Efficient Evaluation of Poly(oxyethylene) Complex Formation with Alkali-Metal Cations

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ABSTRACT: An efficient method is developed for the evaluation of the complexation of poly(oxyethylenes) (POE) with alkali-metal cations in solution. Equations derived from equilibria controlling the chromatographic retention allow us to determine the complex formation constants of a variety of POE oligomers contained in polydisperse POE samples. Statistical consideration shows that compounds having less than 16 repeating oxyethylene (EO) units form only 1:1 complexes whereas those having more than 17 EO units form 1:1 and 2:1 complexes (cation–POE) with K^+ or Rb^+ and that the POEs tested do not form 3:1 or higher multiple complexes.

Introduction

In the presence of some metal ions, poly(oxyethylenes) (POEs) form coordination shells at the optimum distance required by the metal ions.[1] Although this complexation is similar to that of a cyclic ether (crown ether), uses of POEs in chemistry are less common than those of crown ethers because of certain disadvantages of POEs, such as poorer selectivity, lower complexation ability, difficulty in the syntheses of the pure compounds, etc.[2,3] Most of these chemical properties of POEs stem from their flexible structures. Yanagida et al.[4] found that the ability of POEs in the solvent extraction of K^+ increases with an increasing number of EO units and becomes almost equivalent to that of 18-crown-6 when the mean number of repeating EO units increased to 23. In addition, complexation ability toward small metal ions, such as Na^+, Li^+, etc., showed the maximum when the number of EO units corresponds to the suitable coordination number of the metal ion. These facts may indicate that selectivity of a polyether toward complexation with a metal ion is governed not only by a match of the cavity size of the polyether with the crystalline diameter of the metal ion but also by the coordination number of the metal ion and the facility of the polyether in forming a coordination shell. Thus, although the complexation ability of POEs also appears to increase with increasing EO units, the magnitude of the increase has not been known; i.e., the formation constants of POE–metal ion complexes have not been determined except for short POEs with less than eight EO units or polydisperse POE samples[5-7] because of the lack of effective methods.

To evaluate complexation in solution, it is important to study the stoichiometry and the precise complex formation constants. The complexation of POEs with metal ions has been discussed by using a number of methods, namely, nuclear magnetic resonance (NMR),[8-10] conductometry,[5,11-13] viscometry,[14] etc. Xu and Smid[6] determined the formation constants of POE (glymes) complexes with Na^+ and Li^+ in toluene using ligands immobilized on a polymer support and established an increase in the formation constants with increasing number of EO units owing to a statistical factor. Conductometry has also provided useful information on the POE–metal ion complexation. Ono and co-workers reported conductometric determination of the formation constants of a POE with the average molecular weight of 20 000 with alkali-metal ions[11] and presented a one-dimensional lattice model to interpret the complexation.[15] They stated that four oxygen atoms are necessary for POE–K^+ complexation at the high ionic strength limit.[11] On the other hand, it was reported that K^+ adopts 6, 8, and 10 coordination sites.[16] POEs with 6 or 7 EO units were shown to be capable of forming K^+ complexes by means of solvent extraction[4] and NMR.[8] Thus, there is disagreement between the approaches to POE–M^+ complexation. Stoichiometry of metal complexes of POEs containing more EO units also remains uncertain.

The author developed a chromatographic method for the separation of POE oligomers by utilizing the complexation with K^+ bound on a silica-based cation-exchange resin in methanolic solution.[17] This method permits the determination of the complex formation constant of each oligomer contained in polydisperse POE samples together with the stoichiometry. In the present contribution, the author describes the principle of this evaluation and discusses the results obtained for POE complexation with alkali-metal ions.

Experimental Section

Instruments and Materials. The chromatographic system was composed of a Tosoh computer-controlled pump, Model CCPD, a Rheodyne model injection valve equipped with a 100-μL sample loop, a column oven CO-8000 (Tosoh), a conductometric detector CM-8000 (Tosoh), a cation-exchange column TSK-gel IC-Cation-SW (4.6 × 50 mm packed with a silica-based resin of 5-μm particle size with 0.3 mequiv/g ion-exchange capacity), and a Jasco refractive index detector Model 830-RI. Temperature was kept at 25 °C. The flow rate was 1 mL/min. Data were processed with an NEC personal computer Model PC-9801 VX.

Methanol of analytical-grade reagent was distilled and stored over molecular sieves. Distilled methanol was redistilled each day before each experiment. Iodides of alkali-metal ions were dried in vacuo at 110 °C and stored in a desiccator. Mixtures of poly(ethylene glycol) (PEG 400 and 1000) were purchased from Wako Chemicals. Poly(oxyethylene) dodecyl ethers (POE(n)-D, n = 9 and 25) were gifts from Nikko Chemicals. These were used as received.

Method. A 0.1-mL methanolic sample solution containing 50 μg of polydisperse POEs was injected into a methanolic mobile phase containing a given concentration of KI. POEs were separated on the column according to the number of EO units. Eluted POEs were detected with refractive index or conductivity. Refractive index detection was employed for a purely methanolic mobile phase, whereas POEs eluted with KI-containing mobile phases were conductometrically detected on the basis of a difference in mobility between K^+ and K^+–POE complexes.[18] The elution of POEs resulted in negative conductometric changes because of the lower mobility of a K^+–POE complex than solvated K^+. The retention time (t_R) of each oligomer was read from chromatograms and converted into a capacity factor (k') according to the usual relation, $k' = (t_R - t_0)/t_0$, where t_0 is an elution time

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of an unretained analyte. These values were obtained for mobile phases containing 0–2.5 mM KI and processed by the method described below.

Results and Discussion

The method developed for the POE oligomer separation[17] is based on the complexation of POEs with metal cations (M^+) bound on a cation-exchange resin. POEs injected were separated according to the number of EO units and eluted in the order of increasing EO units. Elution peaks of POEs were identified by mass spectrometric measurements of effluents and injection of monodisperse POEs. The retention of POEs was reduced in the presence of M^+ in methanolic mobile phases because of the formation of unretained or weakly retained complexes in mobile phases. Relating the change in the retention times to the POE–M^+ complex formation finally permits us to determine the complex formation constants in solution, as shown below. In the present study, it was assumed that the following equilibria control the retention of POE

$$\left.\begin{array}{c} \mathrm{POE(m)} + \mathrm{M^+(s)} \underset{K_{R1}}{\rightleftarrows} \mathrm{POE{-}M^+(s)} \\ \mathrm{POE{-}M^+(m)} + \mathrm{M^+(s)} \underset{K_{R2}}{\rightleftarrows} \mathrm{POE{-}M^+_2(s)} \\ \vdots \qquad \vdots \qquad \vdots \\ \mathrm{POE{-}M^+_{\mathit{i}-1}(m)} + \mathrm{M^+(s)} \underset{K_{Ri}}{\rightleftarrows} \mathrm{POE{-}M^+_{\mathit{i}}(s)} \end{array}\right\} \quad (1)$$

$$\left.\begin{array}{c} \mathrm{POE(m)} + \mathrm{M^+(m)} \underset{K_1}{\rightleftarrows} \mathrm{POE{-}M^+(m)} \\ \mathrm{POE{-}M^+(m)} + \mathrm{M^+(m)} \underset{K_2}{\rightleftarrows} \mathrm{POE{-}M^+_2(m)} \\ \vdots \qquad \vdots \qquad \vdots \\ \mathrm{POE{-}M^+_{\mathit{j}-1}(m)} + \mathrm{M^+(m)} \underset{K_j}{\rightleftarrows} \mathrm{POE{-}M^+_{\mathit{j}}(m)} \end{array}\right\} \quad (2)$$

$$\mathrm{POE{-}M^+(m)} + \mathrm{POE(m)} \underset{K_s}{\rightleftarrows} \mathrm{POE_2{-}M^+(m)} \quad (3)$$

where s and m in parentheses represent stationary and mobile phases, respectively, and K_{R1}, K_{R2}, ..., K_{Ri}, K_1, K_2, ..., K_j, and K_s are the equilibrium constants. A series of eq 1 is related to the retention mechanism on the stationary phase, while eqs 2 and 3 are related to the complexation in the solution phase. Experimental results were reasonably described by these equilibria, as shown later. Equation 3 may be important for short POEs but does not contribute to the retention under the condition of $[M^+(m)] >> [POE(m)]$. A capacity factor of a POE is thus given by

$$k' = \phi\sum_i[\mathrm{POE{-}M^+_{\mathit{i}}(s)}]/([\mathrm{POE(m)}] + \sum_j[\mathrm{POE{-}M^+_{\mathit{j}}(m)}]) \quad (4)$$

where ϕ represents the phase ratio. Substituting equilibrium constants in eq 4 yields eq 5

$$k' = \frac{\phi[\mathrm{POE(m)}][\mathrm{M^+(s)}]\sum_i K_{Ri}K_0K_1...K_{i-1}[\mathrm{M^+(m)}]^{i-1}}{[\mathrm{POE(m)}] + [\mathrm{POE(m)}]\sum_j K_1K_2...K_j[\mathrm{M^+(m)}]^j} \quad (5)$$

where K_0 (=1) was introduced to simplify the equation. $\phi[M^+(s)]$ can be replaced by m_M/V_m, where m_M is the amount of a metal cation bound on the stationary phase and V_m is the volume of a mobile phase in a column. V_m can be determined from the retention time of unretained compound, and m_M is also determined by measuring the concentration of M^+ eluted out from the M^+-loaded column with another cation such as H^+. V_m and m_M determined for the present system were 0.48 mL and 1.01 × 10^{-4} mol, respectively. We can thus use 4.75 for the following calculation in place of $1/[M^+(s)]\phi$ and finally obtain

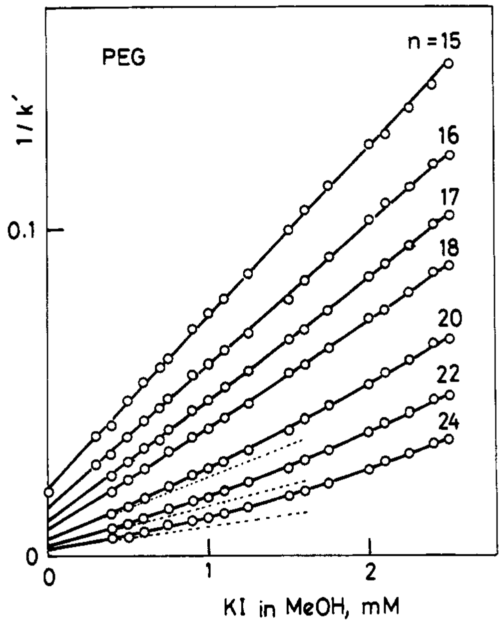

Figure 1. Plots of $1/k'$ vs C_K obtained for PEG. *n* represents the number of repeating EO units. Broken lines are limiting slopes of the corresponding plots. Solid curves are illustrated by using the calculated equilibrium constants.

$$1/k' = 4.75(1 + \sum_j K_1K_2...K_jC_M^{\ j})/\sum_i K_{Ri}K_0K_1...K_{i-1}C_M^{\ i-1} \quad (6)$$

where $[M^+(m)]$ is replaced by C_M, which represents the concentration of M^+ initially added in a mobile phase; this replacement is valid if $C_M >> [POE(m)]$. If a POE forms only a 1:1 complex, eq 7 is reduced to

$$1/k' = 4.75(1 + K_1C_M)/K_{R1} \quad (7)$$

In this specific case, the K_1 value is calculated from a ratio of the slope to the intercept of the plot of $1/k'$ vs C_M.

Plots of $1/k'$ vs C_K obtained for PEG 15–PEG 24 are shown in Figure 1. At least 6 EO units were required for the retention on K^+- and Rb^+-form resins (7 EO units were needed for Cs^+-form resin). Plots for PEG 6–PEG 16 appear to be linear; albeit plots for all oligomers examined are not shown in these figures for simplicity. However, the plots for PEG 17–PEG 24 obviously depart from the limiting slopes, which are represented by broken lines in the figure. To calculate equilibrium constants on the basis of eq 6, the method of least squares was applied together with the simplex method.[19] In all cases, it was not necessary to consider either the formation of 3:1 and higher multiple complexes in the solution phase or the multiple complexation on the stationary phase to fit the data. This will be ensured later in a different manner. This result leads to the reduction of eq 7 to a quadratic equation in C_M as shown by eq 8.

$$1/k' = 4.75(1 + K_1C_M + K_1K_2C_M^{\ 2})/K_{R1} \quad (8)$$

If K_{R1} is the only equilibrium controlling the retention on the stationary phase, this value can be calculated from the intercept of the limiting slope of the plot based on eq 6. When the resulting K_{R1} is used, eq 6 is modified as

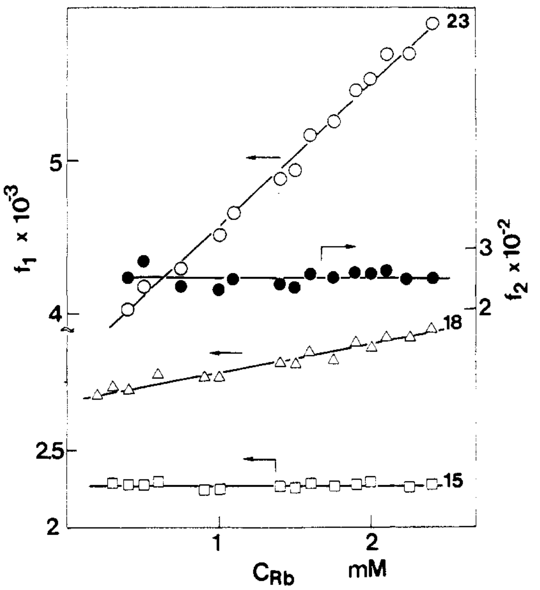

Figure 2. Modified plots (f_1 and f_2) for PEG–Rb^+ complexation: circles, PEG 23; triangles, PEG 18; squares, PEG 15. Open symbols correspond to f_1 plots, and solid circles correspond to f_2 plots.

Table I
Complex Formation Constants of Selected POEs with Alkali-Metal Ions

		K^+	Rb^+	Cs^+
PEG 11	log K_1	3.11 (0.02)[a]	3.08 (0.08)	2.85 (0.02)
PEG 16	log K_1	3.47 (0.05)	3.40 (0.02)	3.21 (0.03)
PEG 21	log K_1	3.57 (0.11)	3.53 (0.06)	3.41 (0.05)
	log K_2	2.16 (0.10)	2.18 (0.07)	1.75 (0.02)
POE(11)D	log K_1	3.08 (0.04)	3.05 (0.03)	2.93 (0.02)
POE(16)D	log K_1	3.36 (0.03)	3.38 (0.04)	3.19 (0.05)
POE(21)D	log K_1	3.52 (0.05)	3.53 (0.07)	3.40 (0.05)
	log K_2	2.05 (0.08)	2.13 (0.09)	1.73 (0.18)

[a] Standard deviation.

follows:

$$f_1 = (K_{R1}/4.75k' - 1)/C_M = \sum_j K_1K_2...K_jC_M^{j-1} \qquad (9)$$

Figure 2 shows modified plots (f_1) for PEG–Rb^+ complexes. The plot for PEG 15 is independent of C_{Rb}. This suggests that only a 1:1 complex is formed in this case. The plots for PEG 18 and PEG 23 appear to be linear. According to eq 9, the intercept of a linear f_1 plot corresponds to the K_1 value. When this value is used, the f_1 equation is further reduced to the lower polynomial in C_M (f_2). An example for PEG 23 is also shown in Figure 2. The plot is basically independent of C_{Rb}. Thus, the quadratic dependence of $1/k'$ on C_M, i.e., the formation of 1:1 and 2:1 complexes, is ensured.

K_1 and K_2 values of selected POEs are listed in Table I along with their standard deviations. K_1 values for K^+ and Rb^+ complexes are almost identical but consistently larger than that for Cs^+. This fact clearly shows that more EO units are needed to form a stable coordination shell around Cs^+ than needed for the other alkali-metal ions because of the large crystalline size of Cs^+. Regardless of whether POE molecules are accompanied with hydrocarbon chains or not, the 2:1 complex is detected. Apparent differences in formation constants between a PEG complex and a POE(n)D complex are not recognized.

Gokel et al.[7] indicated that there was a linear relation between binding constants of Na^+ with POEs and the molecular weights of POEs or between their logarithmic values. In the present work, we also found a linear relationship between K_1 and the number of EO units (EOn) as follows:

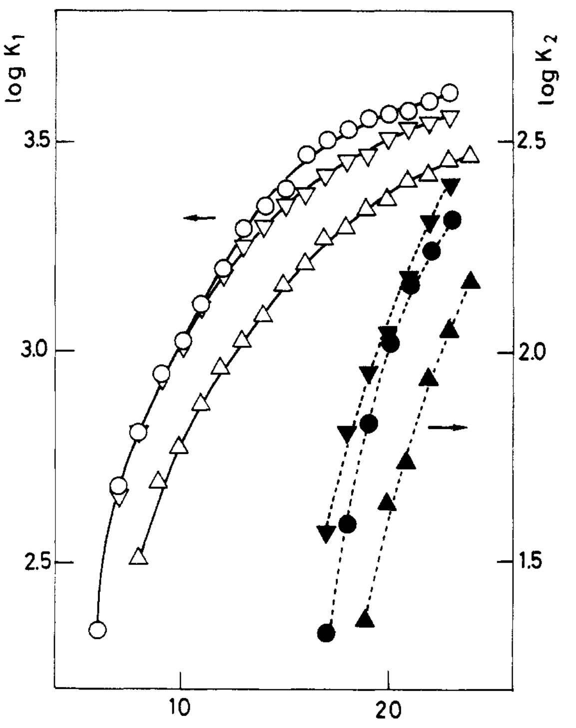

Figure 3. Changes in log K_1 and log K_2 values of PEG–alkali metal complexes with the number of repeating EO units in PEG: circles, K^+ complexes; reversed triangles, Rb^+ complexes; triangles, Cs^+ complexes. Open symbols and solid symbols represent log K_1 and log K_2, respectively.

$$K_1 = 241\mathrm{EO}n - 1280 \qquad r = 0.997, \text{ for } K^+$$

$$K_1 = 213\mathrm{EO}n - 1050 \qquad r = 0.998, \text{ for } Rb^+$$

$$K_1 = 172\mathrm{EO}n - 1130 \qquad r = 0.999, \text{ for } Cs^+$$

Extrapolation of these equations to $K_1 = 0$ will possibly provide the minimum EOn required for POE complexation with these alkali-metal ions: that is, 5.3 for K^+, 4.9 for Rb^+, and 6.5 for Cs^+. It can be concluded from this result that 5–6 EO units are necessary for the complexation with K^+ or Rb^+, and 6–7 EO units are required to form Cs^+ complexes.

Despite the usefulness of these relations, it is essential to discuss the relationship between logarithmic values of formation constants and EOn from thermodynamic viewpoints. Figure 3 shows changes in log K_1 and log K_2 with the number of EO units (EOn, n = 6–24). Slopes of curves become gradual with increasing EOn. It is clearly shown that multiple complex formation becomes important as EOn increases. As mentioned above, a topological effect cannot be expected for the POE complexation because of the flexible structure. The complexation ability of POE therefore depends on whether the number of donor oxygen atoms contained and the size of the coordination shell formed by effective donor atoms meet the requirement of metal ions. Hence, a change in the complexation ability of POE with increasing EOn is attributed to two factors: (1) the increasing number of donor atoms capable of coordinating and (2) increasing facility in building up the coordination shell at the optimum distance required by the metal ion (a statistical effect). The steep change in log K_1 in the small EOn region is ascribed to both effects.

However, the second factor becomes more important in determining the complexation ability, after all coordination sites are occupied by oxygen atoms. This results in the gradual changes of log K_1 in the large EOn region.

The formation of 2:1 complexes is detected between K^+ or Rb^+ and POEs with more than 17 EO units, which contain 18 oxygen atoms, while Cs^+ requires at least 19 EO units for multiple complex formation. This also reflects the large size of Cs^+. Yanagida et al. and Liu indicated that the minimum number of EO units needed to form the K^+ complex is 6 or 7[4,8] and that terminal hydroxyl oxygen is not important for the complexation with K^+.[4] The present study also showed the similar conclusion as mentioned above. In that case, 1:1 complexes should have additional 6 EO units at least to form 2:1 complexes. Further, K^+ adopts 10 coordination sites at the maximum.[16] If these data are applicable to the present case, 16 effective oxygen atoms are required for the formation of the 2:1 complex. This conclusion agrees well with the present result.

Elucidation of POE complexation is expected to be a significant contribution to the coordination chemistry of alkali-metal ions. The author believes that the data obtained and the method presented in this paper will be aids for further understanding of this chemistry.

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