

Complexation of Polyethers in Cation Exchange Resin and Application to Chromatographic Determination of Complexation Constants in Solution

Tetsuo Okada

Department of Chemistry, Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan

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The complex formation of crown ethers with counterions in cation-exchange resin is chromatographically evaluated with a model based on the Poisson–Boltzmann–Gouy–Chapman–Stern theory. In the model, two contributions are taken into account to explain distribution ratios (or chromatographic capacity factors) of crown ethers; one is the ion-pair formation of a cation–crown ether complex with a sulfonate group chemically bonded on silica gel, and the other is the accumulation of cationic complexes in the diffuse layer. To describe this system, at least three equilibrium constants are necessary; a complex formation constant and two ion-pair formation constants between a cation-exchange site and a counteranion and between a cation-exchange site and a cation complexed by a crown ether. The combination of two chromatographic methods, i.e. the crown ether retention and the retention of a probe cation under effects of the crown ether complexation with eluent cations, allows quantitative evaluation of equilibrium constants necessary for numerical calculation. Thus, crown ethers can probe the equilibria not evaluated by other approaches. The results of the calculation are used for the evaluation of the validity of a simple equation previously reported for the chromatographic determination of the complex formation constants of polyethers in solution.

Introduction

The chemistry of polyethers has been one of the most important topics in the last three decades, and it has been studied in a variety of areas in chemistry from various viewpoints.¹ Crown ethers have, above all, attracted many researchers, because these ligands selectively form complexes with hard metal ions, and the selectivity is explained by an intuitively understandable size-fit concept, which has been often mistakenly used for the interpretation of crown ether complex formation. There have thus been published a number of research papers in which syntheses,^{1a} crystal structures,^{1b,c} thermodynamics,^{1d–l} kinetics,^{1g,m} and solution behaviors^{1n–o} of crown ethers and/or crown ether complexes have been studied. Since the ability and the selectivity in crown ether complex formation are a main concern, reliable complex formation constants are bases in most of discussions. A reliable means for the determination of crown ether complex formation constants has been sought for this reason.^{1g–k,2a,b}

The author showed that liquid chromatography could be an efficient tool to study polyether chemistry in solution if the separation was done in appropriate medium² and that this chromatographic method has several advantages over other methods often used for the determination of complex formation constants or other thermodynamic parameters. It is the most important advantage of the developed chromatographic method that impure or even mixed samples can be used to evaluate the complexation ability of polyethers of interest; for example, the thermodynamic parameters for the complex formation of monodispersed poly(ethylene glycols) with alkali metal ions in methanol were determined using polydispersed polyethylene glycols as samples.^{2b,c} The principal mechanism of this chromatographic method is as follows: a polyether is retained by the complex formation with counteranions of a cation-exchange resin; when a mobile phase contains the same cations

as counteranions of the stationary phase, the retention of the polyether decreases with increasing concentration of the cation in the mobile phases according to the complexation ability. If only 1:1 complex formation occurs, the complex formation constants (K) can be determined from the following relation:^{2b}

$$1/k' = (1 + CK)/k'_0 \quad (1)$$

where k' is a capacity factor of a polyether, C is the concentration of the cation, and k'_0 is a capacity factor obtained with a mobile phase not containing the cation. In order to determine various physicochemical parameters from chromatographic data, similar equations have been often derived; it is an underlying idea that the stationary phase is recognized as a phase different from a mobile phase.³ Although the stationary phase itself is certainly a solid skeleton such as synthetic polymers and silica gel, active sites working for the chromatographic retention exist not in the solid phase but at the interface between the stationary phase and the mobile phase. Hydrophilic functional groups must, in particular, exist in a solution phase. In such cases, solutes must successively distribute from the bulk solution to this interface. Long-range mechanisms such as electrostatic interaction affect not only the interaction of solutes with functional groups but the distribution of solutes in solution. When physicochemical values are extracted from chromatographic data, these effects should be taken into account; that is, the accumulation of counterions in the diffuse layer due to the surface electrostatic potential also contributes to overall chromatographic retention. This effect, which has been pointed out by Ståhlberg and co-workers,⁴ implies that a part of the solute is possibly recognized as a retained species even though it exists in a solution phase. It is the main aim of the present paper to develop a chromatographic model for the polyether complexation at the interface between a solution and a cation-exchange resin and evaluate chemistry occurring therein. This

model is expected to allow not only to properly describe the behaviors of polyethers on a cation-exchange resin but to evaluate the validity of the chromatographic approach based on eq 1 for the determination of polyether complex formation constants.

Experimental Section

Chromatographic experiments were done on a similar system as previously described.⁵ The separation column was TSKgel IC-Cation-SW (a 4.6 mm i.d. \times 50 mm PTFE column packed with silica gel-based cation-exchange resin (propylsulfonate as a cation-exchange site) with particle size = 5 μ m, surface area = 200 m² g⁻¹, and ion-exchange capacity = 0.30 m mol g⁻¹). Methanol (MeOH) was distilled after reflux with magnesium. Acetonitrile (AN) was refluxed over CaH₂ and then distilled twice (the second time without additives). The perchlorate salt of ethylviolet (EV⁺) was deposited from EV⁺Cl⁻ aqueous solution by adding HClO₄.

Numerical calculation was done with the program package Mathcad Plus ver. 6.0 on a DEC computer Venturis FX.

Theoretical Section

Retention of Polyethers by the Complexation with Counteranions. The basic starting point of the present paper is the same as shown in previous papers.^{5,6} A single Stern layer was assumed, where both solvated and complexed cations form ion-pairs with sulfonate groups in the cation-exchange resin. The ion-pairs of the cation-exchange sites with complexed cations are usually regarded as the retained polyether species in the phase-separation model. However, we must take the contribution from the accumulation of complexed cations in a diffuse double layer into account. These two contributions to the total retention of polyethers are functions of the Stern layer potential, which is affected by the salt concentrations and the extent of ion-pair formation between cation-exchange sites and counteranions.

An electrical double layer at the surface of an ion-exchange resin, divided into three layers parallel to the surface, is electrically equivalent to the connection of two condensers. For electroneutrality,

$$\sigma_s + \sigma_{st} + \sigma_d = 0 \quad (2)$$

where σ_s , σ_{st} , and σ_d are the charge densities at the surface, at the Stern layer, and at the diffuse layer. These charge densities can be represented by

$$\sigma_s = F(\Gamma_{ie} + \Gamma_{ie-M} + \Gamma_{ie-MCr}) \quad (3)$$

$$\sigma_{st} = -F(\Gamma_{ie-M} + \Gamma_{ie-MCr}) \quad (4)$$

$$\sigma_d = -F\Gamma_{ie} \quad (5)$$

or

$$\sigma_s = C_s(\psi_s - \psi_{st}) \quad (6)$$

$$\sigma_{st} = C_s(\psi_{st} - \psi_s) + C_d(\psi_{st} - \psi_d) \quad (7)$$

$$\sigma_d = C_d(\psi_d - \psi_{st}) \quad (8)$$

where Γ_{ie} , Γ_{ie-M} , and Γ_{ie-MCr} are surface concentrations (mol m⁻²) of free ion-exchange sites, an ion-pair between an ion-exchange site and a counteranion (M), and an ion-pair between an ion-exchange site and a complexed counteranion (M-Cr⁺),

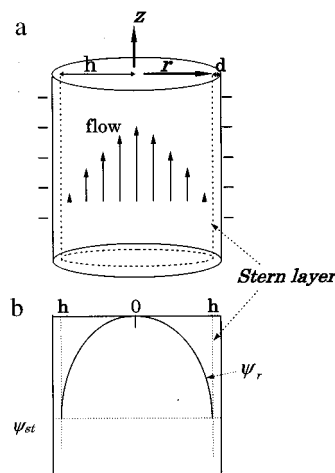
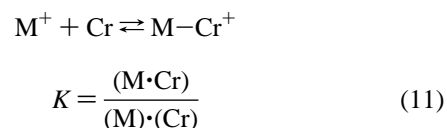
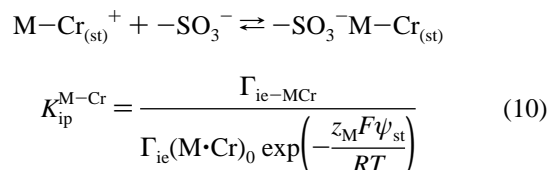
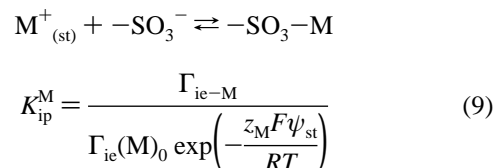


Figure 1. Schematic representation of a cylindrical flow path and coordinates: (a) flow path and the Hagen–Poiseuille flow pattern; (b) changes in the electrostatic potential in the r -direction.

and C_s and C_d are the capacitance of two condensers. We can calculate surface concentration of all species from the following equilibrium constants:



The concentrations in parentheses are given in mol m⁻³. The bulk concentration is represented by a subscript 0.

To solve the above equations, we assumed a cylindrical flow path, having the radius $h + d$ (d is the thickness of the Stern layer), for the fluid in the separation column, as shown in Figure 1. According to the Poisson–Boltzmann equation for cylindrical geometry,

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \psi}{\partial r} \right) = -\frac{F}{\epsilon_0 \epsilon} \sum n_i^0 z_i \exp\left(-\frac{z_i F \psi_r}{RT}\right) \quad (12)$$

where ψ_r is the electrostatic potential at the distance, r , from the center of the cylinder under consideration ($x \leq h$), ϵ_0 and ϵ are the dielectric constant of the vacuum and the relative permittivity of a medium, and n_i^0 and z_i are the bulk concentration and the charge of an ion i . Under the Debye–Hückel approximation for relatively low electrostatic potential, eq 12 can be simplified to⁷

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \psi}{\partial r} \right) = \kappa^2 \psi \quad (13)$$

where $1/\kappa$ is the Debye length. Equation 13 can be analytically

solved as

$$\psi_r = \frac{\sigma_{st}}{\kappa \epsilon_0 \epsilon} \frac{I_0(\kappa r)}{I_1(\kappa h)} \quad (14)$$

where I_0 and I_1 are the modified Bessel function of zeroth and first order. To solve eq 13, we used the relation derived from the G-C theory,

$$\left(\frac{\partial \psi}{\partial r}\right)_{r=h} = -\frac{\sigma_{st}}{\epsilon_0 \epsilon} \quad (15)$$

Thus, we can calculate the Stern layer potential for a given set of equilibrium constants, eqs 9–11.

A stoichiometric capacity factor (contribution from the ion-pair formation between ion-exchange sites and complexed cations) can be calculated from the limiting slope of adsorption isotherms of polyethers.

$$k_{ip} = \frac{A}{V_0} \left(\frac{\partial \Gamma_{ie-MCr}}{\partial C_{r_0}} \right)_{C_{r_0}=0} \quad (16)$$

where A and V_0 are the surface area of the stationary phase and the void volume of the column.

Other than the surface ion-pair formation, we should take the contribution from the accumulation of polyethers participating in the complexation in the electrical double layer. Ståhlberg and co-workers reported the procedure to evaluate the accumulation of ionic compounds in the electrical double layer.⁴ In their treatment, the volume of a mobile phase in a column was separated into several parts. Of these, the stagnant mobile phase was regarded as a part of the stationary phase, where the mobile-phase flow was neglected. In addition, they made another approximation that the effect of the electrostatic potential is negligible outside this stagnant mobile-phase part. These assumptions resulted in a simple equation to explain the contribution from the electrostatic accumulation in the diffuse double layer. However, this treatment is not consistent with their insistence that usual stoichiometric consideration is not applicable to such a long-range mechanism as electrostatic interaction and thus that mobile phases existing in a column cannot be separated into some discrete parts, such as a phase acting as a part of the stationary phase and a real mobile phase.

We assumed a Hagen–Poiseuille flow pattern in the cylinder,⁸

$$v(r) = -\frac{h^2}{4\eta} \frac{dP}{dz} \left(1 - \frac{r^2}{h^2} \right) \quad (17)$$

where η and P are the viscosity of the solution and the pressure, $v(r)$ is the flow velocity at the distance r from the center of the cylinder, and z is the coordinate in the flow direction. To derive eq 17, we assumed that liquids between the Stern layer and the surface are not mobile; the Stern layer corresponds to the slipping layer, meaning $\psi_{st} = \zeta$. This assumption may not be correct in a strict physical sense⁹ but does not cause serious error because h must be much larger than the distance between the Stern and the real slipping layer.

Thus, the contribution from the accumulation of a solute in the diffuse layer to overall k' is described by

$$k_{DL} = \frac{2\pi \int_0^h r v(r) dr}{2\pi \int_0^h r dr} \frac{2\pi \int_0^h r c(r) dr}{2\pi \int_0^h r c(r) v(r) dr} \quad (18)$$

where $c(r)$ is the radial concentration of a solute. For a usual ion, $c(r)$ can be written as

$$c(r) = c^\circ \exp\left(-\frac{zF\psi_r}{RT}\right) \quad (19)$$

Similarly, $c(r)$ for a crown ether, denoted by $Cr(r)$, is given by

$$\begin{aligned} Cr(r) &= Cr\{1 + KM(r)\} \\ &= Cr\left\{1 + K(M)_0 \exp\left(-\frac{z_M F \psi_r}{RT}\right)\right\} \end{aligned} \quad (20)$$

where Cr is the equilibrium concentration of a crown ether not forming complexes, the distribution of which is not affected by the electrostatic potential. Thus, we can calculate k_{DL} by substituting eqs 17 and 20 in eq 18. Overall k' is given by a sum of k_{ip} and k_{DL} .

Evaluation of K_{ip}^M and K_{ip}^{M-Cr} by Nonaqueous Cation-Exchange Chromatography. Information on the ion-pair formation constants is necessary to calculate the retention of crown ethers. We studied the effects of crown ethers on ion-exchange chromatographic behaviors of cations to get information on the ion-pair formation constants, K_{ip}^M and K_{ip}^{M-Cr} . It is well-known that the cation-exchange chromatographic selectivity can be modified by polyether complex formation, and the affinity of a cation to the cation-exchange resin is usually lowered by the complexation.¹⁰ There are some possible experiments for the present purpose: (1) both an eluent and a solute cation are complexed; (2) only a solute cation is complexed; (3) only an eluent cation is complexed. Although case 1 is a general case, the interpretation of the result must be very complex. In case 2, it was difficult to find a suitable eluent not forming complexes under any conditions. After some experiments, we concluded that case 3 is most preferable for the present purpose. We selected ethylviolet (EV^+) as a noncomplexed cationic solute and Na^+ and K^+ as complexed eluents in MeOH and AN.

Results are shown in Figures 2 and 3. The retention of the probe cation increases with increasing concentration of a crown ether in mobile phases, suggesting that the affinity of complexed cations to cation exchange sites is weaker than that of solvated counterparts as expected. When only a 1:1 complex is formed, the following equation can be derived according to a phase-separation scheme free from effects of electrostatic potentials,

$$k_{EV}' = \alpha_1 k_1 + \alpha_2 k_2 \quad (21)$$

where α_1 and α_2 are the fractions of a noncomplexed eluent cation and a complexed eluent cation, and k_1 and k_2 are capacity factors obtained with the former and with the latter eluent cation, respectively. The fraction of a complexed eluent cation is given by

$$\alpha_2 = \frac{(KC_L + KC_M + 1) - \sqrt{(KC_L + KC_N + 1)^2 - 4K^2 C_L C_M}}{2KC_M} \quad (22)$$

where C_L and C_M are the analytical concentration of a ligand and an eluent cation. The combination of eqs 21 and 22 basically gives a simple increase (or decrease) in overall capacity factors with increasing C_L ; obviously eq 21 cannot explain real increases in the retention of EV^+ with increasing C_L in any cases. Figures 2 and 3 show that the increases in k_{EV}' values

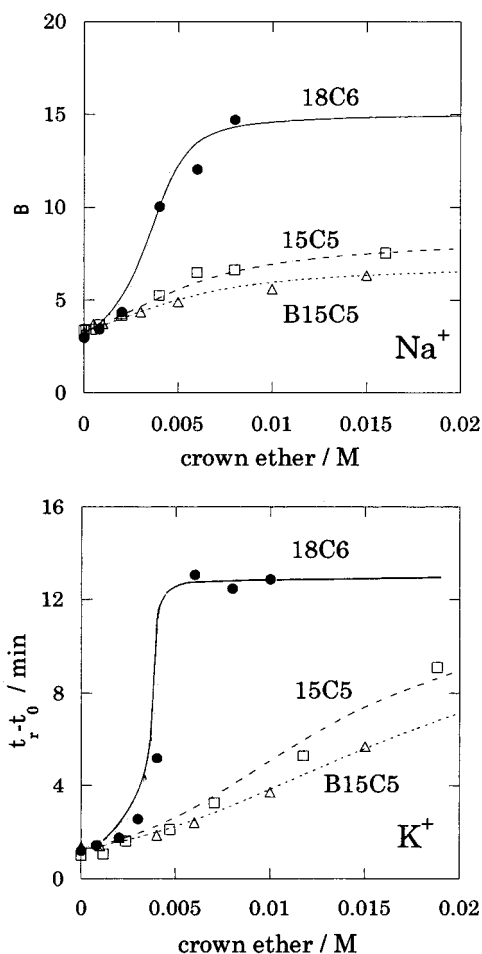


Figure 2. Changes in corrected retention times (equal to volume in mL) with the concentration of crown ethers in MeOH. Mobile phase, the upper 4 mM NaClO₄, the lower 4 mM KClO₄. The h and σ values are set to 2.7×10^{-7} m and -0.1206 C m⁻². The curves in the figures were drawn with parameters listed in Table 1.

with increasing C_L are sigmoidal rather than simple convex curves. To explain this sigmoidal dependence of k_{EV}' on C_L , necessary equations are derived in a manner similar to the above equation development. By solving simultaneous equations, we can simulate changes in k_{EV}' with increasing C_L where the contributions from both ion-pair formation and the diffuse layer accumulation term were taken into account, although the latter contribution was so small in comparison with the former one that we can neglect this contribution in some instances.

Curves in Figures 2 and 3 were drawn using suitable sets of parameters. However, there are many possible parameter sets capable of similar explanation of changes in k_{EV}' ; if one, for example, gives a particular ion-pair formation constant for the probe cation, the curve-fitting procedure always finds appropriate values for the other equilibrium constants. Unfortunately, the absolute constants were not determined, since there are no significant differences in reliability among these values. However, it should be noted that K_{ip}^M/K_{ip}^{M-Cr} ratios are almost identical irrespective of the absolute values. Details are discussed again in the following section.

Relation between k' of a Polyether and $(M)_0$ and Validity of Eq 1. When the complex formation of crown ethers and polyoxyethylenes were previously evaluated using eq 1, we found linear relations between $1/k'$ and $(M)_0$ in almost all instances except for the case where multiple complex formation occurs.² However, as mentioned above, it is possible that K determined on the basis of eq 1 involves some errors even when

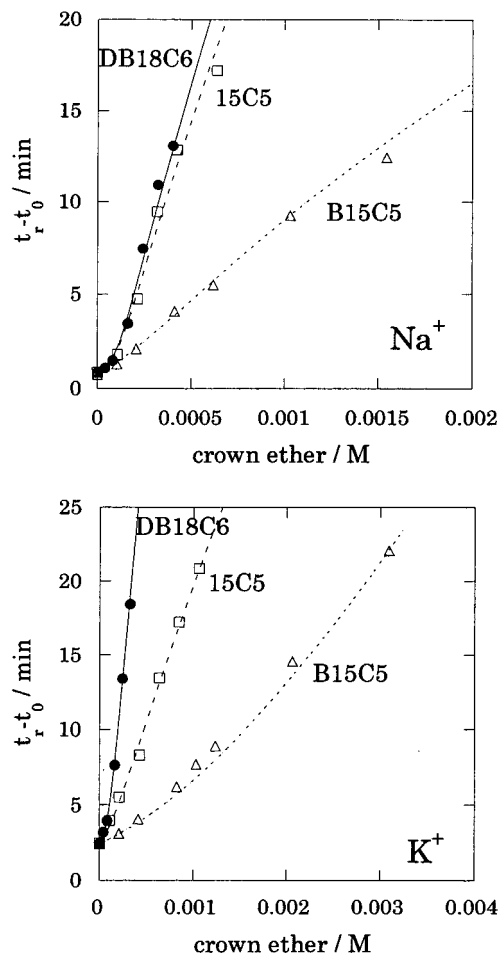


Figure 3. Changes in corrected retention times (equal to volume in mL) with the concentration of crown ethers in AN. Mobile phase, the upper 0.156 mM NaClO₄, the lower 0.167 mM KClO₄. The h and σ values are set to 2.7×10^{-7} m and -0.1206 C m⁻². The curves in the figures were drawn with parameters listed in Table 1.

$1/k'-(M)_0$ plots are linear. To evaluate the validity of eq 1 and errors involved in the method, the dependence of k' of a crown ether on $(M)_0$ was calculated for various sets of parameters. The change in the bulk concentration of a metal ion brings about several effects on this system. The surface (the Stern layer also) potential is numerically lowered by enhanced ion-pair formation with increasing $(M)_0$. This effect results in a decrease in the Stern layer concentrations of a metal-polyether complex and thus lowers k_{ip} . In addition, the low Stern layer potential decreases k_{DL} as well. However, the most drastic effect is seen in decreases in the equilibrium concentration of a polyether by a factor of $1/\{1 + K(M)_0\}$. The last contribution is the fundamental of chromatographic determination of K based on eq 1.

Calculation was done for K_{ip}^M set to $1-10^5$ M⁻¹, K_{ip}^{M-Cr}/K_{ip}^M to $10^{-3}-1$, K to $10-10^3$ M⁻¹, and various h and σ values. The calculated plots were basically linear over the $(M)_0$ range 0.1–1 mM with correlation factors > 0.999 . However, the slope/intercept ratio is not exactly equal to K in many instances. This deviation mainly comes from k_{DL} rather than from k_{ip} ; the slope/intercept ratios of $1/k_{ip}-(M)_0$ plots are not exactly equal to K because of the effects of ψ_{st} . Therefore, as the relative contribution from k_{DL} increases, the difference between K and the slope/intercept ratio becomes large (e.g., for a small K_{ip}^{M-Cr}/K_{ip}^M ratio). Figure 4 shows expected errors of complex formation constants determined by eq 1. This deviation is marked for small K_{ip}^{M-Cr}/K_{ip}^M ratios or large K_{ip}^M values. As K

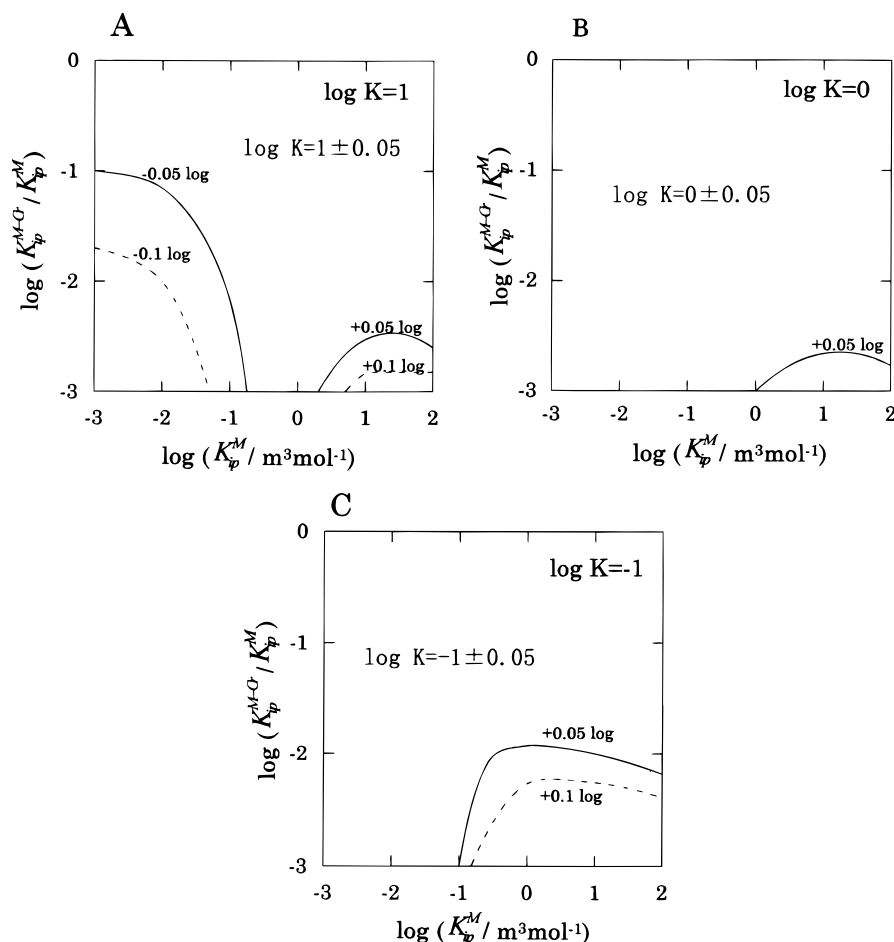


Figure 4. Applicability of eq 1. The h and σ values are set to 2.7×10^{-7} m and -0.1206 C m $^{-2}$. All parameters are given in m 3 mol $^{-1}$.

becomes large, unfavorable regions grow up because the weaker ion-pair formation ability of a complexed cation is emphasized. Thus, the inapplicability of eq 1 basically stems from the large contribution from k_{DL} to overall k' .

Judging from Figure 4, the applicability of eq 1 is better for the complexation of ca. $K = 1000$ M $^{-1}$. This favorable applicability of eq 1 is changed by other parameters such as h and σ (particularly affected by h). The unfavorable regions grew up for smaller h , suggesting that chromatographic stationary phases with larger h are preferably applicable to the determination of complex formation constants based on eq 1. In contrast, the effect of σ is not very serious. However, since this value is a main factor governing absolute retention times, the optimization of this value is important in actual application of eq 1; σ should be optimized so as to obtain appropriate and reliable retention times of polyethers of interest.

It can be concluded that eq 1 basically gives complex formation constants within 5% error in the logarithmic scale as long as K_{ip}^{M-Cr}/K_{ip}^M ratios are not very small. As shown below, this ratio is rather large in MeOH, while seriously small in AN, suggesting that eq 1 possibly provides unreliable K values in the latter solvent.

Crown Ether as a Probe to the Determination of Ion-Pair Formation between Cation-Exchange Sites and Counter Ions. In a previous paper, we showed that crown ethers can probe the ion-pair formation between ammonium ion chemically bonded on the silica gel and its counteranion.⁵ In this case, it was not necessary to take the diffuse layer accumulation effects into account. The precise evaluation of ion-pair formation with crown ether probes was difficult since the system is more

complex in the present case. As shown above, cation-exchange chromatographic retention can be modified by crown ethers added in mobile phases. Although this can be explained by the present model, we could not determine individual ion-pair formation constants, suggesting that at least one ion-pair formation constant be known to determine all individual values.

The curves depicted in Figures 2 and 3 are rather sensitive to changes in the ratio of ion-pair formation constants, K_{ip}^{M-Cr}/K_{ip}^M , but insensitive to changes in individual values. Referring to literature values for K , we determined ratios for K_{ip}^{M-Cr}/K_{ip}^M by curve fitting for the cation-exchange data shown in Figures 2 and 3. After the determination of the ratio, individual values were evaluated by comparing calculated and experimental k' values for crown ethers. Figure 5 shows changes in calculated k' with varying K_{ip}^M and constant K_{ip}^{M-Cr}/K_{ip}^M . Experimental k' values are shown by horizontal lines. Unfortunately, k' values lie on the flat part in calculated curves for Na $^+$ complexation, suggesting that possible K_{ip}^{M-Cr} and K_{ip}^M values range over more than 2 orders. In contrast, we can determine these values for K $^+$ complexation from the lower curves. Since we can calculate the ratio of the ion-pair formation constant for Na $^+$ to that for K $^+$, K_{ip}^M and K_{ip}^{M-Cr} for both cations can finally be evaluated. However, it is expected that these values involve much ambiguity. Errors involved in the values finally determined could not be calculated because of very complex relations between the model and resulting parameters. A similar procedure was applied to the complexation and ion-pair formation in AN. Results are summarized in Table 1.

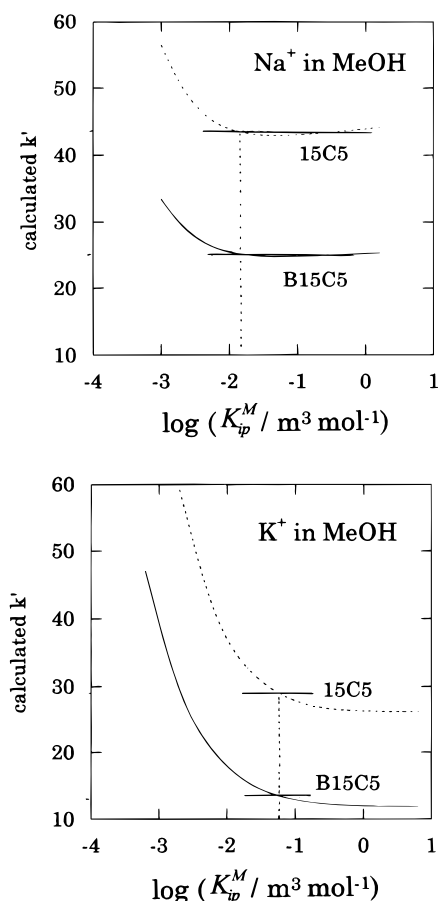


Figure 5. Changes in calculated k' for crown ethers with K_{ip}^M values in MeOH. Experimental k' values are shown by horizontal lines. K_{ip}^{M-Cr}/K_{ip}^M ratios, determined from data shown in Figures 2 and 3, were set to 0.398 for Na^+ -B15C5, 0.316 for Na^+ -15C5, and 0.126 for K^+ -B15C5 and K^+ -15C5. The h and σ values are set to 2.7×10^{-7} m and -0.1206 C m $^{-2}$.

In the above discussions, 1:1 stoichiometry was assumed for crown ether complexation with Na^+ and K^+ . As reported in some instances,^{1g,m} crown ethers having small cavity sizes possibly form sandwich-like complexes with relatively large ions; the complexation between K^+ and B15C5 or 15C5 must be the case especially when crown ether concentration is much higher than that of complexed cations. In the present case, 1:2 complexation gave better fitting to the complexation of K^+ with B15C5 in MeOH and AN, and with 15C5 in MeOH. Results are included in Table 1 as well as those based on the 1:1 stoichiometry assumption.

The parameters listed imply various facts. As is well-known, K^+ is in general preferably complexed by crown ethers in MeOH, while Na^+ more favorably forms complexes with crown ethers in AN^{1f} because higher charge density of smaller Na^+ becomes important for the complex formation in less structured solvents such as AN. The same is true for ion-pair formation of these cations with cation-exchange sites (sulfonate groups); K_{ip}^M for Na^+ in AN is ca. 4 times as large as that for K^+ , but reversed in MeOH. Interestingly, K_{ip}^{M-Cr} depends on the size of a crown ring rather than on the character of a centered ion; e.g., K_{ip}^{M-Cr} values in MeOH are ca. 10 M $^{-1}$ for Na^+ -B15C5 and Na^+ -15C5 complexes, but ca. 4 M $^{-1}$ for Na^+ -18C6 complexes. This must be due to the lower charge density of the latter complex. The ratios K_{ip}^{M-Cr}/K_{ip}^M range from 0.105 to 0.398 in MeOH, but from 3.2×10^{-3} to 5.0×10^{-3} in AN, suggesting the better applicability of eq 1 in MeOH.

TABLE 1: Equilibrium Constants (in M $^{-1}$) Calculated from Crown Ether Retention and Cation-Exchange Chromatography

	log K	log K_{ip}^M	log K_{ip}^{M-Cr}
In MeOH			
EV $^+$		-0.52	
Na $^+$		1.4	
Na $^+$ -B15C5	2.9		1.0
Na $^+$ -15C5	3.0		0.90
Na $^+$ -18C6	4.3		0.60
K $^+$		1.9	
K $^+$ -B15C5 1:1 ^a	2.8		0.90
1:1 & 1:2	2.7 (2.3) ^b		1.0 (0.60) ^b
K $^+$ -15C5 1:1	3.0		0.80
1:1 & 1:2	3.0 (2.5)		1.0 (0.60)
K $^+$ -18C6	6.0		0.7
In AN			
EV $^+$		1.2	
Na $^+$		4.8	
Na $^+$ -B15C5	4.3		2.3
Na $^+$ -15C5	5.0		2.3
Na $^+$ -DB18C6	5.1		2.3
K $^+$		4.2	
K $^+$ -B15C5 1:1	3.7		1.9
1:1 & 1:2	3.3 (2.7)		1.9 (1.6)
K $^+$ -15C5	4.2		1.9
K $^+$ -DB18C6	4.8		1.9

^a Stoichiometry assumed. ^b Values for 1:2 complexes are given in parentheses.

Thus, modeling the complex formation of crown ethers with counterions in cation-exchange resins allowed the evaluation of ion-pair formation constants of counterions as well as of complexed counterions. Although electrically neutral crown ethers themselves are not affected by electrostatic potential, the distribution of their cationic complexes is put under the control by this potential. By this, crown ethers can be probes to explore the ion-pair formation at the ion-exchange resin surface. This modeling also gives the theoretical foundation for the applicability of eq 1 to the determination of the complex formation constants.

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References and Notes

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