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Water Enhanced Solubilities of Succinic Acid in Reactive Extraction Using Tertiary Amines/Alcohols Systems

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Abstract−Tertiary amines were used as the extractants for reactive extraction in alcohol diluents. Equilibrium and hydration data for various alcohol diluents and tertiary amines were obtained. From these data, the effect of coextracted water on extractability was investigated. For the measurement of the water-enhanced solubilities of succinic acid, the sensitivity index was introduced. The amount of coextracted water into organic phase was increased with the chain length of alcohol diluents. However, the water-enhanced solubility of succinic acid was almost constant with the chain length of alcohol diluents. The sensitivity indices were proportional to the chain length of tertiary amines; thus, the water-enhanced solubilities of succinic acid were increased.

Key words: Amine, Chain Length, Extraction, Succinic Acid, Water Solubility

INTRODUCTION

The recovery of succinic acid has recently been drawing much interest due to its use as the monomer of biodegradable polymer. Tertiary amines are known to be effective extractants for carboxylic acids and metal salts from aqueous media [Fahim et al., 1998; Hong and Hong, 2000a; Hong et al., 2000].

Investigations on reactive extraction using tertiary amines have mainly focused on the selection of appropriate extractants and diluents, the development of equilibrium models, and the spectroscopic analysis for the reaction mechanism [Tamada et al., 1990; Tamada and King, 1990a; Han and Hong, 1996; Han et al., 2000]. The phenomenon of water coextraction was reported by some researchers but was not investigated systematically [Tamada and King, 1990b; Han and Hong, 1998].

As the acid molecules transfer from the aqueous to the organic phase during reactive extraction, they may be accompanied by the molecules of water. The solubilities of carboxylic acids in certain organic solvents increase markedly as the water content in the organic phase increases. Under these circumstances the solubility can considerably exceed the solubility in either water or solvent alone. An example is the case of adipic acid and methylcyclohexanone. The solubilities of adipic acid are 1.6, 9.7 and 1.4 wt%, in anhydrous methylcyclohexanone, water-saturated methylcyclohexanone, and water, respectively at 25 °C [Apelblat and Manzurola, 1987; Starr and King, 1992]. Water-enhanced solvation is a manifestation of a phenomenon where the intermolecular interaction in a solute-solvent system containing water is stronger than in the water-free solute-solvent binary system. The implication is that the water and solute interact more strongly than do the solute and solvent. In cases such as the adipic acid-water-methylcyclohexanone, where the solubility of a solute is greater in a water-containing solvent than in water or solvent alone, the further implication is that the solute, water, and solvent form a ternary solvate or complex in which the interactions are stronger than in the solute-water and solute-solvent binaries. This conclusion can be generalized to any case where the activity coefficient of a solute reaches a lower value in a solvent-water mixture than in water or solvent alone [Lee et al., 1994].

Determining the amount of this coextracted water is useful because organic-phase water potentially affects the distribution of acid into the solvent by interacting with the acid-amine complex. Furthermore, to the extent that the amount of water extracted into the organic phase is high, the product acid will require further concentration, thereby influencing process economics [Tamada and King, 1990b].

For these reasons, the effect of coextracted water is considered important in reactive extraction of carboxylic acids. Bizek et al. interpreted the reactive extraction using thermodynamic concepts and predicted the concentration of water in the organic phase [Bizek et al., 1992]. Han and Hong considered the coextracted water as the reaction species and predicted the equilibrium and the hydration curves. And they introduced the concept of sensitivity index for the quantitative analysis on the water-enhanced solubility of lactic acid [Han and Hong, 1996, 1998]. Starr and King applied the effect of coextracted water on the extraction to the stripping process of physical extraction. They found that water removal from the organic phase could decrease the solubility of carboxylic acid. This phenomenon was applied for the stripping method of carboxylic acid by the removal of water from the organic phase [Starr and King, 1992]. Bizek et al. studied the effect of active diluent on the reactive extraction of carboxylic acid using amines and the coextraction of water, but they did not consider the water-enhanced solubilities of carboxylic acid [Bizek et al., 1993].

In this study, we investigated the effect of the coextraction of water as the polarity of alcohol diluents and the chain length of tertiary amine on the extraction characteristics, and explained the water-

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enhanced solubilities of succinic acid quatitatively by introducing of the concept of solubility index.

EXPERIMENTAL

1. Materials

Tripropylamine (TPA), tributylamine (TBA), tripentylamine (TPeA) and trioctylamine (TOA) were used as the extractants. They were used without further purification. TOA, a C_8 straight-chain tertiary amine, was obtained from Acros Co. TPA, TBA, and TPeA were purchased from Aldrich Co.

Diluents were used in reactive extraction of succinic acid because of the high boiling point, the high viscosity, and the corrosive property of tertiary amines. Alcohols such as 1-butanol, 1-hexanol and 1-octanol were used as active diluents. They can be classified as carbon bonded active diluents. All reagents were GR grade.

Tertiary amines and alcohol diluents except for 1-butanol used in this study are little solvable in water. Therefore, the effect of the solvation of these materials into aqueous phase could be negligible. In general, in the case of 1-butanol, its solubility in water is about 7 wt%. But, in the systems used in this study, no significant volume change of both phases was observed.

Succinic acid (99 wt%) was obtained from SIGMA. It was diluted to various concentrations in Aqueous Phase.

2. Experimental Procedures

Succinic acid from aqueous phase was extracted as follows.

The 10 ml solution of succinic acid and the 10 ml organic phase were charged into a 30 ml vial. To maintain the vial at constant temperature, the vial was immersed in a water bath for 30 min. before phase mixing. Phase mixing was carried out by stirring with magnetic bar at 1,000 rpm for 2 hr. The operating temperature was 25 °C. For clear separation of two phases after each extraction, mixed phases were centrifuged at 4,000 rpm for 15 min. The samples of each phase were taken out for analysis of the concentrations of water and succinic acid.

The concentration of succinic acid was titrated by 0.05 N NaOH by using the phenolphthalein indicator. The water concentration in the organic phase was determined by a Coulometric Karl-Fisher Titrimeter.

RESULTS AND DISCUSSION

1. The Effect of the Amine Concentration and the Polarity of Diluent

According to the following reaction in reactive extraction, the solubilities of succinic acid by the mixed solvents that are composed of the amine and the active diluents are divided into two classes. First, succinic acid is extracted by reaction with amines, as in Eq. (1). Second, as can be seen in Eq. (3), succinic acid is physically extracted by the characteristic groups of active diluents.

$$\text{a succinic acid} + \overline{\text{Amine}} + \text{pH}_2\text{O} \leftrightarrow \overline{\text{Succinic acid}_a \cdot \text{Amine} \cdot (\text{H}_2\text{O})_p} \quad (1)$$

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

$$\text{Succinic acid} \leftrightarrow \overline{\text{Succinic acid}} \quad (3)$$

Table 1. Distribution coefficients in physical extraction of succinic acid

	1-Butanol	1-Hexanol	1-Octanol	1-Decanol
D	1.4248	0.8096	0.4347	0.3873

First of all, the reaction of succinic acid with amines does not have large influence on the total solubility of succinic acid because the active diluents used in this experiment have good solubilities for the complex formed by the reaction. Second, the physical extraction of succinic acid strongly influences the equilibria and hydration curves because the physical extraction of succinic acid and water varies with the type of characteristic group of active diluents. The distribution coefficients (D) as determined by physical extraction are listed in Table 1.

As seen in Table 1, the alcohol diluents have good physical solubilities for succinic acid water due to the hydrogen bonds. In the physical extraction complex, the hydrogen of succinic acid is hydrogen bonded to the oxygen of water, and the oxygen atom of the alcohol diluents is also to the hydrogen of water.

Fig. 1 shows the effect of the moles of tripropylamine (TPA) on the amount of extraction in various alcohol diluents. In TPA/1-hexanol and TPA/1-octanol system, the amount of coextracted water is almost constant and independent of the concentration of TPA. However, in the case of 1-butanol, the amount of coextracted water is proportional to the TPA concentration. It is due to the higher solubility for water and for acid-amine-water complex than that of other diluents.

The hydration curves with the polarity of alcohol diluents are represented in Fig. 2. The amount of hydration increases with the polarity of diluent. But, the amount of coextracted water is not largely influenced by the concentration of succinic acid in raffinate phase.

The slopes shown in Fig. 3 are the water-enhanced solubilities of succinic acid in reactive extraction. The lower slopes mean higher

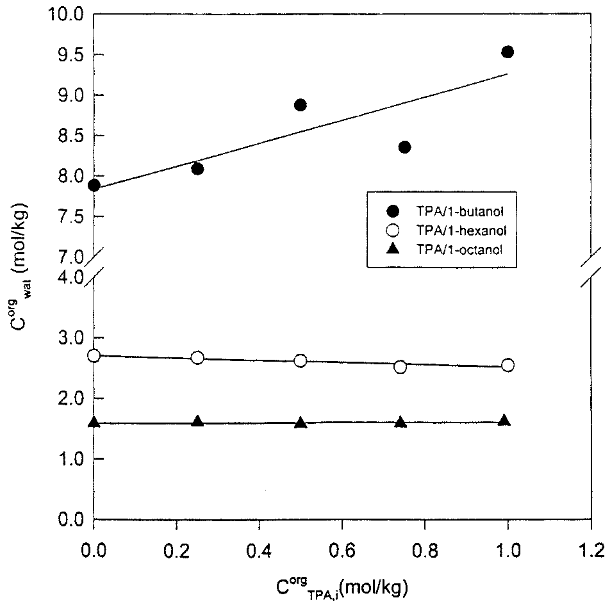

Fig. 1. Effect of TPA concentration on the amount of coextracted water.

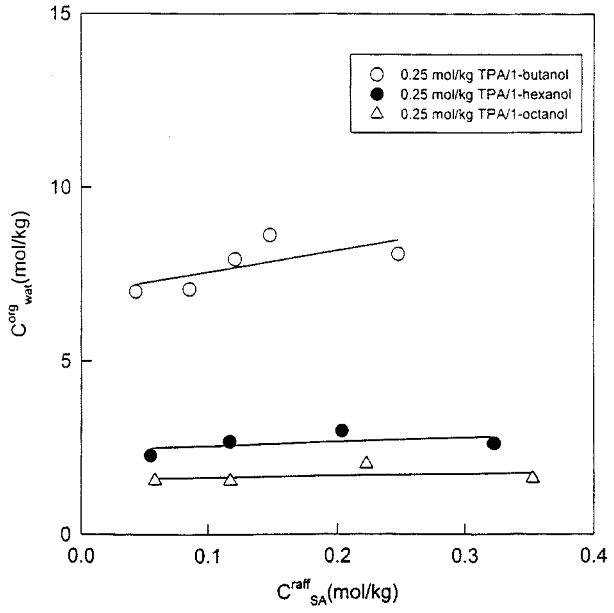

Fig. 2. Hydration curves with the polarity of alcohol diluents.

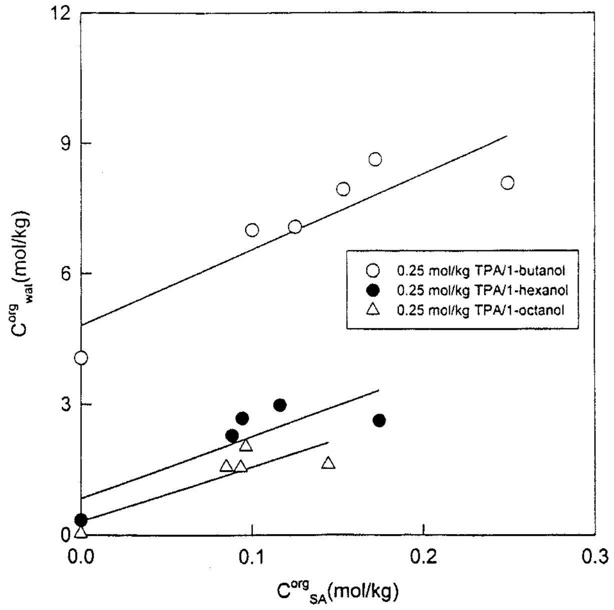

Fig. 3. Water-enhanced solubilities of succinic acid in TPA/alcohol diluents.

water-enhanced solubilities of succinic acid. The sensitivity index was introduced as the measure of the water-enhanced solubilities of each active diluent and defined as follows:

$$S = 1/\text{slope} = \Delta C^{Org}_{SA} / \Delta C^{Org}_{Water} \quad (4)$$

These values indicate the increase of the solubility of succinic acid by an increase of the solubility of water in the organic phase.

As seen in Fig. 3, the slopes of each diluent are almost same. It is indicated that the diluents having the same characteristic group have a similar value of the sensitivity indices, thereby the sensitivity indices are the characteristics due to the characteristic groups of active diluents.

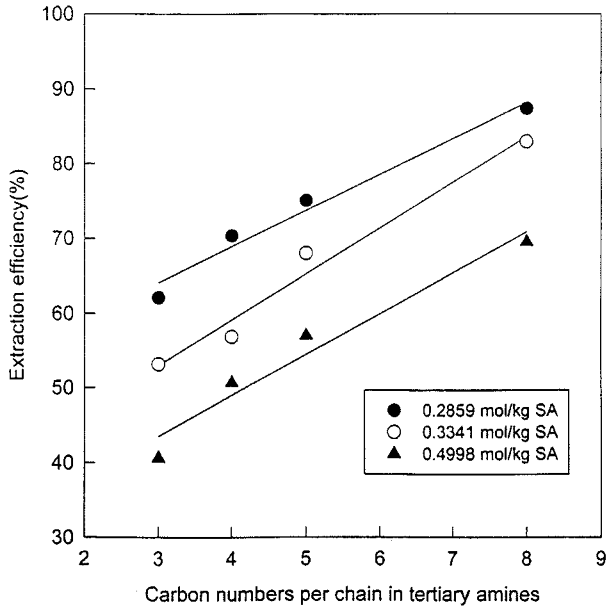

Fig. 4. Effect of the chain length of tertiary amines on extraction efficiency in 1-octanol.

2. Effect of the Chain Length of Tertiary Amines

There are various basic factors affecting the extractability for carboxylic acid in reactive extraction. The chain length of amine is an important one among them. The extractabilities of primary and secondary amines slightly change with increasing of their chain length. However, the extractabilities of tertiary amines increase with their chain length [Hong and Hong, 2000b]. As seen in Fig. 4, the extractabilities of tertiary amines in active diluent are proportional to their chain length. It is not only due to the basicity of tertiary amine but also due to the water-enhanced solubility by coextracted water.

Fig. 5 shows the hydration data with the chain length of tertiary amines dissolved in 1-octanol. The amount of hydration increases

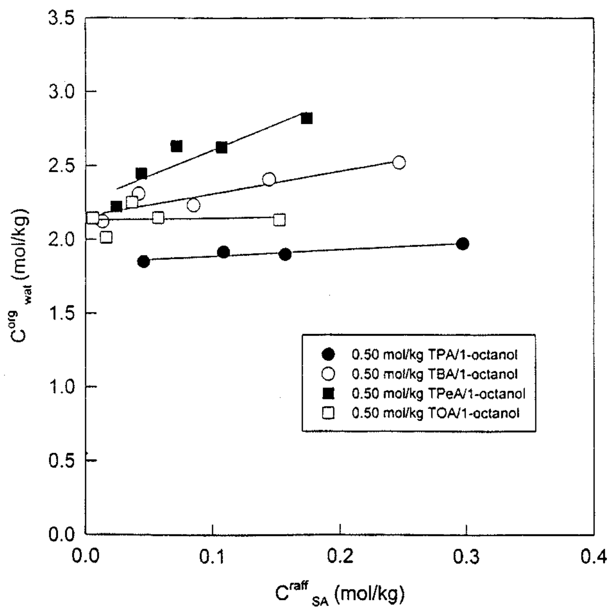

Fig. 5. Hydration curves with the chain length of tertiary amines.

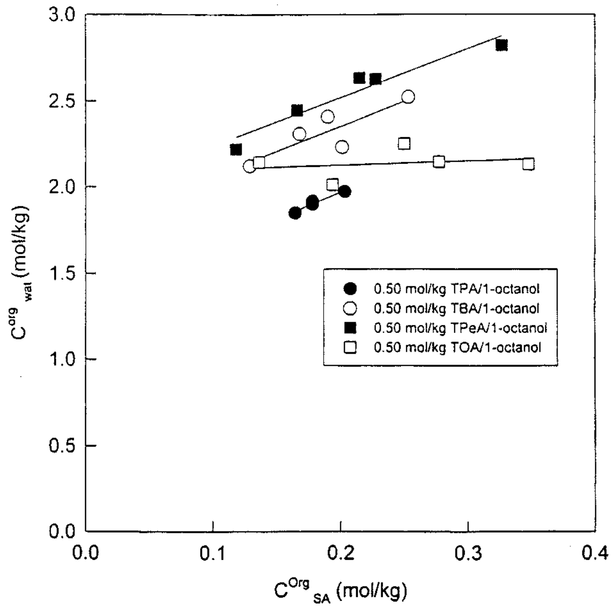

Fig. 6. Water-enhanced solubilities of succinic acid in tertiary amines/1-octanol.

Table 2. Solubility indices of tertiary amines in 1-octanol

Extractant	Slope	Sensitivity index (S)
TPA	3.08	0.32
TBA	2.90	0.34
TpeA	2.81	0.36
TOA	0.24	4.15

with the chain length of tertiary amines until TPeA. But, in TOA/1-octanol system, the amount of coextracted water is lower than that in TPeA and TBA.

Fig. 6 shows the coextracted water in the organic phase in 0.5 mol/kg tertiary amines/1-octanol. The slopes are slightly decreased as the chain length of tertiary amine increases up to TPeA. However, the slopes for TOA are abruptly lower than those for other tertiary amines. It means that the sensitivity index for TOA is larger and the water-enhanced solubility of TOA is higher than that of other amines. In the case of TOA, although the amount of coextracted water is lower than that of other amine, the interaction between TOA and succinic acid is highly enhanced by the coextracted water because of the high basicity of TOA.

CONCLUSION

The water-enhanced solubilities of succinic acid were explained by the action of the polarity of alcohol diluents and the chain length of tertiary amines. The water-enhanced solubilities were almost constant with the polarity of alcohol diluents and the concentration of tertiary amine. The chain length of tertiary amines has large influence on the water-enhanced solubilities of succinic acid.

The sensitivity index, which represents the amount of succinic acid extracted with the variation of water content in organic phase, was defined as the inverse of the slope. The sensitivity index increased with the chain length of tertiary amines.

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REFERENCES

Apelblat, A. and Manzurola, E., "Solubility of Oxalic, Malonic, Succinic, Maleic, Malic, Citric, and Tartaric Acids in Water from 278.15 to 338.15 K," *J. Chem. Thermodyn.*, **19**, 317 (1987).

Bizek, V., Horacek, J., Kousova, M., Heyberger, A. and Prochazka, J., "Mathematical Model of Extraction of Citric Acid with Amine," *Chem. Eng. Sci.*, **47**, 1433 (1992).

Bizek, V., Horacek, J. and Kousova, M., "Amine Extraction of Citric Acid: Effect of Diluent," *Chem. Eng. Sci.*, **48**, 1447 (1993).

Fahim, M. A., Qader, A. and Hughes, M. A., "Extraction Equilibria of Acetic and Propionic Acids from Dilute Aqueous Solution by Several Solvents," *Sep. Sci. Techn.*, **27**, 1809 (1992).

Lee, J. H., Brunt, V. V. and King, C. J., "Water-Enhanced Solvation of Organic Solutes in Ketone and Ester Solvents," *Ind. Eng. Chem. Res.*, **33**, 1373 (1994).

Han, D. H., Hong, Y. K. and Hong, W. H., "Separation Characteristics of Lactic Acid in Reactive Extraction and Stripping," *Korean J. Chem. Eng.*, **17**, 528 (2000).

Han, D. H. and Hong, W. H., "Reactive Extraction of Lactic Acid in a Packed Column," *Korean J. Chem. Eng.*, **15**, 324 (1998a).

Han, D. H. and Hong, W. H., "Reactive Extraction of Lactic Acid with Trioctylamine(TOA)/Methylene Chloride(MC)/n-Hexane," *Sep. Sci. Techn.*, **31**, 1123 (1996).

Han, D. H. and Hong, W. H., "Water Enhanced Solubilities of Lactic Acid in Reactive Extraction Using Trioctylamine/Various Active Diluents System," *Sep. Sci. Techn.*, **33**, 271 (1998).

Hong, Y. K. and Hong, W. H., "Reactive Extraction of Lactic Acid with Mixed Tertiary Amine Extractants," *Biotechn. Techn.*, **13**, 915 (1999).

Hong, Y. K. and Hong, W. H., "Reactive Extraction of Succinic Acid with Tripropylamine (TPA) in Various Diluents," *Biopro. Eng.*, **22**, 281 (2000a).

Hong, Y. K. and Hong, W. H., "Equilibrium Studies on the Reactive Extraction of Succinic Acid from Aqueous Solutions with Tertiary Amines," *Biopro. Eng.*, **22**, 477 (2000b).

Hong, Y. K., Hong, W. H. and Chang, H. N., "Selective Extraction of Succinic Acid from Binary Mixture of Succinic Acid and Acetic Acid," *Biotech. Lett.*, **22**, 871 (2000).

Starr, J. N. and King, C. J., "Water-Enhanced Solubility of Carboxylic Acids in Organic Solvents and its Application to Extraction Processes," *Ind. Eng. Chem. Res.*, **31**, 2572 (1992).

Tamada, J. A., Kertes, A. S. And King, C. J., "Extraction Of Carboxylic Acids with Amine Extractants. 1. Equilibria and Law of Mass Action Modeling," *Ind. Eng. Chem. Res.*, **29**, 1319(1990).

Tamada, J. A. and King, C. J., "Extraction of Carboxylic Acids with Amine Extractants. 2. Chemical Interactions and Interpretation of Data," *Ind. Eng. Chem. Res.*, **29**, 1327 (1990a).

Tamada, J. A. and King, C. J., "Extraction of Carboxylic Acids with Amine Extractants. 3. Effect of Temperature, Water Coextraction, and Process Considerations," *Ind. Eng. Chem. Res.*, **29**, 1333 (1990b).