Influence of Chain Length of Tertiary Amines on Extractability and Chemical Interactions in Reactive Extraction of Succinic Acid

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Abstract−Reactive extraction of succinic acid from aqueous solutions with various tertiary amines dissolved in 1-octanol and in n-heptane has been studied as a function of the chain length of the tertiary amine. In the tertiary amine extractants in 1-octanol, the extractabilities of tertiary amines were proportional to their chain length. But, in n-heptane, the extractabilities of tertiary amines decreased with their chain length. In order to analyze chemical interactions involved in the complexation of succinic acid with amine extractants in 1-octanol and n-heptane, infrared (IR) spectroscopy was used. From IR spectroscopy, it was found that the difference of extractability in 1-octanol and in n-heptane was mainly due to the different degree of intramolecular hydrogen bonding of succinic acid with the polarity of diluents. And the possible stoichiometry of acid-amine-diluent complex was predicted as (1,1), (2,1), (1,1,1).

Key words: Succinic Acid, Chain Length of Amine, Intramolecular Hydrogen Bond, Polarity

INTRODUCTION

Succinic acid is a dicarboxylic acid produced as an intermediate of the tricarboxylic acid cycle (TCA) and also as one of the fermentation products of anaerobic metabolism [Gottschalk, 1986]. Fermentation-derived succinic acid has the potential to become a large-volume industrial chemical that could form the basis for supplying many intermediates and specialty chemicals for the consumer product industry [Zeikus et al., 1999]. Recently, succinic acid has been drawing much interest due to its use as the monomer of polysuccinate, which is biodegradable polymer [Hong et al., 2002].

In general, most carboxylic acids, except for acetic acid, are non-volatile; therefore, distillation is not a useful recovery process. The classical recovery method for these is the precipitation of the calcium salt after the addition of calcium hydroxide to the aqueous fermentation broth. The precipitation method also has disadvantages such as the substantial cost of chemicals, a low yield in crystallization and product loss [Tung and King, 1994].

A reactive extraction method has been proposed to be an effective primary separation step for the recovery of succinic acid from a dilute fermentation process [Hong et al., 2002; Kim et al., 2002]. This separation process uses the reaction between extractant and succinic acid. The extractant in the organic phase reacts with succinic acid in the aqueous phase and then the reaction complex that is formed is solubilized into the organic phase [Han and Hong, 1998; Han et al., 2000].

Three categories of extractants are used in reactive extraction: carboxylic acid extraction by solvation with carbon-bonded oxygen-bearing extractants, by solvation with phosphorous-bonded oxygen-bearing extractants, and by proton transfer or by ion-pair formation using high molecular weight aliphatic amines [Han et al., 2000]. It has been reported that aliphatic amine extractants are more effective than other extractants. Among the aliphatic amines, tertiary amines are the most widely used for the recovery of carboxylic acids because the primary and the secondary amines tend to react irreversibly with carboxylic acid and stripping the solvent becomes difficult [Ricker et al., 1979]. In general, tertiary amines extract only the undissociated form of the carboxylic acid. However, quaternary amines can extract both the undissociated and dissociated acids; moreover, the regeneration of extracted acids is difficult [Yang et al., 1991].

The extractability of acid, in contrast to that of anionic acidic metal complexes, depends more on the composition of the organic phase and the property of amine and diluent than on the aqueous phase conditions. Especially, the chain lengths of amine and the amine class are important in reactive extraction [Hong and Hong, 2000].

Grinstead investigated the behavior and base strength of various amine types and classes in the reactive extraction of hydrochloric acid in toluene diluent. He reported that the base strength decreased in the order primary>secondary>tertiary [Grinstead, 1967]. Rieux et al. investigated the effect of amine class and properties of diluent on amine basicity. They found that the effect of amine class on the extractability was changed with the type of diluent. In benzene and chloroform, the basicities of the amines followed the order, secondary=tertiary>primary, in ketones secondary>tertiary>primary [Rieux et al., 1964].

However, the primary and the secondary amine are not used in reactive extraction, although they have higher extractability than that of tertiary amine. As in the previous description, this is due to the irreversible reaction and the amide formation by primary and secondary amine. The tertiary amine reacts reversibly with carbox-

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‡This paper is dedicated to Professor Hyun-Ku Rhee on the occasion of his retirement from Seoul National University.

Table 1. The properties of tertiary amines used in this study

Chemicals	Molecular weight	Structure	Density	Manufacturing Co.
Tripropylamine (TPA)	143.27	$(CH_3(CH_2)_2)_3N$	0.735	Aldrich
Tributylamine (TBA)	185.36	$(CH_3(CH_2)_3)_3N$	0.778	Aldrich
Tripentylamine (TPeA)	227.44	$(CH_3(CH_2)_4)_3N$	0.782	Aldrich
Trioctylamine (TOA)	353.66	$(CH_3(CH_2)_7)_3N$	0.809	Aldrich

ylic acid; thereby the recovery of extracted acid and extractant is easy [San-Martin et al., 1992].

In general, as the chain length of tertiary amine increases, its dipole moments increase. So, the basicity of tertiary amine increases with its chain length. The reactivity of tertiary amines with carboxylic acids depends not only on the properties of diluent but also on their chain length. However, there are few studies on the effect of the chain length of amine on the extractability.

Recently, we reported that in the amine-based extraction of succinic acid the extractabilities of tertiary amines are proportional to their chain length in active diluent and vice versa in inactive diluent [Hong and Hong, 2000; Hong et al., 2002]. However, a spectroscopic study was not carried out in that study. Therefore, interpretation of equilibrium data and chemical interactions between acid and amine in active diluent and inactive diluent was carried out by IR spectroscopy. Furthermore, the stoichiometry of acid-amine complexes were proposed by the analysis of IR spectra.

EXPERIMENTAL

1. Materials

The properties of tertiary amines used in this study are represented in Table 1. Due to their high purity, they were used as an extractant without further purification. Succinic acid was purchased from SIGMA. The initial concentration of succinic acid in aqueous phase was varied from 0.14 mol/kg to 0.5 mol/kg to obtain the equilibrium data. The concentration of tertiary amine in organic phase was 0.5 mol/kg as the basis of diluents. Diluents used in this study were 1-octanol and n-heptane, which can be classified as a carbon bonded active diluent and as an inactive diluent, respectively.

2. Experimental Procedure

Extraction procedures were as follows. The 10 ml aqueous succinic acid solution and the 10 ml amine-diluent mixture were charged into a 25 ml vial. To maintain the temperature of the vials at 25 °C, vials were immersed in the water bath for 30 min, before phase mixing. Phase mixing was carried out by stirring with a magnetic bar at 1,000 rpm and 25 °C for 2 hr. For the clear separation of two phases after each extraction, mixed phases were centrifuged at 5,000 rpm for 15 min. Samples of each phase were taken for the analysis of the concentration of succinic acid.

The concentration of succinic acid in the aqueous phase was determined by HPLC with an ion exchange column (Supercogel C-601H, 300 mm×7.8 mm, SUPELCO, USA) using 0.1 wt% H_2PO_3 as the mobile phase.

IR spectroscopy (Bomen, Model MB 100-C15) was used to investigate the chemical interaction of acid-amine complex. KBr powder was pressed into tablets and then, organic phase was examined as a thin liquid film on a KBr surface.
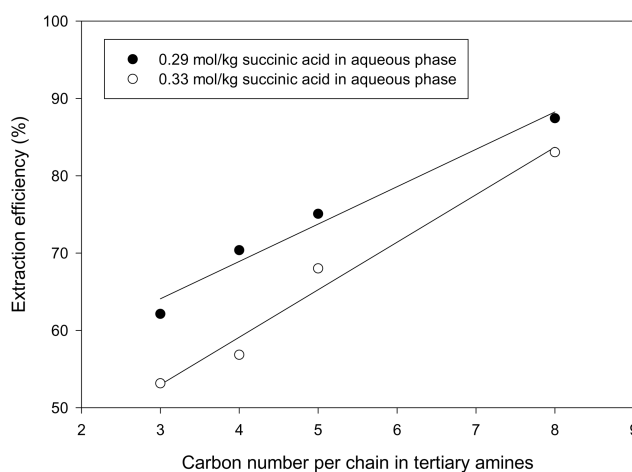

Fig. 1. Extraction efficiency of succinic acid with various tertiary amines in 1-octanol (0.5 mol/kg tertiary amine/1-octanol) [Hong and Hong, 2000].

RESULTS AND DISCUSSION

1. Equilibrium Distribution of Succinic Acid

The effect of the chain length of tertiary amine in active diluent on extraction efficiency has already reported in previous papers [Han et al., 2000; Hong and Hong, 2000]. As seen in Fig. 1, the extraction efficiency increased with the chain length of tertiary amine in 1-octanol diluent. The basicity of primary and secondary amines slightly changes with increasing chain length; however, that of the tertiary amines increases with their chain length. Because the amount of succinic acid physically extracted by only 1-octanol can be neglected in comparing with the amount of succinic acid by tertiary amine, the extractability of amines is determined by the ability to form the amine-acid complex and increased in 1-octanol with increasing their chain length [Hong and Hong, 2000]. The same result was also reported in the amine-based extraction of lactic acid that is monocarboxylic acid [Han et al., 2000].

In the case of inactive diluent, the distribution of succinic acid into organic phase decreases with the chain length of tertiary amines (Fig. 2). It is due to the poor solvating power for acid-amine complex of n-heptane and the increased degree of aggregation in the order TPA<TBA<TPeA<TOA. In the inactive diluent such as a n-heptane, the more polar the acid-amine complex, the more favorable it is to form aggregates. The dipole moments of TPA and TBA are 0.58 and 0.78 debyes, respectively [Weast, 1998]. It can be predicted that the dipole moments of tertiary amines increase with their chain length. The basicity of amines increases with their dipole moments; thus, the aggregate formation is more favorable with increasing their chain length. Moreover, the aggregate formation in reac-
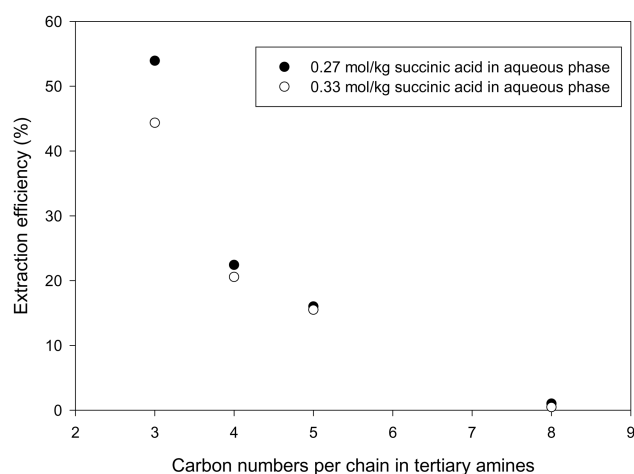
Fig. 2. Extraction efficiency of succinic acid with various tertiary amines in n-heptane (0.5 mol/kg tertiary amine/n-heptane) [Hong et al., 2002].

Fig. 3. Two type of bisuccinate anion.

tive extraction of dicarboxylic acids such as a succinic acid is possible because they have two carboxyl groups. The aggregate formation between succinic acid and tertiary amine makes solvation of acid-amine complexes into organic phase difficult. However, in the active diluent such as a 1-octanol, aggregate formation is not present due to the polarity of the active diluent and its good solvating power for acid-amine complex. In the amine-based extraction of lactic acid by nonpolar diluent, the same results were reported [Han et al., 2000]

2. Formation of Succinic Acid-amine Complex

The fundamental difference between oxygen- and nitrogen-bearing basic extractants in the reactive extraction of carboxylic acids is the behavior of the acid proton during the transfer from an aqueous into an organic phase. In systems with oxygen-bearing solvents, whether carbon, phosphorus, or sulfur bound, the acid strength in the aqueous solutions and that of the hydrogen bond in the organic phase is the measure of extractability. On the other hand, the acid extracted into an amine-containing organic phase is no longer regarded as an acid but as an ammonium salt. It is thus the extent of ion pair association between the alkylammonium cation and the acid radical that is the measure of extractability, or more precisely, the stability of the organic phase species [Kertes and King, 1986]. Thus, the extraction process is based on an acid-base type reaction between the alkylamine and the acid.

In investigation of the characteristics of the -COOH group of the acid by IR spectroscopy, two of the most useful peaks are the asymmetric peak of the carboxylate stretch at 1,550-1,620 cm^{-1} and the carbonyl stretch, C=O peak of the carboxyl (-COOH) group at 1,700-1,780 cm^{-1}. For aliphatic carboxylic acids, a hydrogen-bonded carbonyl and a non-hydrogen bonded carbonyl can be assigned as 1,700-1,720 cm^{-1} and as 1,760-1,780 cm^{-1}, respectively [Barrow and Yerger, 1954; Tamada, 1989].

In addition to those mentioned above, the carboxyl group gives two bands arising from the -C-O stretch coupled with -O-H in-plane deformation, a weak band at 1,350-1,440 cm^{-1} and a stronger band at 1,210-1,320 cm^{-1}. The O-H stretch may appear at 3,500-3,550 cm^{-1} for a free -OH group or as a broad band at 2,500-3,300 cm^{-1}
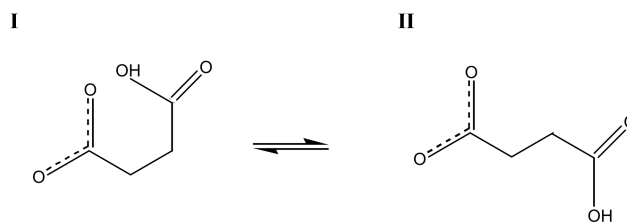
for a hydrogen-bonded -OH group. These carboxyl bands are all generally associated with an acid-dimer [Bizek et al., 1992].

There are several peaks of interest for the amine or ammonium ion. The N-H stretch of the tertiary ammonium salt gives a broad band at 2,250-2,700 cm^{-1}, which signals that the amine has been protonated [Bizek et al., 1992].

There are fumaric (trans-butenedioic), maleic (cis-butenedioic) acid which is similar to succinic (butenedioic) acid. These four-carbon dicarboxylic acids have different configuration and freedom of rotation about the central C-C bond; thereby the degree of their intramolecular hydrogen bonding is different. Fig. 3 illustrates the intramolecular hydrogen bonding in succinic acid [Tamada, 1989; Hong et al., 2000].

In the reactive extraction of dicarboxylic acid, the intramolecular hydrogen bonding plays an important role in determining the stoichiometry of the acid-amine complex. Intramolecular hydrogen bonding is based on the strong interaction between two carboxylic groups in dicarboxylic acid. Among the dicarboxylic acids, the bimaleate anion can form very strong intramolecular hydrogen bonds, because the double bond fixes the proton-donating and proton-accepting groups in close proximity to each structure. This stabilizes the singly deprotonated form of the acid, so that removal of the first proton is favored and removal of the second proton is discouraged.

Table 2. Peak assignments for IR studies in tertiary amines/1-octanol

Peak	Assignment
3,352 m	-OH
	intermolecular hydrogen bonding of the O-H--N type or between acid-amine complex and 1-octanol
2,967-2,858 vs	-CH$_2$, CH$_3$
1,650 m	COO-
	Hydrogen-bonded carboxyl group
1,463 s	CH$_2$, CH$_3$
1,413 s	COO-
	COO- in succinic acid
1,380 s	OH---O
	Hydrogen bonding between succinic acid and 1-octanol
1,207 s	C-N
960-900 w	C-O-H
	C-O-H deformation of dimer in succinic acids
727 w	C=O
	C=O in succinic acid

However, in the bifumarate anion, the carboxylic groups are fixed on opposite sides of the central C=C double bond, and cannot form intramolecular hydrogen bonds. The bisuccinate anion can orient itself to form intramolecular hydrogen bonds, but the central single bond allows floppiness of carboxyl and carboxylate groups. Thus, the tendency to intramolecular hydrogen bond formation is not as strong as that in maleic acid. The intramolecular hydrogen-bonded complex of dicarboxylic acids is stabilized as the proton-donor or acceptor ability of diluent decreases. It is well known that dicar-

Table 3. Peak assignments for IR studies in tertiary amines/n-hep-tane

Peak	Assignment
2,967-2,858 vs	CH$_2$, CH$_3$
	CH$_3$ attached to O or N
2,800 s	NH$_3^+$
2,742 w	COO-
1,471 s	COO- in succinic acid
1,380 s	-OH
	-OH in succinic acid
1,265 s	COO-
	COO- in succinic acid
727 w	C=O
	C=O in succinic acid

boxylic acids form intramolecular hydrogen bonds in several organic solvents [Tamada, 1989].

The assignments for the IR peaks obtained for tertiary amines in 1-octanol and n-heptane are tabulated in Tables 2 and 3, respectively. In Fig. 4 are represented IR spectra for solutions containing tertiary amine in 1-octanol. In principle, carbonyl complexes (hydrogen bond between succinic acid and amine) and carboxylate complexes might exist [Ziegenfuβ and Maurer, 1994]. The spectra of tertiary amines in 1-octanol prove an intermolecular hydrogen bond of the O-H--N type with one nearly symmetrical broad band centered around 3,400 cm^{-1}. The increase of intensity of the broad peak at 3,400 cm^{-1} can be explained both by the formation of hydrogen bonds between amine and acid and by the OH bonds of 1-octanol. And this peak is also associated with an acid-dimer. It means that the (2,1) acid-amine complex is possible. The increase in the area 2,960-2,850 cm^{-1} could refer to a limited formation of alkylammonium cations [Bizek et al., 1992]. Increasing and broadening of the peak at 1,650 cm^{-1} can be interpreted as the increase of carboxylate [Eyal and Sergei, 1999]. It is the evidence that the degree of hydrogen bond between succinic acid and tertiary amine increases.

From this interpretation, the possible complex structures between succinic acid and tertiary amine are shown in Fig. 5. Complex I is dominant in TOA/1-octanol system due to increase of the 1,413 cm^{-1} peak. As the chain length of tertiary amines increases, the steric hindrance by tertiary amine in acid-amine complex increases, and thereby the hydrogen bonding with 1-octanol is difficult. The sec-

Fig. 4. IR spectra for solutions containing succinic acid and tertiary amine in 1-octanol.

Complex I

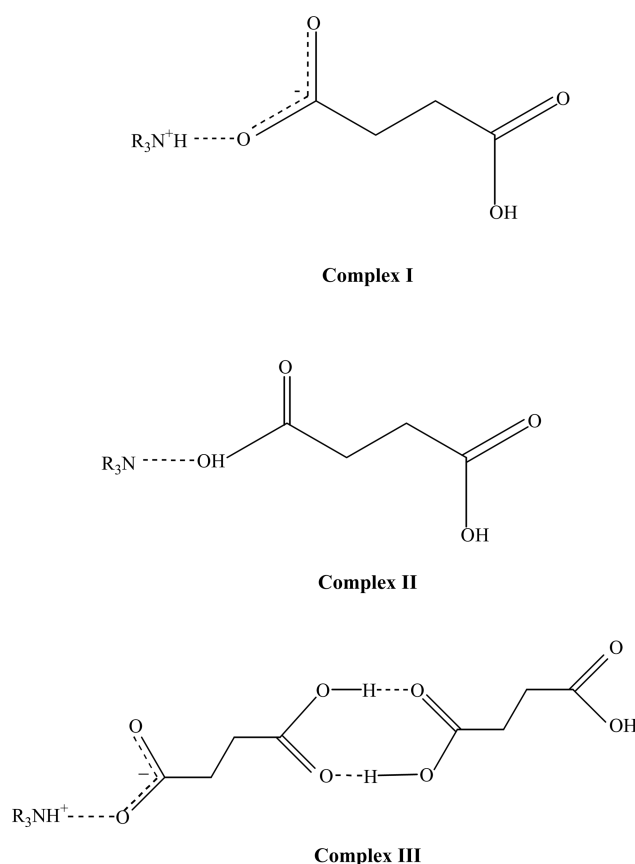**Complex II**

Complex III

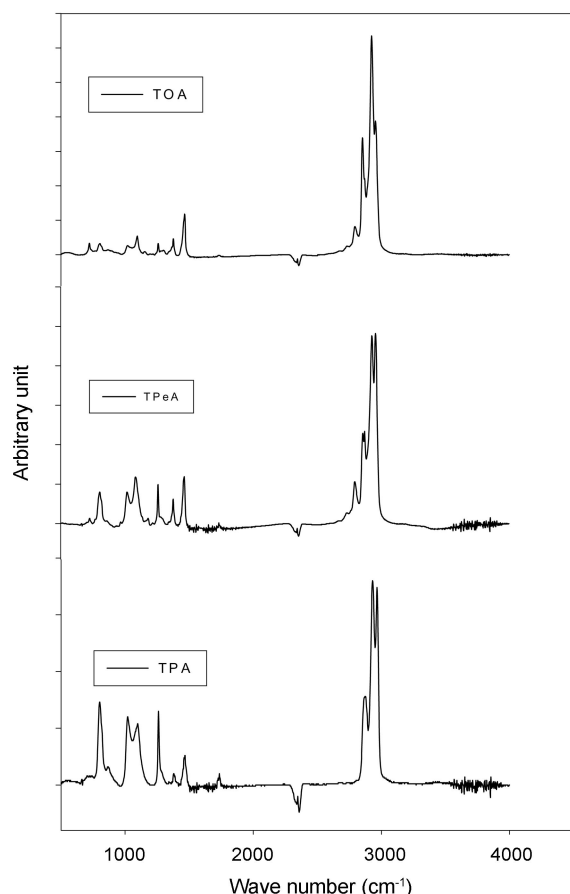**Fig. 5. Possible complexes between a tertiary amine and a succinic acid.**

Fig. 6. IR spectra for solutions containing succinic acid and tertiary amine in n-heptane.

ond molecule of the amine in a (1,2) complex is neutrally hydrogen bonded. However, there is the possibility that intramolecular hydrogen bonding plays an important role in discouraging (1,2) complex formation.

Fig. 6 shows the IR spectra of tertiary amine dissolved in n-heptane and succinic acid mixtures. A hydrogen-bonded carboxyl group (1,650 cm^{-1}) decreases with the chain length of amines. This can be explained by their small extractability for succinic acid in n-heptane and non-polar property of n-heptane. However, the fact that in spite of low extractability of n-heptane the peak at 727 cm^{-1} increases with amine chain length, C=O group in organic phase increases. This result indicates the intramolecular hydrogen bonding of succinic acid itself in organic phase increases. Therefore, the low extractability of tertiary amine dissolved in n-heptane is due to both the low solubility of n-heptane for succinic acid-amine complex and the intramolecular hydrogen bonding of succinic acid itself. Di- and tricarboxylic acids show tendency to aggregate when extracted by amines, differently from monocarboxylic acids. This may be because dicarboxylic acids have two potential binding sites, so they can act as a link between other amines and acids to form a large aggregate. The more inert the diluent, the more favorable it is for the polar complexes to form aggregates shielding themselves from the nonpolar environment [Tamada and King, 1990]. However, monocarboxylic acids, having only one site, cannot link two amines together.

CONCLUSIONS

The extractabilities of tertiary amine in 1-octanol increase with its chain length in 1-octanol diluent. From IR spectroscopy, it could be found that (1,1), (2,1) and (1,1,1) complexes are possible in the tertiary amine/1-octanol system. The acids in acid-amine complexes have two different forms, such as carboxylate form and carbonyl form. However, there were (1,1) and aggregate in tertiary amine/n-heptane because of the intramolecular hydrogen bond of succinic acid in nonpolar diluent. It is concluded that in reactive extraction of dicarboxylic acids, the intramolecular hydrogen bonding played an important role in determining the stoichiometries of acid-amine complexes.

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