Thermodynamic Origin of Selectivity in Polyoxyethylene Complexes with Alkali Cations

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Selectivity in polyoxyethylene complexes with alkali metal cations principally originates from a desolvation process of the alkali cations.

Complex formation with acyclic polyethers has been discussed on the basis of comparison with that of the corresponding cyclic polyethers such as crown ethers.[1-3] Larger complex formation constants of the latter than the former are explained by the term 'macrocyclic effect,' the thermodynamic origin of which still remains somewhat uncertain.[1-3] Systematic thermodynamic studies of polyoxyethylene (POE) complex formation are of fundamental importance not only to elucidate the macrocyclic effect but also to understand the solvation of alkali cations, but work has been limited by a lack of effective methods. The author has recently reported a chromatographic method, which permitted the determination of complex formation constants of POE with an alkali metal ion in solution,[4,5] and now reports the thermodynamic origin of selectivity in POE complexes with alkali cations in methanol.

If the number of oxyethylene (EO) units increases up to 16–17, multiple complexation must be taken into account.[5] POEs having 6–14 EO units were therefore investigated as ligands. Since the terminal lipophilic groups which are a part of the structure of POEs did not affect the complexation, results obtained for polyethylene glycol (PEG), which has no lipophilic termini, are shown instead. Fig. 1 depicts changes in ΔG for PEG–metal ion complex formation with the number of EO units. ΔG decreases with increasing number of EO units, indicating that PEG complexes become more stable with increasing length of POE chain. Table 1 shows $-\Delta H$ and $-\Delta S$ values for PEG complex formation with three alkali cations: K^+, Rb^+ and Cs^+. ΔH and ΔS were obtained from van't Hoff plots. As shown previously,[5] complex formation with Na^+ or Li^+ could not be detected by the present method. Both ΔH and ΔS systematically decrease with increasing number of EO units.

According to Fig. 1, the stability of PEG complexes decreases in the order $Rb^+ > K^+ > Cs^+$. Cs^+ complex formation is disfavoured owing to the negative entropy change. ΔS is a combination of coordination bond formation (ΔS_{bf}), desolvation of metal ion (ΔS_d), and desolvation of ligand. The third contribution is independent of the cation, because marked differences in complex structure for different alkali cations have not been reported.[6] Although we cannot estimate the contribution from ΔS_{bf}, strong bond formation usually causes a large negative entropic change. Since $O-M^+$ coordination bonds become weaker in the order $K^+ > Rb^+ >$

Cs^+, ΔS_{bf} should increase in this order. ΔS values in Table 1, however, shown an opposite trend. Therefore, the differences observed must be due to differences in ΔS_d. The transfer entropy values from an ideal solution to methanol are reported to be -92.4, -67.2 and -50.4 J mol^{-1} K^{-1} for K^+, Rb^+ and Cs^+, respectively.[7] Since alkali metal ions adopt 10 coordination sites,[8] PEGs having more than 10 donor atoms saturate the coordination sites. For the PEG having 12 EO units, ΔS for the K^+ complex is 8.6 ± 2.6 J mol^{-1} K^{-1} larger than that for Rb^+, which is 8.9 ± 2.8 J mol^{-1} K^{-1} larger than that for Cs^+. These values and solvation entropy permit $\Delta\Delta S_{bf}$ to be estimated; $\Delta\Delta S_{bf}$ between K^+ and Rb^+ complexes is 16.3 J mol^{-1} K^{-1}, and that between Rb^+ and Cs^+ complexes is 24.5 J mol^{-1} K^{-1}. After saturation of the coordination sites of
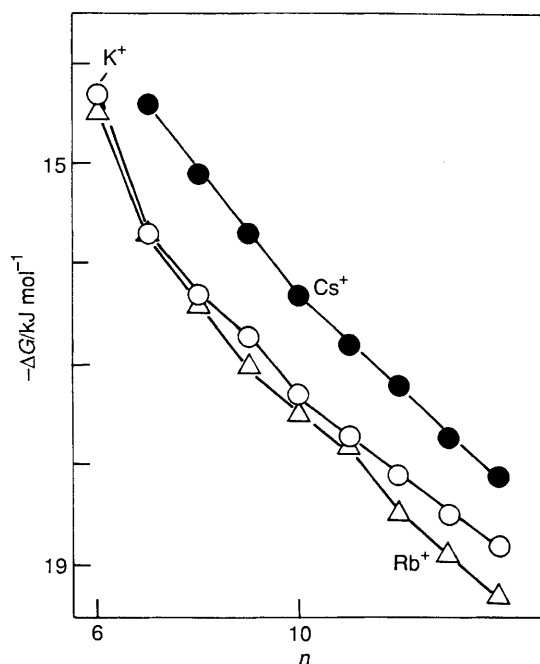

Fig. 1 Variation in $-\Delta G$ at 25 °C with the number of EO units

Table 1 $-\Delta H$ and $-\Delta S$ values for PEG complex formation with K^+, Rb^+ and Cs^+

| n^a | K^+ | | Rb^+ | | Cs^+ | |
	$-\Delta H^b$	$-\Delta S^c$	$-\Delta H$	$-\Delta S$	$-\Delta H$	$-\Delta S$
6	26.3 ± 0.4	40.0 ± 1.3	27.9 ± 0.4	45.1 ± 1.4	—	—
7	30.5 ± 0.4	49.6 ± 1.5	31.9 ± 0.5	54.2 ± 1.5	30.6 ± 0.7	54.5 ± 2.4
8	30.8 ± 0.4	48.7 ± 1.5	34.1 ± 0.5	59.4 ± 1.7	34.4 ± 0.5	64.8 ± 1.8
9	31.8 ± 0.5	50.7 ± 1.5	34.5 ± 0.5	58.8 ± 1.7	36.0 ± 0.5	68.1 ± 1.9
10	33.1 ± 0.5	53.1 ± 1.6	35.9 ± 0.5	61.7 ± 1.7	37.3 ± 0.6	70.4 ± 1.9
11	34.7 ± 0.5	57.0 ± 1.7	37.2 ± 0.5	64.3 ± 1.8	38.8 ± 0.6	73.9 ± 2.0
12	35.9 ± 0.5	59.6 ± 1.7	38.8 ± 0.5	68.2 ± 1.9	40.2 ± 0.6	77.1 ± 2.1
13	36.1 ± 0.7	59.0 ± 2.4	40.0 ± 1.9	73.6 ± 2.7	41.7 ± 0.6	80.5 ± 2.1
14	37.4 ± 1.1	62.4 ± 3.8	41.2 ± 1.9	73.6 ± 6.2	42.8 ± 0.9	83.0 ± 3.1

^{a} Number of EO units. ^{b} In kJ mol^{-1}. ^{c} In J mol^{-1} K^{-1}.

the metal cations, ΔS still systematically decreases. The decrease in ΔS is due to processes other than desolvation of the metal cation, because ΔS values between metal cations are almost constant for POEs containing more than 10 EO units.

Desolvation processes similarly affect ΔH for POE complex formation. A large solvation enthalpy is disadvantageous for complex formation; ΔH for K^+ complexation is larger than the others; the solvation enthalpy in methanol is reported to be -271, -239 and -208 kJ mol^{-1} for K^+, Rb^+ and Cs^+, respectively.[7] In a similar manner to the above discussion on entropic effects, it is possible to estimate differences in bond formation enthalpy ($\Delta\Delta H_{bf}$) between alkali cations. For PEG having 12 EO units, $\Delta\Delta H_{bf}$ between K^+ and Rb^+ is estimated to be 29.1 kJ mol^{-1}, and that between K^+ and Cs^+ is 58.7 kJ mol^{-1}. These values are slightly smaller than those calculated for pentaethylene glycol dimethyl ether by molecular mechanics; $\Delta\Delta H_{bf}$ between K^+ and Rb^+ was estimated to be 44.9 kJ mol^{-1} and that between K^+ and Cs^+ was 83.1 kJ mol^{-1}.[1] Thus, selectivity of POE complexation principally originates

from desolvation of the metal ion, and the POEs can be a probe for investigation of solvation.

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