Measurement of Partition Coefficients of Carboxylic Acids between Water and Triisooctylamine Dissolved in Various Diluents

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Tertiary amines dissolved in organic diluents are attractive extractants for the recovery of carboxylic acids from dilute aqueous solutions. This paper reports experimental results for liquid−liquid equilibrium in organic/aqueous two-phase systems containing a tertiary amine (triisooctylamine) and five carboxylic acids, aconitic, citric, lactic, malic, and oxalic acid. Triisooctylamine (tris[6-methylheptyl]amine) was dissolved in various diluents such as chloroform, a mixture (heptane (50 vol %) + 1-hexanol (50 vol %)), and 1-octanol. Partition coefficients for individual acids were determined at a temperature of 25 °C over a range of amine concentration in each diluent between 2.5 vol % and 60 vol %. Thus, for aconitic, citric, lactic, malic, and oxalic acid the maximum values of partition coefficient were found to be 92.7, 47.0, 28.2, 65.2, and 76.0, respectively. For dilute solutions containing less than 3 mass % of acid, it is energetically preferable to remove the solute from the water through liquid−liquid extraction. Owing to the significant partition coefficients obtained with amine diluent systems, the process generates a small extract stream for subsequent regeneration processing. On the other hand, the recovery of solute by evaporation requires the energy intensive vaporization of water. Liquid−liquid extraction can be considered as an effective process for the recovery organic acids present in wastewater from industries such as distilleries, canneries, and wineries.

Introduction

In recent years, solvent extraction processes have received increasing attention for recovery of carboxylic acids from dilute aqueous solutions, notably with hydrophobic tertiary amines dissolved in various organic diluents (Tamada et al., 1990; Yang et al., 1991; Kirsch and Maurer, 1997; Yabannavar and Wang, 1991; Malmary et al., 1994). Conventional solvents such as alcohols, ketones, and ethers give low partition coefficients and moreover are relatively soluble in water (Kertes and King, 1986). Compared with these solvents, the strong interactions of amines with acids allow for the formation of acid−amine complexes and thus give rise to high partition coefficients. The specific affinity of long-chain tertiary amines for carboxylic acids gives high selectivity for this type of solute with respect to water and eventually nonacidic species in the mixture (King and Poole, 1991). The formation of acid−amine complexes also depends on the nature of diluents, which affect the basicity of the amine and the stability of the ion pair formed in the extract phase. These diluents can hydrogen bond with the oxygen accessible on the complexed carboxylic acid. Since the presence of the hydroxyl and carboxylic groups increases the solubility of acids in the water phase, the strong interactions of solvent with solutes were necessary to extract carboxylic acids from dilute aqueous solutions. Interaction energies between the amine molecules and organic acids must be in the range of the hydrogen bonds that exist between water molecules and acids. Furthermore, since the extracting power of a solvent is dictated by the basicity of the amine, tertiary amines seem to be more suitable extractants for organic acids compared to the primary and secondary amines. In addition, primary amines are too soluble in water, and secondary amines form amides upon regeneration of solvent by distillation. In the present case, at low concentration of acid in the aqueous solution (0.5 mass %), the dominant complex corresponds to a stoichiometric association between the acid and the tertiary amine (Juang and Huang, 1997). Polar diluents that enhance the extracting power of amines are more favorable than nonpolar diluents as shown in the extraction of citric, lactic, and succinic acid (King, 1993). In this work, various diluents such as chloroform, a mixture (heptane (50 vol %) + 1-hexanol (50 vol %)), and 1-octanol were investigated for their abilities to improve the extractive properties of tertiary amines. The experimental determination of partition coefficients of various carboxylic acids allowed one to quantify the effect of the concentration of extractant in the mixture extractant−diluent upon the transfer of solutes in the organic phase.

Experimental Section

Chemicals. Triisooctylamine (tris[6-methylheptyl]amine), chloroform, heptane, 1-hexanol, 1-octanol, aconitic, citric, lactic, malic, and oxalic acids were supplied by Aldrich Chemical Co. The purity of these products close to 99% was given by analysis with the high-performance liquid chromatography (HPLC) method. The volume fraction solubility of triisooctylamine in water is less than 20×10^{-6}. Distilled water that had been passed through a Milli-Q purification system (Millipore Corp.) was used to dilute the carboxylic acids.

Procedures. Batch extraction experiments were carried out at 25 °C in glass-stoppered separatory funnels with an organic to aqueous mass phase ratio of 2. On the basis of the average acid concentration of real effluents, synthetic solutions of individual carboxylic acid that contain 0.5 mass % of solute were prepared. The percentage of triisooctyl-

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amine in the mixture amine−diluent varied in a range of 2.5 vol % to 60 vol %. Thus, 25 g of aqueous solution of acid was contacted with 50 g of solvent (amine + diluent) by shaking in a thermostated device for 3.5 h, which was a widely considered sufficient time to reach equilibration between the organic and aqueous phases. After settling for over a period of 1.5 h, the aqueous and organic phases were analyzed. Carboxylic acid in the aqueous phase was titrated with standard sodium hydroxide solutions (0.01 M and 0.1 M), and phenolphthalein was used as an indicator. The organic layer was washed with a known excess amount of sodium hydroxide (0.1 M) in another separating funnel. The carboxylic acid present in the organic phase was then extracted into a sodium hydroxide solution as the corresponding sodium salt. After the two layers were separated, the alkaline solution containing the organic salt was back-titrated with hydrochloric acid solution (0.05 M) to find the excess amount of sodium hydroxide. The error induced from titrating and weighing was less than 2%. The partition coefficient (m) is defined as the ratio of acid concentration (mass %) in the organic phase to acid concentration (mass %) in the aqueous phase. HPLC analyses were carried out to confirm the carboxylic acid concentrations in both liquid phases at equilibrium. The HPLC system consisted of a pump (Spectra-Physics SP 8800), an integrator (Chromjet SP 4400), an UV spectrophotometer (Spectra 100 UV−vis detector: wavelength = 210 nanometers), and an organic acid column (BIO-RAD AMINEX ion exclusion HPX-87H) operated at 41 °C. The mobile phase was 0.005 M H_2SO_4, and its flow rate was 0.5 mL/min. The peak area on the chromatogram was used to compare with known standards to determine the acid concentration in the sample examined. The percentage standard deviation of the partition coefficients mentioned in Tables 1 to 3 was estimated to be 2% for all batch experiments.

Results and Discussion

The selection of solvent affects the design of a continuous process both in the extraction section and in the solvent regeneration cycle. The use of traditional carbon-bonded oxygen donor extractants requires large solvent flow rates because the partition coefficients of carboxylic acids obtained with these solvents are low (Kertes and King, 1986; Smagghe et al., 1991; Faizal et al., 1990; Duarte et al., 1989). Moreover, these extractants are relatively soluble in water and sometimes form azeotropes with water. Consequently, the regeneration of these components is costly. In the present work, experimental results for the liquid−liquid equilibrium involved with the reactive extraction of carboxylic acid with triisooctylamine dissolved in various diluents are given in Tables 1 to 3. The high partition coefficients obtained with tertiary amines result to a great extent from the ion pair association between alkylammonium cation and acid anion. Moreover, as complexes of carboxylic acids and amine are often hydrated, the coextraction of water was a significant feature in such a solvent extraction process. Formation of clusters of water molecules associated with the complexation sites occurs (King, 1993). A change in the diluent mixed with the tertiary amine can cause changes in the complexation equilibrium. The extractability of malic, aconitic, and citric acids is much greater in octanol and heptane−hexanol than in chloroform (Tables 1 to 3). With regard to malic acid, alcohol breaks the intramolecular hydrogen bond in bimalate ion: $HA^- + (ROH)_n \rightleftharpoons (ROH)_nHA^-$. The base can proceed further and abstract a proton from HA^- to form the dianion as an ion pair $(BH^+)_2A^{2-}(ROH)_n$ (Tamada et al., 1990). Since the two negative charges on A^{2-} are close together, the extracted 1:2 dicarboxylic acid:amine complex would be strongly alcoholated and hydrated. Lactic acid presumably extracts as a 1:1 complex. Chloroform favors 1:1 complex formation through strong hydrogen bonding with the available oxygen on the complex (King, 1993). Whatever the diluent used, we observed that the partition coefficient of individual carboxylic acids passes through a

Table 1. Partition Coefficients (m) of Aconitic, Citric, Lactic, Malic, and Oxalic Acids between Aqueous Solution (0.5 mass %) and Triisooctylamine Dissolved in Chloroform at 25 °C

	partition coefficients (m)				
concn of amine in the mixture, vol %	aconitic acid	citric acid	lactic acid	malic acid	oxalic acid
2.5	15.9	0.9	1.7	2.9	3.7
5.0	34.4	1.5	4.4	4.1	8.9
7.5	50.7	2.6	9.6	7.0	15.2
10.0	54.4	5.2	13.7	15.5	23.3
15.0	46.6	11.1	17.9	21.5	36.3
20.0	38.1	14.4	18.1	25.5	32.3
25.0	32.2	14.1	19.2	30.7	25.5
30.0	24.8	13.0	18.1	36.6	20.7
35.0	21.5	11.8	16.3	34.0	18.1
40.0	19.2	11.1	14.8	29.2	16.3
45.0	16.3	9.6	12.2	24.0	14.4
50.0	15.2	8.5	10.4	20.7	13.3
55.0	14.4	6.7	7.4	18.9	12.2
60.0	14.1	3.7	5.2	15.9	10.4

Table 2. Partition Coefficients (m) of Aconitic, Citric, Lactic, Malic, and Oxalic Acids between Aqueous Solution (0.5 mass %) and Triisooctylamine Dissolved in (Heptane (50 vol %) + 1-Hexanol (50 vol %)) at 25 °C

	partition coefficients (m)				
concn of amine in the mixture, vol %	aconitic acid	citric acid	lactic acid	malic acid	oxalic acid
2.5	19.0	2.8	2.8	7.8	2.8
5.0	38.8	4.9	3.7	8.6	3.1
7.5	58.3	6.6	4.1	11.8	3.2
10.0	65.2	8.8	5.5	19.5	6.8
15.0	86.0	10.5	8.4	38.1	13.5
20.0	92.7	15.6	9.9	55.7	15.1
25.0	71.0	23.9	11.3	65.2	19.8
30.0	44.0	28.6	14.0	43.0	23.4
35.0	32.0	23.9	12.6	32.0	26.0
40.0	27.0	17.4	11.2	27.5	31.3
45.0	24.0	15.5	9.8	23.0	35.8
50.0	22.0	13.9	7.0	19.7	44.0
55.0	18.0	9.2	5.7	15.5	38.0
60.0	17.6	6.2	3.1	13.1	35.0

Table 3. Partition Coefficients (m) of Aconitic, Citric, Lactic, Malic, and Oxalic Acids between Aqueous Solution (0.5 mass %) and Triisooctylamine Dissolved in 1-Octanol at 25 °C

	partition coefficients (m)				
concn of amine in the mixture, vol %	aconitic acid	citric acid	lactic acid	malic acid	oxalic acid
2.5	8.0	12.8	5.1	3.1	4.6
5.0	23.9	20.3	8.6	6.1	11.7
7.5	39.1	33.8	9.4	16.2	16.2
10.0	53.5	36.0	11.4	22.0	20.8
15.0	71.0	37.9	15.2	38.3	29.6
20.0	55.0	39.5	28.2	43.7	37.0
25.0	43.0	41.5	25.9	59.0	46.0
30.0	41.0	47.0	18.6	30.7	51.0
35.0	36.3	41.9	16.0	27.8	56.6
40.0	33.0	37.2	13.3	23.9	76.0
45.0	27.0	28.9	13.0	19.7	73.0
50.0	25.3	26.0	12.6	16.7	71.5
55.0	21.0	21.1	12.1	15.0	65.6
60.0	21.6	19.0	10.6	13.9	57.5

maximum with increasing amine concentration, which can be explained as follows. Since the undissociated form of carboxylic acids was the only one extracted by the solvent, the acidic pH of the initial aqueous solution that contains 0.5 mass % of acid was favorable to the transfer of solute into the organic phase. However, at lower carboxylic acid concentration in the aqueous phase, there is a substantial effect of the amine on the aqueous phase pH. Indeed, on increasing the amine concentration in the organic phase, a small amount of amine dissolved in water. Since triisooctylamine is a base, the pH of the aqueous phase increased (Kirsch et al., 1997). Consequently, the dissociation of carboxylic acid becomes predominant, and a decreasing amount of solute was extracted by the solvent. With regard to the regeneration of this class of solvent, the back-extraction with an aqueous base such as sodium or calcium hydroxide appears the most obvious method; however, this process produces carboxylate salts rather than carboxylic acids. To obtain the carboxylic acid, the process requires a displacement of carboxylic acid with a stronger acid such as sulfuric acid, which involves consumption of this latter acid and also the production of salt. An alternative method of solvent recovery consists of displacing the carboxylic acid from the solvent by a hydrochloric acid solution to produce an undissociated carboxylic acid solution. However, to obtain a high recovery of carboxylic acid, it was necessary to use more than the stoichiometric amount of hydrochloric acid (Yabannavar and Wang, 1991). Then, since the tertiary amines do not form amides, it is possible to regenerate the solvent by distilling off the volatile hydrochloric acid. Finally, even though the extracting power of tertiary amine is limited by the stoichiometry of complexation, in view of its quasi-insolubility in water, its slight toxicity, and its possible recovery through back-extraction, this type of solvent tends to be a complexant of choice for recovery of carboxylic acids from dilute aqueous solutions.

Literature Cited

Duarte, M. L.; Lozar, J.; Malmary, G.; Molinier, J. R. Equilibrium diagrams at 19 °C of water + malic acid + 2-methyl-1-propanol, water + malic acid + 1-pentanol, and water + malic acid + 3-methyl-1-butanol ternary systems. *J. Chem. Eng. Data* **1989**, *34*, 43−45.

Faizal, M.; Smagghe, F.; Malmary, G.; Lozar, J.; Molinier, J. Equilibrium diagrams at 25 °C of water + oxalic acid + 2-methyl-1-propanol, water + oxalic acid + 1-pentanol, and water + oxalic acid + 3-methyl-1-butanol ternary systems. *J. Chem. Eng. Data* **1990**, *35*, 352−354.

Juang, R. S.; Huang, R. H. Equilibrium studies on reactive extraction of lactic acid with an amine extractant. *Chem. Eng. J.* **1997**, *65*, 47−53.

Kertes, A. S.; King, C. J. Extraction chemistry of fermentation product carboxylic acids. *J. Biotechnol. Bioeng.* **1986**, *28*, 269−282.

King, C. J. Advances in separation techniques: recovery of polar organics from aqueous solution. *11th International Congress of Chemical Engineering,* Chisa, Praha, 1993; Paper P2.1, p 1062.

King, C. J.; Poole, L. J. Regeneration of carboxylic acid-amine extracts by back-extraction with an aqueous solution of volatile amine. *Ind. Eng. Chem. Res.* **1991**, *30*, 923−929.

Kirsch, T.; Maurer, G. Distribution of binary mixtures of citric, acetic and oxalic acids between water and organic solutions of tri-*n*-octylamine. *Fluid Phase Equilib.* **1997**, *131*, 213−231.

Kirsch, T.; Ziegenfuss, H.; Maurer, G. Distribution of citric, acetic and oxalic acids between water and organic solutions of tri-*n*-octylamine. *Fluid Phase Equilib.* **1997**, *129*, 235−266.

Malmary, G.; Vezier, A.; Robert, A. Mourgues, J.; Conte, T.; Molinier, J. Recovery of tartaric and malic acids from dilute aqueous effluents by solvent extraction technique. *J. Chem. Technol. Biotechnol.* **1994**, *60*, 67−71.

Smagghe, F.; Faizal, M.; Malmary, G.; Molinier, J. Equilibrium diagrams at 20 °C of water + tartaric acid + 2-methyl-1-propanol, water + tartaric acid + 1-pentanol, and water + tartaric acid + 3-methyl-1-butanol ternary systems. *J. Chem. Eng. Data* **1991**, *36*, 65−67.

Tamada, J. A.; Kertes, A. S.; King, C. J. Extraction of carboxylic acids with amine extractants. *Ind. Eng. Chem. Res.* **1990**, *29*, 1319−1326.

Yabannavar, V. M.; Wang, D. I. C. Extractive fermentation for lactic acid production. *J. Biotechnol. Bioeng.* **1991**, *37*, 1095−1100.

Yang, S. T.; White, S. A.; Hsu, S. T. Extraction of carboxylic acids with tertiary and quaternary amines: Effect of pH. *Ind. Eng. Chem. Res.* **1991**, *30*, 1335−1342.

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