

Chromatographic determination of Gibbs free energy of transfer for crown ether and monodispersed polyoxyethylene complexes with alkali cations from methanol to acetonitrile

Tetsuo Okada* and Shamshad B. Quraishi

Department of Chemistry, Tokyo Institute of Technology, Meguro-ku, Tokyo 152-8551, Japan.
E-mail: tokada@chem.titech.ac.jp; Fax: +81 3 5734 2612; Tel: +81 3 5734 2612

Received 10th July 2000, Accepted 10th October 2000

First published as an Advance Article on the web 22nd November 2000

Several chromatographic methods are cooperatively employed to determine the Gibbs free energies of transfer (ΔG_{tr}°) for alkali cation complexes with crown ethers and monodispersed polyoxyethylene (POE) oligomers having 6–13 oxyethylene units. In all cases, polyether complexation is enhanced in acetonitrile (AN) relative to methanol (MeOH). This enhancement is most pronounced for Li^+ complexation, and becomes marginal with increasing the sizes of alkali cations. The enhancement of crown ether complexation in AN dominantly comes from the smaller energy loss in the desolvation process of a cation in this solvent. The preferable free energies of transfer for POE complexes from MeOH to AN is another important factor in the enhancement of POE complexation in AN. The comparison of thermodynamic data with conductivity data imply that there are structural differences between POE complexes in MeOH and in AN, and that strong coordination occurs between POE and a metal ion in AN.

Introduction

A number of well-established tools, such as spectrometry, electrochemistry, calorimetry *etc.*, have been applied to study the nature of polyethers in solution.^{1–8} Developments of these approaches have given a variety of insights into the behaviors of polyethers in condensed phases, and allowed the current establishments of polyether chemistry. Individual approaches have some limitations as well as advantages; *e.g.* conductometry is inapplicable if the molar conductivity of a complex is the same as that of a solvated ion, and calorimetry cannot detect athermal reaction. In order to explore unknown areas in polyether chemistry and find novel aspects therein, it is essential to develop new methods, which are capable of covering fields that no one has elucidated because of the lack of applicable methods. One of the authors pointed out that separation techniques have great advantages over other methods in the evaluation of polyether complexation, and developed several means based on chromatography and electrophoresis.^{9–12} The applicability to impure or even mixed samples is the most important advantage of these separation approaches. The thermodynamic parameters of monodispersed polyoxyethylenes (POE) in methanol were, for example, determined by a chromatography-based method, and it was revealed that the desolvation entropy plays a decisive role in determining complexation selectivity among heavy alkali cations.¹³

As seen in the origin of POE complexation selectivity, the nature of the solvents is generally one of the most important factors governing polyether complexation in a solution phase, albeit complexation has often been discussed on the basis of the size fit theory. The nature of the solvation and structural aspects of all the species involved in equilibrium should be known for the complete understanding of solvent effects on polyether complexation. It is in general more versatile and significant to discuss solvent effects on polyether complexation on the basis of the transfer thermodynamic parameters.^{14–17}

Kolthoff and coworkers,^{16,17} for example, reported the free energies of transfer for usual 18-membered crown ethers and their complexes, and discussed origins in the complexation selectivity. Although several attempts have been reported to elucidate the origin of polyether complexation selectivity based on transfer thermodynamic parameters, there have been very few discussions of Li^+ complexes and of acyclic polyethers because of the lack of the relevant thermodynamic data. In the present paper, we discuss the transfer free energies of acyclic polyether complexes from methanol to acetonitrile as well as those of some crown ether complexes with alkali metal ions including Li^+ . Various separation techniques are cooperatively employed to determine these parameters and to elucidate transfer properties of polyethers.

Experimental

Apparatus

The chromatographic system was the same as previously used.^{9–10,12} Several different separation columns were used; (1) aminopropyl-silica (Si-NH_2), which was synthesized according to the literature¹⁸ from Wako Sil 5-SIL (5 μm particle size and specific surface area 300 $\text{m}^2 \text{g}^{-1}$ packed in a 7.6 mm \times 150 mm stainless steel column), (2) aminomethylated polystyrene-divinylbenzene copolymer gel (Re-NH_2), synthesized from MCI GEL 5HP, packed in a 4.6 mm \times 50 mm PTFE column, and (3) reversed-phase column (ODS), L-column (Chemicals Evaluation Research Institute, Japan), 4.6 mm \times 150 mm. The Si-NH_2 and Re-NH_2 stationary phases were fully protonated by passing aqueous perchloric acid before use. Ammonium ions formed on the stationary phase surface allowed the retention of polyethers by surface complexation.¹² Conductivity changes upon polyether complexation were monitored by a Tosoh conductometric detector Model CM-8000 connected with UV detector in tandem. All the columns were immersed in thermostated water to keep the

temperature at 25 °C. Electrophoretic data were taken from the literature.¹¹

Reagents

Dodecylpolyoxyethylene [POE(*n*)D, polydispersed POE(9)D and monodispersed POE(6)D and POE(8)D] was allowed to react with chloroanthraquinone in the presence of sodium hydride; *n* denotes the average number of repeating oxyethylene units. The anthraquinonePOE(*n*)D formed was purified by silica gel chromatography.¹⁹ The introduction of the anthraquinone moiety allowed spectrometric determination and detection of POE(*n*)D. Benzo-15-crown-5 (B15C5), benzo-18-crown-6 (B18C6), dibenzo-18-crown-6 (DB18C6), dibenzo-24-crown-8 (DB24C8), and dibenzo-30-crown-10 (DB30C10), were synthesized according to the literature. Methanol (MeOH) of analytical grade was refluxed with magnesium, and then distilled. Acetonitrile (AN) was refluxed with calcium hydride and then distilled. Other reagents were of analytical grade.

Determination of polyether complexation constants

Polyether complexation constants were determined by the following very simple equation.^{9,10,12}

$$k = \frac{k_0}{1 + KC} \quad (1)$$

where *k* and *k*₀ are the retention factors of a crown ether obtained with mobile phases containing and not containing a complex-forming cation, and *K* and *C* are the 1 : 1 complexation constant and the concentration of the cation in the mobile phase. This equation is valid when polyether concentration is much lower than *C*. The initial concentration of a polyether introduced into the column was typically 0.05 mM, and *C* ranged from 0.2 mM to 1 mM. The distribution coefficients for most polyethers were more than 2, suggesting that an introduced polyether is dominantly present in the stationary phase. Taking dilution of a solute into account, the ratio of the polyether concentration to *C* is not more than 0.1. Thus, *K* can simply be determined by studying the dependence of *k* on *C*. The Si-NH₂ column was used to determine *K* for POE, while the Re-NH₂ column was for crown ethers. Although the retention mechanisms on these stationary phases are basically identical, the former one has higher separation ability but lower chemical stability whereas the latter one has lower separation ability but higher chemical stability. These two columns were thus used for different purposes.

In AN, anions possibly form the ion-pairs with alkali cations and their complexes; ion-association should be enhanced for smaller ions. Perchlorate salts were used in this study to avoid (or minimize) this effect. It has been reported that the ion-association constant for LiClO₄ is 20 M⁻¹,²⁰ indicating that no association occurs in diluted (sub-mM level) electrolytes.

Determination of free energy of transfer for polyethers

The Gibbs free energy of transfer for B15C5 was determined by the solvent extraction between dodecane and MeOH or AN. After shaking the solvent mixtures for 10 min, the concentration of B15C5 in the polar phase was spectrometrically determined ($\epsilon = 6000 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{max}} = 276 \text{ nm}$).

The Gibbs free energy of transfer of monodispersed POE was also determined with solvent extraction using the same solvent systems. However, the simple determination of partition coefficients (*P*) between dodecane and a polar solvent of interest was difficult because of the very low partition of POE in the dodecane phase. The procedure for determining *P* is as follows: (1) dodecane and a polar solvent containing POE was shaken for 10 min (phase ratio; ϕ_1); after equilibration,

dodecane phase was shaken with the fresh polar solvent (ϕ_2); POE contained in the polar phase after this back extraction was separated into monodispersed components with reversed phase chromatography (detection at 300 nm). The ratio (*r*) of the peak intensity of a monodispersed POE contained in a final solution to that in an original solution is given by

$$r = \frac{\phi_2 P}{(1 + \phi_1 P)(1 + \phi_2 P)} \quad (2)$$

P is thus given by a solution of eqn. (2).

Results and discussion

Gibbs free energy of transfer for crown ether complexes

Table 1 lists complexation constants of crown ethers determined at 25 °C. The chromatographic method using Si-NH₂ or Re-NH₂ stationary phase has a great advantage that it is applicable to the evaluation of rather weak complexation. This chromatographic method was capable of evaluating Li⁺ complexation with some crown ethers. Li⁺ complexation with crown ethers having large cavities was not detected in MeOH even with this rather sensitive method. The complexation constants are in general larger in AN than in MeOH. This enhancement becomes more marked as the size of an alkali cation decreases; taking B15C5 as an example, $\Delta \Delta \log K_{(\text{MeOH} \rightarrow \text{AN})} = 3.06 \pm 0.04$ for Li⁺, 1.18 ± 0.02 for Na⁺, and 0.47 ± 0.03 for K⁺.

The Gibbs free energies of transfer for complexes ($\Delta G_{\text{tr}(\text{LM}^+; \text{MeOH} \rightarrow \text{AN})}^\circ$) were calculated to verify the origin of enhanced complexation in AN:

$$\Delta G_{\text{tr}(\text{LM}^+; \text{MeOH} \rightarrow \text{AN})}^\circ = -2.303RT[(\log K_{\text{AN}}) - (\log K_{\text{MeOH}})] + \Delta G_{\text{tr}(\text{L}; \text{MeOH} \rightarrow \text{AN})}^\circ + \Delta G_{\text{tr}(\text{M}^+; \text{MeOH} \rightarrow \text{AN})}^\circ \quad (3)$$

where *K*_{AN} and *K*_{MeOH} are the complexation constants in AN and MeOH, and $\Delta G_{\text{tr}(\text{L}; \text{MeOH} \rightarrow \text{AN})}^\circ$ and $\Delta G_{\text{tr}(\text{M}^+; \text{MeOH} \rightarrow \text{AN})}^\circ$ are the Gibbs free energies of transfer of a ligand and a metal ion. The $\Delta G_{\text{tr}(\text{M}^+; \text{MeOH} \rightarrow \text{AN})}^\circ$ values were taken from the literature; 20.6, 6.9 and -1.5 kJ mol^{-1} for Li⁺, Na⁺ and K⁺, respectively.²¹ These $\Delta G_{\text{tr}(\text{M}^+; \text{MeOH} \rightarrow \text{AN})}^\circ$ values were determined on the basis of the tetraphenylborate tetraphenylarsonium assumption. The $\Delta G_{\text{tr}(\text{L}; \text{MeOH} \rightarrow \text{AN})}^\circ$ values for most crown ethers except B15C5 are also taken from the literature;^{16,17} -2.98 , -9.41 , -7.09 and $-7.98 \text{ kJ mol}^{-1}$ for B18C6, DB18C6, DB24C8, and DB30C10, respectively. $\Delta G_{\text{tr}(\text{L}; \text{MeOH} \rightarrow \text{AN})}^\circ$ for B15C5 was determined by dodecane extraction as $-0.82 \text{ kJ mol}^{-1}$. These crown ethers are solvated better in AN than in MeOH, and this trend is clearer for dibenzo crown ethers than for monobenzo crown ethers. A crown ring should be solvated through hydrogen bonding, but the solvation of benzo groups should

Table 1 Crown ether complexation constants with alkali cations^a

	Li ⁺	Na ⁺	K ⁺
In MeOH			
B15C5	1.33(0.03)	2.99(0.02)	2.90(0.02)
B18C6	—	4.53(0.15)	4.71(0.09)
DB18C6	0.81(0.02)	4.52(0.11)	5.25(0.06)
DB24C8	—	2.25(0.03)	3.46(0.01)
DB30C10	—	2.14(0.01)	4.67(0.03)
In AN			
B15C5	4.39(0.03)	4.17(0.01)	3.37(0.02)
B18C6	2.56(0.24)	4.69(0.14)	5.29(0.19)
DB18C6	1.38(0.01)	4.88(0.07)	5.18(0.30)
DB24C8	1.26(0.03)	3.75(0.03)	3.77(0.01)
DB30C10	1.06(0.02)	3.15(0.05)	4.67(0.12)

^a Standard deviations are in parentheses (*n* = 6–7).

be due to dispersion force and π - π interaction. The above $\Delta G_{\text{tr(L; MeOH} \rightarrow \text{AN)}}^{\circ}$ data may reflect the dominant contribution from the solvation of benzo groups rather than that of crown rings.

$\Delta G_{\text{tr(LM}^+; \text{MeOH} \rightarrow \text{AN)}}^{\circ}$ values were summarized in Table 2. Li^+ -complexation with some crown ethers in MeOH is too weak to be detected by the present method; thus, in such cases, $\Delta G_{\text{tr(LM}^+; \text{MeOH} \rightarrow \text{AN)}}^{\circ}$ is represented by " $<$ ". The positive $\Delta G_{\text{tr(LM}^+; \text{MeOH} \rightarrow \text{AN)}}^{\circ}$ values for Li^+ indicate the weaker solvation for the Li^+ complexes in AN. $\Delta G_{\text{tr(LM}^+; \text{MeOH} \rightarrow \text{AN)}}^{\circ}$ decreases in the order of $\text{Li}^+ > \text{Na}^+ > \text{K}^+$. This disagrees with the fact that enhancement of Li^+ complexation is most pronounced, suggesting that the desolvation of cations governs the entire free energy changes in crown ether complexation. This will be discussed later in more detail.

Transfer parameters for POE complexes

Table 3 lists the complexation constant of POE with Li^+ , Na^+ and K^+ in MeOH and AN. As previously described, the terminal groups do not cause significant shifts in POE complexation ability.⁹ An anthraquinone group introduced in a POE molecule hardly affects complexation. Although $\log K$ increases with increasing number of repeating oxyethylene units (n) in either solvent, the increments are obviously different; $\log K$ more steeply increases in MeOH than in AN.

Table 2 Gibbs free energy of transfer of crown ethers complexes from MeOH to AN

	$\Delta G_{\text{tr(LM}^+; \text{MeOH} \rightarrow \text{AN)}}^{\circ}/\text{kJ mol}^{-1}$		
	Li^+	Na^+	K^+
B15C5	2.4	-0.64	-5.0
B18C6	<3.0	0.67	-7.8
DB18C6	4.1	-4.9(-7.4) ^a	-12.6(-10.8) ^a
DB24C8	<6.3	-8.7	-10.4
DB30C10	<6.6	-6.8	-9.5

^a Taken from ref. 16.

There have been some discussions on the systematic increase in $\log K$ for POE complexation with increasing n ; a statistical effect has been pointed out as a possible origin.²² However, the statistical effect cannot explain different trends in $\log K$ increases in AN and MeOH, because it predicts the identical change regardless of solvents. This difference may imply differences between the structures of POE complexes in MeOH and in AN.

In order to clarify solvent effects on POE complexation, the Gibbs free energies of transfer for POE and POE-complexes were evaluated using chromatographic techniques. The partition coefficients for POE between MeOH and AN were determined by the procedure described in the Experimental section. The determined partition coefficients for monodispersed POE chains are listed in Table 4. The POE derivatives used in this work are well partitioned in AN compared to in MeOH probably due to the preferable solvation of the terminal anthraquinone and dodecyl groups in the former solvent. The partition coefficients ($c_{\text{MeOH}}/c_{\text{AN}}$) decrease with increasing n up to $n = 9$, then increases; the maximum difference corresponds to *ca.* $1.5 \pm 0.5 \text{ kJ mol}^{-1}$ over the entire range of n . This rather small dependence of $\Delta G_{\text{tr(L; MeOH} \rightarrow \text{AN)}}^{\circ}$ on n strongly suggests that the negative values are mainly due to the terminal effect and there is no clear differences between POE solvation in MeOH and in AN. The $\Delta G_{\text{tr(LM}^+; \text{MeOH} \rightarrow \text{AN)}}^{\circ}$ values for POE complexes, calculated based on eqn. (3), are also listed in Table 4; POE complexation with Li^+ in MeOH was not confirmed with any methods attempted, and no data for Li^+ are listed. It should be noted that $\Delta G_{\text{tr(LM}^+; \text{MeOH} \rightarrow \text{AN)}}^{\circ}$ also depends on the nature of the terminal groups similar to $\Delta G_{\text{tr(L; MeOH} \rightarrow \text{AN)}}^{\circ}$. However, $\Delta G_{\text{tr(LM}^+; \text{MeOH} \rightarrow \text{AN)}}^{\circ}$ is more negative than $\Delta G_{\text{tr(L; MeOH} \rightarrow \text{AN)}}^{\circ}$ by *ca.* 5 kJ mol^{-1} , indicating that, apart from the contribution from the solvation of the terminal groups, the complex becomes stable on going from MeOH to AN. Interestingly, the $\Delta G_{\text{tr(LM}^+; \text{MeOH} \rightarrow \text{AN)}}^{\circ}$ values both for Na^+ - and for K^+ -complexes increase with increasing n by *ca.* 0.5 kJ mol^{-1} . Although relatively large errors in $\Delta G_{\text{tr(LM}^+; \text{MeOH} \rightarrow \text{AN)}}^{\circ}$ are possibly involved, this trend is significant. Very small differences in

Table 3 POE complexation constants with alkali cations

n	Li^+		Na^+				K^+			
	AN		AN		MeOH ^a		AN		MeOH	
	$\log K$	σ^b	$\log K$	σ	$\log K$	σ	$\log K$	σ	$\log K$	σ
6	2.65	0.00	3.28	0.00	0.63	0.27	3.39	0.00	2.34	0.00
7	2.75	0.00	3.33	0.00	0.93	0.25	3.43	0.00	2.69	0.00
8	2.77	0.00	3.36	0.00	1.09	0.21	3.48	0.00	2.76	0.01
9	2.79	0.00	3.39	0.00	1.24	0.18	3.54	0.00	2.95	0.00
10	2.82	0.00	3.42	0.00	1.34	0.13	3.58	0.00	3.02	0.00
11	2.84	0.00	3.45	0.00	1.42	0.14	3.63	0.00	3.08	0.01
12	2.87	0.00	3.49	0.00	1.42	0.04	3.68	0.01	3.20	0.00
13	2.89	0.00	3.52	0.00	1.49	0.06	3.73	0.01	3.29	0.00

^a Determined by capillary electrophoresis (ref. 11). ^b Standard deviation.

Table 4 Partition coefficients of monodispersed POE and Gibbs free energies of transfer of POE complexes with Na^+ and K^+

n	$\ln P$ ($P = c_{\text{MeOH}}/c_{\text{AN}}$)	σ^a	$\Delta G_{\text{tr(L; MeOH} \rightarrow \text{AN)}}^{\circ}$ / kJ mol^{-1}	$\Delta G_{\text{tr(LM}^+; \text{MeOH} \rightarrow \text{AN)}}^{\circ}/\text{kJ mol}^{-1}$	
				Na^+ complex	K^+ complex
6	-4.40	0.17	-10.9	-19.1	-18.4
7	-4.63	0.06	-11.5	-18.2	-17.2
8	-4.76	0.03	-11.8	-17.8	-17.4
9	-4.91	0.04	-12.6	-17.5	-17.0
10	-4.89	0.09	-12.1	-17.0	-16.8
11	-4.62	0.13	-11.4	-16.1	-16.1
12	-4.55	0.19	-11.3	-16.1	-15.5
13	-4.30	0.15	-10.6	-15.3	-14.6

^a Standard deviation for $\ln P$.

$\Delta G_{\text{tr}}^{\circ}(\text{Li}^+; \text{MeOH} \rightarrow \text{AN})$ between Na^+ -POE and K^+ -POE complexes are also noticeable. This may imply that the structures of POE complexes with these cations are similar to each other; *i.e.* the cationic nature is effectively shielded by complexation with POE. In contrast, $\Delta G_{\text{tr}}^{\circ}(\text{Li}^+; \text{MeOH} \rightarrow \text{AN})$ for crown ether complexation with Na^+ is more positive than that of K^+ as shown in Table 2. This difference between POE and crown ether complexes must come from their different molecular flexibility. POE can almost completely wrap a cation, and effectively shields the nature of the cation, whereas crown ethers cannot flexibly change their structures to allow complete wrapping.

Conductometric measurements were carried out to obtain more information on the solvation nature of POE complexes. Although conductometry has been extensively utilized for the evaluation of crown ether complexation in solution,^{3,4} its application to acyclic polyethers have been very few because of the limited availability of monodispersed acyclic polyether. In the present research, spectrometric and conductometric detectors connected in tandem were used to monitor the elution of monodispersed POE after chromatographic separation. The former detector monitors the anthraquinone moiety bonded to a POE chain; its response is proportional to the concentration of POE. The elution of POE causes a change (usually a decrease) in the conductivity of effluents containing an appropriate alkali cation, depending on the complexation ability of the POE and ionic conductivity of a POE complex. The conductometric detector responses (ΔA) are proportional to the concentration of the complex formed in the effluents ($[\text{M} \cdot \text{POE}]$):

$$\begin{aligned} \Delta A &= \alpha(\lambda_{\text{M} \cdot \text{POE}} - \lambda_{\text{M}})[\text{M} \cdot \text{POE}] \\ &= \alpha(\lambda_{\text{M} \cdot \text{POE}} - \lambda_{\text{M}})[\text{M}^+][\text{POE}]K \end{aligned}$$

where α is a proportional constant, λ_{M} and $\lambda_{\text{M} \cdot \text{POE}}$ are the molar ion conductivity of a cation and its complex with POE, respectively. When the concentration of a cation in the mobile phase is sufficiently larger than that of POE, the equilibrium concentration of a cation ($[\text{M}^+]$) equals its initial concentration in the mobile phase (C_{M}). Thus,

$$\Delta A = \alpha(\lambda_{\text{M} \cdot \text{POE}} - \lambda_{\text{M}}) \frac{KC_{\text{M}}C_{\text{P}}}{1 + KC_{\text{M}}}$$

where C_{P} is the total concentration of POE. Dividing ΔA by the spectrometric detector response (A), which is also proportional to C_{P} , we obtain

$$\frac{\Delta A}{A} = \alpha'(\lambda_{\text{M} \cdot \text{POE}} - \lambda_{\text{M}}) \frac{KC_{\text{M}}}{1 + KC_{\text{M}}}$$

Since K and C_{M} are known, we can thus calculate $\alpha'(\lambda_{\text{M} \cdot \text{POE}} - \lambda_{\text{M}})$ from the ratios of two detector responses. Assuming the absorptivity of anthraquinone is independent of the chain lengths of bonded POE moieties, $(\lambda_{\text{M}} - \lambda_{\text{M} \cdot \text{POE}})$ can be compared for different systems because α' is common to all the POE oligomers. This scheme was applicable to complexation of three alkali cations studied in AN and that of K^+ in MeOH. Results are summarized in Fig. 1.

An alternative way was applied to the estimation of the ionic conductivity of Na^+ complexes in MeOH. We previously reported capillary electrophoretic evaluation of polyether complexation in MeOH.¹¹ This method is based on the following relation:

$$\mu_{\text{app}} - \mu_{\text{eo}} = \frac{\mu_{\text{M} \cdot \text{POE}} C_{\text{M}}}{1 + KC_{\text{M}}}$$

where μ_{app} , μ_{eo} and $\mu_{\text{M} \cdot \text{POE}}$ are the apparent mobility, the mobility of an electroosmotic flow, and the mobility of a POE complex. From the dependence of μ_{app} on C_{M} , we can evaluate $\mu_{\text{M} \cdot \text{POE}}$ and in turn $\lambda_{\text{M} \cdot \text{POE}}$. Results are also plotted in Fig. 1, where for the consistency with other data, $(\lambda_{\text{M} \cdot \text{POE}} - \lambda_{\text{M}})$ is

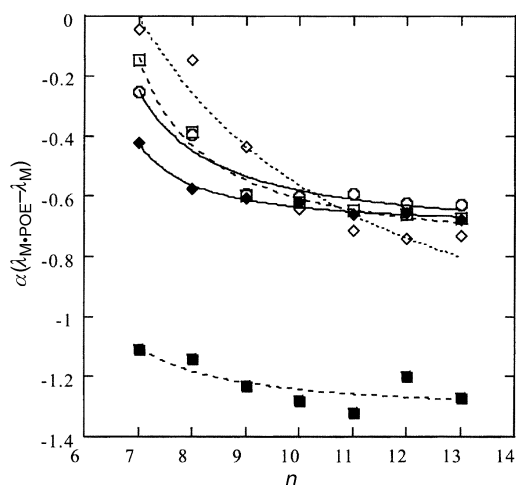


Fig. 1 Ionic molar conductivity changes for POE complexes. Open symbols in AN. Solid symbols in MeOH. Circles, Li^+ ; squares, Na^+ ; diamonds, K^+ . Curves are guidelines for the eye.

plotted for Na^+ -POE complexes in MeOH; λ_{M} was calculated based on an Onsager equation. The lower shift of the plot for Na^+ -POE is due to a different proportional factor (α'), and thus not essential.

The dependence of $(\lambda_{\text{M} \cdot \text{POE}} - \lambda_{\text{M}})$ on n in AN clearly reflects differences in size (or the coordination number) of alkali cations; $(\lambda_{\text{M} \cdot \text{POE}} - \lambda_{\text{M}})$ becomes almost constant for Li^+ and Na^+ at $n = 9$, while that for K^+ continues to change up to $n = 12$ – 14 . It has been reported that K^+ cations have ten coordination sites in polyether complexes while Li^+ and Na^+ cations have less.²³ The dependence of $(\lambda_{\text{M} \cdot \text{POE}} - \lambda_{\text{M}})$ on n in AN suggests that increasing POE chain length causes the changes in the coordination numbers and in the structures of complexes. In contrast, $(\lambda_{\text{M} \cdot \text{POE}} - \lambda_{\text{M}})$ becomes almost constant at $n = 8$ in MeOH even for K^+ . It appears that the structures of POE complexes in MeOH are independent of POE chain lengths and ethereal oxygen atoms occupy all the coordination sites, when n exceeds 8.

Origin of enhanced complexation in AN compared to in MeOH

The results listed in Tables 1 and 3 show that the complexation of polyethers is generally enhanced in AN compared to that in MeOH, and that poorer complexation selectivity among alkali cations emerges in the former solvent. There are four possible origins in solvent effects on polyether complexation: (1) metal cation desolvation; (2) ligand desolvation; (3) the solvation of a formed complex; (4) coordination bond strength. Fig. 2 shows the components of differences in the overall Gibbs free energy changes for complexation between in MeOH and in AN ($\Delta\Delta G^{\circ}$). Taking B15C5 as an example of a crown ether, the enhancement of Li^+ complexation on going from MeOH to AN is most pronounced, and the enhancement becomes marginal in the order of $\text{Li}^+ > \text{Na}^+ > \text{K}^+$. Fig. 2 shows that this enhancement is due to changes in the solvation energy of an alkali cation; the solvation changes of ligands and complexes are not very important in the determination of $\Delta\Delta G^{\circ}$. Thus, the desolvation energy of a metal ion is a main factor governing crown ether complexation selectivity. In this connection, it is predictable that crown ethers show poorer selectivity but higher complexation ability in nitromethane (NM) than in AN, because much smaller desolvation energy losses are expected for smaller alkali cations; $\Delta G_{\text{tr}}^{\circ}(\text{Li}^+; \text{MeOH} \rightarrow \text{NM}) = 44 \text{ kJ mol}^{-1}$, $\Delta G_{\text{tr}}^{\circ}(\text{Na}^+; \text{MeOH} \rightarrow \text{NM}) = 18 \text{ kJ mol}^{-1}$ and $\Delta G_{\text{tr}}^{\circ}(\text{K}^+; \text{MeOH} \rightarrow \text{NM}) = 9 \text{ kJ mol}^{-1}$.¹⁹ However, since ion-pair formation is greatly enhanced in this solvent, complexation constants could not be evaluated either with separation techniques or with conductivity measurements.

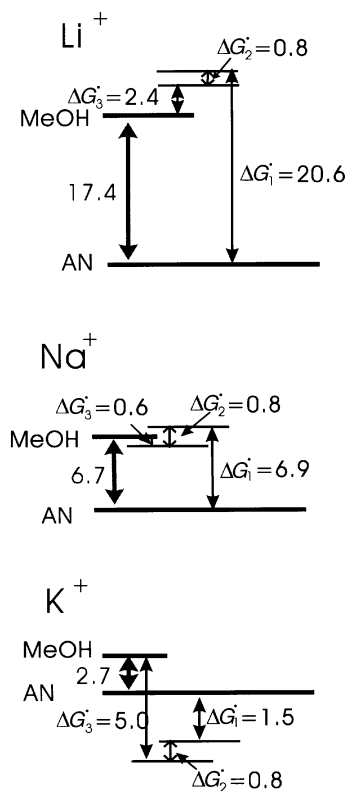


Fig. 2 Components of $\Delta\Delta G^\circ$ between B15C5 complexation in MeOH and in AN. $\Delta G_1^\circ = \Delta G_{\text{tr}}^\circ(\text{M}^+; \text{MeOH} \rightarrow \text{AN})$, $\Delta G_2^\circ = \Delta G_{\text{tr}}^\circ(\text{L}; \text{MeOH} \rightarrow \text{AN})$ and $\Delta G_3^\circ = \Delta G_{\text{tr}}^\circ(\text{LM}^+; \text{MeOH} \rightarrow \text{AN})$. Energies in kJ mol^{-1} .

Similar contribution from cation desolvation can be seen for POE complexation as well. The complexation selectivity basically follows the preference in the desolvation energy of a metal ion. However, both $\Delta G_{\text{tr}}^\circ(\text{L}; \text{MeOH} \rightarrow \text{AN})$ and $\Delta G_{\text{tr}}^\circ(\text{LM}^+; \text{MeOH} \rightarrow \text{AN})$ also comprise rather large sectors in $\Delta\Delta G^\circ$ as shown in Fig. 3. Taking POE(10) as an example, the enhancement of K^+ com-

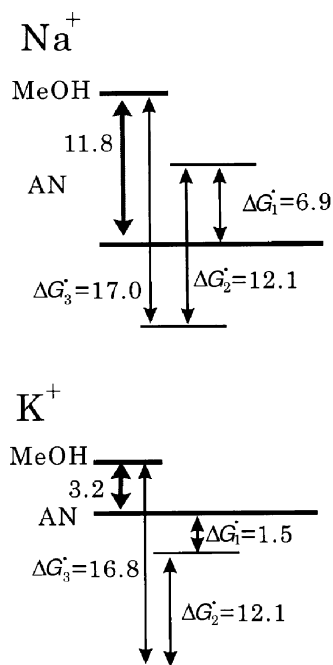


Fig. 3 Components of $\Delta\Delta G^\circ$ between POE ($n = 10$) complexation in MeOH and in AN. $\Delta G_1^\circ = \Delta G_{\text{tr}}^\circ(\text{M}^+; \text{MeOH} \rightarrow \text{AN})$, $\Delta G_2^\circ = \Delta G_{\text{tr}}^\circ(\text{L}; \text{MeOH} \rightarrow \text{AN})$ and $\Delta G_3^\circ = \Delta G_{\text{tr}}^\circ(\text{LM}^+; \text{MeOH} \rightarrow \text{AN})$. Energies in kJ mol^{-1} .

plexation in AN relative to in MeOH is solely due to the preferable $\Delta G_{\text{tr}}^\circ(\text{LK}^+; \text{MeOH} \rightarrow \text{AN})$. For Na^+ , both $\Delta G_{\text{tr}}^\circ(\text{Na}^+; \text{MeOH} \rightarrow \text{AN})$ and $\Delta G_{\text{tr}}^\circ(\text{LNa}^+; \text{MeOH} \rightarrow \text{AN})$ make significant contributions to the complexation enhancement in AN. Since $\Delta G_{\text{tr}}^\circ(\text{LK}^+; \text{MeOH} \rightarrow \text{AN})$ are almost equal to $\Delta G_{\text{tr}}^\circ(\text{LNa}^+; \text{MeOH} \rightarrow \text{AN})$, Na^+ complexation is more markedly enhanced in AN than K^+ complexation by the preferential shift in the desolvation energy of a cation. Although no Li^+ complexation occurs in MeOH, similar discussion must be applicable to Li^+ complexation as well.

If a POE complex is transferred from MeOH to AN, two effects are expectable: (1) the interaction of the complex with solvent molecules changes and (2) the structure of the complex changes. Kolthoff and coworkers^{16,17} stated that the solvation of crown ether complexes would be kind of hydrophobic, because the outer surfaces of the complexes are covered by hydrocarbon groups. The outer surface of a POE complex is also covered by methylene groups, and interacts with solvent molecules mainly by dispersion forces. Differences between $\Delta G_{\text{tr}}^\circ(\text{L}; \text{MeOH} \rightarrow \text{AN})$ and $\Delta G_{\text{tr}}^\circ(\text{LM}^+; \text{MeOH} \rightarrow \text{AN})$ (ca. 5 kJ mol^{-1}) may indicate that a POE complex is more favorably solvated in AN than a POE ligand itself.

Another possible explanation for negative $\Delta G_{\text{tr}}^\circ(\text{LM}^+; \text{MeOH} \rightarrow \text{AN})$ is the stronger coordination bond formation in AN. When a POE complex is transferred from MeOH to AN, not only is the structure of a complex changed but also the coordination bond strength. If this effect is responsible for negative $\Delta G_{\text{tr}}^\circ(\text{LM}^+; \text{MeOH} \rightarrow \text{AN})$, a change in $\Delta G_{\text{tr}}^\circ(\text{LM}^+; \text{MeOH} \rightarrow \text{AN})$ with n implies that a relatively short POE chain forms more stable coordination bond than that of the longer counterpart in AN. It is understandable that this trend, coming from the structure changes of POE complexes in AN, diminishes as the POE chain length increases, because all the coordination sites are occupied by the ethereal oxygen atoms in a sufficiently long POE chain and structural changes no longer occur. This is confirmed by the comparison of $\Delta G_{\text{tr}}^\circ(\text{LM}^+; \text{MeOH} \rightarrow \text{AN})$ and $(\lambda_{\text{M-POE}} - \lambda_{\text{M}})_{\text{MeOH} \rightarrow \text{AN}}$. If the negative $\Delta G_{\text{tr}}^\circ(\text{LM}^+; \text{MeOH} \rightarrow \text{AN})$ were due to the strong solvation of POE complexes in AN, there should be positive correlation between $\Delta G_{\text{tr}}^\circ(\text{LM}^+; \text{MeOH} \rightarrow \text{AN})$ and $(\lambda_{\text{M-POE}} - \lambda_{\text{M}})_{\text{MeOH} \rightarrow \text{AN}}$, because stronger solvation usually results in smaller mobility. However, $\Delta G_{\text{tr}}^\circ(\text{LM}^+; \text{MeOH} \rightarrow \text{AN})$ becomes less negative with increasing n , while $(\lambda_{\text{M-POE}} - \lambda_{\text{M}})_{\text{MeOH} \rightarrow \text{AN}}$ becomes smaller. Thus, strong solvation does not occur for short POE complexes in AN, and the stabilization of short POE complexes in AN is due to the strong coordination bond formation rather than to their strong solvation.

In conclusion, separation approaches have revealed various thermodynamic aspects of polyether complexation in solution, and are particularly effective for mixed solutes, such as POE, because systematic studies are feasible. The present study has pointed out that the structural differences between complexes in AN and in MeOH are well reflected in thermodynamic data, but cannot provide any direct structural information. Cooperative uses of efficient spectroscopic methods with the present approach should be useful to elucidate these aspects.

References

- 1 T. Hayashita, H. Sawano, T. Higuchi, M. Indo, K. Hiratani, Z.-Y. Zhang and R. A. Bartsch, *Anal. Chem.*, 1999, **71**, 791.
- 2 O. A. Raevsky, V. P. Solov'ev, A. F. Solotnov, H. J. Schneider and V. Rüdiger, *J. Org. Chem.*, 1996, **61**, 8113.
- 3 M. Hasani and M. Shamsipur, *J. Solution Chem.*, 1994, **23**, 721.
- 4 A. D'Aprano, B. Sesta, A. Princi, C. Filippi and M. Iammarino, *J. Electroanal. Chem.*, 1994, **365**, 119.
- 5 K. Ohtsu, T. Kawashima and K. Ozutsumi, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 4375.
- 6 M. Shamsipur and M. R. Ganjali, *J. Inclusion Phenom. Mol. Recognit. Chem.*, 1997, **28**, 315.
- 7 A. Göçmen and Ç. Erk, *Fresenius' J. Anal. Chem.*, 1993, **347**, 471.
- 8 M. Hasani and M. Shamsipur, *J. Chem. Soc., Perkin Trans. 2*, 1998, 1277.

- 9 T. Okada, *Macromolecules*, 1990, **23**, 4216.
- 10 T. Okada and T. Usui, *Anal. Chem.*, 1994, **66**, 1654.
- 11 T. Okada, *J. Chromatogr. A*, 1995, **695**, 309.
- 12 S. B. Quraishi and T. Okada, *Anal. Sci.*, 1999, **15**, 1059.
- 13 T. Okada, *J. Chem. Soc., Chem. Commun.*, 1991, 1209.
- 14 S. Katsuta, C. Takagi, M. Tanaka, N. Fukada and Y. Takeda, *J. Chem. Soc., Faraday Trans.*, 1998, **93**, 365.
- 15 A. F. D. de Namor, J. C. Y. Ng, M. A. L. Tanco and M. Salomon, *J. Phys. Chem.*, 1996, **100**, 14485.
- 16 M. K. Chantooni, Jr., G. Roland and I. M. Kolthoff, *J. Solution Chem.*, 1988, **17**, 175.
- 17 I. M. Kolthoff and M. K. Chantooni and Jr., *Anal. Chem.*, 1980, **52**, 1039.
- 18 C. P. Jaroniec, R. K. Gilpin and M. Jaroniec, *J. Phys. Chem. B*, 1997, **101**, 6861.
- 19 S. B. Qraishi, T. Okada and A. Ikeya, *J. Electroanal. Chem.*, 2000, **489**, 84.
- 20 A. D'Aprano, M. Goffredi and R. Triolo, *J. Chem. Soc., Faraday Trans. 1*, 1975, 1188.
- 21 Y. Marcus, *Ion Solvation*, John Wiley, Chichester, 1985.
- 22 W.-Y. Xu and J. Smid, *J. Am. Chem. Soc.*, 1984, **106**, 3790.
- 23 M. R. Truter, *Struct. Bonding*, 1973, **16**, 71.