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Ion-Pair Solvent Extraction of *EDTA* Anions with Tetraalkylammonium Ions in Various Organic Solvents

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Summary. The ion-pair solvent extraction behavior of ethylenediaminetetraacetate (*EDTA*) anion by various tetraalkylammonium ions was investigated at 25.0 ± 0.1°C. The extraction of *EDTA* exceeded 90% from the basic aqueous solution into the organic solvents such as *n*-hexane and benzene derivatives containing tri-*n*-octylmethylammonium chloride, but *EDTA* was hardly extracted from acidic solution. Among the chemical species of *EDTA* in aqueous solution, $edta^{4-}$ is the most extractable one. On the other hand, the extraction of *EDTA* was less than 1% into chloroform and 1,2-dichloroethane even from the basic aqueous solution. The effect of the structure of alkylammonium ion was also examined. Tetra-*n*-hexylammonium and tetra-*n*-octylammonium ions could not extract *EDTA* even from the basic aqueous solution, while the use of tri-*n*-octylmethylammonium and di-*n*-lauryldimethylammonium ions enhances the extraction of *EDTA*. These results suggest that the steric hindrance in the ion-pair of alkylammonium and *EDTA* anion in the organic phase affects the extractability of *EDTA* containing ion-pair. The solution structure of ion-pair in the organic phase was calculated by MMFF force field and the steric effect in the ion-pair was also suggested. From the extraction constants obtained, the possibility of the extraction separation of *EDTA* has been shown.

Keywords. Ion-Pair; *EDTA*; Molecular modelling; Solvent effect; Solvent extraction.

Introduction

Ethylenediaminetetraacetate, *EDTA* or is called as edethic acid, has been widely used as a powerful metal chelating agent in wide aspects of industrial processes such as chemical, pharmaceutical, and cosmetic, paper milling and pulp, metal, photography and textile, and as additives of household detergents and foods. *EDTA* is one of the high production volume chemicals [1] and thus *EDTA* occurs as a water

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pollutant substance because it is discharged after use by wastewaters. On the other hand, since *EDTA* does not undergo biodegradation in wastewater treatment plants [2, 3], it is suspected that the accumulation of *EDTA* into surface waters has an environmental impact [2–4]. Although environmental concentrations of *EDTA* are thought to be non-toxic to mammals, the potential removal of metal ions necessary for living organs from natural waters affects the biosphere of surface waters [5–8].

Thus, the separation, determination, and speciation of *EDTA* and its metal complexes in surface waters as well as wastewaters from sewage effluents has been widely investigated [9–16]. Although, the most popular method in *EDTA* analysis may be high-performance liquid chromatography [9–12, 15], the mechanism of separation process is still obscure and the optimization of analytical conditions based on two-phase equilibria is requested. There has also been interest in the removal of *EDTA* from sewage of water treatment systems [17]. As the interest and the importance of the behavior of ethylenediaminetetraacetic acid (*EDTA*) in surface and waste waters is increasing, the two phase distribution of *EDTA* and its metal complexes has been thus becoming important.

In the present paper, the two phase equilibria of *EDTA* with various tetraalkylammonium ions have been investigated by means of solvent extraction. The results are discussed by the extractability of the chemical species of *EDTA* into the aqueous phase and the structure of the alkylammonium ion in the organic phase. The results gave the foresight of extraction removal of *EDTA* from waste waters and sediments.

Results and Discussion

Effect of pH on the Extraction

In Fig. 1, the change of the distribution ratios of *EDTA* ($D \equiv C_{EDTA,\mathrm{org}}/C_{EDTA,\mathrm{aq}}$) between *n*-hexane solution containing $0.01\,M$ of Capriquat and aqueous phase is plotted as a function of *pH*. The extraction of *EDTA* from an acidic aqueous solution ($pH < 5$) was low, *i.e.*, less than 10% *EDTA* could be extracted into the *n*-hexane phase. The extractability gradually increases as the *pH* of the aqueous phase increase and at $pH > 10$, the extraction of *EDTA* exceeded 90%. Similar extraction curves were obtained for benzene, xylene, chlorobenzene, and tetrachloromethane. For these solvents, the extractabilities of *EDTA* were less than 10% from acidic solution, but were increased as the *pH* of the aqueous phase increased and exceeded 90%. In contrast to these solvents, the extractability of *EDTA* into 1,2-dichloroethane and chloroform did not exceed 1% even from strong basic aqueous solution ($pH > 12$).

These extraction curves were analyzed by considering the protonation equilibria of the *EDTA* anion in the aqueous phase. In aqueous solution, *EDTA* exists in multiple protonated species such as $edta^{4-}$, $Hedta^{3-}$, H_2edta^{2-}, H_3edta^{-},

$$H_n edta^{(4-n)-} \xrightleftharpoons{K_a} H^+ + H_{(n-1)} edta^{(5-n)-} \tag{1}$$

and H_4edta depending on the *pH* of the aqueous phase as shown in Eq. (1). Thus, the distribution of each *EDTA* species can be written as Eq. (2), by considering the

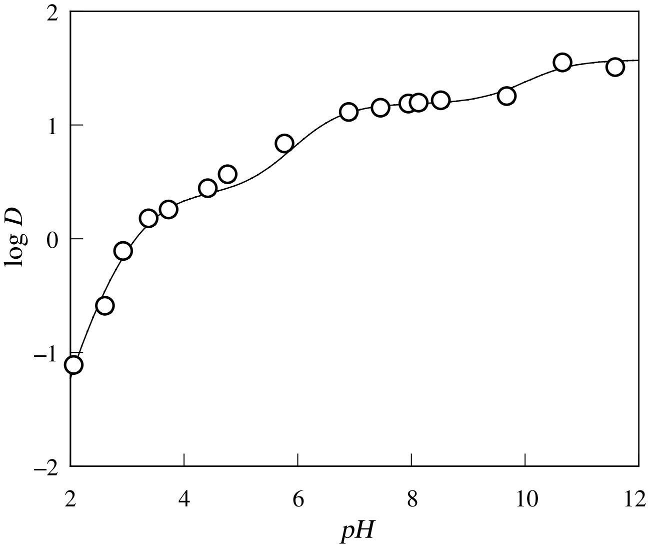

Fig. 1. Plots of the logarithmic distribution ratio of *EDTA*, log *D*, into *n*-hexane as a function of *pH* of the aqueous solution; solid line is calculated from the extraction constants obtained form the least square analysis and the acid dissociation constants

extraction of the *EDTA* anion as a non-charged ion-pair with tetraalkylammonium ion of Capriquat.

In Eq. (2), "*TOMA*" denotes tri-*n*-octylmethylammonium ion, the major

$$\mathrm{H}_n edta^{(4-n)-} + (4-n)TOMA \cdot \mathrm{Cl}_{\mathrm{org}} \xrightleftharpoons{K_{\mathrm{ex},n}} (TOMA)_{(4-n)} \cdot \mathrm{H}_n edta^{(4-n)-}{}_{\mathrm{org}} + (4-n)\mathrm{Cl}^- \tag{2}$$

constituent alkylammonium ion of Capriquat, and subscript "org" denotes the species which exist in the organic phase. By considering Eqs. (1) and (2), the distribution ratio D_{calc} can be written in Eq. (3), where R^+ denotes an alkylammonium ion such as $TOMA^+$.

$$\begin{aligned} D_{\mathrm{calc}} &= \frac{C_{EDTA,\mathrm{org}}}{C_{EDTA,\mathrm{aq}}} \\ &= \frac{[(R^+)_4 edta^{4-}]_{\mathrm{org}} + [(R^+)_3\mathrm{H}edta^{3-}]_{\mathrm{org}} + [(R^+)_2\mathrm{H}_2 edta^{2-}]_{\mathrm{org}} + [(R^+)\mathrm{H}_3 edta^{-}]_{\mathrm{org}} + [\mathrm{H}_4 edta]_{\mathrm{org}}}{[edta^{4-}]_{\mathrm{aq}} + [\mathrm{H}edta^{3-}]_{\mathrm{aq}} + [\mathrm{H}_2 edta^{2-}]_{\mathrm{aq}} + [\mathrm{H}_3 edta^{-}]_{\mathrm{aq}} + [\mathrm{H}_4 edta]_{\mathrm{aq}}} \\ &= \frac{K_{\mathrm{ex},0} + [\mathrm{H}^+]K_{\mathrm{ex},1}K_{\mathrm{a},4}{}^{-1} + [\mathrm{H}^+]^2K_{\mathrm{ex},2}(K_{\mathrm{a},3}K_{\mathrm{a},4})^{-1} + [\mathrm{H}^+]^3K_{\mathrm{ex},3}(K_{\mathrm{a},2}K_{\mathrm{a},3}K_{\mathrm{a},4})^{-1} + [\mathrm{H}^+]^4K_{\mathrm{ex},4}(K_{\mathrm{a},1}K_{\mathrm{a},2}K_{\mathrm{a},3}K_{\mathrm{a},4})^{-1}}{1 + [\mathrm{H}^+]K_{\mathrm{a},4}{}^{-1} + [\mathrm{H}^+]^2(K_{\mathrm{a},3}K_{\mathrm{a},4})^{-1} + [\mathrm{H}^+]^3(K_{\mathrm{a},2}K_{\mathrm{a},3}K_{\mathrm{a},4})^{-1} + [\mathrm{H}^+]^4(K_{\mathrm{a},1}K_{\mathrm{a},2}K_{\mathrm{a},3}K_{\mathrm{a},4})^{-1}} \end{aligned} \tag{3}$$

The acid dissociation constants, $K_{\mathrm{a},n}$, are independent of extraction process, such values were obtained separately and the conditional extraction constants, $K_{\mathrm{ex},n}$, for

Table 1. Logarithmic conditional extraction constants of each *EDTA* species (log $K_{ex,n}$) into benzene, chlorobenzene, xylene, tetrachloromethane, chloroform, 1,2-dichloroethane, and *n*-hexane with 0.01 *M* Capriquat

	log $K_{ex,0}$	log $K_{ex,1}$	log $K_{ex,2}$	log $K_{ex,3}$	log $K_{ex,4}$
Benzene	9.38	6.34	2.10	−7.7	<−10
Chlorobenzene	9.15	5.66	2.65	−8.6	<−10
Xylene	9.40	7.17	3.48	−8.6	<−10
Tetrachloromethane	9.44	6.89	3.38	−5.0	−8.5
Chloroform	5.65	3.42	1.5	<−10	
1,2-Dichloroethane	5.65	3.52	1.4	<−10	
n-Hexane	9.57	7.19	4.40	−8.6	<−10

each *EDTA* species were obtained from least square analysis of the extraction curve that minimized the error square sum as shown in Eq. (4) and they are given in Table 1 for various organic solvents. Due to the dimerization and the polymerization reaction of *TOMA* · Cl (or other tetraalkylammonium salts) in the organic phase, only conditional extraction constants were evaluated. The values for chloroform and 1,2-dichloroethane could be obtained only for $K_{ex,0}$ and $K_{ex,1}$ due to the low extractability. The solid line in Fig. 1 shows the calculated extraction curve of *EDTA* with considering the acid dissociation constants and the extraction constants, $K_{ex,n}$, of each species of *EDTA* in aqueous phase.

$$U = \Sigma(\log D_{\mathrm{calc}} - \log D_{\mathrm{obsd}})^2 \tag{4}$$

From these analyses, it is apparent that the most extractable species of *EDTA* into organic solvents is the most negatively charged *edta*$^{4-}$ anion. As the addition of protons on *EDTA* proceeds, the extractability decreases and it is the worst for the non-charged H$_4$*edta* species. In general, the interaction between an anion and water molecules in aqueous phase increases as the negative charge of the anion increases. This results in an increased hydrophilicity of the *EDTA* anion and its extractability should be decreased. By considering the hydrophilicity of *EDTA* anions only, the most negatively charged *edta*$^{4-}$ anion is the most disadvantaged species for the extraction since the interaction between anion and water molecules is the strongest. The results of extraction, however, showed the reverse tendency from mentioned above. This fact suggests that another factor enhances the extraction of the *EDTA* anion into the organic phase.

The scheme of ion-pair extraction means that the negatively charged *EDTA* anion is necessarily accompanied by the positively charged tetraalkylammonium ion when extracted into the organic phase. For the most negatively charged *edta*$^{4-}$ anion, it should form the non-charged ion-pair with tetraalkylammonium ion, *e.g.* [*TOMA*$^{+}{}_4$ · *edta*$^{4-}$]. The Capriquat consists of a mixture of some kinds of tetraalkylammonium chlorides but mainly tri-*n*-octylmethylammonium chloride. Thus, the average number of carbon atoms in alkylammonium ion may be thought to be about 25. Accordingly, the addition of more *TOMA*$^+$ cations to the *EDTA* anion results in increased hydrophobicity of the ion-pair. This effect should overcome the hydrophilic effect of the charge of the *EDTA* anion.

From the values of log $K_{ex,n}$ listed in Table 1, it can be seen that the difference of the extraction constants for each species is largest between $K_{ex,2}$ and $K_{ex,3}$. The difference of the values of extraction constants exceeds 10^8, while other differences such as between $K_{ex,0}$ and $K_{ex,1}$ are about 10^2 to 10^3. These phenomena may be described by the protonation and the solution structure of the *EDTA* anion. It is well known that the first and the second protonation occur on the nitrogen atoms of *EDTA* and the proton added *EDTA* anion forms an intramolecular hydrogen bond between NH^+ and the carboxylate group. Thus, until the addition of two protons, the carboxylate groups of the *EDTA* anion still exist essentially as free ionic form and are capable to interact to form the ion-pair with the alkylammonium ion. Contrary to this, the third and the forth protonation occur on the carboxylate groups and the protonated carboxylate group cannot interact with alkylammonium ion anymore. Accordingly, the large decrease in the degree of extraction of *EDTA* is observed.

Effect of Organic Solvents

The extraction constants, $K_{ex,n}$, were measured by volumetric molar concentration and were recalculated into mol fraction scale. The logarithmic extraction constants represented by the mol fraction scale are plotted as a function of *Reichardt*'s $E_T(30)$ [18] values of organic solvents in Fig. 2. Other solvent parameter such as solubility parameter (δ), relative dielectric constant (ε_r), and donor number (*DN*) did not give any relevant change with the extraction constants.

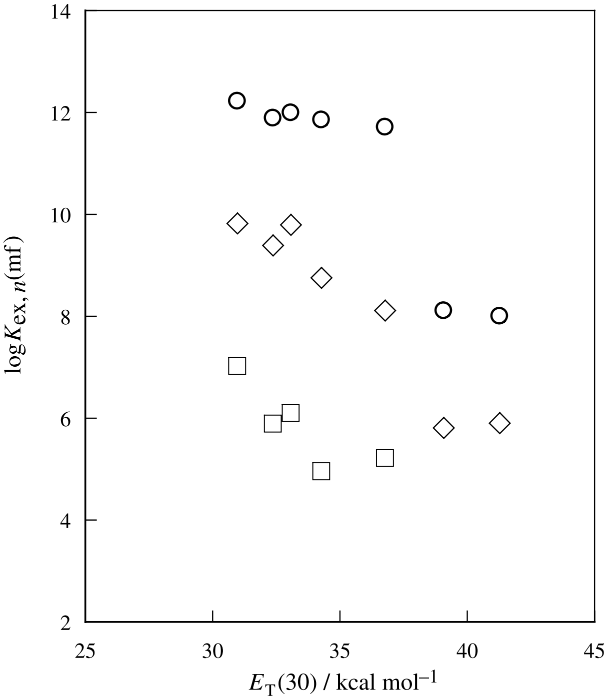

Fig. 2. Plots of the conditional extraction constants for $edta^{4-}$(○), $Hedta^{3-}$ (◇), and H_2edta^{2-} (□) as a function of the values of $E_T(30)$ for various solvents

As can be seen from Fig. 2, the extraction constants decrease with increasing $E_T(30)$ value of organic solvents. These phenomena are interesting, because $E_T(30)$ is a measure of accepter ability of solvent molecule, *i.e.*, the value of $E_T(30)$ increases, when the interaction between anion and solvent molecule increases. Even if *EDTA* itself is extracted as an anion, it is surrounded by many alkylammonium ions and may be hard to interact directly with the molecules of the organic solvent. This extraction process is an anion exchange reaction, *i.e.*, the chloride ion present in the organic phase is exchanged with the *EDTA* anion in the aqueous phase. Thus, even if the *EDTA* anion is hardly interacting with solvent, the chloride ion should have contact with the organic solvent molecules and the exchange of chloride ion by *EDTA* anion is prevented with increasing $E_T(30)$ value.

Effect of Tetraalkylammonium Ion

The extractions of *EDTA* with other tetraalkylammonium ions such as di-*n*-lauryldimethylammonium ion (*DLDMA*$^+$, the number of carbon atoms is 26), tetra-*n*-hexylammonium ion (*THA*$^+$, the number of carbon atoms is 24), and tetra-*n*-octylammonium ion (*TOA*$^+$, the number of carbon atoms is 34) into benzene were examined. The extraction curves for these alkylammonium ions are shown in Fig. 3. The use of *DLDMA* · Cl enhances the extraction of *EDTA* in the whole *pH* range about 10 times from that of Capriquat, while the use of *THA* · Cl and *TOA* · Cl strongly suppress the extraction of *EDTA* even from basic aqueous solutions (Table 2).

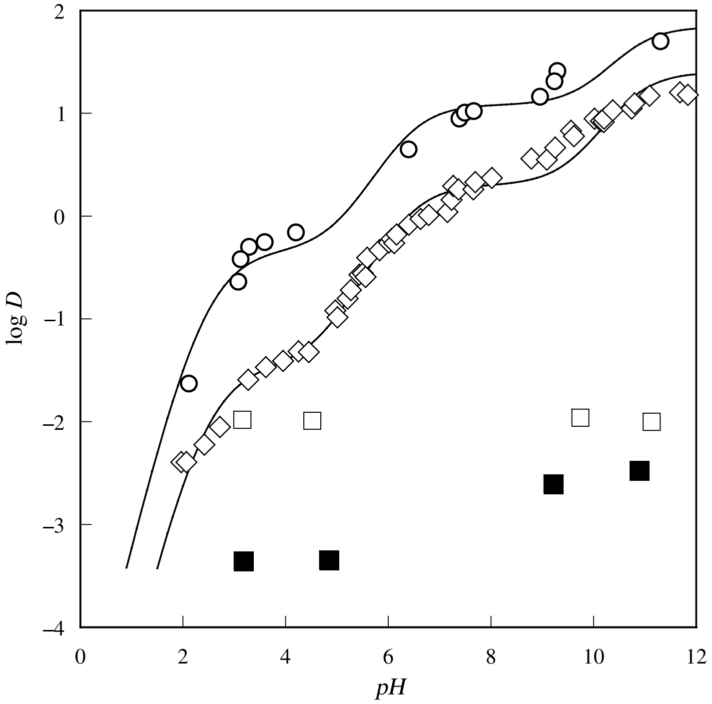

Fig. 3. Plots of the logarithmic distribution ratio of *EDTA*, log *D*, into benzene with *TOMA*$^+$ (◇), *DLDMA*$^+$ (○), *THA*$^+$ (□), and *TOA*$^+$ (■) chloride

Table 2. Logarithmic conditional extraction constants of each *EDTA* species with 0.01 *M* tri-*n*-octylmethylammonium, di-*n*-lauryldimethylammonium, tetra-*n*-octylammonium, and tetra-*n*-hexylammonium chloride into benzene

	$\log K_{ex,0}$	$\log K_{ex,1}$	$\log K_{ex,2}$	$\log K_{ex,3}$	$\log K_{ex,4}$
Tri-*n*-octylmethylammonium	9.38	6.34	2.10	−7.7	<−10
Di-*n*-lauryldimethylammonium	9.84	7.08	3.66	−7.7	<−10
Tetra-*n*-hexylammonium	6.3	3.4			
Tetra-*n*-octylammonium	5.7	0.0			

It is surprising that the number of carbon atoms is almost the same for $TOMA^+$, $DLDMA^+$, and THA^+ or even more hydrophobic (TOA^+), and the extractability of *EDTA* gave such a remarkable difference especially for tetra-*n*-hexyl- and tetra-*n*-octylammonium ion's systems.

The effect of the number of carbon atoms in the ion-pair extraction using alkylammonium has been investigated in various systems. For the tetraalkylammonium of equivalent length of alkyl carbon chain, the effect of the hydrophobicity of carbon atoms on the extraction constants has been investigated and was estimated as about 0.6 logarithmic units per carbon atom [19]. Thus, the observed enhancement of the extraction of *EDTA* with $DLDMA^+$ and disenhancement with THA^+ and TOA^+ cannot be accounted only for the hydrophobicity of the alkylammonium ion. It is also surprising that even TOA^+, a more hydrophobic alkylammonium ion than $TOMA^+$, virtually cannot extract *EDTA* into benzene. These phenomena mean that the ion-pair formation equilibria in the organic phase are strongly affected by the structure of the alkylammonium ion, in other words, the kind of hydrocarbon chain of the ammonium ion.

THA^+ and TOA^+ ions consist of four equal length hydrocarbon chains (hexyl groups for THA^+ and octyl groups for TOA^+), while $DLDMA^+$ consists of two very long hydrocarbon chains (lauryl groups) and two very short methyl groups attached on the nitrogen atom. When the ion-pair is formed in the organic phase, the negatively charged carboxylate group of the *EDTA* anion should access the positively charged nitrogen of the alkylammonium ion. Accordingly, the steric hindrance between the carboxylate group and long alkyl chain occurs for THA^+ and TOA^+ which weakens the formation of the ion-pair. In contrast, the methyl group of $DLDMA^+$ and $TOMA^+$ cannot cause such steric hindrance so that the ion-pair of the *EDTA* anion and $DLDMA^+$ and $TOMA^+$ forms easily. The steric effect on the ion-pair formation may also affect the dissociation process of the alkylammonium chloride ion-pair. Thus, the quantitative discussion should accompany further equilibrium data of the ion-pair of alkylammonium ions in the organic phase.

The molecular mechanics calculations of the structure of the ion-pairs $[(TOMA^+)_2 \cdot H_2edta^{2-}]$ and $[(THA^+)_2 \cdot H_2edta^{2-}]$ using MMFF force field parameters suggest the steric hindrance of the THA^+ cation and the carboxylate group of *EDTA* as shown in Fig. 4. According to the structure, the distances between the nitrogen atoms of THA^+ and the oxygen atoms of the carboxylate group are 4.04–4.55 Å, while those of $TOMA^+$ are 3.33–3.98 Å. Apparently, the interaction between the $TOMA^+$ cation and H_2edta^{2-} anion is stronger than that of TOA^+.

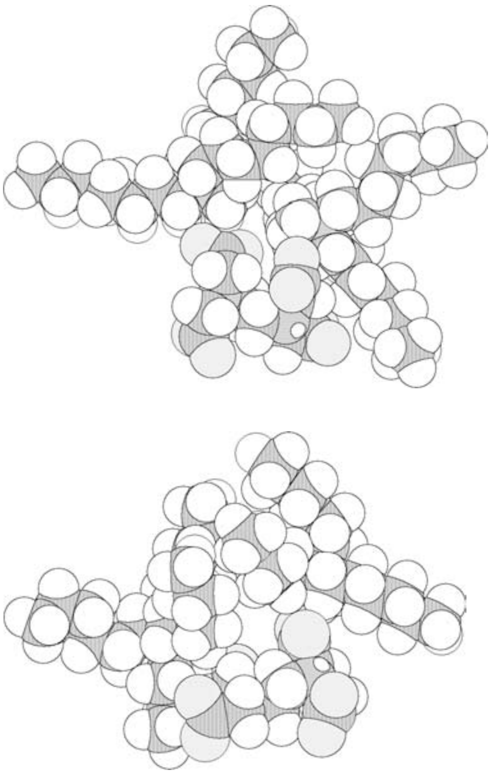

Fig. 4. The structure of the ion-pair of $[(TOMA^{+})_2 \cdot H_2edta^{2-}]$ (up) and $[(THA^{+})_2 \cdot H_2edta^{2-}]$ (bottom) calculated by MMFF force field

It is clear that the THA^{+} cannot access the carboxylate group due to the steric hindrance of the long alkyl chain while $TOMA^{+}$ approches the carboxylate group by the methyl group and gives less steric hindrance.

Experimental

Reagents

All reagents were of analytical grade. The organic solvents, benzene, chlorobenzene, xylene, tetrachloromethane, chloroform, 1,2-dichloroethane, and *n*-hexane, were shaken with distilled water before use to obtain water saturation. Capriquat was purchased from Dojindo and the content was determined by argentometry. Tetra-*n*-hexylammonium chloride ($THA \cdot Cl$), tetra-*n*-octylammonium chloride ($TOA \cdot Cl$), and di-*n*-lauryldimethylammonium bromide ($DLDMA \cdot Br$) were dried under vacuum and the contents were determined by argentometry. The organic solution of $DLDMA \cdot Br$ was shaken with 1 *M* aqueous NaCl solution for at least three times to convert bromide into chloride in the organic solution. The salt $EDTA \cdot 2Na \cdot 2H_2O$ was obtained from Dojindo and dried at 80°C before use.

Extraction Procedure

An aliquot (20 cm^3) of organic solvent containing 0.01 *M* tetraalkylammonium chloride and an aliquot (20 cm^3) of aqueous solution containing 1×10^{-4} *M EDTA* and 0.01 *M* KCl at various *pH* was shaken for 30 min at 25.0 ± 0.1°C in a stoppered centrifuge tube. After the centrifuge separation of each phase, the *EDTA* extracted into organic phase was stripped by back extraction with an equiv volume of 0.1 *M* HNO_3. The concentrations of *EDTA* thus stripped as well as in the aqueous phase were determined spectrophotometrically by the discoloration of iron(II)-2,4,6-tripyridyl-5-triazine (*APTZ*) complex at 593 nm [20].

Molecular Mechanics Calculations

The molecular mechanics calculations for the solution structure of the ion-pairs $[(TOMA^{+})_2 \cdot \mathrm{H}_2 edta^{2-}]$ and $[(THA^{+})_2 \cdot \mathrm{H}_2 edta^{2-}]$ were performed by using MMFF force field [21] by Pentium III based personal computer.

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