

## Nonaqueous anion-exchange chromatography II. Changing anion-exchange selectivity by resin surface complex formation of crown ethers

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### Abstract

Ion-exchange selectivity can be varied with the extent of desolvation, the charge distribution of ion-exchange sites, and the hydrogen bond formation between the ion-exchange site and a counter ion. These are changed by varying the structure of ion-exchange sites. Thus, we can modify the ion-exchange selectivity by changing the chemical structures of ion-exchange sites as can be seen in a variety of references. When an ion-exchange site comprises a primary ammonium ion, the distribution of the charge of the ammonium ion can be modified by complex formation of a crown ether with this anion-exchange site. Though it is difficult to quantitatively describe the electrostatic potential on a molecular basis, a number of data accumulated so far apparently indicate that ion-exchange sites with high charge density force the desolvation of solute ions and form tight ion pairs with small anions while ion-exchange sites with low charge density interact with solvated ions and favorably bind large anions. Comparison of data implies that the surface complex formation of a crown ether apparently lowers hydrogen bond formation ability of the anion-exchange site and the affinity of small anions, and changes anion-exchange selectivity.

*Keywords:* Ion-exchange selectivity; Stationary phases, LC; Surface modification; Complexation; Solvation; Inorganic anions; Crown ethers; Picrate; Ammonium cation

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### 1. Introduction

Ion exchange is one of the most common, most practical and most extensively used methods for the separation of various ionic compounds. Understanding and varying ion-exchange selectivity has therefore been a main topic of fundamental research in this discipline [1–10]. Ion-exchange selectivity has been studied by changing the resin matrices, the degree of crosslinking and the structures of ion-exchange sites [5–10]. A number of distribution (or chromatographic retention) data for anions are available in aqueous solution, though the accumulation of

such data was difficult until the introduction of ion chromatography. This has allowed us to understand qualitatively the relation between the chemical structure of anion-exchange sites and anion-exchange selectivity.

Large and poorly solvated (hydrated) anions are more favorably distributed to an anion-exchange resin than small counterparts when anion-exchange sites are comprised of tetraalkylammonium ions though there is variation in selectivity with the chemical structures of the tetraalkylammonium ions [5,6]. As shown in the preceding paper [11], the interaction between an anion and tetraalkylam-

monium anion-exchange site should be basically electrostatic and other nonspecific interactions such as ion-induced dipole or London dispersion interactions are less important. This usual selectivity implies that the interaction of large and poorly solvated (hydrated) anions with the anion-exchange site is electrostatically stabilized compared to that of small and highly solvated anions; i.e. the desolvation of anions hardly takes place in this instance.

The situation is rather different for small anion-exchange sites of high charge density, which are expected to produce a strong electrostatic field, to act as a hydrogen bond donor, to facilitate the desolvation of anions, and to change anion-exchange selectivity. It has been reported that the selectivity obtained with anion-exchange resins bearing primary ammonium anion-exchange sites is different from that with tetraalkylammonium anion-exchange resin [11–13]. Thus, changes in the chemical structures of anion-exchange sites result in different anion-exchange selectivity.

A solvent plays important roles in determining ion-exchange selectivity. Though it is therefore essential to discuss the balance between the solvation strength and the strength of the interaction of an ion-exchange site with a counter ion, the quantitative description of both is very difficult. However, qualitative consideration of the relation between anion-exchange selectivity and the chemical structure of anion-exchange sites leads to the idea that anion-exchange selectivity can be varied without changing basic structures of anion-exchange resin sites. We reported that polyethers form complexes with primary ammonium ions bound on silica gel [14]. The charge distribution or the hydrogen bond formation ability of the ammonium ion will be greatly changed by the complex formation with crown ethers. This phenomenon is expected to vary the anion-exchange selectivity. In this paper, we study the relation between anion-exchange selectivity and the surface complex formation of crown ethers. In addition, the structure of surface complexes is inferred on the basis of retention data analyses.

## 2. Experimental

The chromatographic system was composed of a Tosoh computer-controlled pump Model CCPD, a

Rheodyne injection valve equipped with a 100- $\mu$ l sample loop, a Tosoh UV-Vis detector Model UV-8020 or a Jasco UV-Vis detector Model 875UV, and a SIC integrator Model Chromatocoder 12. A Tosoh reactive index detector Model RI-8010 was used to monitor the elution of a crown ether. A separation column (50 $\times$ 4.6 mm I.D. PTFE column) was immersed in thermostated water to keep the temperature constant ( $\pm 0.1^\circ\text{C}$ ).

Aminopropylated silica gel (Si-NH<sub>2</sub>) was prepared by the reaction of Wakosil 5 Sil (5  $\mu$ m particle size and 500 m<sup>2</sup> g<sup>-1</sup> specific surface area) with 3-amino-propyl triethoxysilane in dry toluene at room temperature. After being packed in the column, the stationary phase was equilibrated with dilute aqueous HCl to allow full protonation (Si-NH<sub>3</sub><sup>+</sup>Cl) and then with an aqueous or a methanolic solution of an appropriate salt to allow the complete replacement of counter anions (Si-NH<sub>3</sub><sup>+</sup>NO<sub>3</sub><sup>-</sup>).

Tetraethylammonium nitrate was synthesised from tetraethylammonium bromide and recrystallized from acetone containing a small amount of ethanol. Methanol (MeOH) of analytical reagent was distilled twice. Crown ethers [15-crown-5 (15C5) and 18-crown-(18C6)] are purchased from Tokyo Kasei and used as received.

Amounts of adsorbed crown ethers on the stationary phase were measured by a breakthrough method; a mobile phase containing a crown ether of known concentration and 0.01 M tetraethylammonium nitrate or LiNO<sub>3</sub> flowed through the column, the refractive index of effluents was monitored until the reactive index increased to the plateau corresponding to that of the mobile phase, and the amount of an adsorbed crown ether was calculated from an obtained breakthrough curve.

Data analysis was carried out with a graphics application software (Kaleida Graph) on a Macintosh Quadra 650.

## 3. Results and discussion

Since ion-exchange selectivity is strongly affected by the solvation of ion-exchange sites as well as that of counter ions, the choice of a solvent is very important. In the present study, we chose MeOH as a solvent. MeOH has a smaller dielectric constant and slightly smaller acceptor number than water [15], but

anion-exchange selectivity in methanol is basically similar to that in water when polymer based resins are used [11]. Although acetonitrile is also an interesting solvent to study as a medium for ion exchange, various ion pairs are formed mainly because of its very weak acceptor ability [15]. Such strong ion-pair formation results in extreme difficulty in the anion-exchange chromatographic determination of retention times as shown in the preceding paper [11].

In the preceding paper [11], various nonaqueous solvents were tested for anion-exchange chromatography with the  $-\text{NEt}_3^+$  and the  $-\text{NH}_3^+$  resins. Effects of specific adsorption were reduced by use of nonaqueous solvents to substantial extent even when a polymer was used as a matrix. The specific adsorption is weaker for silica gel used in the present study than for polymer matrices. Nonspecific electrostatic interaction is a main factor governing anion-exchange selectivity, and this can be varied by the surface complex formation of crown ethers. Though specific ion-pair formation between an anion-exchange site and a counter anion is also thought to be weak in MeOH, this interaction, if present, is also reduced by the surface complex formation of crown ethers.

When a polyether complexes an  $\text{Si}-\text{NH}_3^+$ , a positive charge of an  $\text{Si}-\text{NH}_3^+$  is dispersed into the entire molecules of the polyether and behaves like tetraalkylammonium ion. We investigated effects of the addition of 15C5 and 18C6 to a mobile phase on anion-exchange behavior; use of these crown ethers allowed us to avoid a problem arising in the UV detection of solute anions because of UV transparency. Results are shown in Fig. 1 and Fig. 2, where the retention times of anions are plotted against the concentration of a crown ether added to 0.01 M  $\text{LiNO}_3$  methanolic solution. Ion-exchange experiments provide relative values to a reference ion (in the present case, an eluent anion,  $\text{NO}_3^-$ ). Therefore, the results shown in Fig. 1 and Fig. 2 should be discussed by comparing the properties of analytes with that of  $\text{NO}_3^-$ . The addition of a crown ether causes decreases in the retention of small anions ( $\text{Cl}^-$  and  $\text{Br}^-$ ) more solvated than  $\text{NO}_3^-$  as well as increases in the retention of bulky anions ( $\text{I}^-$ ,  $\text{SCN}^-$ , picrate and  $\text{ClO}_4^-$ ) less solvated than  $\text{NO}_3^-$ . It appears that these changes well agree with adsorption isotherms of crown ethers (also shown by solid

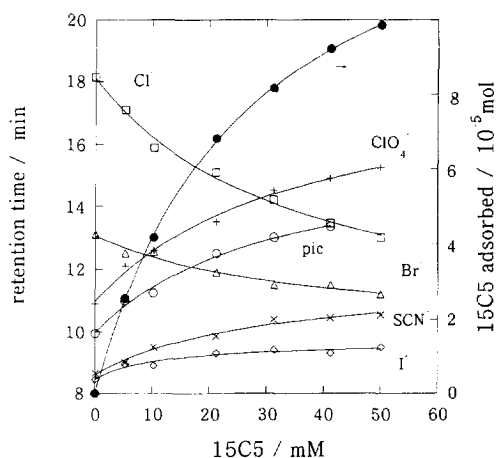


Fig. 1. Changes in retention times of anions with the addition of 15C5 to 0.01 M  $\text{LiNO}_3$  methanolic solution. Solid circles represent amounts of 15C5 adsorbed on  $\text{Si}-\text{NH}_3^+$  stationary phase.

circles in the figures). Fig. 3 shows examples of separation. It can be seen that “unusual selectivity” in the absence of 18C6 in the mobile phase is drastically changed to “usual selectivity” in the presence of 18C6. “Unusual selectivity” in the absence of a crown ether was not observed for polymer resin in MeOH as reported in the preceding paper [11]. As was stated, this will be due to the reduced specific adsorption on silica gel.

The adsorption isotherms of 15C5 and 18C6 are analyzed according to Langmuir type equations:

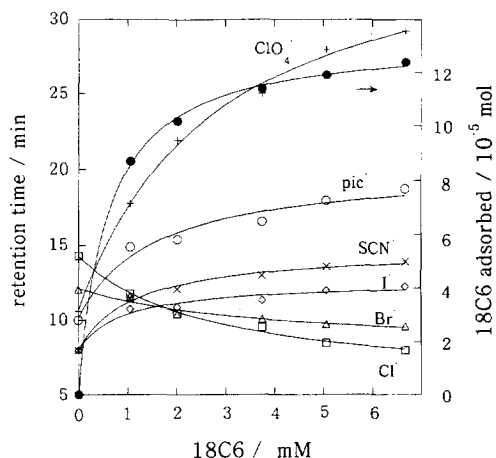


Fig. 2. Changes in retention times of anions with the addition of 18C6 to 0.01 M  $\text{LiNO}_3$  methanolic solution. Solid circles represent amounts of 18C6 adsorbed on  $\text{Si}-\text{NH}_3^+$  stationary phase.

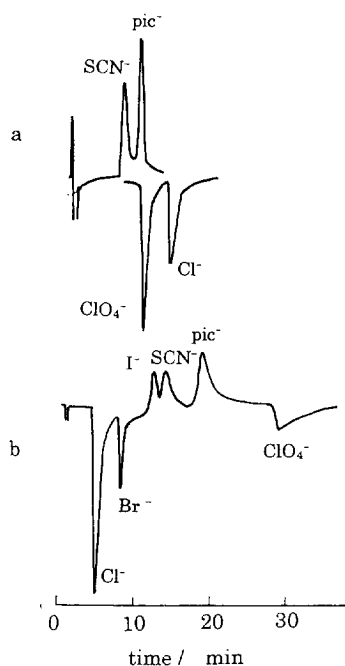
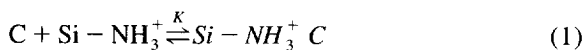


Fig. 3. Change in the selectivity of anion-exchange chromatography by surface complex formation of 18C6 with  $\text{Si-NH}_3^+$ . Mobile phase: (a) 0.01 M tetraethylammonium nitrate in MeOH, (b) 0.01 M tetraethylammonium nitrate + 6.67 mM 18C6 in MeOH. Detection at 247 nm.



$$\text{ADS} = \text{ADS}_{\text{max}} K[\text{C(m)}] / (1 + K[\text{C(m)}]) \quad (2)$$

where ADS and  $\text{ADS}_{\text{max}}$  are the amount of an adsorbed crown ether and the maximum amount of an adsorbed crown ether and  $[\text{C(m)}]$  is the concentration of a crown ether in solution at the equilibrium.  $\text{ADS}_{\text{max}}$  and  $K$  obtained for 15C5 and 18C6 are summarized in Table 1. It appears that the 1:1 interaction between the crown ether and the anion-exchange site was verified by the agreement between  $\text{ADS}_{\text{max}}$  and the amount of  $\text{Si-NH}_3^+$  sites in the column ( $1.5 \cdot 10^{-4}$  mol). However, this is not necessarily correct as shown below.

If only 1:1 complex is formed, total anion-exchange can be described by a linear combination such as

$$k' = X_{\text{NH}_3} k'_1 + X_{\text{NH}_3-\text{C}} k'_2 \quad (3)$$

where  $k'$  is an apparent capacity factor of an anion,

Table 1

Adsorption maximum ( $\text{ADS}_{\text{max}}$ ) and surface complex formation constant ( $K$ ) for 15C5 and 18C6

	$\text{ADS}_{\text{max}}$ (mol)	$K$ ( $M^{-1}$ )	$K_2$ ( $\text{mol}^{-1}$ )
15C5	$1.49 \cdot 10^{-4}$ ( $2 \cdot 10^{-6}$ ) <sup>a</sup>	39.1 (0.1)	
18C6 (1:1) <sup>b</sup>	$1.33 \cdot 10^{-4}$ ( $2 \cdot 10^{-6}$ )	$1.71 \cdot 10^3$ (100)	
(1:2) <sup>c</sup>	$1.46 \cdot 10^{-4}$ ( $2 \cdot 10^{-6}$ )	$1.71 \cdot 10^3$ (60)	$1.17 \cdot 10^4$ ( $1.98 \cdot 10^3$ )

<sup>a</sup> Standard deviations in parentheses.

<sup>b</sup> Only 1:1 surface complex formation is taken into account.

<sup>c</sup> 1:2 surface complex formation is also taken into account.

$X_{\text{NH}_3}$  and  $X_{\text{NH}_3-\text{C}}$  are molar ratios of  $\text{Si-NH}_3^+$  and  $\text{Si-NH}_3^+\text{C}$ ,  $k'_1$  is the intrinsic capacity factor of an anion obtained with uncomplexed  $\text{Si-NH}_3^+$ , and  $k'_2$  is the intrinsic capacity factors of an anion assuming the complete 1:1 complex formation of anion-exchange sites with crown ethers. Eq. (3) suggests that  $k'$  linearly changes with  $X_{\text{NH}_3-\text{C}}$ . Fig. 4 and Fig. 5a show plots based on Eq. (3) using the 1:1 complex formation constants of 15C5 and 18C6 extracted from adsorption isotherms. Eq. (3) holds for the case of 15C5; there are linear relations between  $k'$  and  $X_{\text{NH}_3-\text{C}}$  (instead of  $k'$ ,  $t_r - t_0$  is plotted in the figure) of all anions. Table 2 lists  $k'_1$  and  $k'_2$  obtained with the addition of 15C5. The apparent capacity factor  $k'_2$  decreases with decreasing numerical solvation energy (or increasing solvation energy) of anions, i.e. complex formation of 15C5 results in the "usual" anion-exchange selectivity.

In contrast, changes in  $k'$  obtained with the

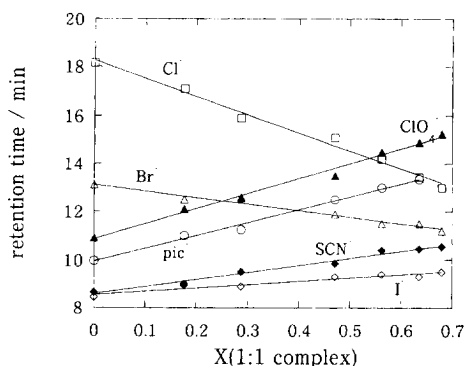


Fig. 4. Plots based on Eq. (3) for the addition of 15C5.

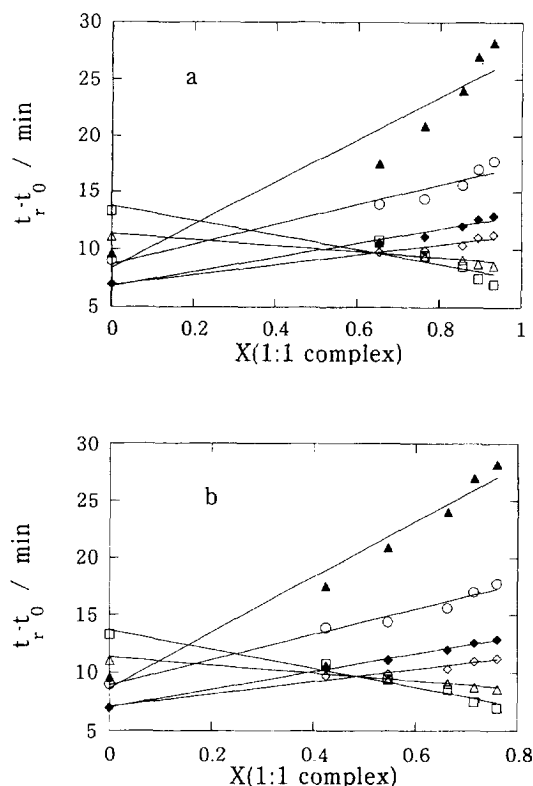
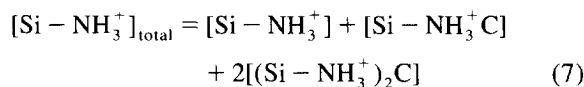
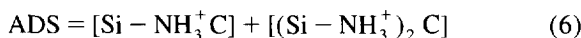
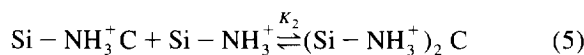
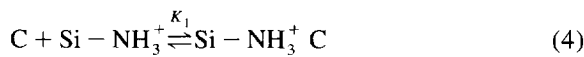


Fig. 5. Plots based on Eq. (3) and Eq. (8) for the addition of 18C6. In (a) only 1:1 complex formation is taken into account, and (b) 1:1 and 1:2 complex formation are assumed. Symbols are given in Fig. 4. Details are given in Section 3.

addition of 18C6 cannot be explained by Eq. (3) (Fig. 5a). The adsorption isotherm of 18C6 is steeply changed over a lower concentration range in comparison with corresponding changes in the retention of anions. This implies that mechanisms other than

1:1 should be considered for 18C6 complex formation. Taking 1:2 (18C6: Si-NH<sub>3</sub><sup>+</sup>) complex formation into account, we restudied the adsorption isotherm of 18C6. In solution, crown ethers of relatively small ring sizes (smaller than 18-membered ring) form sandwich-like 2:1 complexes rather than 1:2 complexes [16,17]. However, in the present case, since the ammonium ion is anchored on the silica gel surface, a sandwich-like complex cannot be formed because of extremely large steric hindrance. Therefore, we did not take this type of complex formation into account. A crown ether having such a relatively small ring size as 18C6 will possibly have difficulty in accommodating two cations in its cavity. However, the surface concentration of ammonium ion is rather high (if the interface thickness is assumed to be 2 Å, the concentration of Si-NH<sub>3</sub><sup>+</sup> is estimated 3.7 M), and thus the electrostatic repulsion will be minimized at such high ionic strength. In addition, as inferred below, the structure of the 1:2 complex is much different from that known in solution [17]. The following equations were used for analysis.



The final equation, including three adjustable param-

Table 2  
Intrinsic  $k'$  calculated from linear combination (e.g. Eq. (3))

		Cl <sup>-</sup>	Br <sup>-</sup>	I <sup>-</sup>	SCN <sup>-</sup>	pic <sup>-</sup>	ClO <sub>4</sub> <sup>-</sup>
15C5	$k'_1$ <sup>a</sup>	18.3	13.1	8.5	8.6	9.9	10.9
	$k'_2$	9.4	9.9	9.7	11.8	15.9	18.3
		(1.1) <sup>b</sup>	(0.9)	(0.2)	(0.5)	(1.0)	(0.9)
18C6	$k'_1$	14.3	12.1	8.0	8.1	10.0	10.6
	$k'_2$	5.2	8.0	13.1	15.6	21.2	38.1
		(0.4)	(0.4)	(0.5)	(0.3)	(1.0)	(0.8)
	$k'_3$	18.4	15.1	9.0	8.4	9.0	-2.6
		(0.9)	(1.0)	(1.1)	(0.7)	(2.4)	(2.0)

<sup>a</sup> ( $t_r - t_0$ ) is listed instead of  $k'$ .

<sup>b</sup> Standard deviation.

eters  $K_1$ ,  $K_2$ , and  $[\text{Si-NH}_3^+]_{\text{total}}$ , was obtained by substituting Eq. (4) and Eq. (5) and Eq. (7) in Eq. (6). The equation including 1:2 complex formation gave a better fit to the adsorption isotherm than Eq. (2); complex formation constants are listed in Table 1. Using these values, we determined  $k'_1$ ,  $k'_2$  and  $k'_3$  according to the linear combination;

$$k' = X_{\text{NH}_3} k'_1 + X_{\text{NH}_3\text{-C}} k'_2 + X_{(\text{NH}_3)_2\text{-C}} k'_3 \quad (8)$$

$k'_3$  is an intrinsic capacity factor on 1:2 complex site.

The apparent capacity factors  $k'_1$ ,  $k'_2$  and  $k'_3$  are also listed in Table 2. Interestingly,  $k'_3$  is almost equal to  $k'_1$  rather than  $k'_2$ , suggesting that 1:2 complexes behave like uncomplexed anion-exchange sites. This can be explained by a model depicted in Fig. 6. The average distance between two adjacent anion-exchange sites is estimated to be 15 Å from the specific surface area of the silica gel (500 m<sup>2</sup>) and the anion-exchange capacity (3.7 · 10<sup>-4</sup> mol g<sup>-1</sup>), assuming the homogeneous modification of the silica gel surface. Since the ring size of 18C6 ranges from ca. 4 to ca. 6 Å, depending on its conformation,

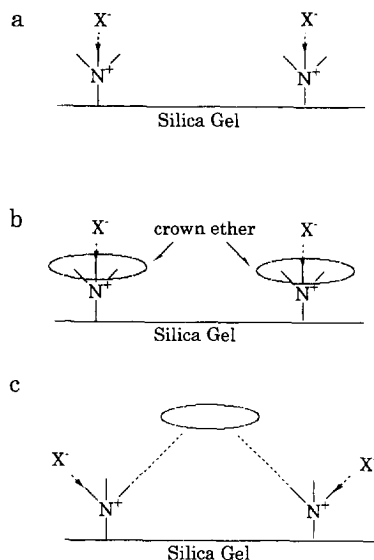


Fig. 6. Possible mechanism of the change in anion-exchange selectivity by the surface complex formation of crown ethers: (a) electrostatic interaction between an anion ( $X^-$ ) and  $\text{Si-NH}_3^+$ , (b) electrostatic interaction between an anion ( $X^-$ ) and a 1:1 complex of  $\text{Si-NH}_3^+$  with a crown ether, (c) electrostatic interaction between anions ( $X^-$ ) and a 1:2 complex involving two  $\text{Si-NH}_3^+$  and a crown ether.

the distance between two adjacent  $\text{Si-NH}_3^+$  sites is too great for 18C6 to simultaneously interact with these. Coordination bonds in 1:2 complex are thus thought to be rather weak; this complex easily dissociates into 1:1 complexes at high crown ether concentration. Such weak bonds lengthen the distance between the crown ether and the cationic site, and allow the electrostatic interaction of an anion with an uncomplexed ammonium ion (Fig. 6c). Fig. 5b shows the plot based on Eq. (3) except that  $X_{\text{NH}_3\text{-C}}$  was calculated by taking 1:2 complex formation into account. Linear relations are obtained for all anions, implying that the above model is correct and 1:2 complex sites behave like uncomplexed sites in the overall anion-exchange mechanism.

A  $k'_2$  value of a large and poorly solvated anion obtained with 15C5 is smaller than the corresponding value with 18C6, while that of a small and highly solvated anion obtained with 15C5 is larger than with 18C6. A positive charge of  $\text{Si-NH}_3^+$  is more dispersed when 18C6 complexes the ammonium ion because of the larger molecular size of 18C6. This more dispersed charge results in weaker electrostatic field and better binds a bulky and less solvated anion.

Thus, the surface complex formation of crown ethers allows the dispersion of the charge of a cationic anion-exchange site, lowers the hydrogen bond formation ability of the anion-exchange site, and finally causes great changes in anion-exchange selectivity. Unfortunately, such phenomena have not been observed in an aqueous medium, and this interrupts practical application.

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