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Extraction Equilibria of Acrylic Acid from Aqueous Solutions by Amberlite LA-2 in Various Diluents

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Amberlite LA-2 (a secondary amine mixture) has been studied for its ability to extract acrylic acid at different amine concentrations. The extraction of acrylic acid by Amberlite LA-2 dissolved in seven single solvents (cyclohexane, 2-octanone, toluene, methyl isobutyl ketone (MIBK), iso-octane, hexane, and 1-octanol) has been investigated with respect to different amine concentrations at 298.15 K. In the extraction, two acid−amine complexes, $(HO):(R_2N)$ and $(HO):(R_2N)_2$, have been assumed to exist in the organic phase in the case of proton-donating diluents, while the complexes $(HO):(R_2N)$ and $(HO)_2:(R_2N)_3$ have been suggested in the case of nonproton-donating diluents. Important data for the design and analysis of different separation processes have been obtained as a result of batch experiments. These important data are distribution coefficients (D), loading factors (Z), extraction efficiency (E), and overall extraction constants (K_{11}, K_{12}, K_{23}). The maximum removal of acrylic acid is 98.22 % with MIBK at 0.93 $\text{mol}\cdot\text{L}^{-1}$ initial concentration of Amberlite LA-2.

Introduction

Acrylic acid or prop-2-enoic acid ($CH_2 = CHCOOH$) is the simplest unsaturated carboxylic acid with a vinyl group at the α-carbon. Acrylic acid is a clear, colorless liquid with a characteristic odor. Its formula weight is 72.06 $\text{g}\cdot\text{mol}^{-1}$. Acrylic acid and its salt and esters are principal raw materials in the manufacturing of polymeric products. The polymers made of acrylic acid and its derivatives are specified by colorless transparency, easy adhesion, elasticity, and stability to light and moderate heat as well as weathering. They are widely used in surface coatings, textiles, adhesives, paper treatment, polishes, leather, fibers, detergents, and superabsorbent materials, and so forth.[1–3]

Fermentation processes, being the ideal method to produce carboxylic acids, have been proven to be environmentally friendly and use renewable resources. The most important problem of fermentation in the production of these carboxylic acids is their low concentration (< 10 %),[4] and separation of the acid is difficult and expensive.

Reactive extraction is receiving increasing interest for the recovery of organic acids from fermentation product mixtures or dilute aqueous streams because of its various advantages over conventional and other recovery methods.[2–13] For carboxylic acids, the classical method for recovery from an aqueous solution has been to add calcium hydroxide to form the calcium salt, to which an acid is added to liberate the acid. This method consumes chemicals such as lime and sulfuric acid and produces a huge amount of waste salt. Therefore, this method is falling out of favor. Acid−amine interaction allows the fermentation of a complex, and this complex provides high-distribution coefficients. Also, the high affinity of an amine for the carboxylic acid provides selectivity for the acid over other components in the mixtures.[14,15] Various extractants (tri-*n*-butyl phosphate,[8] trioctylphosphine oxide,[9] Alamine 336,[13] tri-*n*-octylamine,[6–8] Aliquat 336,[2,7,8] Amberlite LA-2,[11,12] etc.) have been used in reactive extraction for recovery processes that can chemically complex with the acid to form acid−extractant complexes. The complexation gives higher yields and selectivities of acid over nonacidic components. Because these extractants are either solid or viscous, they should be used when dissolved/mixed in diluents. A diluent is usually added along with the extractant for enhancement of its physical properties by providing general solvation and affects the extraction power of the extractant by providing specific interactions. The diluent may consist of one or more components, inert or active. Various active polar and proton- or electron-donating diluents (halogenated aliphatic/aromatic hydrocarbons, ketones, nitrobenzenes, higher alcohols) enhance the extraction. On the other hand, inert diluents (long-chain paraffins, benzene, etc.) limit the solvent capacity.[5]

The effect of diluent on extraction is usually explained qualitatively as a sequence of diluents corresponding to increasing or decreasing carboxylic acid distribution. The influence of diluents on reactive amine extraction have explained by Tamada et al.[16] They have found that the structure of the acid−amine complex is diluent-dependent. The acid−amine complexes are stabilized by the hydrogen bonding with the diluent. A complex structure has been given by Yerger and Barrow.[17] As a result of this work, the effect of diluent can be understood in terms of the ability to solvate the complex organic phase. Therefore, it should distinguish general solvation from other types of mechanisms such as electrostatic, dispersion, and specific solvation due to hydrogen bonding.[18]

There are lots of articles about the recovery of carboxylic acids.[2–10] Particularly, Uslu et al. has studied the extraction of carboxylic acids with Amberlite LA-2.[11,12] However, there are not sufficient data in relation to the acrylic acid and Amberlite LA-2/diluent system.

The purpose of this work was to explore the reactive extraction of acrylic acid from aqueous solutions using Amberlite LA-2 dissolved in different solvents. The extraction of acrylic acid from aqueous solutions by the Amberlite LA-2

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extractant in a variety of diluents was examined over a wide range of amine concentration [(0.19 to 0.93) mol·L^{-1}]. Batch extraction experiments were performed with Amberlite LA-2 dissolved in diluents of various types: ketones (methyl isobutyl ketone (MIBK), 2-octanone), alkanes (iso-octane, cyclohexane, hexane), alcohols (1-octanol), and aromatic hydrocarbons (toluene). Distribution coefficients were calculated from the results of the batch extraction experiments. Also, extraction efficiencies and loading factors have been obtained. Furthermore, they were used to obtain conclusions about the stoichiometry of complex formation.

Theoretical Section

Reactive extraction of acrylic acid (HA) with an amine (R_2N) can be described by the following set of reactions:

$$i(\mathrm{HA})^{\mathrm{R}} + j(\mathrm{R_2N})^{\mathrm{E}} \rightleftarrows ((\mathrm{HA})_i \cdot (\mathrm{R_2N})_j)^{\mathrm{E}} \qquad (1)$$

$$i = 1, p; j = 1, q$$

where HA represents the undissociated part of the acid present in the raffinate or aqueous phase ($^{\mathrm{R}}$) and extract (organic) phase species are marked with superscript E ($^{\mathrm{E}}$). Because no overloading of the amine has been observed, i is expected to be less than or equal to j for any p and q. The reaction given by eq 1 can be specified by the overall thermodynamic extraction constant:

$$(K_{ij})^{\mathrm{E}} = [(\mathrm{HA})_i \cdot (\mathrm{R_2N})_j]^{\mathrm{E}}/([\mathrm{HA}]^i)^{\mathrm{R}}([\mathrm{R_2N}]^j)^{\mathrm{E}} \qquad (2)$$

where square brackets mean activities.

Equation 1 can be given in terms of dissociated species, hydrogen ions and anions, as it is used in the literature on the amine extraction of acids. Taking into account the dissociation equilibrium, one can derive that both concepts are equivalent, the only difference being in the values of equilibrium constants.[13] Replacing the activities by the products of molalities (mol·kg^{-1} of solvent) and molar activity coefficients, eq 2 can be written as:

$$(K_{ij})^{\mathrm{E}} = (b_{ij})^{\mathrm{E}} \cdot a_{ij}/(b_a a_a)^{i\mathrm{E}}(b_e a_e)^{j\mathrm{E}} \qquad (3)$$

where water and diluents are understood as diluents for the aqueous or organic phases, respectively.

Levien offered that the activity coefficients of undissociated citric acid in water can be neglected as a first approximation.[13,19] Also, supposing the ratio of the activity coefficients of organic phase species are constant allows them to incorporated into the equilibrium constants. The conditional overall extraction constants are written as:

$$K_{ij} = (b_{ij})^{\mathrm{E}}/(b_{\mathrm{a}}{}^i)^{\mathrm{R}}(b_{\mathrm{e}}{}^j)^{\mathrm{E}} \qquad (4)$$

$$i = 1, p; j = 1, q$$

Combining eq 4 with the mass balance equations of acid and amine in the organic phase, the mathematical model of equilibrium can be obtained as:

$$(b_{\mathrm{a}})^{\mathrm{E}} = \sum \sum i K_{ij} (b_{\mathrm{a}}{}^i)^R (b_{\mathrm{e}}{}^j)^{\mathrm{E}} \qquad (5)$$

$$i = 1, p; j = 1, q$$

where the molality of free amine is characterized by the equation:

$$(b_{\mathrm{e}})^{\mathrm{E}} + \sum \sum j K_{ij} (b_{\mathrm{a}}{}^i)^{\mathrm{R}} (b_{\mathrm{e}}^j - b_{\mathrm{e}}^0)^{\mathrm{E}} = 0 \qquad (6)$$

$$i = 1, p; j = 1, q$$

where $b_{\mathrm{e}}{}^0$ is the total molality of amine in the organic phase. Equation 6 has a solution between zero and the aqueous phase molalities of the undissociated acid, with respect to the dissociation equilibrium. It can be seen from the results by Vanura and Kuca that all possible (i,j) combinations for $i = 1$, p and $j = 1$, q need not to be taken into account.[13–20] It is possible to investigate the extraction of carboxylic acids by pure diluents to obtain the distribution coefficient, but there is no evidence of the true value of this coefficient in the presence of amine and its complexes with the acid. The changes of the K_{ij} with respect to amine concentration can be caused by both the conditional character of the K_{ij} constant and the stoichiometry of complex formation. The loading of the extractant, Z, is described as the total concentration of acid in the organic phase divided by the total concentration of amine in the organic phase. The expression for loading, Z, can be obtained from eqs 5 and 6 in the form:

$$Z = (b_{\mathrm{a}})^{\mathrm{E}}/(b_{\mathrm{e}}{}^0)^{\mathrm{E}} \rightleftarrows [\sum i K_{i1} (b_{\mathrm{a}}{}^i)^{\mathrm{R}}]/[1 + \sum K_{i1} (b_{\mathrm{a}}{}^i)^{\mathrm{R}}] \qquad (7)$$

$$i = 1, p; j = 1, q$$

The acid and amine concentrations have been given different symbols for each phase: $(c_{\mathrm{a}})^{\mathrm{R}}$, concentration of acid in the aqueous phase; $(c_{\mathrm{a}})^{\mathrm{E}}$, concentration of acid in the organic phase; and $(c_{\mathrm{e}})^{\mathrm{E}}$, concentration of amine in the organic phase.

Distribution coefficients for acrylic acid extracted from water into the organic phase were specified as:

$$D = (b_{\mathrm{a}})^{\mathrm{E}}/(b_{\mathrm{a}})^{\mathrm{R}} \qquad (8)$$

The efficiency of extraction, E, is expressed as

$$E = (1 - (C_{\mathrm{a}}/C_{\mathrm{ao}})) \cdot 100 \qquad (9)$$

where C_{a} is the concentration of acid in the aqueous phase after extraction and C_{ao} is the initial concentration of acid in the aqueous phase. An E value of 100 % means that all of the acid in the aqueous phase has been removed and is present in the organic phase.[11]

Materials and Methods

All of the solvents (hexane, cyclohexane, toluene, iso-octane, MIBK, 2-octanone, 1-octanol) and acrylic acid were reagent grade and used without pretreatment. Amberlite LA-2, a commercial product (Henkel Co.) was used: a mixture of straight-chain secondary amines ($M = 374$ g·mol^{-1}).

An acrylic acid solution was prepared using by analytical purity distilled water (1.59 mol·L^{-1}). We have prepared the organic phases by mixing Amberlite LA-2 with the diluents at five different concentrations in the range of (0.19 to 0.93) mol·L^{-1}. Aqueous and organic solutions of 3 mL of known concentration were added to Erlenmeyer flasks (50 mL) and have been shaken in a Nuve Shaker ST402 bath at 298.15 K for 3 h, which preliminary tests demonstrated to be a sufficient time for equilibration. After equilibration, both phases were separated by centrifugation at 1200 rpm for about 30 min for better phase separation. The acid concentration of aqueous phase samples was analyzed by the use of titration with 0.1 N sodium hydroxide (relative uncertainty: 1 %) by means of phenolphthalein as an indicator with each measurement being performed in duplicate.[19] Almost in all experiments, the deviation between the amount of acid analyzed and the amount of acid known by preparing the solutions by mass did not exceed 3 %. The solubilities of amine salts and diluents in the aqueous phase were negligible in the range of variables investigated.

Table 1. Experimental Results of the Extraction of Acrylic Acid with Amberlite LA-2/Individual Diluents at 25 °C

diluent	concentration of amine in the organic phase $\text{mol}\cdot\text{L}^{-1}$	concentration of acid in the aqueous phase $\text{mol}\cdot\text{L}^{-1}$	concentration of acid in the organic phase $\text{mol}\cdot\text{L}^{-1}$	D	Z	E %
cyclohexane	0.19	0.78	0.81	1.04	4.37	50.9
	0.37	0.43	1.16	2.68	3.13	72.8
	0.56	0.27	1.32	4.93	2.40	83.1
	0.74	0.14	1.45	10.1	1.96	91.0
	0.93	0.11	1.48	13.5	1.60	93.1
iso-octane	0.19	0.76	0.83	1.10	4.49	52.3
	0.37	0.47	1.12	2.39	3.03	70.5
	0.56	0.25	1.34	5.25	2.43	84.0
	0.74	0.14	1.45	10.1	1.96	91.0
	0.93	0.09	1.50	16.3	1.62	94.2
MIBK	0.19	0.25	1.34	5.36	7.24	84.3
	0.37	0.16	1.43	9.19	3.88	90.2
	0.56	0.09	1.50	17.2	2.73	94.5
	0.74	0.05	1.54	30.7	2.08	96.8
	0.93	0.03	1.56	55.2	1.69	98.2
1-octanol	0.19	0.37	1.22	3.29	6.59	76.7
	0.37	0.22	1.37	6.13	3.69	86.0
	0.56	0.16	1.43	8.64	2.59	89.6
	0.74	0.10	1.49	15.5	2.02	93.9
	0.93	0.07	1.52	23.3	1.65	95.9
2-octanone	0.19	0.38	1.21	3.24	6.57	76.4
	0.37	0.19	1.40	7.20	3.77	87.8
	0.56	0.12	1.47	12.4	2.68	92.6
	0.74	0.07	1.52	22.5	2.06	95.7
	0.93	0.04	1.55	37.4	1.67	97.4
toluene	0.19	0.64	0.95	1.48	5.13	59.7
	0.37	0.29	1.30	4.43	3.51	81.6
	0.56	0.15	1.44	9.49	2.62	90.5
	0.74	0.09	1.50	16.3	2.02	94.2
	0.93	0.06	1.53	27.0	1.66	96.4
hexane	0.19	0.83	0.76	0.91	4.09	47.5
	0.37	0.43	1.16	2.73	3.15	73.2
	0.56	0.23	1.36	5.95	2.48	85.6
	0.74	0.13	1.46	11.5	1.98	92.0
	0.93	0.09	1.50	16.7	1.62	94.4

Results and Discussion

Table 1 lists the results of the experimental studies. The concentrations of amines in the diluents were between 0.19 $\text{mol}\cdot\text{L}^{-1}$ and 0.93 $\text{mol}\cdot\text{L}^{-1}$. The acrylic acid concentration in the initial aqueous phase was 1.59 $\text{mol}\cdot\text{L}^{-1}$ ($w = 10.27$ %).

The equilibrium complexation constants on the distribution of acrylic acid between water and Amberlite LA-2 dissolved in hexane, cyclohexane, toluene, methyl isobutyl ketone, iso-octane, 2-octanone, and 1-octanol are given in Table 2. The synergistic effect obtained with reactive extraction can be seen by comparing Table 1 with physical extraction values (Table 3).

Figure 1 presents the effect of the organic diluent on acrylic acid distribution between water and Amberlite LA-2. That the extraction power of Amberlite LA-2−diluent mixture changes by increasing the initial concentration of Amberlite LA-2 in the organic phase. As given in Figure 1 and Table 1, the effect of the diluents on the extraction of acrylic acid were found as,

$$\text{MIBK} > \text{2-octanone} > \text{toluene} > \text{1-octanol} > \text{hexane} > \text{iso-octane} > \text{cyclohexane}$$

This effect can be explained theoretically as the formation of two or three acid−amine complexes, which are affected by the diluents in different ways. In this study, using Bizek's approach,three acid−amine complexes, $(\text{HO})\cdot(\text{R}_2\text{N})$, $(\text{HO})\cdot(\text{R}_2\text{N})_2$, and $(\text{HO})_2\cdot(\text{R}_2\text{N})_3$, have been supposed to exist in the organic phase.[13]

Solvation of the complex by the diluent is the most investigated factor in the extraction of the carboxylic acid. The mutual effect between the complex and the diluent can be separate general solvation interactions and specific interactions of the diluent with the complex. Inert diluents, such as the nonpolar alkanes hexane, iso-octane, and cyclohexane, provide very low solvation of the polar complex.

For systems with only one amine per complex, no effect of total amine concentration on the loading can be seen. If there is more than one amine per complex, the loading increases with increasing amine concentration. Systems that display aggregation, that is, formation of complexes with large numbers of acid and amine molecules, exhibit an abrupt increase in loading. In this work, loading factors of all diluents decrease with increasing amine concentration, indicating that complexes include more than one amine per complex. Thus, they do not contribute significantly to the distribution of the acid into the diluent phase and give low values of distribution coefficients. The aromatic diluent (toluene) shows a higher distribution coefficient than nonpolar diluents. This case has been rationalized in terms of solvation due to the interaction of the aromatic π-electrons with the complex. MIBK and 2-octanone are polar and can promote extraction by providing a good medium for the ion pair. However, polarity (or polarizability) alone does not completely account for the solvating ability. In the case of using alcohol as a diluent, the capability for hydrogen bonding is important as well;[13] thus, 1-octanol has given high distribution coefficients in this work.

In Figure 2, the effect of Amberlite LA-2 concentration on loading is shown. The loading curve is a plot of Z versus amine concentration. Overloading (loading greater than unity) indicates

Table 2. Values of Changing the Overall Extraction Constants for Different Diluents

diluent	concentration of amine in the organic phase mol·L^{-1}	K_{11} L·mol^{-1}	K_{23} L^4·mol^{-4}	K_{12} L^2·mol^{-2}
cyclohexane	0.19	5.47	194	
	0.37	7.24	122	
	0.56	8.81	105	
	0.74	13.7	176	
	0.93	14.5	154	
iso-octane	0.19	460	211	
	0.37	186	100	
	0.56	199	118	
	0.74	287	176	
	0.93	355	221	
MIBK	0.19	28.2	3129	
	0.37	24.9	1164	
	0.56	30.7	1119	
	0.74	41.5	1512	
	0.93	59.3	2425	
1-octanol	0.19	17.3	1298	91.0
	0.37	16.6	543	44.8
	0.56	15.4	299	27.6
	0.74	21.0	398	28.3
	0.93	25.0	442	26.9
2-octanone	0.37	17.1	1261	
	0.37	19.5	734	
	0.56	22.2	599	
	0.74	30.4	821	
	0.93	40.2	1124	
toluene	0.19	7.80	337	
	0.37	12.0	299	
	0.56	17.0	357	
	0.74	22.0	438	
	0.93	29.1	593	
hexane	0.19	4.78	159	
	0.37	7.40	127	
	0.56	10.6	148	
	0.74	15.5	223	
	0.93	18.0	232	

Table 3. Distribution of Acrylic Acid between Diluents and Water at 25 °C

diluent	concentration of acid in the aqueous phase mol·L^{-1}	$(C_a)^E$ mol·L^{-1}	D	E %
cyclohexane	0.90	0.69	0.76	43.1
iso-octane	0.80	0.79	0.99	49.7
MIBK	0.27	1.32	4.85	82.9
1-octanol	0.29	1.30	4.39	81.5
2-octanone	0.73	0.86	1.17	53.9
toluene	0.36	1.23	3.40	77.3
hexane	0.95	0.64	0.67	40.1

that complexes with more than one acid per amine have been formed. Overloading can be observed with all of the solvents for all Amberlite LA-2 concentrations (Figure 2).

In the case of the nonproton-donating diluents (hexane, cyclohexane, iso-octane, toluene, 2-octanone, MIBK) the process can be described by the reaction:

$$2(\mathrm{HA})^{\mathrm{R}} + 3(\mathrm{R_2N})^{\mathrm{E}} \rightleftarrows ((\mathrm{HA})_2\cdot(\mathrm{R_2N})_3)^{\mathrm{E}} \quad K_{23}$$

Only the values of K_{11} and K_{12} for 1-octanol have been presented in Table 2. Reaction 11 can be explained as a result of three consecutive reactions: 10, 11, and 12;

$$(\mathrm{HA})^{\mathrm{R}} + (\mathrm{R_2N})^{\mathrm{E}} \rightleftarrows ((\mathrm{HA})\cdot(\mathrm{R_2N}))^{\mathrm{E}} \quad K_{11} \qquad (10)$$

$$(\mathrm{HA})^{\mathrm{R}} + 2(\mathrm{R_2N})^{\mathrm{E}} \rightleftarrows ((\mathrm{HA})\cdot(\mathrm{R_2N})_2)^{\mathrm{E}} \quad K_{12} \qquad (11)$$

$$(\mathrm{HA}\cdot(\mathrm{R_2N})_3)^{\mathrm{E}} + ((\mathrm{HA})\cdot(\mathrm{R_2N})_2)^{\mathrm{E}} \rightleftarrows ((\mathrm{HA})_2\cdot(\mathrm{R_2N})_5)^{\mathrm{E}} \quad K_{\mathrm{A}} \qquad (12)$$

The values of the overall extraction constants, K_{11}, K_{12}, and K_{23}, are calculated using eq 5 and given in Table 2. In the case of a proton-donating diluent (1-octanol), the extraction process can be described by reactions 10 and 11.

The resulting acid−amine complexes are supposed to be stabilized because of hydrogen bonding with the diluent.

Experimental aggregation of highly polar primary acid−amine complexes according to reaction 12 are supposed to proceed almost completely. As the $((\mathrm{HA})\cdot(\mathrm{R_2N})_2)^{\mathrm{E}}$ complex is the minor component in the studied range of concentrations, its presence is not indicated.

The distribution data of acrylic acid between water and the diluents used in this study (1-octanol, 2-octanone, cyclohexane,

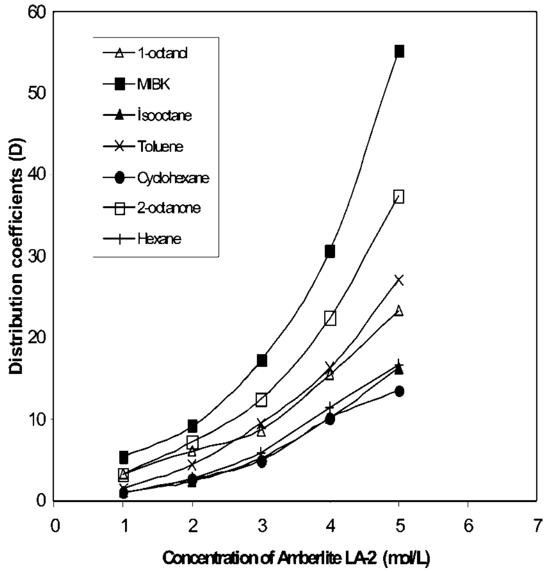

Figure 1. Variation of distribution coefficients with concentration of Amberlite LA-2 in different individual diluents at 25 °C. △, 1-octanol; ■, MIBK; ▲, iso-octane; ×, toluene; ●, cyclohexane; □, 2-octanone; +, hexane.

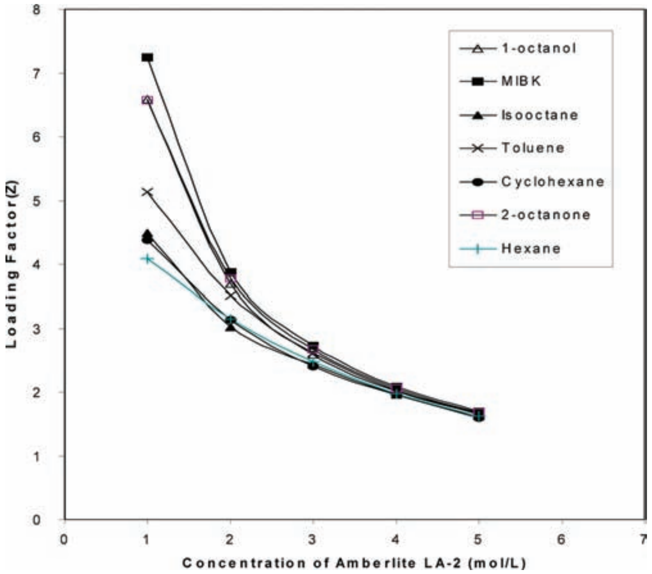

Figure 2. Variation of loading factors with concentration of Amberlite LA-2 in different diluents at 25 °C. △, 1-octanol; ■, MIBK; ▲, iso-octane; ×, toluene; ●, cyclohexane; □, 2-octanone; +, hexane.

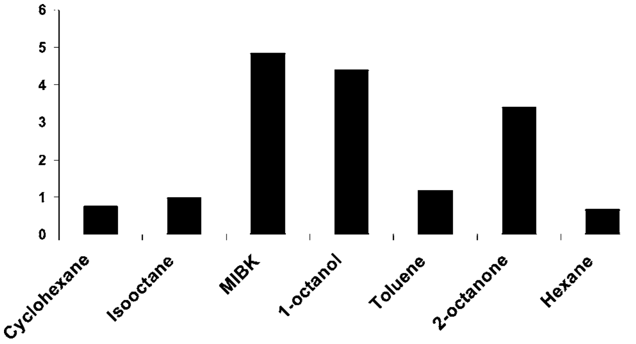

Figure 3. Distribution coefficients of acrylic acid between water and diluents used in this study.

iso-octane, hexane, cyclohexane, MIBK) are presented in Table 3 and shown in Figure 3.

Conclusions

In this work, the extraction characteristics of acrylic acid by Amberlite LA-2 with different diluents were examined. Hexane, cyclohexane, iso-octane, toluene, MIBK, 1-octanol, and 2-octanone have been used as solvents. The extraction of acrylic acid increases with increasing amine concentration, for all of the diluents. Among the diluents used in this study the largest distribution coefficients were obtained with MIBK, 2-octanone, and toluene. In the experiments, the concentration of acrylic acid in the aquous phase varied between 0.24 $mol \cdot L^{-1}$ and 0.28 $mol \cdot L^{-1}$ for 1-octanol. The best distribution ratio of acrylic acid is obtained with MIBK as 98.86 %. For other solvents E % values are the following: hexane, 94.4 %; cyclohexane, 93.1 %; iso-octane, 94.2 %; toluene, 96.4 %; 1-octanol, 95.9 %; and 2-octanone, 97.4 %.

The maximum extraction efficiencies for diluents used at the maximum Amberlite LA-2 (0.93 $mol \cdot L^{-1}$) concentration were determined as

MIBK > 2-octanone > toluene > 1-octanol > hexane > iso-octane > cyclohexane

Glossary

Symbols and Abbreviations

a_a	molal activity coefficient of acid
a_e	molal activity coefficient of amine
a_{ij}	molal activity coefficient of complex
$(c_a)^R$	concentration of acid in the aqueous phase, $mol \cdot L^{-1}$
$(c_a)^E$	concentration of acid in the organic phase, $mol \cdot L^{-1}$
$(c_e)^E$	concentration of amine in the organic phase, $mol \cdot L^{-1}$
D	distribution coefficient
E	efficiency of extraction
HA	acrylic acid
K_A	aggregation constant
K_{ij}	overall thermodynamic extraction constant
$(b_a)^R$	molality of acid in the aqueous phase, $mol \cdot kg^{-1}$
$(b_a)^E$	molality of acid in the organic phase, $mol \cdot kg^{-1}$
$(b_e)^R$	molality of amine in the aqueous phase, $mol \cdot kg^{-1}$
$(b_{eo})^E$	total molality of amine in the organic phase, $mol \cdot kg^{-1}$
MIBK	methyl isobutyl ketone
p	number of acid molecules
q	number of amine molecules
R_2N	secondary amine
w	mass fraction
Z	loading factor
$()^E$	organic phase
$()^R$	aqueous phase

Literature Cited

(1) *Kirk-Othmer Encyclopedia of Chemical Technology*; Wiley Interscience: New York, 1981.
(2) Keshav, A.; Wasewar, K. L.; Chand, S. Extraction of acrylic, propionic, and butyric acid using Aliquat 336 in oleyl alcohol: Equilibria and effect of temperature. *Ind. Eng. Chem. Res.* **2009**, *48* (2), 888–893.
(3) Xiaobo, X.; Jianping, L.; Peilin, C. Advances in the Research and Development of Acrylic Acid Production from Biomass. *Chin. J. Chem. Eng.* **2006**, *14* (4), 419–427.
(4) Aşçı, Y. S.; Hasdemir, İ. M. Removal of some carboxylic acids from aqueous solutions by hydrogels. *J. Chem. Eng. Data* **2008**, *53*, 2351–2355.
(5) Keshav, A.; Wasewar, K. L.; Chand, S. Recovery of propionic acid from an aqueous stream by reactive extraction: effect of diluents. *Desalination* **2009**, *244* (1), 12–23.
(6) Keshav, A.; Wasewar, K. L.; Chand, S. Extraction of propionic acid with tri-n octyl amine in different diluents. *Sep. Purif. Technol.* **2008**, *63*, 179–183.
(7) Keshav, A.; Wasewar, K. L.; Chand, S.; Uslu, H. Effect of binary extractants and modifier-diluents systems on equilbria of propionic acid extraction. *Fluid Phase Equilib.* **2009**, *275* (1), 21–26.
(8) Keshav, A.; Wasewar, K. L.; Chand, S. Extraction of propionic acid using different extractants (Tri-*n*-butylphosphate, Tri-*n*-octylamine, and Aliquat 336. *Ind. Eng. Chem. Res.* **2008**, *47* (16), 6192–6196.
(9) Kumar, S.; Wasewar, K. L.; Babu, B. V. Intensification of nicotinic acid separation using organophosphorous solvating extractants: Reactive extraction. *Chem. Eng. Technol.* **2008**, *31* (11), 1584–1590.
(10) Kumar, S.; Babu, B. V. Propionic acid production via fermentation route using renewable sources. *Chem. Ind. Dig.* **2008**, *9*, 76–81.
(11) Uslu, H.; Bayat, C.; Gökmen, S.; Yorulmaz, Y. Reactive Extraction of Formic Acid by Amberlite LA-2 Extractant. *J. Chem. Eng. Data* **2009**, *54* (1), 48–53.
(12) Beyazit, Ş. S.; Uslu, H.; İnci, İ. Comparative Equilibrium Studies for Citric Acid by Amberlite LA-2 or Tridodecylamine (TDA). *J. Chem. Eng. Data* **2009**, *54* (7), 1991–1996.
(13) İnci, İ. Extraction of gluconic acid with organic solutions of alamine 336. *Chem. Biochem. Eng. Q.* **2002**, *4*, 185–189.
(14) İnci, I.; Aydın, A. Extraction of Hydroxycarboxylic Acids with MIBK/Toluene Solutions of Amines. *J. Sci. Ind. Res.* **2003**, *62*, 926–930.
(15) Barrow, G. M.; Yerger, E. A. Acid-Base Reactions in Nondissociating Solvents: n-Butyl Amine and Acetic Acid in Carbon Tetrachloride. *J. Am. Chem. Soc.* **1955**, *77*, 6201.
(16) Tamada, J. A.; Kertes, A. S.; King, C. J. Extraction of Carboxylic Acids with Amine Extractants 1: Equilibria and Law of Mass Action Modelling. *Ind. Eng. Chem. Res.* **1990**, *29*, 1319–1326.
(17) Yerger, E. A.; Barrow, G. M. Acid-Base Reactions in Non-dissociating Solvents n-Butylamine and Acetic Acid in Carbon Tetrachloride and Chloroform. *J. Am. Chem. Soc.* **1955**, *77* (23), 6206–6207.
(18) Inci, I.; Uslu, H.; Ayhan, S. T. Partitioning of Gluconic Acid between Water and Trioctyl Methylammonium Chloride and Organic Solvents. *J. Chem. Eng. Data* **2005**, *50*, 961–965.
(19) Levien, B. A. A physicochemical study of aqueous citric acid solutions. *J. Phys. Chem.* **1955**, *59*, 640–644.
(20) Vanura, P.; Kuca, L. Extraction of Glycolic Acid by the Toluene Solutions of Trilaurylamine. *Collect. Czech. Chem. Commun.* **1976**, *41*, 2857–2877.

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