric loading factor; S_f is the separation factor; and E is the extraction efficiency.

a diluent interacts with the complex strongly, it can be presented as below

$$p[A] + q[B] + r[D]_{org} \leftrightarrow [A_pB_qD_r]_{org} \qquad (2)$$

where D is the diluent molecule. The diluents used in the extraction can be classified as "active" and "inert" diluents. Active diluents contain functional groups that interact strongly with the complex, e.g., 1-octanol and methyl isobutyl ketone (MIBK), as shown in reaction 2. Inert diluents do not interact with the complex, e.g., cyclohexane and 2,2,4-trimethylpentane (isooctane). Aliphatic hydrocarbons are generally inert diluents.[5]

A tertiary amine and a secondary amine were chosen as extractants in this study. Complex formation reactions of these

Table 2. Results for Extraction of Lactic Acid by (a) TDA and (b) Amberlite La-2 with Solvent Mixtures at 298 K[a]

(a) diluent mixtures (in 50/50 % volume)	$C_{B,org}$ mol·L^{-1}	C_A mol·L^{-1}	$C_{A,org}$ mol·L^{-1}	pH	K_d	Z_t	Z_s	S_f	100E
1-octanol−toluene	2.62	0.27	0.82	2.52	2.99	0.312	0.287	0.433	75.23
1-octanol−MIBK	2.62	0.22	0.87	2.58	3.98	0.332	0.298	0.482	79.82
MIBK−toluene	2.62	0.28	0.81	2.48	2.84	0.309	0.307	0.408	74.31

(b) diluent mixtures (in 50/50 % volume)	$C_{B,org}$ mol·L^{-1}	C_A mol·L^{-1}	$C_{A,org}$ mol·L^{-1}	pH	K_d	Z_t	Z_s	S_f	100E
1-octanol−toluene	3.70	0.05	0.56	3.97	19.63	0.137	0.131	0.936	95.14
1-octanol−MIBK	3.70	0.02	1.07	4.49	58.40	0.135	0.130	0.989	98.35
MIBK−toluene	3.70	0.03	1.06	4.26	31.60	0.135	0.134	0.981	97.25

[a] $C_{B,org}$ is the amine concentration of the organic phase; C_A is the acid concentration int the aqueous phase; $C_{A,org}$ is the acid concentration in the organic phase; K_d is the distribution coefficient; Z_t is the loading factor; Z_s is the stoichiometric loading factor; S_f is the separation factor; and E is the extraction efficiency.

extractants with carboxylic acids based on reaction 1 are shown below. For TDA, a tertiary amine[10]

$$[H_pA]_{aq} + i[R_3N]_{org} \leftrightarrow [R_3NH]_i H_{p-i}A \qquad p = 1, 2, 3 \quad i = 1, 2, 3 \tag{3}$$

For Amberlite LA-2, a secondary amine[11]

$$[H_pA]_{aq} + i[R_2NH]_{org} \leftrightarrow [R_2NH_2]_i H_{p-i}A \qquad p = 1, 2, 3 \quad i = 1, 2, 3 \tag{4}$$

If the interaction between the acid and amine is strong, the reactive extraction is more effective.

For the comparison of extraction experiments results, distribution coefficient (K_d), loading factor (Z), and extraction yield (E) are used.

The distribution coefficient is defined as the ratio of the concentration of organic acid in the organic phase to organic acid in the aqueous phase.

$$K_d = \frac{C_{A,\,org}}{C_{A,\,aq}} \tag{5}$$

The loading factor (Z) of extractant is defined as the total concentration of acid in the organic phase, $C_{A,org}$, divided by the total concentration of amine in the organic phase, C_B.

$$Z_t = \frac{C_{A,\,org}}{C_{B,\,org}} \tag{6}$$

The stoichiometric loading factor, Z_s, is the ratio of the overall complexed acid to total amine in the organic phase. This factor includes a correction term ($\nu \cdot C^{s}_{A,org}$), for the amount of acid extracted by the modifiers in the solvent mixture.

$$Z_s = \frac{(C_{A,\,org} - \nu \cdot C^{*s}_{A,\,org})}{C_B} \tag{7}$$

Extraction yield is the determined percentage of extracted acid.

$$E = \left(1 - \frac{(C_{A,\,aq})}{C_{Ao}}\right) \cdot 100 \tag{8}$$

In eq 8, $C_{A,aq}$ is the concentration of acid in the aqueous phase after extraction, and C_{Ao} is the initial acid concentration in the aqueous phase.[12]

If an extractant is suitable for the chosen acid, the distribution coefficient should be bigger than 1. Also, for more economic extraction, complexes with more than one acid per amine should be formed. In other words, loading factors have high values.

The relative proportion between physical interaction and chemical reaction was evaluated with respect to a modified separation factor which is expressed as the ratio of the complexed acid to overall extracted acid

$$s_f = \frac{C_{A,\,org}}{C_{A,\,org} + C_{A^-}} \tag{9}$$

EXPERIMENTAL SECTION

The purpose of the presented investigations was to compare different amine extractants and solvents and find the most effective amine−solvent composition for lactic acid purification. The experiments involved two types of amines, tridodecylamine, Amberlite LA-2, and five types of solvents. TDA is a long-chain tertiary amine, and Amberlite LA-2 is a normal and dodecyl secondary amine mixture. TDA is a liquid extractant, with a melting point of 16 °C, density of 0.82 g·cm^{-3}, and molecular weight of 522.01 g·mol^{-1}. Amberlite LA-2 is a yellow liquid, with an acid binding capacity of (2.6 to 2.9) mg·g^{-1}, viscosity of 18 Pa·s at 25 °C, and density of 0.83 g·cm^{-3}. The molecular weight of Amberlite LA-2 is between (353 and 395) g·mol^{-1}, but its mean molar mass of 374 has been offered.[13] Methyl isobutylketone (MIBK), 1-octanol, toluene, cyclohexane, and 2,2,4-trimethylpentane were used for diluting the amine extractants.

Lactic acid (Merck) (pK_a: 3.86) was diluted into distilled water to approximately a mass fraction of 10 % like produced by the fermentation process. In the extraction, the organic phase was prepared by diluting the amine extractants in five solvents, and the aqueous phase acid solutions had a mass fraction of 10 % acid. Aqueous and organic solutions were added to Erlenmeyer flasks and equilibrated in a thermostatted shaker bath (Nüve ST402) at 298 K for 4 h. This equilibrium period was found in preliminary experiments. After achieving an equilibrium state, aqueous phase acid concentrations were determined by titration with 0.1 mol·L^{-1} NaOH solution (relative uncertainty: ± 1 %) with phenolphthalein as an indicator at 298 K. In most cases, the deviation between the amount of acid analyzed and the amount of acid known by preparing the solutions by mass did not exceed

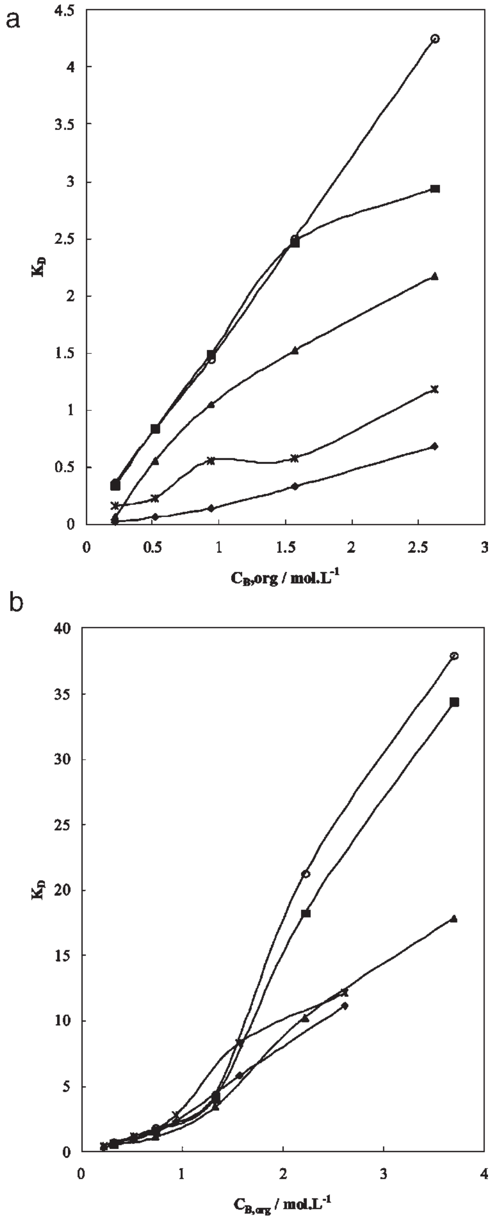

Figure 1. Variation of distribution coefficients (K_d) with concentration of (a) TDA (C_B) and (b) Amberlite La-2 ($C_{B,org}$) in different solvents. ▲, Toluene; ○, 1-octanol; □, MIBK; ∗, 2,2,4-trimethylpentane; ◆, cyclohexane.

± 1 %. Aqueous phase pH measurements were performed with a Hanna Instruments pH 211 Microprocessor pH meter with deviation ± 0.01.

RESULTS AND DISCUSSION

Lactic acid was extracted by two different amine extractants which were diluted at five different solvents. Tables 1a and b show the results of the extraction experiments when TDA and Amberlite La-2 were used, respectively. The concentration of TDA in the solvents was between 0.22 $\mathrm{mol \cdot L^{-1}}$ and 2.62 $\mathrm{mol \cdot L^{-1}}$, and Amberlite La-2 concentration was changed in the range of 0.32 $\mathrm{mol \cdot L^{-1}}$ to 3.60 $\mathrm{mol \cdot L^{-1}}$. The initial lactic acid concentration was 1.11 $\mathrm{mol \cdot L^{-1}}$ mass fraction of lactic acid 10 %, and the initial pH value of the acid was 1.75.

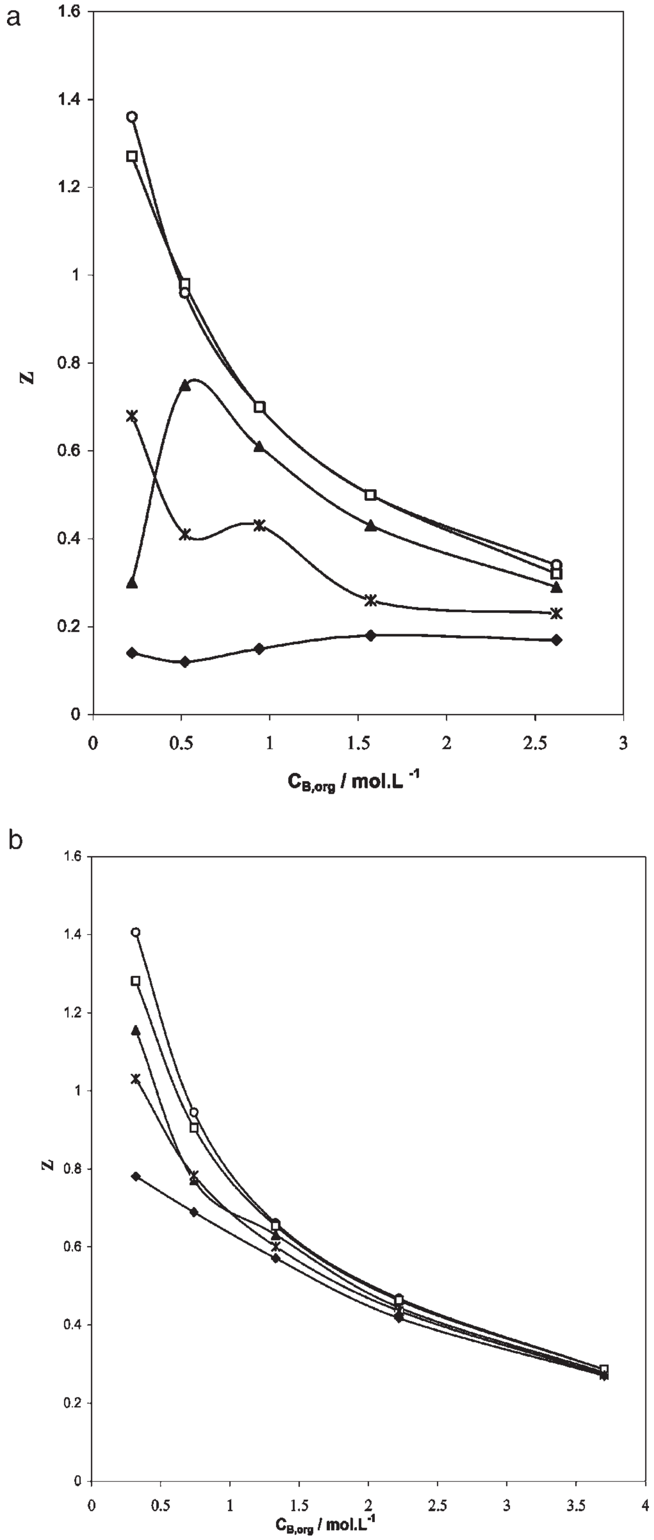

Figure 2. Variation of loading factors (Z) with concentration of (a) TDA ($C_{B,org}$) and (b) Amberlite La-2 ($C_{B,org}$) in different diluting solvents at 298 K. ▲, Toluene; ○, 1-octanol; □, MIBK; ∗, 2,2,4-trimethylpentane; ◆, cyclohexane.

The data for the distribution of lactic acid between water and TDA or Amberlite La-2 dissolved in toluene, 1-octanol, MIBK, cyclohexane, and 2,2,4-trimethylpentane are shown in Tables 1 and 2 are illustrated in Figures 1a and b. The tables show that

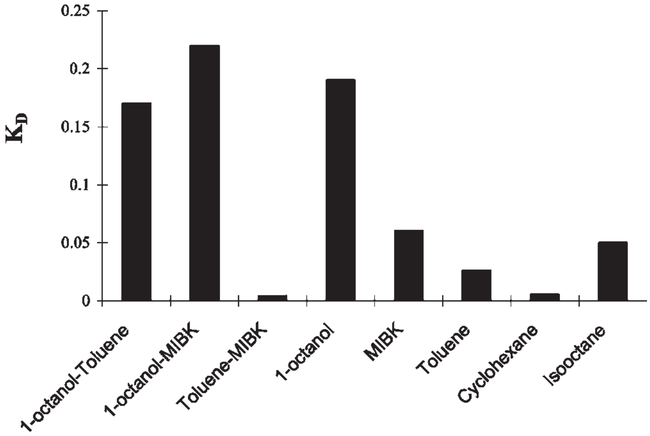

Figure 3. Results of physical extraction of lactic acid.

Table 3. Results of Physical Extraction of Lactic Acid at 298 K[a]

	C_A	$C_{A,org}$			
diluent	$\mathrm{mol \cdot L^{-1}}$	$\mathrm{mol \cdot L^{-1}}$	pH	K_d	100E
cyclohexane	1.10	0.01	1.76	0.01	0.90
2,2,4-trimethylpentane	1.05	0.06	1.76	0.05	5.41
MIBK	1.04	0.07	1.89	0.06	6.31
1-octanol	0.94	0.17	1.74	0.19	15.32
toluene	1.08	0.03	1.75	0.03	2.70
MIBK−1-octanol	0.89	0.21	2.02	0.22	19.09
MIBK−toluene	1.09	0.01	1.94	0.004	0.91
1-octanol−toluene	0.94	0.16	1.98	0.17	14.55

[a] C_A is the acid concentration in the aqueous phase; $C_{A,org}$ is the acid concentration in the organic phase; K_d is the distribution coefficient; and E is the extraction efficiency.

TDA and Amberlite La-2 are very effective extractants. The maximum extracted lactic acid was 81.08 % with TDA dissolved in 1-octanol and 97.43 % with Amberlite La-2. This result was achieved when the organic phase concentration was the highest value, 2.62 $\mathrm{mol \cdot L^{-1}}$ of TDA and 3.70 $\mathrm{mol \cdot L^{-1}}$ of Amberlite La-2. At the lowest concentration value, the extraction yield was 22.94 % with Amberlite La-2, and this result shows that K_d increased with an increasing amount of amine. Choudhury et al. reported that the distribution coefficient increased with increasing amount of amine extractant, and they reported that the increasing amine concentration might have a toxic effect on microorganisms in the in situ extractive fermentation. That is why the loading factor is an important expression.

The distribution coefficients increase from 0.37 to 4.25 with increasing concentration of TDA (0.22 $\mathrm{mol \cdot L^{-1}}$ to 2.62 $\mathrm{mol \cdot L^{-1}}$) with 1-octanol. When using cyclohexane, it was observed that the distribution coefficient changed between 0.02 and 0.68. This comparison shows that 1-octanol was the most effective solvent for lactic acid extraction by TDA. On the other hand, the reactive extraction of lactic acid by Amberlite La-2 with 1-octanol gave values of distribution coefficients between 0.72 and 37.93 with increasing Amberlite La-2 concentration from (0.32 to 3.70) $\mathrm{mol \cdot L^{-1}}$.

In the extraction of carboxylic acids by TDA or Amberlite La-2, an acid−amine complex occurs. Solvents interact with the complex. This interaction can be classified as "general solvation" and "specific interaction". Cyclohexane and 2,2,4-trimethylpentane are nonpolar diluents, so they affect the complex very slightly. That is why cyclohexane and 2,2,4-trimethylpentane gave lower distribution coefficients than 1-octanol and MIBK.[5]

MIBK has a high relative permittivity, 13.1 D at 20 °C, and has a reactive functional group. These properties cause a very effective interaction between the polar complex and MIBK, as an example of general solvation. As Tables 1a and b show, the distribution coefficient changed between 0.34 and 34.36 when MIBK was used as solvent. These values were second highest distribution coefficients for lactic acid extraction by TDA or Amberlite La-2. The third highest value was with toluene. Toluene has aromatic π electrons that interact with the complex specifically, and distribution coefficients ranged between 0.06 and 17.86.

Polarity is not the only factor for solvating ability. Alcohol diluents give unexpected distribution coefficients and hydrogen bonding occurs between the proton of the diluent and the complex. This characteristic of the alcohol provides extra solvation for the complex. For this reason, 1-octanol had the best results for lactic acid extraction, even though its dielectric constant is 10.3 D at 20 °C.

The maximum extraction efficiencies for the diluents are found to be in the following order for both amines:

1-octanol > MIBK > toluene > 2,2,4-trimethylpentane > cyclohexane.

The loading curve is a plot of Z vs extractant concentration. In Figures 2a and 2b, the effect of TDA or Amberlite La-2 concentration on loading is shown. As shown in Figures 2a and 2b, except for cyclohexane, the other solvents show decreasing loading with increasing amine concentration. For nonaggregating systems in inert diluents, for example, monocarboxylic acids in alkane or aromatic diluents, there was no effect of amine concentration on loading. So, in the present work, cyclohexane has no effect on amine concentration loading.

Overloading, loading greater than unity, indicates that complexes with more than one acid per amine have been formed. With 1-octanol and MIBK, overloading was observed.

Systems that exhibit aggregation, formation of complexes with a large numbers of acid and amine molecules, exhibit an abrupt increase in loading at a critical acid concentration. In this study, toluene showed an abrupt increase in loading after that loading started to decrease.

The pH of the aqueous phase is an important parameter for the reactive extraction of organic acids. Yang et al. reported that lower pH values result in good separation of lactic acid by long-chain tertiary amines.[14] The most effective extraction is carried out when the pH value is below the pK_a of the acid. The pK_a value of lactic acid is 3.86. In this study, the pH values of the aqueous phase ranged from 1.79 to 2.32 when TDA was used and from 2.24 to 4.57 when Amberlite La-2 was used.

Tables 2a and 2b present K_d, Z, and E values of the extraction of lactic acid by TDA when solvent mixtures were used for diluting the TDA or Amberlite La-2. Used solvent mixtures were 1-octanol−toluene, 1-octanol−MIBK, and toluene−MIBK. As shown in Figure 3, the 1-octanol−MIBK mixture is more effective than the other mixtures. Its distribution coefficient was 3.98, and its extraction yield was 79.82 % when TDA was used. When Amberlite La-2 was used, its value increased from 3.98 to 58.40. However, the most effective one is 1-octanol by itself. Its distribution coefficient was 4.25, and its extraction yield is 81.08 % for TDA.

Table 4. Results of Extraction of Lactic acid by (a) TDA and (b) Amberlite La-2 at Different Initial Lactic Acid Concentrations at 298 K[a]

(a) initial acid conc. (mol·L^{-1})	$C_{B,org}$ mol·L^{-1}	C_A mol·L^{-1}	$C_{A,org}$ mol·L^{-1}	pH	K_d	Z	100E
2.32	2.62	0.84	1.48	2.01	1.76	0.56	63.8
0.57	2.62	0.09	0.48	2.80	5.31	0.18	84.21
0.28	2.62	0.04	0.24	3.27	6.87	0.09	87.14

(b) initial acid conc. (mol·L^{-1})	$C_{B,org}$ mol·L^{-1}	C_A mol·L^{-1}	$C_{A,org}$ mol·L^{-1}	pH	K_d	Z	100E
2.32	3.70	0.250	2.07	3.17	8.13	0.56	89.22
0.57	3.70	0.007	0.56	-	79.00	0.98	98.73
0.28	3.70	0.003	0.27	5.77	90.43	0.07	98.89

[a] C_A is the acid concentration in the aqueous phase; $C_{A,org}$ is the acid concentration in the organic phase; K_d is the distribution coefficient; Z_t is the loading factor; Z_s is the stoichiometric loading factor; S_f is the separation factor; and E is the extraction efficiency.

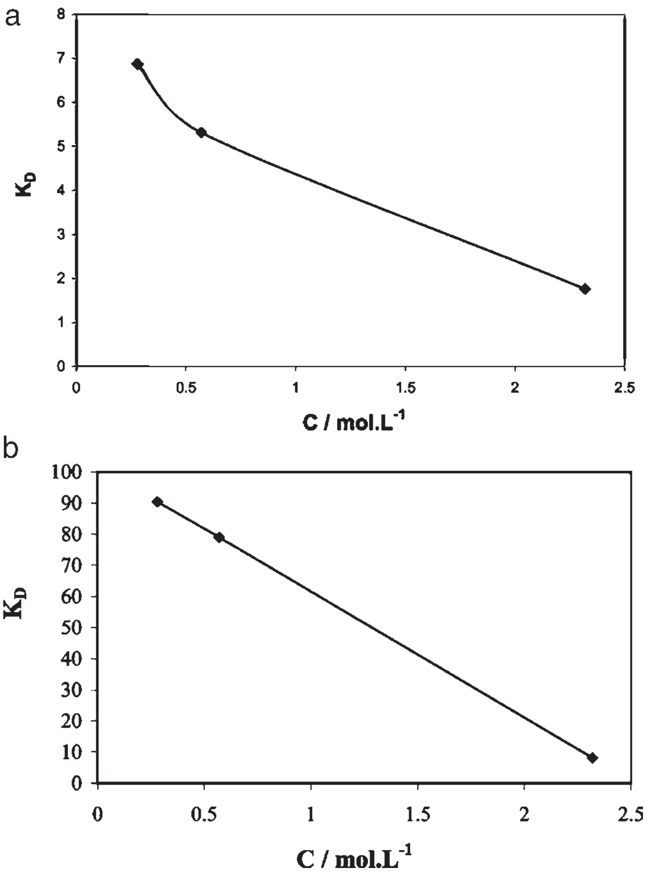

Figure 4. (a) Variation of distribution coefficients (K_d) in 2.62 mol·L^{-1} concentration of TDA ($C_{B,org}$) in different initial lactic acid concentrations (C). (b) Variation of distribution coefficients (K_d) in 3.70 mol·L^{-1} concentration of Amberlite La-2 ($C_{B,org}$) in different initial lactic acid concentrations (C).

The physical extraction of lactic acid was studied for better understanding of the effect of the amine. The pure solvents (not containing amine) used in this study (cyclohexane, 2,2,4-trimethylpentane, MIBK, 1-octanol, toluene, 1-octanol−toluene, 1-octanol−MIBK, and toluene−MIBK) are presented in Table 3 and shown in Figure 3. All pure solvents gave poor distribution coefficients. The 1-octanol + MIBK mixture gave the highest distribution coefficient with a value of 0.22, whereas this solvent mixture gave a 58.40 distribution value when using Amberlite La-2.

The effects of modified separation factors on the concentration of TDA and Amberlite La-2 are presented in Tables 1 and 2. The separation factor (S_f) shows the relative proportion between physical interaction and chemical reaction. For all solvents with increasing concentration of amine (TDA and Amberlite La-2), increasing separation factors were observed. At the amine concentration ranges (0.32 to 2.22) mol·L^{-1} for Amberlite La-2 and (0.22 to 0.94) mol·L^{-1} for TDA, the separation factor showed a sharp increase in 1-octanol, MIBK, and toluene.

The initial organic acid concentration is also an important parameter for the extraction of organic acids. In the investigations of Yabannavar and Wang on lactic acid, they reported that K_d decreased with increasing initial acid concentration.[15] In a recent study, the distribution coefficient decreased with the increasing initial acid concentration, as shown in Tables 4a and 4b and Figures 4a and 4b.

CONCLUSION

The reactive extraction of lactic acid by both TDA and Amberlite La-2 with different diluents was studied. The comparative work showed that Amberlite La-2 was a more effective extractant than tridodecyl amine (TDA). Among the used solvents, to dilute amines, the most effective synergistic effect belonged to 1-octanol + Amberlite La-2. It has 37.93 distribution coefficients and has a 97.43 extraction yield. The physical extraction showed how important it is to use amine on the extraction of carboxylic acids. As a result of experiments, the Amberlite LA-2 and 1-octanol mixture which has the best result for both acids is recommended for the design of reactors for the extraction process.

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