

Crown Ether Complexation in Electrical Double Layer of Anion-Exchange Resin

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The complex formation of crown ethers with ammonium ions chemically bonded on the silica gel surface is affected by the nature of a counteranion and by the concentration of an anion in solution. Equations based on the Gouy–Chapman–Stern model for electrical double layers are derived to describe the adsorption isotherms of crown ethers and to elucidate effects of anion concentration on their chromatographic behaviors. Although the derived equations are not analytically solved, numerical solutions well describe experimental results. In the present case, the various types of interaction between the ammonium ion and counterions, i.e., the ion-pair (and triple ion) formation between the ammonium ion and a counteranion and the ion-pair formation between the ammonium ion complexed by a crown ether and a counteranion, are important and essential factors governing the overall adsorption of crown ethers. These constants are evaluated on the basis of the derived equation.

Much attention has been paid to the complex formation of crown ethers with cations in a variety of media.¹ Studies on the complexation in solution have been most extensively conducted and brought about important knowledge on thermodynamic, kinetic, and structural features. There are many possible factors governing and influencing the crown ether complexation. Of these, solvent effects have been thought to be one of the most important and essential factors when discussing this chemistry in solution.^{1h–n} Electrostatic (ion–dipole) interaction between a cation and oxygen atoms in a polyether molecule, which is a major mechanism in the polyether complexation, is affected by the permittivity of a solvent. The desolvation from a metal cation and changes in solvation to the ligand are also involved in the complex formation and often play a decisive role in determining the total thermodynamic energy.^{1k–n} Thus, effects of a solvent in the complex formation of polyethers in solution have been often discussed as an inevitable issue in the consideration of the complex formation ability or selectivity of polyethers.

Crown ethers, acting as Lewis bases, interact with Lewis acids, mainly metal ions. In such interaction, anions effects usually are not very important and thus have received much less interest than solvent effects, while anions are accommodated in complexes of macrocycles containing nitrogen atoms discussed often as compounds parallel to crown ethers.² In some low-permittivity media, anions form ion-pairs with cations and reduce the apparent complex formation. Studies on polyether complex formation have mostly been done in water, methanol, and aprotic solvents; in most of these media, ion-pair formation is not important, or conditions where ion-pair formation is negligible have been selected. In the previous papers,³ we indicated that anion effects should be taken into account to interpret the complexation of polyethers with ammonium ions chemically bonded on silica gel even in methanol; ion-pair formation, which is not detected in a bulk solvent, plays important roles to determine the overall complex formation because of the local high concentration of ions at the interface. To understand this phenomena more precisely, a model based on electrical double-layer assumption has been developed in the present paper. The Gouy–Chapman–Stern electrical double-layer (GCS) model was selected because of the simplicity

in equation derivation, albeit there are some criticisms of this theory.⁴ The GCS model has been applied to the interpretation of phenomena occurring at various solid/liquid interfaces and has elucidated ion distributions in electrical double layers of electrodes, ion-exchange resins, micellar surfaces, etc.⁵ Though the distribution of crown ethers, which are electrically neutral compounds, is not affected by the potentials in an electrical double layer of charged surfaces, that of counteranions should be a function of potential. Since ion-pair formation equilibria contribute to a substantial extent in the total complex formation in the present case, phenomena observed as adsorption or chromatographic retention of crown ethers should be described as a function of potential.

Experimental Section

Silica gel (WakoSil 5-SIL; particle size = 5 μm , average pore size = 60 Å, and specific surface area = 500 m^2/g) was used for experiments after the reaction with (3-aminopropyl)triethoxysilane in dry toluene. After packing aminopropylsilanized silica gel ($\text{Si}-\text{NH}_2$) in a PTFE column (4.6 mm i.d. \times 50 mm), 0.01 M HClO_4 aqueous solution was passed to a column to allow the protonation ($\text{Si}-\text{NH}_3^+\cdot\text{ClO}_4^-$) of amino groups. The counterion (ClO_4^-) was exchanged by passing an appropriate solution containing an anion (X^-) of interest to obtain $\text{Si}-\text{NH}_3^+\cdot\text{X}^-$. Alternatively, the preparation of $\text{Si}-\text{NH}_3^+\cdot\text{X}^-$ stationary phase was done simply by passing aqueous HX solution. The column contained 0.40 g of silica gel. The ion-exchange capacity was determined by UV-absorbance measurements of NO_3^- in the effluent eluted from a $\text{Si}-\text{NH}_3^+\cdot\text{NO}_3^-$ column with an appropriate UV-transparent salt (e.g. NaClO_4). Acetonitrile (AN) was distilled three times; first with P_2O_5 , second with CaH_2 , and finally without additives. Methanol was refluxed with Mg and then distilled. Tetraethylammonium (Et_4N^+) salts were synthesized in the usual manner. Crown ethers were synthesized according to Pedersen's methods.⁶

Experiments were basically done with the chromatographic system, composed of a computer-controlled pump Tosoh model CCPD or Shimadzu model, a UV-detector Tosoh model UV-8020, a thermostated water bath, and an integrator SIC model Chromatocoder 12. The temperature of the column was kept at 25.0 $^\circ\text{C}$ by immersing the column in thermostated water. The flow rate was kept at 1.00 mL min^{-1} . Retention times were measured with the integrator and converted to capacity factors

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TABLE 1: Langmuir Parameters for B15C5

$\sigma_s = 0.0579 \text{ C m}^{-2}$ (1.20×10^{-4} mol ammonium ion per column) $X = \text{ClO}_4^-$		
	MeOH	AN
K/M^{-1}	43.9	117
$\text{Ads}_{\text{max}}/\text{mol}$	8.16×10^{-5}	7.44×10^{-5}
$\sigma_s = 0.118 \text{ C m}^{-2}$ (2.45×10^{-4} mol ammonium ion per column) $X = \text{Cl}^-$		
	0.01 mM Cl^- in AN	0.5 mM Cl^- in AN
K/M^{-1}	70.4	68.0
$\text{Ads}_{\text{max}}/\text{mol}$	6.52×10^{-5}	6.21×10^{-5}
$X = \text{Br}^-$		
	0.01 mM Br^- in AN	0.5 mM Br^- in AN
K/M^{-1}	83.6	104.7
$\text{Ads}_{\text{max}}/\text{mol}$	9.18×10^{-5}	5.68×10^{-5}
$X = \text{NO}_3^-$		
	5 mM NO_3^- in AN	10 mM NO_3^- in AN
K/M^{-1}	70.5	54.3
$\text{Ads}_{\text{max}}/\text{mol}$	9.32×10^{-5}	1.00×10^{-4}

(or corrected retention volume, $V_r - V_o$) by the usual relation, $k' = (V_r - V_o)/V_m$ where V_r , V_o , and V_m are the retention volume, the void volume equal to the retention volume of an unretained solute, and the volume of a mobile phase contained in the column. The amounts of adsorbed crown ethers were determined from breakthrough curves.

Numerical calculation was carried out with Mathcad Plus 6.0 on a DEC computer Venturis FX.

Results and Discussion

Equation Derivation. The adsorption isotherms of a neutral compound such as a crown ether on the solid surface usually obey the following Langmuir equation if only 1:1 interaction takes place:

$$\text{Ads} = \text{Ads}_{\text{max}} K C_r / (1 + K C_r) \quad (1)$$

where Ads , Ads_{max} , K , and C_r refer to the adsorption amount of a crown ether, the maximum amount of adsorbed crown ether, the adsorption constant of a crown ether on the surface, and the concentration of a crown ether at an adsorption equilibrium. If eq 1 is applicable to the cases involving ionic complex formation, the adsorption of crown ethers on the ammonium-ion-modified silica gel surface may also obey eq 1. Selected Langmuir parameters obtained for B15C5 adsorption on the $\text{Si-NH}_3^+\text{X}^-$ ($X = \text{Cl}^-$, Br^- , NO_3^- , and ClO_4^-) in MeOH are summarized in Table 1. Though it seems that the adsorption isotherms can be well represented by eq 1, one must find several strange aspects in these Langmuir parameters. Very few data have been reported for the complex formation between crown ethers with alkylammonium ions; e.g. $\log K$ values for 18-crown-6 complex formation with various aliphatic primary ammonium ions range from 3.5 to 4.2 in MeOH^{1k}, and it can be reasonably expected that corresponding values in AN will be larger than in MeOH. We also determined some complex formation constants of propylammonium ion with crown ethers by chromatography⁷ or electrophoresis;⁸ $\log K$ values are 2.17 for B15C5 in AN, 2.51 for DB18C6 in AN, 1.49 for B15C5 in MeOH, and 2.40 for DB18C6 in MeOH. K values determined by curve fitting based on eq 1 fairly agree with those determined in solution. However, K values vary with the kind of counterion and the concentration of a counterion in solution. It is difficult

to include these effects in usual Langmuir equation such as eq 1. The further problem with eq 1 is seen in another parameter, i.e., maximum adsorption amounts. In the present study, two Si-NH_3^+ stationary phases differing in surface charge densities (σ_s) were used; σ_s values are 0.0579 and 0.118 C m^{-2} corresponding to 1.20×10^{-4} mol ammonium ion per column and 2.45×10^{-4} mol per column. If the adsorption isotherms obey Langmuir's equation and only 1:1 complex formation occurs, the maximum amount of adsorbed crown ethers should be equal to these values. For any $\text{Si-NH}_3^+\text{X}^-$ phases, the maximum amounts of adsorbed crown ethers are smaller than that expected from the surface charge densities as shown in Table 1 and vary with the nature of a counterion and the concentration of a counterion in solution. Thus, usual complex formation equilibrium not involving counterion effects is not applicable to the present case.

As pointed in a previous paper,³ the ion-pair formation between the ammonium ion and a counterion and between the ammonium ion complexed by a crown ether and a counterion should be taken into consideration to interpret the results obtained in the present case. Crown ether complex formation with the ammonium ion competes with the ion-pair formation of the ammonium ion with a counterion but is stabilized by the ion-pair formation after the complex formation. For this purpose, the SGC model for electrical double layers is a possible choice to describe the crown ether adsorption (or complexation) on Si-NH_3^+ because of its simplicity.

To model the complex formation of crown ethers with the Si-NH_3^+ , we assumed three layers at the interface between solution and the modified silica gel surface, where the only one Stern layer was assumed, which means that the minimum approach for anions is not changed even after the complex formation of crown ethers with ammonium ions. The complex formation constant of a crown ether with the ammonium ion chemically bonded on silica gel (K_s), the ion-pair formation constant of the ammonium ion with a counterion ($K_{\text{IP}}^{\text{NH}_3}$), and the ion-pair formation constant of the complexed ammonium ion with a counterion ($K_{\text{IP}}^{\text{NH}_3-\text{C}}$) are defined by

$$K_s = \frac{\Gamma_{\text{NH}_3-\text{C}}}{\Gamma_{\text{NH}_3} C_{r0}} \quad (2)$$

$$K_{\text{IP}}^{\text{NH}_3} = \frac{\Gamma_{\text{NH}_3-\text{X}}}{\Gamma_{\text{NH}_3} X_0 \exp(F\psi_{\text{st}}/RT)} \quad (3)$$

$$K_{\text{IP}}^{\text{NH}_3-\text{C}} = \frac{\Gamma_{\text{NH}_3-\text{C}-\text{X}}}{\Gamma_{\text{NH}_3-\text{C}} X_0 \exp(F\psi_{\text{st}}/RT)} \quad (4)$$

where Γ_{NH_3} , $\Gamma_{\text{NH}_3-\text{C}}$, $\Gamma_{\text{NH}_3-\text{X}}$, and $\Gamma_{\text{NH}_3-\text{C}-\text{X}}$ denote the surface concentration (in mol m^{-2}) of the free ammonium ion, the ammonium ion complexed by a crown ether, the ion-pair between the ammonium ion and a counterion (X), and the ion-pair between the ammonium ion complexed by a crown ether and a counterion, C_{r0} and X_0 are the bulk concentrations (in mol m^{-3}) of a crown ether and an added anion, which is the same anion as a counterion, ψ_{st} is the potential at the Stern layer, and R , F , and T refer to the gas constant, the Faraday constant, and the absolute temperature. It has been well-known that triple ion formation occurs in inert solvents.⁹ Hojo et al.¹⁰ have recently indicated the existence of such equilibria even in AN. Triple ion formation has been criticized from several viewpoints; e.g. minima observed in molar conductance measurements are due not to the triple ion formation but to the

decreased permittivity of a medium used with increasing salt concentration¹¹ or to the changes in ion-pair activity coefficients.¹² However, in the present case, the interaction between the ammonium ion and counterions should involve hydrogen bond formation other than usual electrostatic interaction. The hydrogen bond formation must support the existence of triple ions ($\text{Si-NH}_3^+2\text{X}^-$) at the interface between the stationary phase and AN. This equilibrium constant is defined by

$$K_{\text{TI}}^{\text{NH}_3-\text{X}_2} = \frac{\Gamma_{\text{NH}_3-\text{X}_2}}{\Gamma_{\text{NH}_3}\{X_0 \exp(F\psi_{\text{st}}/RT)\}^2} \quad (5)$$

Though the structures of complexes of ammonium ions with crown ethers have not been well elucidated, it is reasonable that three N–H bonds in ammonium ions participate in the bond formation with crown ethers.¹³ Since the strong ion-pair (and triple ion as well) formation also takes place through N–H bonds as stated above, the contribution of triple ions formed across crown ethers to overall stability of crown ether complexation is negligible. Thus, four equilibria shown by eqs 2–5 will be sufficient to model the present phenomena. Finally, we obtain the following three equations (see Appendix for the detail derivation of these equations).

$$\sigma_s - C_d(\psi_{\text{st}} - \psi_d) = X_0 \exp\left(\frac{F\psi_{\text{st}}}{RT}\right) \left(K_{\text{IP}}^{\text{NH}_3} + K_{\text{IP}}^{\text{NH}_3-\text{C}} K_s C_{\text{r0}} + K_{\text{IP}}^{\text{NH}_3} K_{\text{IP}}^{\text{NH}_3-\text{X}_2} X_0 \exp\left(\frac{F\psi_{\text{st}}}{RT}\right) \times \left[\sigma_s \left\{ 1 + K_s C_{\text{r0}} + \left(K_{\text{IP}}^{\text{NH}_3} + K_{\text{IP}}^{\text{NH}_3-\text{C}} K_s C_{\text{r0}} + K_{\text{IP}}^{\text{NH}_3} K_{\text{TI}}^{\text{NH}_3-\text{X}_2} X_0 \exp\left(\frac{F\psi_{\text{st}}}{RT}\right) \right\} X_0 \times \exp\left(\frac{F\psi_{\text{st}}}{RT}\right) \right] \right) \quad (6)$$

$$\sinh\left(\frac{F\psi_{\text{st}}}{2RT}\right) \cdot \sqrt{8RT\epsilon\epsilon_0 X_0} = (1 + K_s C_{\text{r0}}) \sigma_s \left\{ 1 + K_s C_{\text{r0}} + \left(K_{\text{IP}}^{\text{NH}_3} + K_{\text{IP}}^{\text{NH}_3-\text{C}} K_s C_{\text{r0}} + K_{\text{IP}}^{\text{NH}_3} K_{\text{TI}}^{\text{NH}_3-\text{X}_2} X_0 \exp\left(\frac{F\psi_{\text{st}}}{RT}\right) \right) X_0 \times \exp\left(\frac{F\psi_{\text{st}}}{RT}\right) \right\} \quad (7)$$

$$C_d = \cosh\left(\frac{F\psi_{\text{st}}}{2RT}\right) \cdot \sqrt{\frac{2F^2\epsilon\epsilon_0 X_0}{RT}} \quad (8)$$

where ϵ_0 and ϵ are the dielectric constant of vacuum and the relative permittivity of a medium, C_d is the capacitance of the diffuse layer (F m^{-2}), ψ_d is the potential of the diffuse layer, and σ_s is the surface charge density (C m^{-2}). ψ_d , ψ_{st} , and C_d are calculated for a given set of C_{r0} , X_0 , σ_s , ϵ , T , $K_{\text{IP}}^{\text{NH}_3-\text{C}}$, $K_{\text{IP}}^{\text{NH}_3}$, $K_{\text{TI}}^{\text{NH}_3-\text{X}_2}$, and K_s by solving simultaneously eqs 6–8. We can predict the adsorption isotherms of crown ethers under various conditions differing in salt concentrations, surface charge densities, ion-pair formation constants, and complex formation constants from the solutions. The amount of adsorbed crown ethers is described by

$$Ad = A(\Gamma_{\text{NH}_3-\text{C}} + \Gamma_{\text{NH}_3-\text{C-X}}) = \left[A\sigma K_s C_{\text{r0}} \left(1 + K_{\text{IP}}^{\text{NH}_3-\text{C}} X_0 \exp\left(\frac{F\psi_{\text{st}}}{RT}\right) \right) \right] / \left[F \left(1 + K_s C_{\text{r0}} + \left(K_{\text{IP}}^{\text{NH}_3} + K_{\text{IP}}^{\text{NH}_3-\text{C}} K_s C_{\text{r0}} + K_{\text{IP}}^{\text{NH}_3} K_{\text{TI}}^{\text{NH}_3-\text{X}_2} X_0 \exp\left(\frac{F\psi_{\text{st}}}{RT}\right) \right) X_0 \exp\left(\frac{F\psi_{\text{st}}}{RT}\right) \right) \right] \quad (9)$$

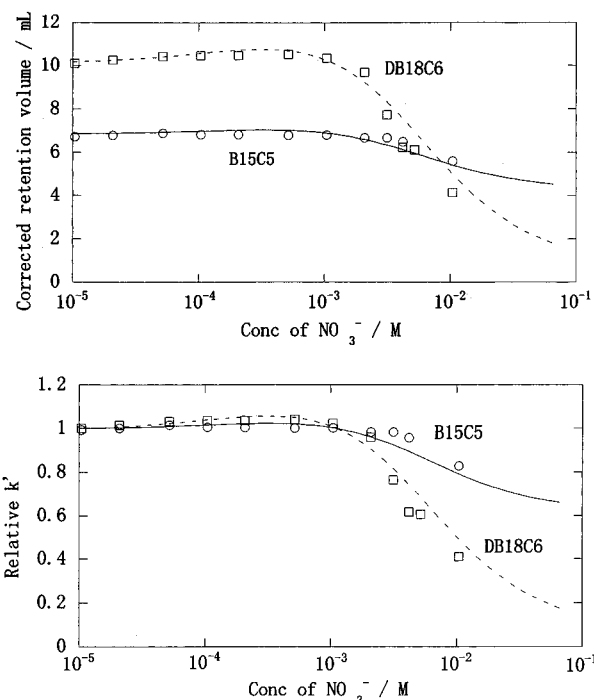


Figure 1. Changes in corrected retention volumes and k'_{rel} values of B15C5 and DB18C6 in AN with the concentration of NO_3^- ; $\sigma_s = 0.118 \text{ C m}^{-2}$.

where A is the total surface area of the silica gel used for experiments.

Thus, it is expected that studies on the adsorption isotherm of crown ethers on the Si-NH_3^+ under various conditions are expected to provide useful information on the electrical double layer as well as on the ion-pair and complex formation. In the present study, in addition to adsorption isotherms, the chromatographic retention behaviors of crown ethers were also investigated in detail. Adsorption isotherms can be regarded as linear over the very low concentration range of crown ethers; for chromatographic experiments, the concentration of crown ethers in a sample solution was kept as low as $5 \times 10^{-5} \text{ M}$, and the actual concentration of a crown ether in a chromatographic column should be lower than this concentration. Chromatographic retention should be constant over the concentration range where the adsorption isotherms are linear. A dimensionless capacity factor (k'), which is one of the most useful and extensively used retention parameters, is defined by the following equation.

$$k' = \phi \left(\frac{\partial(\Gamma_{\text{NH}_3-\text{C}} + \Gamma_{\text{NH}_3-\text{C-X}})}{\partial C_{\text{r0}}} \right)_{C_{\text{r0}}=0} \quad (10)$$

where ϕ is the phase ratio, equal to A/V_m . To avoid the ambiguity of experimentally determined V_m , the comparison of experimental retention with calculated values was done with corrected retention volume ($k'V_m$) rather than k' itself for discussion below.

The relative k' values (k'_{rel}) for B15C5 and DB18C6 are plotted against the concentrations of NO_3^- , Br^- , and Cl^- in Figures 1–3, where a reference concentration was set to $1 \times 10^{-5} \text{ M}$ (hereafter, this reference concentration of an anion will be used for discussion). The k'_{rel} values first slightly increase and then decrease with increasing salt concentration to the extent dependent on the nature of anions. The decreases in k'_{rel} values at the higher salt concentration become marked in the order $\text{ClO}_4^- < \text{NO}_3^- = \text{Br}^- < \text{Cl}^-$. Cl^- is the most solvated and

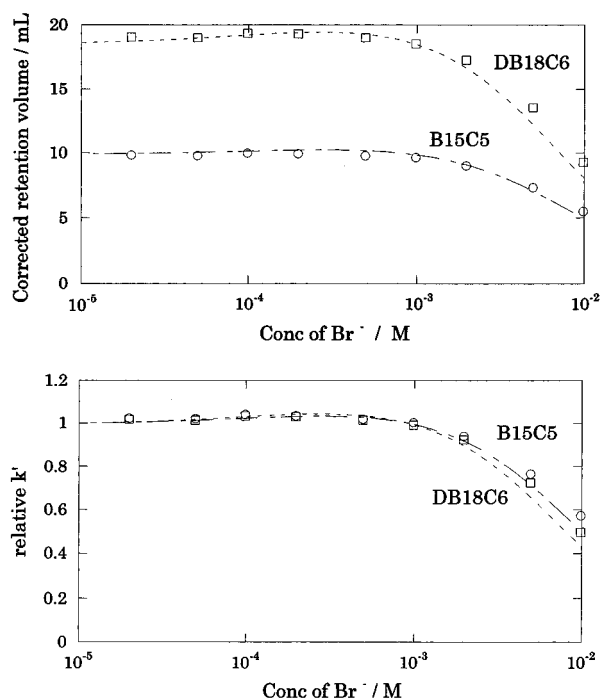


Figure 2. Changes in corrected retention volumes and k'_{rel} values of B15C5 and DB18C6 in AN with the concentration of Br⁻ $\sigma_s = 0.118$ C m⁻².

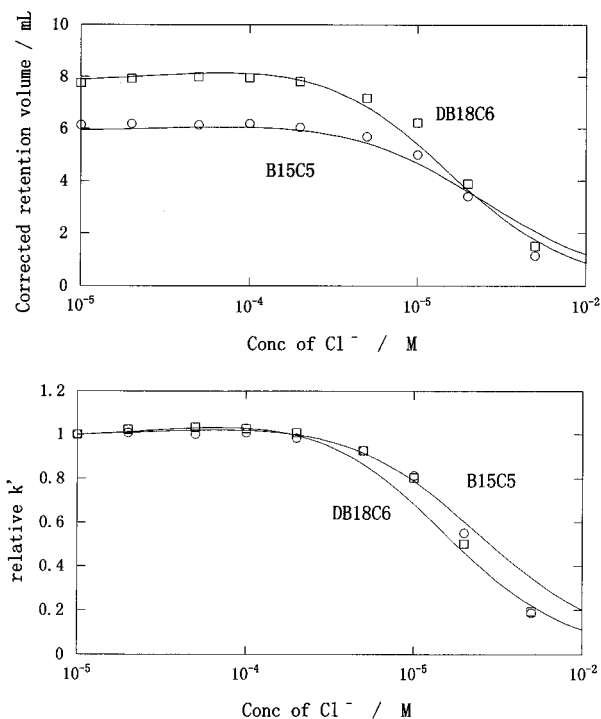


Figure 3. Changes in corrected retention volumes and k'_{rel} values of B15C5 and DB18C6 in AN with the concentration of Cl⁻ $\sigma_s = 0.118$ C m⁻².

ClO₄⁻ is the least solvated anions of these. Since hydrogen bond formation is one of the most important mechanisms in anion solvation, this order should basically be the same as increasing hydrogen bond formation ability or, in the present case, the ion-pair formation ability of an anion with the ammonium ion.

It should be noted that though B15C5 and DB18C6 have different complex formation ability and thus the corrected retention volume are much different for these, changes in k'_{rel} values of these crown ethers with the salt concentration is

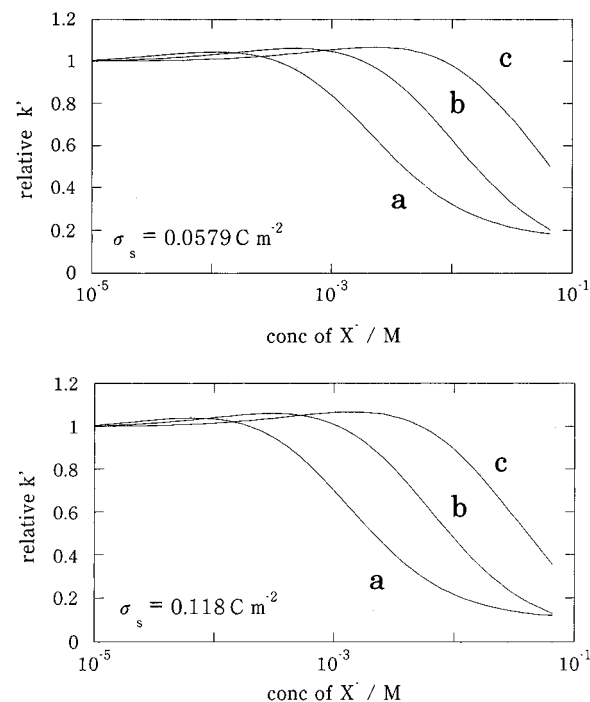


Figure 4. Effects of $K_{IP}^{NH_3}$ and σ_s on k'_{rel} values. $K_{IP}^{NH_3}/K_{IP}^{NH_3-C}$ and $K_{IP}^{NH_3-X_2}$ are set to 1000 and 0, respectively. a, $K_{IP}^{NH_3} = 10^5$ M⁻¹; b, $K_{IP}^{NH_3} = 10^4$ M⁻¹; c, $K_{IP}^{NH_3} = 10^3$ M⁻¹.

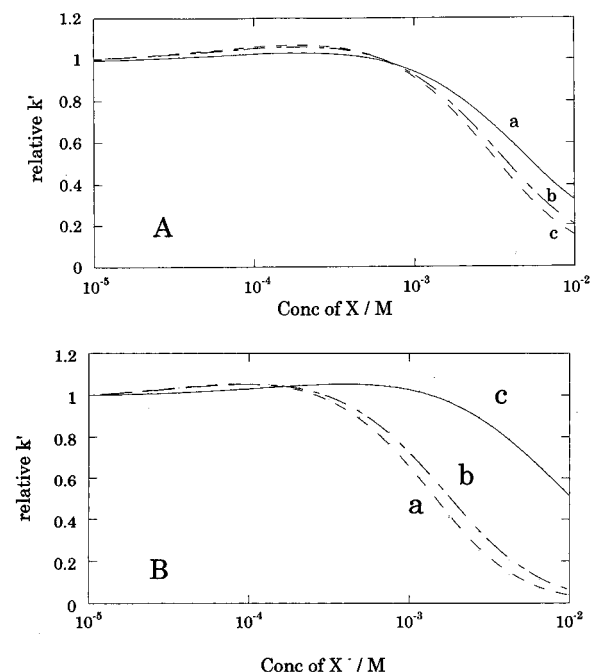


Figure 5. Effects of $K_{IP}^{NH_3-C}$ and $K_{IP}^{NH_3-X_2}$ on k'_{rel} values. (A) $K_{IP}^{NH_3}$, $K_{IP}^{NH_3-X_2}$, and σ_s are set to 10^4 M⁻¹, 10^3 M⁻¹, and 0.118 C m⁻²; a, $K_{IP}^{NH_3-C} = 10^3$ M⁻¹; b, $K_{IP}^{NH_3-C} = 10^2$ M⁻¹; c, $K_{IP}^{NH_3-C} = 10^1$ M⁻¹. (B) $K_{IP}^{NH_3}$, $K_{IP}^{NH_3-C}$, and σ_s are set to 10^4 M⁻¹, 10^2 M⁻¹, and 0.118 C m⁻²; a, $K_{IP}^{NH_3-X_2} = 10^4$ M⁻¹; b, $K_{IP}^{NH_3-X_2} = 10^3$ M⁻¹; c, $K_{IP}^{NH_3-X_2} = 10^2$ M⁻¹.

similar. The k'_{rel} for DB18C6 is more markedly increased over the lower salt concentration range, and more decreased over the higher salt concentration range, than that for B15C5. However, k'_{rel} values for both DB18C6 and B15C5 return to unity at the same concentration of an anion.

To quantitatively explain experimental results shown above, numerical calculation were carried out. Figures 4 and 5 show examples of calculated results, where changes in relative k'_{rel} are plotted against the salt concentration in a solvent of $\epsilon =$

TABLE 2: Anion Concentration Giving $k'_{\text{rel}} = 1$ and Differences in the Stern Layer Potential^a

	concn giving $k'_{\text{rel}} = 1/M$	$\psi_{\text{st-ref}} - \psi_{\text{st}}/mV$
X = Cl ⁻	1.9×10^{-4}	75.8
X = Br ⁻	9.0×10^{-4}	115
X = NO ₃ ⁻	1.1×10^{-3}	121

^a $\sigma_s = 0.118 \text{ C m}^{-2}$. The reference concentration is 1×10^{-5} .

35.95 (AN is assumed). A k'_{rel} value is given by the following equation

$$k'_{\text{rel}} = \left\{ \left[1 + X_{\text{ref}} K_{\text{IP}}^{\text{NH}_3} \exp\left(\frac{F\psi_{\text{st-ref}}}{RT}\right) + K_{\text{IP}}^{\text{NH}_3} K_{\text{TI}}^{\text{NH}_3-\text{X}_2} X_{\text{ref}}^2 \exp\left(\frac{2F\psi_{\text{st-ref}}}{RT}\right) \right] \left\{ 1 + X K_{\text{IP}}^{\text{NH}_3-\text{C}} \exp\left(\frac{F\psi_{\text{st}}}{RT}\right) \right\} / \left\{ 1 + X_{\text{ref}} K_{\text{IP}}^{\text{NH}_3-\text{C}} \exp\left(\frac{F\psi_{\text{st-ref}}}{RT}\right) \right\} \left\{ 1 + X K_{\text{IP}}^{\text{NH}_3} \exp\left(\frac{F\psi_{\text{st}}}{RT}\right) + K_{\text{IP}}^{\text{NH}_3} K_{\text{TI}}^{\text{NH}_3-\text{X}_2} X^2 \exp\left(\frac{2F\psi_{\text{st}}}{RT}\right) \right\} \right\} \quad (11)$$

where the subscript “ref” denotes the reference concentration. Equation 11 does not involve K_s , suggesting that k'_{rel} are independent of K_s unlike k' itself. However, eq 11 includes $K_{\text{IP}}^{\text{NH}_3-\text{C}}$, which is possibly changed by the size and/or other natures of a crown ether molecule (or a crown ether complex). Figures 4 and 5 show effects of a single parameter, $K_{\text{IP}}^{\text{NH}_3}$, $K_{\text{IP}}^{\text{NH}_3-\text{C}}$, and $K_{\text{TI}}^{\text{NH}_3-\text{X}_2}$ with the other two parameters constant. Figure 4 illustrates effects of $K_{\text{IP}}^{\text{NH}_3}$. Larger $K_{\text{IP}}^{\text{NH}_3}$ values result in the faster decay of k'_{rel} values. The similar results are illustrated in Figure 5B, where effects of $K_{\text{TI}}^{\text{NH}_3-\text{X}_2}$ are shown. Thus, both strong ion-pair formation and triple ion formation cause marked decreases in k'_{rel} values. As shown in Figure 5A, the k'_{rel} values return to unity at the same concentration irrespective of $K_{\text{IP}}^{\text{NH}_3-\text{C}}$ values, while the larger $K_{\text{IP}}^{\text{NH}_3-\text{C}}$ value results in a marked increase followed by a marked decrease in k'_{rel} values. We can conclude from eq 11 that the k'_{rel} values return to unity at the concentration of

$$X = X_{\text{ref}} \exp\left\{ \frac{F(\psi_{\text{st-ref}} - \psi_{\text{st}})}{RT} \right\} \quad (12)$$

This naturally indicates that equal k'_{rel} values mean equal Stern layer concentrations of a counterion. The Stern layer potential is determined only by the nature of a counterion (or alternatively by $K_{\text{IP}}^{\text{NH}_3}$ and $K_{\text{TI}}^{\text{NH}_3-\text{X}_2}$) but is independent of $K_{\text{IP}}^{\text{NH}_3-\text{C}}$ under the condition that the concentration of crown ethers is very low. Thus, it is understandable that k'_{rel} values return to the unity at a particular concentration shown by eq 12 irrespective of the nature of crown ethers. Table 2 summarizes the iso- k' concentration and $(\psi_{\text{st-ref}} - \psi_{\text{st}})$ for X⁻ = Cl⁻, Br⁻, and NO₃⁻ ($1 \times 10^{-5} \text{ M}$ is again selected as the reference concentration). The concentration of $k'_{\text{ref}} = 1$ becomes lower with increasing $K_{\text{IP}}^{\text{NH}_3}$, because the strong ion-pair formation (and triple ion formation) between Si-NH₃⁺ sites and counteranions makes $(\psi_{\text{st-ref}} - \psi_{\text{st}})$ smaller. Though effects of surface charge density are also shown in Figure 4, basic trends are not affected by surface charge density. The trends of the calculation agree well with those of the experimental results shown in Figures 1–3.

The k'_{rel} vs salt concentration (X) curves are thus free from K_s . We can therefore estimate $K_{\text{IP}}^{\text{NH}_3}$, $K_{\text{TI}}^{\text{NH}_3-\text{X}_2}$, and $K_{\text{IP}}^{\text{NH}_3-\text{C}}$ values from k'_{ref} vs salt concentration curves. After the estimation of these parameters, we determined K_s values by

TABLE 3: Equilibrium Constants Determined for $\sigma_s = 0.118 \text{ C m}^{-2}$ Modified Silica Gel^a

	$\log K_{\text{IP}}^{\text{NH}_3}$	$\log K_{\text{IP}}^{\text{NH}_3-\text{C}}$	$\log K_{\text{TI}}^{\text{NH}_3-\text{X}_2}$	$\log K_s$
X = Cl ⁻				
B15C5	5.04	3.53	2.85	3.06
DB18C6		2.70		3.68
X = Br ⁻				
B15C5	4.00	2.98	2.49	2.95
DB18C6		2.48		3.58
X = NO ₃ ⁻				
B15C5	4.30	2.48		3.07
DB18C6		1.30		3.62

^a Equilibrium constants in M⁻¹ in this table.

fitting the retention data (k' or corrected retention volumes) with calculated values. However, we obtained several possible sets of parameters, which similarly well describe k'_{rel} vs X curves but mostly failed to describe the adsorption isotherms of crown ethers. Therefore, the optimum set of parameters was selected so as to simultaneously explain both the k'_{rel} -X curve and an adsorption isotherm. The parameters obtained for Cl⁻, Br⁻, and, NO₃⁻ are summarized in Table 3, where K_s and $K_{\text{IP}}^{\text{NH}_3-\text{C}}$ values for DB18C6 are also listed, which were estimated from corrected retention volumes after the determination of $K_{\text{IP}}^{\text{NH}_3}$ and $K_{\text{TI}}^{\text{NH}_3-\text{X}_2}$ values based on the data for B15C5. These constants for ClO₄⁻ were not determined because our calculation cannot be applicable to such a weak ion-pair formation constant between ammonium ions and ClO₄⁻. The $K_{\text{IP}}^{\text{NH}_3}$ values for Cl⁻ are larger than those for Br⁻ and NO₃⁻ by ca. 1 order of magnitude. Similar results have been observed in the ion-pair formation constants between an ammonium ion and an anion in acetonitrile^{3b,14} or in the heteroconjugated anion formation constants between an anion and a phenol.¹⁵

We previously studied anion-exchange chromatographic behaviors of these anions in AN and confirmed the same selectivity, i.e., Cl⁻ > Br⁻ ≈ NO₃⁻ > ClO₄⁻ on both -NH₃⁺ and -NR₃⁺ (R = an alkyl group) type anion-exchange resins.¹⁶ Thus, anion-exchange chromatographic selectivity basically reflects the extent of ion-pair formation at the anion-exchange resin surfaces. The anion-exchange selectivity to the Si-NH₃⁺ sites complexed by crown ether in methanol was also previously studied.¹⁷ The anion-exchange sites behave like tetraalkylammonium ion type anion-exchange resin after the complex formation with crown ethers. Since the smaller anion gave the larger ion-pair formation constants even with tetraalkylammonium ions, the order of $K_{\text{IP}}^{\text{NH}_3-\text{C}}$ values (Cl⁻ > Br⁻ > NO₃⁻) is also reasonable. It is interesting that there is a difference in $K_{\text{IP}}^{\text{NH}_3-\text{C}}$ values for B15C5 and for DB18C6; $K_{\text{IP}}^{\text{NH}_3-\text{C}}$ values for B15C5 are generally larger than for DB18C6 irrespective of anions, suggesting that the ion-pair formation across a smaller crown ether more easily occurs than across a larger molecule. Triple ion formation should be taken into consideration for Cl⁻ and Br⁻, but not for NO₃⁻. Though there must be argument as to whether triple ion is really formed in AN or not, this should be included to explain the adsorption isotherms of crown ethers on Si-NH₃⁺Cl⁻ and Si-NH₃⁺Br⁻. It is due to the molecular shape of planar NO₃⁻ (or steric problems) that triple ion formation was not detected for the -NH₃⁺NO₃⁻ silica gel.

Figure 6 shows the calculated adsorption isotherms of B15C5 on the Si-NH₃⁺Cl⁻. Calculated results agree well with adsorption data. It should be noted that the ion-pair between the ammonium ion and the counterion across crown ethers occupies a substantial part in overall surface-adsorbed crown ether species. Thus, the adsorption of crown ethers on the modified silica gel is enhanced by this ion-pair formation.

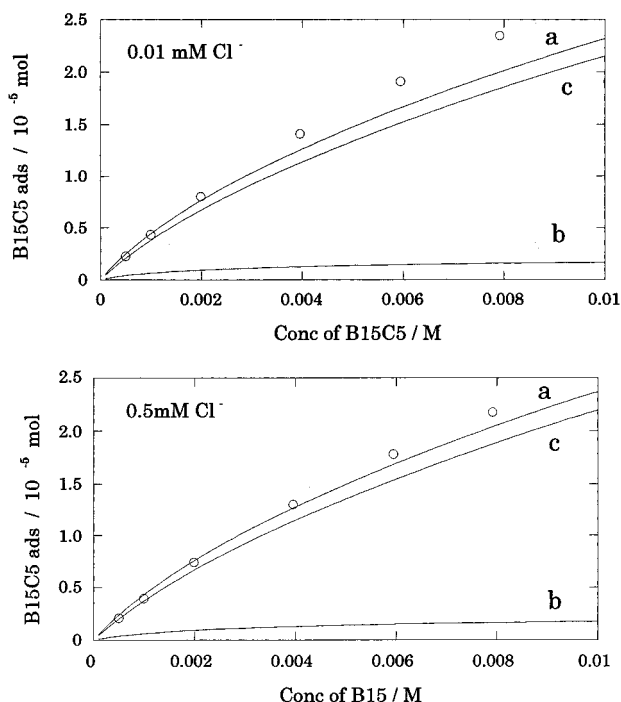


Figure 6. Adsorption isotherms of B15C5 on the Si-NH₃⁺Cl⁻. Circles, experimental values. a, calculated values (total adsorbed amount of B15C5); b, ion-pair between a counterion and the ammonium ion complexed by B15C5; c, complex of B15C5 with the ammonium ion (not ion-pair).

Simple equations presented in this paper well explain the experimental results for crown ether complex formation on the modified silica gel surface and allow the estimation of some equilibrium constants at this interface. The developed model thus indicates that crown ethers are possible probes to study not only the complex formation of themselves but also various equilibria such as ion-pair formation taking place on the surface.

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Appendix

An electrical double layer at the surface of the modified silica gel, divided into three layers, is electrically equivalent to the connection of two condensers. Total differential capacitance of the electrical double layer (C_t) is represented by

$$1/C_t = 1/C_s + 1/C_d \quad (\text{A1})$$

According to the Gouy–Chapman model, C_d is given by

$$C_d = \frac{\partial \sigma_d}{\partial \psi} = \cosh\left(\frac{F\psi_{st}}{2RT}\right) \cdot \sqrt{\frac{2F^2 \epsilon \epsilon_0 X_0}{RT}} \quad (\text{A2})$$

where σ_d is the charge density at the diffuse layer. For electroneutrality

$$\sigma_s + \sigma_{st} + \sigma_d = 0 \quad (\text{A3})$$

where σ_{st} is the charge density at the Stern layer. These charge densities can be represented by

$$\sigma_s = F(\Gamma_{\text{NH}_3} + \Gamma_{\text{NH}_3\text{-C}} + \Gamma_{\text{NH}_3\text{-X}} + \Gamma_{\text{NH}_3\text{-C-X}} + \Gamma_{\text{NH}_3\text{-X}_2}) \quad (\text{A4})$$

$$\sigma_{st} = -F(\Gamma_{\text{NH}_3\text{-X}} + \Gamma_{\text{NH}_3\text{-C-X}} + \Gamma_{\text{NH}_3\text{-X}_2}) \quad (\text{A5})$$

$$\sigma_d = -F(\Gamma_{\text{NH}_3} + \Gamma_{\text{NH}_3\text{-C}}) \quad (\text{A6})$$

or

$$\sigma_s = C_s(\psi_s - \psi_{st}) \quad (\text{A7})$$

$$\sigma_{st} = C_s(\psi_{st} - \psi_s) + C_d(\psi_{st} - \psi_d) \quad (\text{A8})$$

$$\sigma_d = C_d(\psi_d - \psi_{st}) = \sinh\left(-\frac{F\psi_{st}}{2RT}\right) \cdot \sqrt{8RT\epsilon\epsilon_0 X_0} \quad (\text{A9})$$

On the other hand, we can calculate surface concentration of all species from eqs 2–4. Thus, eqs A4–A6 can be written by functions of ψ_{st} . From eqs A5, A7, and A8, we obtain

$$-F(\Gamma_{\text{NH}_3\text{-X}} + \Gamma_{\text{NH}_3\text{-C-X}} + \Gamma_{\text{NH}_3\text{-X}_2}) = C_d(\psi_{st} - \psi_d) - \sigma_s \quad (\text{A10})$$

Also, from eqs A6 and A9, we obtain

$$-F(\Gamma_{\text{NH}_3} + \Gamma_{\text{NH}_3\text{-C}}) = \sinh\left(-\frac{F\psi_{st}}{2RT}\right) \cdot \sqrt{8RT\epsilon\epsilon_0 X_0} \quad (\text{A11})$$

Thus, we can calculate ψ_d , ψ_{st} , and C_d by solving simultaneously eqs A10, A11, and A2 corresponding to eqs 6–8.

Supporting Information Available: Adsorption isotherms of B15C5 on Si-NH₃⁺X⁻ (X = ClO₄⁻, NO₃⁻, and Br⁻) and changes in k' on Si-NH₃⁺ClO₄⁻ with ClO₄⁻ concentration (5 pages). Ordering information is given on any current masthead page.

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