Metal-ion Complexation of Noncyclic Poly(oxyethylene) Derivatives. II. PMR Studies of the Complexation with Alkali and Alkaline-earth Metal Cations*

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The complexation of homogeneous polyethylene glycols and their dimethyl ethers(glymes) with alkali and alkaline-earth metal cations was studied by PMR spectroscopy on the basis of a comparison with crown ethers. The ethylene proton signal of octaethylene glycol in methanol-d_4 was split into three lines by the addition of a potassium, rubidium, caesium, strontium, or barium cation. The latter two cations also caused large downfield shifts of the signals, which are quite comparable with those of 15-crown-5 and 18-crown-6 caused by the same metal cations. As for heptaethylene glycol, a splitting was observed in the presence of a strontium ion or an alkali metal cation except for a lithium ion. A large downfield shift was also observed in the presence of a strontium or barium ion. As for hexaethylene glycol, the signal was split only by a sodium ion, and the optimal interaction with a calcium ion was confirmed on the basis of the downfield shift. In methanol-d_4, lithium and magnesium ions did not cause any change in the PMR spectra of either the crown ethers or the glycols. The PMR downfield-shift method also disclosed the metal-ion complexation of the glycols in water. The terminal hydroxyl groups play an important role in the complexation.

In the preceding paper,[1] we clarified, by solvent extraction, that acyclic poly(oxyethylene)(POE) derivatives with at least seven oxyethylene units complex fairly well with alkali metal ions in water and that their extracting power is comparable with that of 18-crown-6. In the cases of alkaline-earth metal ions, however, the solvent-extraction method was found inadequate to evaluate their complexation because of the poor solubility of the complexes in dichloromethane.

Of the instrumental methods used for the evaluation of the metal-ion complexation of organic ligands, NMR spectroscopy has proven to be the most facile and informative under various conditions.[2–8] In general, complexation with metal cations or the ion pairs leads to a change in the conformation of the ligands and, as a result, the splitting or broadening of the absorption signals. When the charged complex and the anion are separately solvated and the ion pairing is negligible, which means the absence of an anion effect, a downfield shift can be exclusively expected due to the increased electronegativity of the donor atoms in the ligands. Thus, the change in the PMR spectra can be a qualitative measure of the extent of the complexation in a series of ligands.

With these facts in mind, we have undertaken the present studies to ascertain the complexation of relatively short but homogeneous polyethylene glycols (PEG) and their dimethyl ethers(glymes) with alkali and alkaline-earth metal cations in methanol and in water. The thiocyanates again turned out to be convenient salts for these studies because of their high solubility in methanol.

Experimental

Materials. RuSCN, CsSCN, and $Sr(SCN)_2$ were prepared according to the method reported for $Ba(SCN)_2$.[9] $LiSCN \cdot 2H_2O$ was obtained from Mitsuwa Pure Chemicals. The other salts were the same materials as in the preceding paper. The anhydrous thiocyanates were prepared by vacuum dehydration at 100 °C. The following chemicals were obtained in the highest available purity from the sources indicated: methanol-d_4 and deuterium oxide(CEA products through Nakarai Chemicals, Ltd.); ethylene glycol(EO1), ethylene glycol dimethyl ether(glyme)(MeEO1Me), diethylene glycol(EO2), and triethylene glycol(EO3)(Wako Pure Chemicals Industries, Ltd.); diethylene glycol dimethyl ether(diglyme)(MeEO2Me) (Yoneyama Chemical Industries Ltd.); triethylene glycol dimethyl ether (triglyme)(MeEO3Me)-(Nakarai Chemicals, Ltd.); tetraethylene glycol (EO4) (Japan Catalytic Chemical Industry, Ltd.); tetraethylene glycol dimethyl ether(tetraglyme)(MeEO4Me)(Tokyo Kasei Kogyo Co., Ltd.) and 12-crown-4(Bokusui Brown Co., Ltd.). They were all used after distillation.

Penta-, hexa-, hepta-, and octaethylene glycols(EO5—EO8) were prepared according to the method reported previously;[10] bp(°C/mmHg) EO5, 165—168/0.2; EO6, 180—189/0.3; EO7, 210—212/0.35; EO8, 214—218/0.27. Their dimethyl ethers, *e.g.*, penta-, hexa-, hepta-, and octaglymes (MeEO5Me, MeEO6Me, MeEO7Me, and MeEO8Me) were prepared similarly the from sodium salt of EO1 monomethyl ether and the dichloride of EO3, from the sodium salt of EO2 monomethyl ether and the dichloride of EO2, from the sodium salt of EO2 monomethyl ether and the dichloride of EO3, and the from sodium salt of EO2 monomethyl ether and the dichloride of EO4, respectively; bp(°C/mmHg): MeEO5Me, 120—123/0.25; MeEO6Me, 145—148/0.1; MeEO7Me, 175—180/0.5; MeEO8Me, 215—218/0.45. Hexaethylene glycol monomethyl ether(137—141/0.05) and octaethylene glycol monomethyl ether (MeEO8)(212—216/0.16) were prepared from EO2 chloroethyl methyl ether and the sodium salt of EO3, and that of EO5, respectively.

Measurment of PMR Spectra. The PMR spectra were obtained using a JEOL LMN-PS-100 spectrometer on an expanded scale(sweep width, 270 Hz), with 8% dioxane in benzene as the external reference. The chemical shifts are expressed in Hz downfield, without any bulk magnetic susceptibility correction. The differences in the chemical shifts of the main oxyethylene protons and methyl protons were determined by the successive measurement of the signals of

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a plain 1% POE solution and those of 1% POE solution containing metal salt(0.04—0.05 mol/kg). The molar ratio of the salt to POE ranged from about 2 to 7, depending on the molecular weight of the POE. For the measurement in deuterium oxide, the salt concentration was increased to 0.2 mol/kg.

Results and Discussion

Downfield Shifts for Crown Ethers in the Presence of Alkali or Alkaline-earth Thiocyanates. In Table 1 we summarize the downfield shifts for 15-crown-5 and 18-crown-6 caused by the presence of alkali and alkaline-earth metal thiocyanates. Alkali and ammonium ions caused small downfield shifts in methanol, but all alkaline-earth metal ions except the magnesium ion caused downfield shifts which are large enough to be a measure of metal-ion complexations both in methanol and in water. These facts are consistent with the recent observations made using 220 MHz PMR spectroscopy.[7]

On the other hand, lithium and magnesium ions did not bring about any observable shifts in methanol-d_4, not even for 12-crown-4.

Recently, Izatt *et al.*[11] have reported the association constants for the reactions of several crown ethers with alkali and alkaline-earth metal cations in water and in aqueous methanol. Compared with the log K values, the downfield shifts are not necessarily proportional to the corresponding log K values; also, surprisingly, the calcium ion induced larger downfield shifts for both the crown ethers than would be expected from the respective log K values. Further, the shift induced by the calcium ion for 18-crown-6 is larger than that for 15-crown-5 both in methanol and in water, and the barium ion caused a larger shift for 15-crown-5 than for 18-crown-6. These facts are quite in conflict with the ion radius cavity concept.[13,14] The ioslation of some stable calcium ion-crown ethers complexes[15,16] substantiates the strong interaction with the crown ethers as well as the large downfield shifts. The interaction of the crown ethers with the calcium ion seems to have been underestimated thus far.[17]

Interaction of Polyethylene Glycols(PEG) and Their Dimethyl Ethers (Glymes) with Alkali Metal and Ammonium Ions in Methanol. The downfield shift in the 60 MHz PMR spectra of PEG in the presence of potassium iodide was too small to draw any decisive conclusion on their interaction.[3] A reinvestigation of the high resolution PMR spectroscopy(100 MHz) using various thiocyanate salts has, however, revealed the following facts: (1) the downfield shifts are all quite small, just as for the crown ethers(Table 2); (2) the spectrum of hexaethylene glycol was changed into two partially resolved peaks in the presence of sodium thiocyanate (Table 2, Fig. 1); (3) the sharp signal of heptaethylene glycol was split into two or three peaks by all alkali metal thiocyanates except lithium thiocyanate (Table 2, Fig. 1); (4) the sharp signal of octaethylene glycol was changed into three partially resolved peaks, accompanied by small downfield shifts in the presence of potassium, rubidium, and caesium thiocyanates (Table 2, Fig. 1); (5) the potassium ion caused downfield shifts for glymes which are proportional to the log K values (Table 3); (6) in the presence of ammonium

TABLE 1. ASSOCIATION CONSTANTS AND CATION-INDUCED DOWNFIELD SHIFTS FOR CROWN ETHER COMPLEXES IN METHANOL AND IN WATER

Metal ions	Ionic radius (Å)[a]	15-Crown-5			18-Crown-6			
		Log K[b]	Downfield shift (Hz)[c]		Log K		Downfield shift (Hz)[c]	
		in H_2O	in CD_3OD (Concn)[d]	in D_2O (Concn)[d]	in 70 wt% CH_3OH[e]	in H_2O[b]	in CD_3OD (Concn)[d]	in D_2O (Concn)[d]
Li^+		—	0.5 (0.07)	—	—	—	—	—
Na^+	0.95	0.7	2.6 (0.04)	—	2.76(4.32[f])	0.80	−0.7 (0.05)	—
K^+	1.33	0.74	−0.2 (0.04)	—	4.33(6.10[f])	2.03	0.3 (0.04)	0.9 (0.18)
NH_4^+	1.48	1.71	0.3 (0.04)	—	—	1.23	3.7 (0.05)	—
Rb^+	1.48	0.62	0.7 (0.04)	—	3.46	1.56	0.4 (0.05)	—
Cs^+	1.69	0.8	0.8 (0.05)	—	2.84(4.62[f])	0.99	−0.3 (0.05)	—
Mg^{2+}	0.78	—	0.7 (0.05)	—	—	—	1.7 (0.05)	—
Ca^{2+}	1.06	—	19.2 (0.05)	8.6 (0.20)	2.51	<0.5	21.7 (0.05)	11.4 (0.19)
Sr^{2+}	1.27	1.95	23.4 (0.05)	13.0 (0.20)	5.0	2.72	22.6 (0.05)	17.8 (0.20)
Ba^{2+}	1.43	1.71	24.3 (0.05)	16.6 (0.19)	6.0	3.87	18.8 (0.05)	13.1 (0.18)

a) 1Å=0.1 nm. b) Determined at 25 °C. See Ref. 11a. c) Minus means upfield shift. Measured at 23 °C. d) mol/kg. e) Determined at 25 °C. See Ref. 11b. f) Determined in methanol at 25 °C. See Ref. 12.

Table 2. Alkali metal ion-induced downfield shifts for homogeneous PEG in methanol-d_4

Metal ions	Downfield shifts (Hz)a)			
	EO5 (Concn)b)	EO6 (Concn)b)	EO7 (Concn)b)	EO8 (Concn)b)
Li^+	−0.4 (0.05)	−0.1 (0.05)	—	—
Na^+	0.3 (0.0)	2.8, 1.8 (0.05)	1.7, 0.7 (0.05)	2.4 (0.04)
K^+	—	0.1 (0.05)	2.8, 0.8 (0.05)	4.1, 3.1 0.8(0.04)
NH_4^+	—	1.6 (0.05)	1.9 (0.04)	2.1 (0.04)
Rb^+	—	−0.1 (0.04)	1.3, 0.3 (0.04)	6.1, 4.9 3.1(0.05)
Cs^+	—	0.6 (0.05)	0.2, −0.6 (0.05)	4.9, 3.8 2.7(0.04)

a) Measured at 23 °C. Minus means upfield shift.
b) mol/kg.

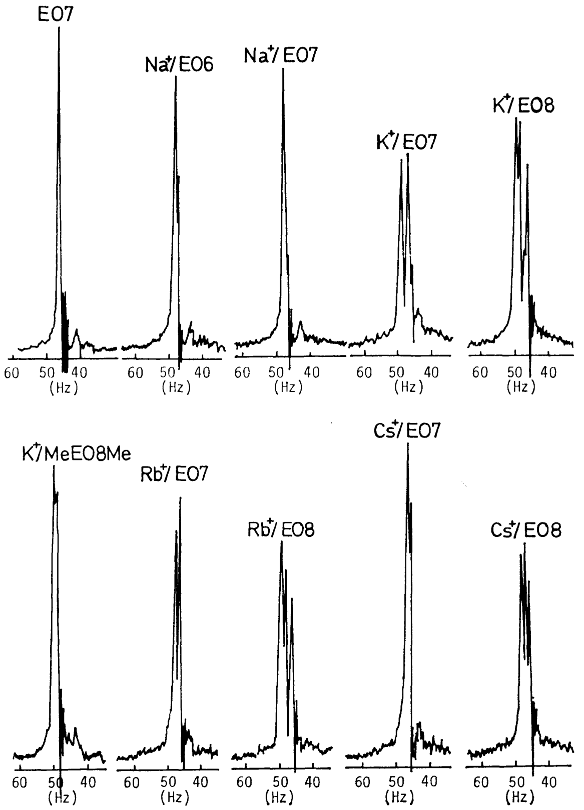

Fig. 1. NMR signals in methanol-d_4 of oxyethylene protons of the homogeneous PEG and glymes in the absence or the presence of alkali metal cation.

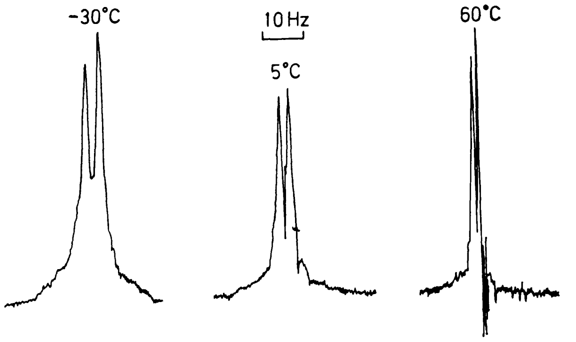

Fig. 2. PMR signals at various temperature of Hexaethylene glycol with KSCN in methanol-d_4.

thiocyanate, small shifts were observed for the higher glycols as well as for the crown ethers(Table 2); (7) the potassium ion caused partial splitting in octaglyme (Table 3, Fig. 1), and (8) the resolved spectrum of heptaethylene glycol in the presence of potassium thiocyanate was identical with that observed in the presence of potassium iodide and showed a tendency to coalesce with the elevation of the temperature (Fig. 2).

Liu[3] also reported the partial splitting for heptaethylene glycol in the presence of potassium iodide. However, the splitting was strangely ascribed to the drastic conformational change which originally exists rather than to that provoked by the interaction with potassium iodide.[19] On the other hand, Reinhoudt *et al.*[8] recently noted the splitting of the PMR signal of the alkali metal ion-crown ether complexes, in which the size of the crown ether cavity is more than sufficient to accommodate the cation. Considering these facts and the similar phenomena caused by some alkaline-earth metal ions (Fig. 6), the splitting of the signals in the presence of metal cations can be ascribed to the strong complexation with the metal cations. Therefore, it can be concluded that, in methanol, the complexation with the sodium ion becomes significant for hexaethylene glycol, while those with potassium, rubidium, or caesium are significant for heptaethylene glycol.

Complexation of PEG and Glymes with Alkaline-earth Metal Cations in Methanol. As expected, calcium, strontium, and barium ions caused appreciable downfield shifts for PEG and glymes, while the magnesium ion did not. In Figs. 3, 4, and 5, their shifts are plotted as a function of the number of oxyethylene units(n).

The calcium ion caused the maximum downfield shift for hexaethylene glycol, which is comparable with that of 15-crown-5. In the cases of hexaglyme and heptaglyme, small shifts were recorded, indicating their

Table 3. Potassium ion-induced downfield shifts for glymes and association constants in methanol

Glymes	Downfield shifts (Hz)a)				
	MeEO3Me	MeEO5Me	MeEO6Me	MeEO7Me	MeEO8Me
Oxyethylene protons	1.3	1.9	2.7	3.2	4.1, 3.4
Methyl protons	1.8	2.9	3.4	4.2	4.1
log K in CH_3OHb)	—	2.20	2.55	2.87	

a) Concentration of KSCN is 0.04 mol/kg. b) See Ref. 18.

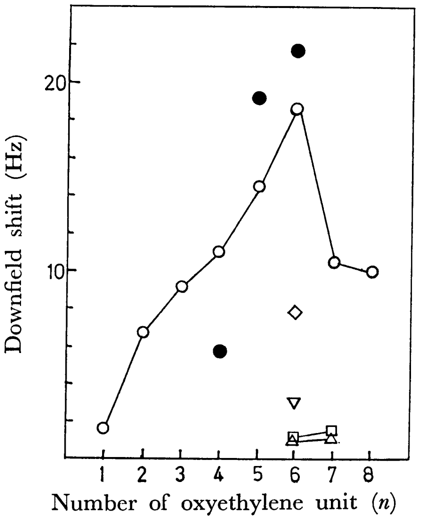

Fig. 3. Calcium-ion induced Downfield shifts for homogeneous poly(oxyethylene) derivatives in methanol-d_4.
●, Oxyethylene protons of the crown ethers; ○, oxyethylene protons of the PEG; □, oxyethylene protons of the glymes; ◇, oxyethylene protons of hexaethylene glycol monomethyl ether; △, methyl protons of the glymes; ▽, methyl protons of hexaethylene glycol monomethyl ether.

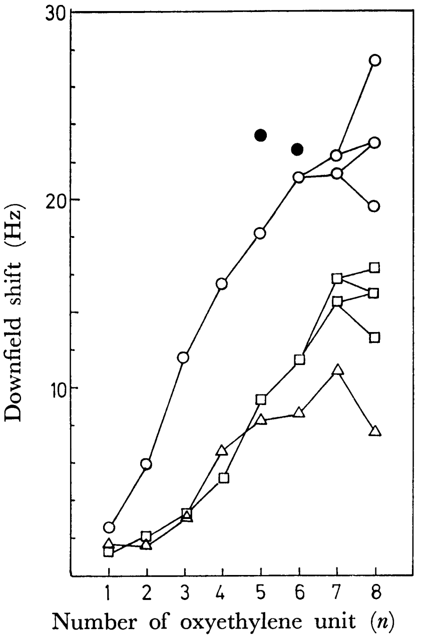

Fig. 4. Strontium-ion induced downfield shifts for homogeneous poly(oxyethylene) derivatives in methanol-d_4.
●, Oxyethylene protons of the crown ethers; ○, oxyethylene protons of the PEG; □, oxyethylene protons of the glymes; △, methyl protons of the glymes.

weak interaction. On the other hand, hexaethylene glycol monomethyl ether showed a medium shifts, accompanied by the splitting of the main signal. These facts suggest that the terminal hydroxyl groups play an important role in the complexation with the calcium ion in methanol (Fig. 3).

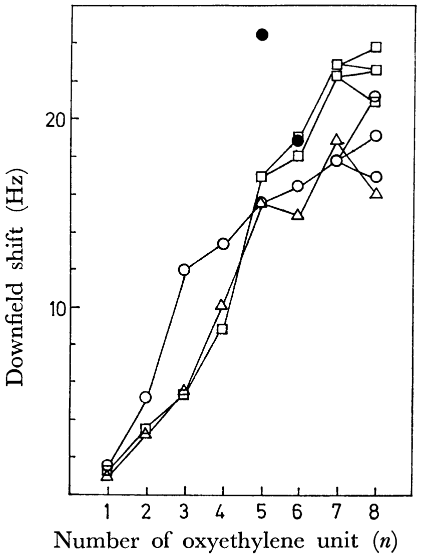

Fig. 5. Barium-ion induced Downfield shifts for the homogeneous poly(oxyethylene) derivatives in D_2O.
●, Oxyethylene protons of the crown ethers; ○, oxyethylene protons of the PEG; □, oxyethylene protons of the glymes; △, methyl protons of the glymes.

In the case of the strontium ion (Fig. 4), the interaction becomes significant above triethylene glycol and the complexing tendency increases remarkably with the number of oxyethylene units. Interestingly, the downfield shifts for hepta- and octaethylene glycols are quite comparable with those for the crown ethers, and their signals are split into two or three peaks respectively (Fig. 6). Heating at 60 °C led to the coalescence of the split signal of heptaethylene glycol with a slight upfield shift. (The difference between the chemical shifts with and without the strontium ion was found to be 21 Hz.) Since it was reported that the splitting due to the conformational change for heptaethylene glycol in a nonpolar solvent does not disappear easily with an increase in the temperature,[19] the easy coalescence supports the cation-induced splitting.

Glymes with more than four oxyethylene units also interact strongly with the strontium ion, and the averaged downfield shifts for hepta- and octaglymes and the shifts for their methyl protons indicate that the heptaglyme attain the optimal interaction. Judging from the differences in the downfield shifts between PEG and glymes, the terminal hydroxyl groups are important to some extent in creating effective interaction with the strontium ion.

With regard to the barium ion (Fig. 5), the series of PEG and glymes showed quite similar downfield shifts, which turned out to be more than that of 18-crown-6 when they have more than seven oxyethylene units. The main signal of pentaglyme broadened and those of hexaglyme and heptaglyme split into two peaks, while that of heptaethylene glycol resulted in broadening, and that of octaethylene glycol, in three resolved lines(Fig. 6). The rather large shifts and splitting for glymes imply that the terminal hydroxyl groups do not already play a characteristic role in the

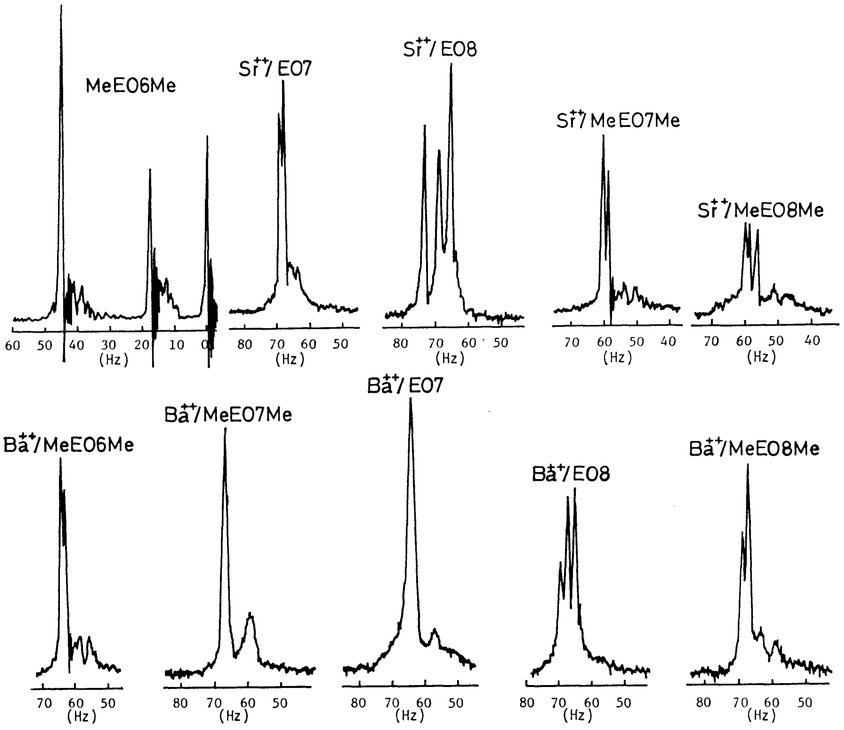

Fig. 6. NMR signals in methanol-d_4 of oxyethylene protons of the homogeneous PEG and glymes in the absence or the presence of alkaline-earth metal cation.

complexation with the barium ion in methanol.

It is interesting to note that one of the three split lines for octaethylene glycol in the presence of the strontium or barium ion was observed upfield (Fig. 6). The eighth oxyethylene unit may not be utilized in complexation, probably because of the crowding in the complexed ion.

Metal-ion Complexation of PEG in Water. Hitherto, no one has succeeded in observing by PMR the metal-ion complexation of acyclic POE derivatives in water.3) As is shown in Table 1, we found that calcium strontium, and barium ions caused appreciable downfield shifts of the crowns' proton signals even in water, while the potassium ion did not.

In the presence of calcium thiocyanate, hexaethylene glycol, which showed the maximum interaction with the calcium ion in methanol, gave partially resolved peaks in water with a slight downfield shift (Fig. 7). The signal of heptaethylene glycol was shifted 5.6 Hz downfield by the strontium ion(0.12 mol/kg) and 7.9 Hz downfield by the barium ion (0.02 mol/kg). In view of the larger shift by the barium ion, the shifts for a series of polyethylene glycols were determined; they are plotted as a function of the oxyethylene units(n)

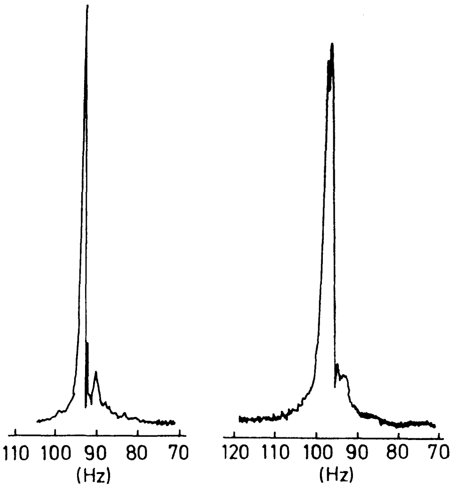

Fig. 7. PMR signals in D_2O of hexaethylene glycol in the absence (the left) and the presence (the right) of calcium thiocyanate.

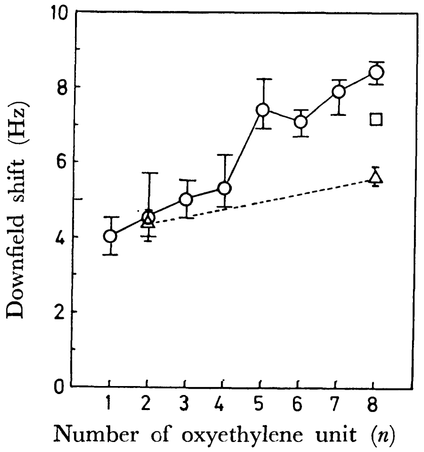

Fig. 8. Barium-ion induced downfield shifts for the homogeneous poly(oxyethylene) derivatives in D_2O. ○, Oxyethylene protons of the PEG; △, oxyethylene protons of the glymes; □, oxyethylene protons of the octaethylene glycol monomethyl ether.

in Fig. 8. The downfield shifts increased rapidly at pentaethylene glycol and then gradually with the increase in the number of oxyethylene units. The shift for monomethyl octaethylene glycol is reduced slightly, but the shift for octaglyme dropped to the extent of that for tetraethylene glycol. It is apparent that the terminal hydroxyl group is important in obtaining a high complexation in water. The smaller downfield shifts for PEG than those for the crown ethers, however, imply that the topology control, *e.g.*, the macrocyclic effect, plays a much more important role in the complexation in water.

Conclusion. It is now clear that polyethylene glycols show a strong ion-dipole binding affinity in methanol, especially toward the potassium, rubidium, caesium, calcium, strontium and barium ions, in spite of the absence of the topology control based on the ionic radius and the cavity size. In addition, there seem to be an optimum number of oxyethylene units in the glycols for a given cation; *e.g.*, the sodium and calcium ions are for six oxyethylene units; the potassium, rubidium, caesium, and strontium ions, for seven oxyethylene units, and the barium ion, for five or seven oxyethylene units.

The conformation of the oxyethylene unit in PEG has recently been clarified to favor the TGT conformation, even in an aqueous medium.[20] Such a conformation is apparently convenient to form stable five-membered ring chelates.[14] The optimal arrangement of the repeating oxyethylene units with the TGT conformation would work cooperatively and would lead to effective complexation with alkali and alkaline-earth cations. In other words, the energetically favorable TGT conformation and entropically favorable[21] oxyethylene chain must be the origins of the chelating ability of POE.

The isolation of some homogeneous PEG–metal cation complexes substantiating the PMR studies will be disclosed in a subsequent paper.

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References

1) S. Yanagida, K. Takahashi, and M. Okahara, *Bull. Chem. Soc. Jpn.*, **50**, 1386 (1977).

2) a) D. Nicholls and M. Szwarc, *J. Phys. Chem.*, **71**, 2727 (1967); b) E. Schaschel and M. C. Day, *J. Am. Chem. Soc.*, **90**, 504 (1968).

3) K. Liu, *Macromolecules*, **1**, 308 (1968).

4) a) K. H. Wong, G. Konizer, and J. Smid, *J. Am. Chem. Soc.* **92**, 666 (1970); b) L. L. Chan, K. H. Wong, and J. Smid, *ibid.*, **92**, 1955 (1970).

5) a) J-M. Lehen, J. P. Saurage, and B. Dietrich, *J. Am. Chem. Soc.*, **92**, 2916 (1970); b) B. Dietrich, J. M. Lehn, and J. P. Sauvage, *Tetrahedron*, **29**, 1647 (1973).

6) a) E. Pretsch, M. Vasak, and W. Simon, *Helv. Chim. Acta*, **55**, 1098 (1972); b) R. Büchi, E. Pretsch, and W. Simon, *ibid.*, **59**, 2327 (1976); c) R. Büchi, E. Pretsch, and W. Simon, *Tetrahedron Lett.*, **1976**, 1709.

7) D. Live and S. I. Chan, *J. Am. Chem. Soc.*, **98**, 3769 (1976).

8) D. N. Reinhoudt, R. T. Gray, F. DeJong, and C. J. Smit, *Tetrahedron*, **33**, 563 (1977).

9) K. M. Herstein, *Inorg. Synth.*, Vol. III, 24 (1950).

10) R. Fordyce, E. L. Lovell, and H. Hibbert, *J. Am. Chem. Soc.*, **61**, 1905 (1939).

11) a) R. M. Izatt, R. E. Terry, B. L. Haymore, L. D. Hansen, N. K. Dalley A. G. Avondet, and J. J. Christensen, *J. Am. Chem. Soc.*, **98**, 7620 (1976); b) R. M. Izatt, R. E. Terry, D. P. Nelson, Y. Chan, D. J. Eatough, J. S. Bradshaw, L. D. Hansen, and J. J. Christensen, *ibid.*, **98**, 7626 (1976).

12) H. K. Frenshorf, *J. Am. Chem. Soc.*, **93**, 600 (1971).

13) C. J. Pedersen and H. K. Frensdorf, *Angew. Chem. Int. Ed. Engl.*, **11**, 16 (1972).

14) J-M. Lehn, *Struct. Bonding(Berlin)*, **16**, 1 (1973).

15) J. D. Dunitz and P. Seiler, *Acta Crystallogr., Sect. B*, **30**, 2750 (1974).

16) During the PMR measurments, the complex of 12-crown-4 with $Ca(SCN)_2$ was precipitated. The composition was found to be 12-crown-4·$Ca(SCN)_2 \cdot H_2O$. Unpublished work.

17) R. M. Izatt, D. J. Eatough, and J. J. Christensen, *Struct. Bonding(Berlin)*, **16**, 161 (1973).

18) G. Chaput, G. Jeminet, and J. Jullard, *Can. J. Chem.*, **53**, 2240 (1975).

19) K. Liu, *Macromolecules*, **1**, 213 (1968).

20) a) P. G. Assarsson, P. S. Leung, and G. J. Safford, *Polymer Reprints*, **10**, (2), 1241 (1969); b) T. M. Connor and K. A. Melauchlan, *J. Phys. Chem.*, **69**, 1888 (1965); c) K. Liu and J. L. Parsons, *Macromol. Chem.*, **94**, 194 (1966); d) J. L. Koenig and A. C. Angood, *J. Polym. Sci., Part A-2*, **8**, 1787 (1970).

21) J. Smid, *Angew. Chem. Int. Ed. Engl.*, **11**, 112 (1972).