



## Thermodynamics of Solvation of 18-Crown-6 and Its Alkali-Metal Complexes in Various Solvents

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### Abstract

Heats of solution of 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) in acetonitrile, 1,2-dichloroethane, *N,N*-dimethylformamide, dimethyl sulfoxide, nitromethane, propylene carbonate, pyridine and water were measured at 25 °C and the enthalpies of the transfer of 18-crown-6 from water to the aprotic solvents were derived. The thermodynamic quantities,  $\Delta G_1^\circ$ ,  $\Delta H_1^\circ$  and  $T\Delta S_1^\circ$ , for the formation of the  $[M(18\text{-crown-6})]^+$  ( $M^+ = \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{NH}_4^+$ ) complexes were determined by titration calorimetry in dimethyl sulfoxide containing  $0.1 \text{ mol dm}^{-3}$   $(\text{C}_2\text{H}_5)_4\text{NClO}_4$  as a constant ionic medium at 25 °C. These thermodynamic quantities suggest that the complexation of 18-crown-6 with the alkali-metal ions mainly reflects the different solvation of 18-crown-6 and also the different degree of solvent structure.

### Introduction

The complexation of metal ions in nonaqueous solvents is markedly different from that in water. Aprotic solvents such as acetonitrile (MeCN), propylene carbonate (PC), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and pyridine (PY) are often used in various fields. MeCN and PC have a weaker donor ability than water while the donor property of DMF, DMSO and PY is stronger than that of water [1]. Transferring nickel(II) and copper(II) ions from water to DMF, the metal ions are enthalpically stabilized [2, 3]. On the other hand, transfer of the metal ions from water to MeCN is an endothermic reaction [2, 4]. The acceptor property of MeCN, PC, DMF, DMSO and PY is weaker than that of water [1]. The transfer process of the chloride ion from water to MeCN, PC, DMF and DMSO is endothermic because the chloride ion is strongly hydrated in water [5]. Therefore, the complexation of the metal ions with chloride in MeCN, DMF and DMSO is more pronounced than water, i.e., a series of  $[\text{MCl}]^+$ ,  $[\text{MCl}_2]$ ,  $[\text{MCl}_3]^-$  and  $[\text{MCl}_4]^{2-}$  is extensively formed in the former three solvents [2, 6–10]. Moreover, the formation of the monochloro complex of the copper(II) and nickel(II) ions is exothermic in MeCN, while endothermic in DMF and DMSO [2, 6–10]. This is because the solvation energy of the chloride ion is similar in the three solvents [5]. Thus, the solvation of the divalent metal ions and simple anions and their complexation behavior are mainly explained in terms of the donor and acceptor properties of solvents.

Macrocyclic ligands are flexible and a conformational change sometimes occurs in different phases. For example, 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) has six oxygen atoms, which are the binding sites with metal ions. Without metal ions, these oxygen atoms interact with an acceptor site of solvent molecules. Other methylene sites can also interact with solvent molecules. Interactions of macrocyclic ligands with solvents can alter the conformations of macrocycles and can modify the complexing ability of the ligands. Thus, it is expected that a simple donor and acceptor approach to the solvation and complexation behavior of macrocyclic molecules may not always apply.

We have investigated the complexation of 18-crown-6 with alkali-metal and ammonium ions in water, DMF, PY, MeCN and PC by using a precise calorimetry system and pointed out that the solvation of 18-crown-6 plays an important role [11–14]. For a detailed elucidation of the solvent effect on 18-crown-6 complexation, quantitative thermodynamic parameters concerning the solvation of 18-crown-6 are necessary. This report describes heats of solution of 18-crown-6 measured in water, 1,2-dichloroethane (DCE), nitromethane (NM), MeCN, PC, DMSO, PY and DMF and the resulting enthalpies of transfer of 18-crown-6 from water to the aprotic solvents. Also, we determined the thermodynamic quantities,  $\Delta G_1^\circ$ ,  $\Delta H_1^\circ$  and  $T\Delta S_1^\circ$ , for the formation of  $[M(18\text{-crown-6})]^+$  ( $M^+ = \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{NH}_4^+$ ) by titration calorimetry in DMSO containing  $0.1 \text{ mol dm}^{-3}$   $(\text{C}_2\text{H}_5)_4\text{NClO}_4$  as a constant ionic medium at 25 °C. Combining the formation enthalpies of  $[M(18\text{-crown-6})]^+$  in DMSO as well as those in water, MeCN, PC, DMF and PY

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[11–14] with the enthalpies of transfer of the  $M^+$  ions and 18-crown-6 from water to the aprotic solvents, the enthalpies of transfer of  $[M(18\text{-crown-6})]^+$  from water to the aprotic solvents were derived. By using these thermodynamic quantities, the solvation of 18-crown-6 and  $[M(18\text{-crown-6})]^+$  as well as the solvent effect on the 18-crown-6 complexation will be discussed.

## Experimental

### Reagents

All chemicals used were of reagent grade. 18-Crown-6 was purified as described previously [12]. DMF, PY, PC, NM and DCE were dried over molecular sieves 4A for several weeks and DMSO was dried over  $\text{CaH}_2$  for several days. Then, these solvents were distilled under reduced pressure and stored over molecular sieves 4A in a dark bottle. MeCN was refluxed over  $\text{CaH}_2$  for 1 h to remove water and then distilled under an atmospheric pressure and finally stored over molecular sieves 3A in a dark bottle. The water contents in the solvents have been checked by the Karl–Fischer method and found to be less than 80 ppm. Sodium perchlorate and potassium perchlorate of reagent grade were used without further purification and dried at 100 °C in a vacuum oven. Rubidium perchlorate and cesium perchlorate were prepared by dissolving the relevant carbonates in perchloric acid. The crystals thus obtained were recrystallized from water and dried in a vacuum oven at 100 °C. Ammonium perchlorate and tetraethylammonium perchlorate were recrystallized once from water and dried in a vacuum oven at 50 °C. All solutions were prepared and treated over  $\text{P}_2\text{O}_5$  in a dry box under nitrogen atmosphere.

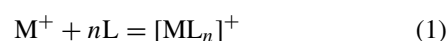
### Measurement of heats of solution

Heats of solution of 18-crown-6 in various solvents were measured at 25 °C using an MPS-11 calorimeter (Tokyo Riko, Japan) [15, 16]. Four Teflon vessels were placed in an aluminum block controlled at  $(25 \pm 0.003)$  °C in an air bath. One of the four vessels was a reference vessel and the temperature differences between three sample vessels and the reference vessel were monitored. Powders of a sample were placed in a glass ampoule in a dry box over  $\text{P}_2\text{O}_5$  and the ampoule was weighted and then sealed. The ampoule containing a given amount of the sample was immersed into a solvent of 50  $\text{cm}^3$  in the Teflon vessel. The ampoule was mechanically broken and the temperature increased or decreased depending on the exothermic or endothermic dissolution of the sample was detected by a thermal sensor which was sandwiched between the bottom of the vessel and the aluminum block. Concentrations of the resulting solutions were in the range of 2–15  $\text{mmol dm}^{-3}$ . The enthalpies of solution were practically independent of the solute concentrations examined.

### Measurement and analysis of heats of complexation

Heats of complexation were measured at 25 °C by using a fully automatic titration-calorimetry system, consisting of a twin-type calorimeter (Tokyo Riko, Japan) [17]. All test solutions contained 0.1  $\text{mol dm}^{-3}$   $(\text{C}_2\text{H}_5)_4\text{NClO}_4$  as a constant ionic medium [18]. A DMSO solution (40  $\text{cm}^3$ ) containing alkali perchlorate or ammonium perchlorate was placed in a stainless-steel vessel, the inside wall of which was coated with Teflon. The vessel was inserted into an aluminum block thermostated at  $(25 \pm 0.0001)$  °C in an air bath. The test solution was titrated with either 0.1 or 0.05  $\text{mol dm}^{-3}$  18-crown-6 DMSO solution by using an APB-118 autoburet (Kyoto Electronics, Japan) under dry nitrogen atmosphere. A metal replacement titration, in which  $\text{NaClO}_4$  and 18-crown-6 in DMSO was titrated with 0.05  $\text{mol dm}^{-3}$   $\text{MClO}_4$  ( $M^+ = \text{K}^+, \text{Rb}^+, \text{Cs}^+$ ) solution, was also performed. Heats of complexation ranging 3.8 J to 0.2 J at each titration point were determined with an error of  $\pm 0.02$  J and were corrected for heat of dilution of the titrants, which had been measured in advance by separate experiments and was found to be very small. The small heats of dilution of 0.05  $\text{mol dm}^{-3}$  metal ion ( $\text{K}^+, \text{Rb}^+, \text{Cs}^+$ ) solutions suggest that metal perchlorate contact ion pairs are hardly formed. The same applies to the 0.06  $\text{mol dm}^{-3}$   $\text{NaClO}_4$  DMSO solution, because according to dielectric relaxation measurements sodium perchlorate does not exist as a contact ion pair in MeCN and DMF having similar relative permittivities [19, 20].

We considered the formation of only mononuclear species in the course of data analyses. The overall complexation of 18-crown-6 (L) with a monovalent cation ( $M^+$ ) is represented by Equations (1) and (2).



$$\beta_n = [ML_n^+]/[M^+][L]^n. \quad (2)$$

The concentrations of free  $M^+$  and L are related to their total concentrations,  $C_{M,i}$  and  $C_{L,i}$  in a solution  $i$  by the following mass-balance equations.

$$C_{M,i} = [M^+]_i + \sum \beta_n [M^+]_i [L]_i^n \quad (3)$$

$$C_{L,i} = [L]_i + \sum n \beta_n [M^+]_i [L]_i^n \quad (4)$$

A heat  $q_i$  measured at a titration point  $i$  is given by the overall formation constant  $\beta_n$  and the enthalpy  $\Delta H_{\beta_n}$  of  $[ML_n]^+$  as Equation (5), where  $V_i$  denotes the volume of the test solution.

$$q_i = -(V_i \sum \beta_n \Delta H_{\beta_n} [M^+]_i [L]_i^n - V_{i-1} \sum \beta_n \Delta H_{\beta_n} [M^+]_{i-1} [L]_{i-1}^n). \quad (5)$$

Formation constants and enthalpies were simultaneously optimized by minimizing the error-square sum  $\sum (\mathbf{q}_{i,\text{obsd}} - \mathbf{q}_{i,\text{calcd}})^2$ , using a nonlinear least-squares program MQCAL [21], according to an algorithm proposed by Marquardt [22].

Table 1. Enthalpies of solution,  $\Delta H_s^\circ(L)$ , of 18-crown-6 in various solvents and enthalpies of transfer,  $\Delta H_{tr}^\circ(L)$ , of 18-crown-6 from water to various solvents at 25 °C.<sup>a</sup>

| Solvent | $\Delta H_s^\circ(L)/\text{kJ mol}^{-1}$ | $\Delta H_{tr}^\circ(L)/\text{kJ mol}^{-1}$ | $A_N^b$ | $D_N^c$ |
|---------|--|---|---------|---------|
| NM      | -25.7 (0.6)                              | -3.6 (0.6)                                  | 20.5    | 2.7     |
| Water   | -22.1 (0.2)                              | 0   | 54.8    | 18.0    |
| MeCN    | -5.2 (0.5)                               | 16.9 (0.5)                                  | 19.3    | 14.1    |
| DCE     | -4.3 (0.6)                               | 17.8 (0.6)                                  |         |         |
| PC      | 24.3 (0.6)                               | 46.5 (0.6)                                  | 18.3    | 15.1    |
| DMSO    | 29.3 (0.5)                               | 51.4 (0.5)                                  | 19.3    | 29.8    |
| PY      | 31.5 (0.5)                               | 53.6 (0.5)                                  | 14.2    | 33.1    |
| DMF     | 34.7 (0.5)                               | 56.8 (0.5)                                  | 16.0    | 26.6    |

<sup>a</sup> Values in parentheses refer to three standard deviations.

<sup>b</sup> The donor number quoted from Ref. [1].

<sup>c</sup> The acceptor number quoted from Ref. [1].

## Results

### Enthalpies of solution of 18-crown-6 in various solvents

Enthalpies of solution of neat 18-crown-6,  $\Delta H_s^\circ(L)$ , in NM, water, MeCN, DCE, PC, DMSO, PY and DMF are summarized in Table 1. Dissolution of 18-crown-6 is exothermic in NM, water, MeCN and DCE, while endothermic in other solvents. Enthalpies of transfer of 18-crown-6,  $\Delta H_{tr}^\circ(L)$ , from water to the solvents are also given in Table 1.

### Complexation in DMSO

Calorimetric titration curves for the complexation of the sodium and ammonium ions with 18-crown-6 in DMSO are depicted in Figure 1 (a and b), respectively. The  $-q/(\delta v C_{L,tit})$  values are plotted against the ratio of the total concentrations of 18-crown-6 to metal ions,  $C_L/C_M$ , where  $q$ ,  $\delta v$  and  $C_{L,tit}$  are the measured heat of complexation, portions of the added volume of the titrant and the concentration of the ligand in the titrant solution, respectively. These calorimetric titration data were analyzed by assuming the formation of a plausible set of complexes and the Hamilton  $R$  factor and the standard deviation of the observed heats ( $\sigma$ ) were compared. The calorimetric titration curves were best explained by considering the formation of  $[M(18\text{-crown-6})]^+$  ( $M^+ = \text{Na}^+, \text{NH}_4^+$ ). The formation constants and enthalpies determined are given in Table 2.

Calorimetric curves obtained by titrating the potassium, rubidium and cesium ions with an 18-crown-6 solution shown in Figure 2 (a, b and c), respectively, were also best reproduced in terms of the formation of  $[M(18\text{-crown-6})]^+$  ( $M^+ = \text{K}^+, \text{Rb}^+, \text{Cs}^+$ ). The results are summarized under 'binary' in Table 2 but the formation constants for the  $[M(18\text{-crown-6})]^+$  complexes are all large. If logarithmic values of formation constants are larger than three, the reliability of the values must be checked. For this purpose, calorimetric data titrating various  $\text{NaClO}_4$  and 18-crown-6 solutions with  $\text{MClO}_4$  ( $M = \text{K}^+, \text{Rb}^+, \text{Cs}^+$ ) shown in Figure 3 were also measured and all of the data were simultaneously analyzed. In the course of the analyses, the formation constant and enthalpy of the  $[\text{Na}(18\text{-crown-6})]^+$

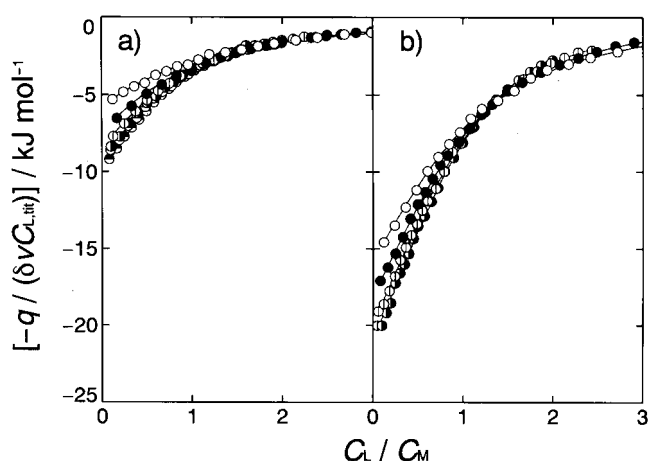


Figure 1. Calorimetric titration curves for (a) sodium-18-crown-6 and (b) ammonium-18-crown-6 systems in DMSO containing  $0.1 \text{ mol dm}^{-3}$   $(\text{C}_2\text{H}_5)_4\text{NClO}_4$  at 25 °C. Concentrations of metal ions in initial test solutions,  $C_{M,init}/\text{mmol dm}^{-3}$ , are 20.91( $\circ$ ), 30.15( $\bullet$ ), 40.07( $\oplus$ ), 50.02( $\ominus$ ), 51.91( $\ominus$ ) and 60.58( $\oplus$ ) for sodium and 20.70( $\circ$ ), 30.15( $\bullet$ ), 41.14( $\oplus$ ) and 50.17( $\oplus$ ) for ammonium. Solid lines were calculated by using the constants in Table 2.

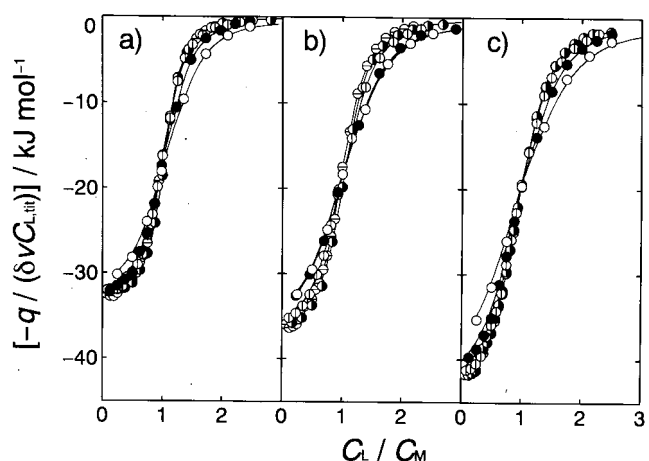


Figure 2. Calorimetric titration curves for (a) potassium, (b) rubidium and (c) cesium ions and 18-crown-6 solutions in DMSO containing  $0.1 \text{ mol dm}^{-3}$   $(\text{C}_2\text{H}_5)_4\text{NClO}_4$  at 25 °C. Concentrations of metal ions in initial test solutions,  $C_{M,init}/\text{mmol dm}^{-3}$ , are 5.106( $\circ$ ), 10.21( $\bullet$ ), 15.05( $\oplus$ ), 20.06( $\oplus$ ) and 20.11( $\circ$ ) for potassium, 5.000( $\circ$ ), 5.432( $\bullet$ ), 10.86( $\oplus$ ), 14.98( $\oplus$ ) and 20.12( $\ominus$ ) for rubidium, and 5.016( $\circ$ ), 10.03( $\bullet$ ), 15.11( $\oplus$ ), 20.11( $\oplus$ ) and 20.18( $\ominus$ ) for cesium. Solid lines were calculated by using the constants under 'ternary' in Table 2.

complex were kept unchanged at the values described above during the least-squares calculations. The thermodynamic parameters obtained are listed under 'ternary' in Table 2 and we accepted these values as a final choice.

The solid lines in Figures 1–3 were calculated by using the parameter values thus obtained and reproduce well the experimental points over the entire range of  $C_L/C_M$  (or  $C_M/C_L$ ) examined.

The formation constants for the potassium complex was in good agreement with that obtained by NMR ( $\log K_1 = 3.4$ ) [23]. Also, the  $\log K_1$  value for the rubidium complex agrees well with that obtained potentiometrically (3.16) [24].

Table 2. Least-squares refinements of formation constants,  $\log(K_1/\text{mol}^{-1} \text{ dm}^3)$ , Gibbs energies,  $\Delta G_1^\circ/\text{kJ mol}^{-1}$ , enthalpies,  $\Delta H_1^\circ/\text{kJ mol}^{-1}$ , and entropies,  $\Delta S_1^\circ/\text{J K}^{-1} \text{ mol}^{-1}$ , of 18-crown-6 complexes in DMSO containing  $0.1 \text{ mol dm}^{-3} (\text{C}_2\text{H}_5)_4\text{NClO}_4$  as a constant ionic medium at  $25^\circ\text{C}$ .<sup>a</sup>

|                    | Na <sup>+</sup> | NH <sub>4</sub> <sup>+</sup> | K <sup>+</sup> | Rb <sup>+</sup> | Cs <sup>+</sup> |
|--------------------|-----------------|------------------------------|----------------|-----------------|-----------------|
|                    |                 |                              | Binary         | Binary          | Binary          |
| $\log K_1$         | 1.39 (0.03)     | 1.78 (0.02)                  | 3.41 (0.02)    | 3.23 (0.02)     | 3.02 (0.01)     |
| $\Delta G_1^\circ$ | -7.9 (0.2)      | -10.2 (0.1)                  | -19.5 (0.1)    | -18.5 (0.1)     | -17.2 (0.1)     |
| $\Delta H_1^\circ$ | -16.2 (0.6)     | -27.3 (0.3)                  | -33.0 (0.1)    | -37.3 (0.2)     | -44.0 (0.2)     |
| $\Delta S_1^\circ$ | -27.9 (2.6)     | -57.4 (1.4)                  | -45.4 (0.7)    | -63.3 (1.0)     | -89.9 (1.0)     |
| $R^b$              | 0.017           | 0.013                        | 0.011          | 0.013           | 0.012           |
| $\sigma^c$         | 0.014           | 0.016                        | 0.015          | 0.018           | 0.018           |
| $N^d$              | 118             | 92                           | 87             | 88              | 93              |
|                    |                 |                              | Ternary        | Ternary         | Ternary         |
| $\log K_1$         |                 |                              | 3.40 (0.01)    | 3.22 (0.01)     | 3.01 (0.01)     |
| $\Delta G_1^\circ$ |                 |                              | -19.4 (0.1)    | -18.4 (0.1)     | -17.2 (0.1)     |
| $\Delta H_1^\circ$ |                 |                              | -32.9 (0.1)    | -37.2 (0.2)     | -43.5 (0.2)     |
| $\Delta S_1^\circ$ |                 |                              | -45.4 (0.6)    | -63.1 (0.8)     | -88.3 (0.9)     |
| $R^b$              |                 |                              | 0.013          | 0.016           | 0.017           |
| $\sigma^c$         |                 |                              | 0.015          | 0.020           | 0.022           |
| $N^d$              |                 |                              | 170            | 179             | 190             |

<sup>a</sup> The values in parentheses refer to three standard deviations.

<sup>b</sup> Hamilton  $R$ -factor.

<sup>c</sup> Standard deviation of the observed heats.

<sup>d</sup> The number of calorimetric data points.

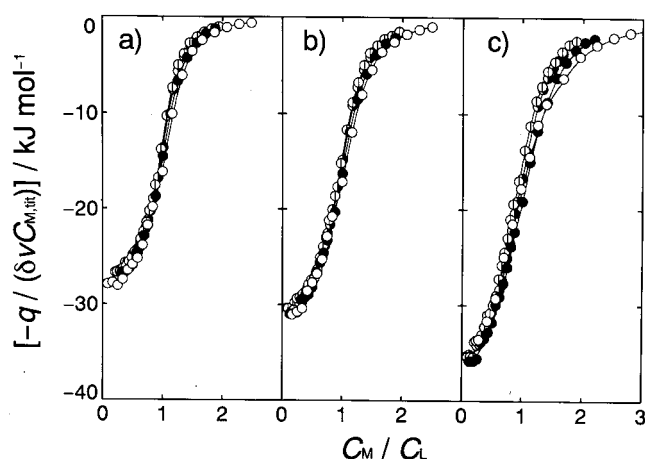


Figure 3. Calorimetric curves titrating test solutions involving sodium ion and 18-crown-6 with (a) potassium, (b) rubidium and (c) cesium ions in DMSO containing  $0.1 \text{ mol dm}^{-3} (\text{C}_2\text{H}_5)_4\text{NClO}_4$ , at  $25^\circ\text{C}$ . Concentrations of sodium ions and 18-crown-6 in initial test solutions,  $C_{M, \text{init}}; C_{L, \text{init}}/\text{mmol dm}^{-3}$ , are 15.13; 15.30(○), 20.05; 20.07(●), 25.88; 25.12(⊕) and 30.01; 30.09(⊙) for potassium, 15.13; 15.30(○), 20.05; 20.07(●), 25.88; 25.12(⊕) and 30.01; 30.09(⊙) for rubidium, and 9.009; 9.002(○), 20.07; 21.11(●), 26.51; 25.04(⊕) and 30.03; 30.01(⊙) for cesium. Solid lines were calculated by using the constants under 'ternary' in Table 2.

#### Enthalpies of transfer of 18-crown-6 complexes from water to various solvents

The enthalpies of transfer of the 18-crown-6 complexes,  $\Delta H_{\text{tr}}^\circ(\text{complex})$ , from water to various solvents were derived by Equation (6),

$$\Delta H_{\text{tr}}^\circ(\text{complex}) = \Delta H_{\text{tr}}^\circ(\text{M}) + \Delta H_{\text{tr}}^\circ(\text{L}) + \Delta H_1^\circ(\text{S}) - \Delta H_1^\circ(\text{W}), \quad (6)$$

where  $\Delta H_{\text{tr}}^\circ(\text{M})$  and  $\Delta H_{\text{tr}}^\circ(\text{L})$  represent the enthalpies of transfer of the metal ion and 18-crown-6, respectively, from water to a given solvent S. The  $\Delta H_{\text{tr}}^\circ(\text{M})$  values were quoted from Refs. [5] and [25]. The terms  $\Delta H_1^\circ(\text{S})$  and  $\Delta H_1^\circ(\text{W})$  denote the formation enthalpies of the 18-crown-6 complexes in S and water, respectively, and these values were taken from Refs. [11–14] except for those in DMSO. The enthalpies of transfer of the 18-crown-6 complexes thus obtained are summarized in Table 3, along with the  $\Delta H_{\text{tr}}^\circ(\text{M})$ ,  $\Delta H_{\text{tr}}^\circ(\text{L})$ ,  $\Delta H_1^\circ(\text{S})$  and  $\Delta H_1^\circ(\text{W})$  values.

## Discussion

### Solvation of 18-crown-6 in various solvents

As seen in Table 1, 18-crown-6 dissolves exothermically in NM, water, MeCN and DCE but the exothermicity is much less for MeCN and DCE. On the other hand, the dissolution process is endothermic and entropy-driven in PC, DMSO, PY and DMF. The enthalpies of solution of 18-crown-6 correlate with neither electron-pair accepting nor electron-pair donating abilities of the solvents.

18-Crown-6 is *ca.*  $50 \text{ kJ mol}^{-1}$  enthalpically more stable in water than in PC, DMF, DMSO and PY. 18-Crown-6 can take three typical conformations,  $C_i$  [26, 27],  $D_{3d}$  [28] and  $C_1$  [29–33] in a solid phase. The total energies of the three conformers without metal ions in an isolated system have been calculated by the molecular mechanical method and were found to be 198, 202 and  $237 \text{ kJ mol}^{-1}$  for the  $C_i$ ,  $D_{3d}$  and  $C_1$ , conformers, respectively [34, 35]. The  $C_i$  conformer is the most stable but the energy difference between the  $C_i$  and  $D_{3d}$  ones is quite small. Among the three, the

Table 3. Enthalpies of transfer,  $\Delta H_{tr}^{\circ}(\text{complex})/\text{kJ mol}^{-1}$ , of complex cations from water to various solvents at 25 °C.

| Solvent | Cation                       | $\Delta H_{tr}^{\circ}(\text{complex})$ | $\Delta H_{tr}^{\circ}(\text{M})^a$ | $\Delta H_{tr}^{\circ}(\text{L})^b$ | $\Delta H_1^{\circ}(\text{S})^c$ | $\Delta H_1^{\circ}(\text{W})^d$ |
|---------|------------------------------|---|-------------------------------------|-------------------------------------|----------------------------------|----------------------------------|
| DMF     | Na <sup>+</sup>              | 16.0                                    | -32.4                               | 56.8                                | -22.2 <sup>e</sup>               | -13.8                            |
|         | K <sup>+</sup>               | 8.6                                     | -35.7                               | 56.8                                | -38.8 <sup>e</sup>               | -26.3                            |
|         | Rb <sup>+</sup>              | -3.0                                    | -36.1                               | 56.8                                | -44.6 <sup>e</sup>               | -20.9                            |
|         | Cs <sup>+</sup>              | -8.5                                    | -34.6                               | 56.8                                | -50.0 <sup>e</sup>               | -19.3                            |
| DMSO    | Na <sup>+</sup>              | 19.8                                    | -29.2                               | 51.4                                | -16.2                            | -13.8                            |
|         | K <sup>+</sup>               | 9.4                                     | -35.4                               | 51.4                                | -32.9                            | -26.3                            |
|         | Rb <sup>+</sup>              | 0                                       | -35                                 | 51.4                                | -37.2                            | -20.9                            |
|         | Cs <sup>+</sup>              | -5.8                                    | -33.0                               | 51.4                                | -43.5                            | -19.3                            |
|         | NH <sub>4</sub> <sup>+</sup> | -3                                      | -41                                 | 51.4                                | -27.3                            | -14.1                            |
| PC      | Na <sup>+</sup>              | 21.3                                    | -10.5                               | 46.4                                | -28.4 <sup>f</sup>               | -13.8                            |
|         | K <sup>+</sup>               | 3.1                                     | -22.5                               | 46.4                                | -47.1 <sup>f</sup>               | -26.3                            |
|         | Rb <sup>+</sup>              | -1.6                                    | -24.9                               | 46.4                                | -44.0 <sup>f</sup>               | -20.9                            |
|         | Cs <sup>+</sup>              | -5.5                                    | -27.5                               | 46.4                                | -43.7 <sup>f</sup>               | -19.3                            |
|         | NH <sub>4</sub> <sup>+</sup> | -7.5                                    | -19.8                               | 46.4                                | -48.2 <sup>f</sup>               | -14.1                            |
| MeCN    | Na <sup>+</sup>              | 18.8                                    | -13.6                               | 16.9                                | 1.7 <sup>f</sup>                 | -13.8                            |
|         | K <sup>+</sup>               | 3.0                                     | -23.2                               | 16.9                                | -17.0 <sup>f</sup>               | -26.3                            |
|         | Rb <sup>+</sup>              | -2.9                                    | -25.7                               | 16.9                                | -15.0 <sup>f</sup>               | -20.9                            |
|         | Cs <sup>+</sup>              | -8.4                                    | -26.1                               | 16.9                                | -18.5 <sup>f</sup>               | -19.3                            |
| PY      | Na <sup>+</sup>              | -5.2                                    | -30.3 <sup>g</sup>                  | 53.6                                | -42.3 <sup>h</sup>               | -13.8                            |

<sup>a</sup> The enthalpy of transfer in  $\text{kJ mol}^{-1}$  of cations from water to a given solvent, quoted from Ref. [5].

<sup>b</sup> The enthalpy of transfer in  $\text{kJ mol}^{-1}$  of 18-crown-6 from water to a given solvent S.

<sup>c</sup> The formation enthalpy in  $\text{kJ mol}^{-1}$  of the 18-crown-6 complexes in a given solvent S.

<sup>d</sup> The formation enthalpy in  $\text{kJ mol}^{-1}$  of the 18-crown-6 complexes in water, quoted from Ref. [11].

<sup>e</sup> Ref. [12].

<sup>f</sup> Ref. [14].

<sup>g</sup> Ref. [25].

<sup>h</sup> Ref. [13].

C<sub>1</sub> conformer is the least stable. When 18-crown-6 is introduced into water, the hydration energies of 18-crown-6 were estimated by the Monte Carlo simulation and the hydration structures of the C<sub>i</sub>, D<sub>3d</sub> and C<sub>1</sub> conformers were predicted [36]. The D<sub>3d</sub> and C<sub>1</sub> conformers are strongly stabilized in water by forming hydrogen bonds between the oxygen atoms of 18-crown-6 and water molecules, while each oxygen atom in the C<sub>i</sub> conformer weakly interacts with a water molecule. The hydration energies of the C<sub>i</sub>, D<sub>3d</sub> and C<sub>1</sub> conformers were found to be -123, -219 and -227  $\text{kJ mol}^{-1}$ , respectively. The hydration of the C<sub>1</sub> conformer is enhanced over the D<sub>3d</sub> one but the latter is intrinsically much more stable than the former. As a result, the D<sub>3d</sub> conformer is the most stable one in water and the stability order in water is D<sub>3d</sub> > C<sub>1</sub> > C<sub>i</sub>. 18-Crown-6 takes the D<sub>3d</sub> conformation in the 18-crown-6·6H<sub>2</sub>O crystal [37]. Our X-ray diffraction measurements have revealed that the D<sub>3d</sub> and C<sub>1</sub> conformations are possible to be present in water but the D<sub>3d</sub> conformation seems to give the best fit to the X-ray diffraction data [38]. The predominance of the D<sub>3d</sub> conformer in water is also predicted by Raman spectroscopy [39]. Due to the strong hydrogen bonding with water, the hydration structure of 18-crown-6 is rigid like metal complexes and the motion of free 18-crown-6 is much restricted in water.

Aprotic solvents are unable to form hydrogen bonds with the oxygen atoms of 18-crown-6 because of their weak electron-pair accepting ability. Therefore, unlike in water, the stabilization of 18-crown-6 by solvation through hydrogen bonding cannot be expected in aprotic solvents. Free 18-crown-6 may even take the C<sub>i</sub> conformation which is intrinsically the most stable and it is also plausible that 18-crown-6 takes the D<sub>3d</sub> conformation because the difference in the intrinsic stability between the C<sub>i</sub> and D<sub>3d</sub> conformation is small and 4  $\text{kJ mol}^{-1}$  [34, 35]. On the other hand, the C<sub>1</sub> conformer is most unlikely, as it is the least stable conformation in an isolated system and the stabilization by solvation through hydrogen bonding is not expected in aprotic solvents. Whichever conformation, C<sub>i</sub> or D<sub>3d</sub>, 18-crown-6 takes in aprotic solvents, 18-crown-6 is expected to be much more weakly solvated in aprotic solvents than in water. Accordingly, the solvation structure is flexible in PC, DMF, DMSO and PY.

MeCN, NM and DCE are also aprotic solvents. However, the enthalpies of transfer of 18-crown-6 from water to these solvents are much less positive as compared with those to PC, DMF, DMSO and PY. The interactions of 18-crown-6 with solvent molecules have been investigated by molecular dynamics simulation [40], NMR [41, 42], molecular mechanics calculation [43] and XRISM methods [44]. For

MeCN and NM, solvate crystals, 18-crown-6·2MeCN and 18-crown-6·2NM, have been isolated and the structures have been determined by X-ray crystallography [45–47]. In both solvates, two solvent molecules bind with 18-crown-6 through a methyl group. Furthermore, the formation of 18-crown-6(MeCN)<sub>n</sub> and 18-crown-6(NM)<sub>n</sub> (*n* = 1, 2) has been revealed in benzene [41]. Thus, NM and MeCN molecules interact strongly with 18-crown-6 in solution as well. In fact, according to the molecular dynamics calculation, a stable solvate species as in a solid state is present with a long lifetime in MeCN [40]. It is also likely that DCE molecules interact strongly with 18-crown-6 in DCE because the Cl—C—H···O (18-crown-6) interaction is present in a crystal of 18-crown-6·2CH<sub>2</sub>Cl<sub>2</sub> [48]. The MeCN, NM and DCE molecules solvate 18-crown-6 well in these solvents and the solvation structure may be rigid like in water.

The solvation behavior of 18-crown-6 is not simply explained in terms of the acceptor property of solvents.

#### Solvation of $[M(18\text{-crown-6})]^+$ ( $M^+ = \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+$ ) in various solvents

Figure 4 compares the enthalpies of transfer of  $[M(18\text{-crown-6})]^+$  and  $M^+$  ( $M^+ = \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+$ ) from water to MeCN, PC, DMF, DMSO and PY. Except for PY, the  $\Delta H_{\text{tr}}^\circ(\text{complex})$  values change from positive for the sodium complex to negative for the cesium one, the values being close to zero for the rubidium ion. On the other hand, the  $\Delta H_{\text{tr}}^\circ(M)$  values are all negative regardless of the stronger or weaker electron-pair donating ability of these solvents than water. Evidently, the more negative  $\Delta H_{\text{tr}}^\circ(M)$  values for DMF and DMSO than for MeCN and PC originate from the fact that the former two solvents have the larger electron-pair donating property than the latter two. The negative  $\Delta H_{\text{tr}}^\circ(M)$  values for all of the aprotic solvents are closely related with the hydrogen-bonded water structure. In both aprotic solvents and water, solvent molecules are endothermically evolved from the solvation sphere of metal ions upon transfer to vacuum. In highly structured water, the liberated molecules then form hydrogen-bonding in the bulk, which significantly compensates the desolvation energy for the monovalent alkali-metal ions. On the other hand, the aprotic solvents are relatively structureless liquids and no enthalpic gain, like the formation of hydrogen-bonding in water, is expected. Thus, the desolvation enthalpies of the  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  ions are more needed in the aprotic solvents than in water and the transfer reactions of these metal ions from water to the solvents are exothermic.

The  $\Delta H_{\text{tr}}^\circ(\text{complex})$  values vary in the order,  $\text{Na}^+ > \text{K}^+ > \text{Rb}^+$  (ca. 0)  $> \text{Cs}^+$ , in MeCN, PC, DMF and DMSO. Moreover, the  $\Delta H_{\text{tr}}^\circ(\text{complex})$  values are all larger than the  $\Delta H_{\text{tr}}^\circ(M)$  ones. Also, the  $\Delta H_{\text{tr}}^\circ(\text{complex})$  values for a given metal ion are slightly dependent on the aprotic solvents. The last fact indicates that the solvation of the 18-crown-6 complexes is similar in the aprotic solvents. The  $M^+$  ions bind with 18-crown-6 and then six hydrophilic oxygen atoms point inside. As a result, the six oxygen atoms are almost isolated from solvent molecules. In water hydrophobic sites of 18-crown-6 contact with water molecules.

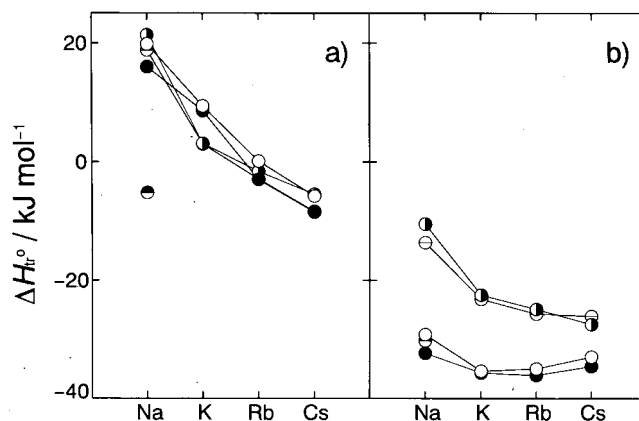


Figure 4. The enthalpies of transfer of (a) 18-crown-6 complexes and (b) metal ions from water to DMSO(○), DMF(●), PC(◐), MeCN(◑) and PY(◒).

Hence, hydrogen bonds among water molecules around the 18-crown-6 complexes are expected to be enhanced due to the hydrophobic interactions. This causes the larger desolvation enthalpies of the metal 18-crown-6 complexes than those of the corresponding free metal ions and makes the  $\Delta H_{\text{tr}}^\circ(\text{complex})$  values larger than the  $\Delta H_{\text{tr}}^\circ(M)$  ones. The large metal ions such as  $\text{Rb}^+$  and  $\text{Cs}^+$  are not fully accommodated in the cavity of 18-crown-6 and much of their surface contacts with water molecules [38]. In the region hydrogen bonds of liquid water are broken although water molecules weakly interact with the metal ions. After removal of the 18-crown-6 complexes from aqueous solution, hydrogen-bond formation occurs in the bulk. Similarly to the free metal ions, the formation in part compensates the desolvation enthalpies of the 18-crown-6 complexes. With increasing the radii of the metal ions, this effect becomes gradually pronounced and leads to the sequence  $\text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$  of the  $\Delta H_{\text{tr}}^\circ(\text{complex})$  values.

#### Solvent effect on 18-crown-6 complexation

Figure 5 shows the plots of the thermodynamic quantities,  $\Delta G_1^\circ$ ,  $\Delta H_1^\circ$  and  $T\Delta S_1^\circ$ , for the formation of 18-crown-6 complexes in MeCN, PC, DMF, DMSO, PY and water. The stability constants of the  $[M(18\text{-crown-6})]^+$  ( $M^+ = \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+$ ) complexes in the aprotic solvents are all larger than those in water. The reaction enthalpies and entropies, however, differ much among the solvents.

The complexation is more exothermic in DMSO, DMF, PC and PY than in water, regardless of their weaker or stronger donor property than water. On the other hand, most of the reaction entropies are similar or more negative in DMSO, DMF, PC and PY than in water. As seen in Table 3, the  $\Delta H_{\text{tr}}^\circ(L)$  values of 18-crown-6 from water to these aprotic solvents are from 45 to 57 kJ mol<sup>-1</sup>, and 18-crown-6 is strongly solvated in water. On the other hand, the  $\Delta H_{\text{tr}}^\circ(M)$  ( $M^+ = \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+$ ) values are from -10 to -40 kJ mol<sup>-1</sup>. Thus, much less energy is needed for the desolvation of 18-crown-6 in these aprotic solvents than in water and makes the complexation more exothermic in the former four solvents than in the latter. The hydrogen-

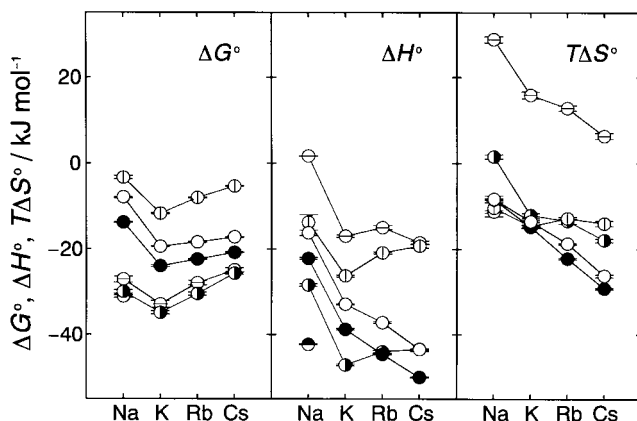


Figure 5. The Thermodynamic quantities,  $\Delta G_1^\circ$ ,  $\Delta H_1^\circ$  and  $T\Delta S_1^\circ/\text{kJ mol}^{-1}$ , for the formation of  $[M(18\text{-crown-6})]^+$  in DMSO( $\circ$ ), DMF( $\bullet$ ), water ( $\diamond$ ), PC( $\blacklozenge$ ), MeCN( $\square$ ) and PY( $\triangle$ ).

bonded hydration structure of 18-crown-6 is rigid similarly to the case of metal 18-crown-6 complexes, while 18-crown-6 is weakly solvated in DMSO, DMF, PC and PY and has a flexible structure. The entropic loss of 18-crown-6 upon complexation with metal ions is much larger in these aprotic solvents than in water, and hence, the complexation is not entropically favorable over water.

The complexation of  $\text{Na}^+$  is the most exothermic in PY. This is not simply explained in terms of the solvation of the sodium ion and 18-crown-6. According to our  $^{23}\text{Na}$  NMR measurements [13], the  $[\text{Na}(18\text{-crown-6})]^+$  complex is solvated with at least one solvent molecule in PY, DMF and MeCN. It is likely that the sodium ion is coordinated with more solvent molecules in PY than in DMF and MeCN. Another possibility for the markedly enhanced stabilization of  $[\text{Na}(18\text{-crown-6})]^+$  in PY is a favorable through-space interaction between the ligand and solvent molecule in the first coordination sphere of the sodium ion.

The formation enthalpies and entropies are much larger in MeCN than in DMSO, DMF, PC and PY. The  $\Delta H_{\text{tr}}^\circ(\text{L})$  value of 18-crown-6 from water to MeCN is much less positive than that to PC, DMF, DMSO and PY because of the relatively strong solvation of 18-crown-6 in MeCN. The larger reaction enthalpies in MeCN than in the other aprotic solvents arise from the more energy required for the desolvation of 18-crown-6 in the former solvent than in the latter ones. Also, an extensive desolvation of 18-crown-6 occurs upon complexation in MeCN, making the complexation in MeCN more favorable entropically.

Despite the fact that the solvation of both metal ions and 18-crown-6 is stronger in water than in MeCN, the complexation is enthalpically favorable in the former than in the latter. Water is a well-structured solvent. Desolvated water molecules upon complexation from the solvation sphere of both metal ions and 18-crown-6 are included in the hydrogen-bonded water structure, which in part cancels the desolvation energy. MeCN is a relatively structureless liquid and no such favorable gain of enthalpy occurs. Thus, the complexation is more endothermic in MeCN than in water [14]. The inclusion of desolvated solvent molecules

in the highly-structured bulk water also makes the reaction unfavorable entropically in water [14].

The complexation in DMSO is less exothermic than in DMF though DMSO and DMF have similar donor and acceptor properties. The fact results from the stronger solvation of 18-crown-6 in DMSO than in DMF. The entropic changes of the complexation are less favorable in DMSO than in DMF. DMSO has a stronger liquid structure due to dipole-dipole interactions than DMF [49]. DMSO molecules are liberated from the solvation sphere of both metal ions and 18-crown-6 and then form the bulk structure like in water. This gives rise to the smaller changes of entropy in DMSO than in DMF.

In conclusion, the complexation of 18-crown-6 with the alkali-metal ions mainly reflects the different solvation of 18-crown-6 and also the different degree of solvent structure.

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