Thermodynamics of Formation of 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-Crown-6) Complexes with Calcium, Strontium and Barium Ions in Water and Dimethylformamide

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The formation of 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) complexes with calcium, strontium and barium ions has been studied by titration calorimetry in water and dimethylformamide (dmf) containing 0.1 mol dm^{-3} NEt_4Cl and NEt_4ClO_4, respectively, as constant ionic media at 25 °C. The formation of the $[M(18\text{-crown-}6)]^{2+}$ ($M = Ca^{2+}$, Sr^{2+} or Ba^{2+}) complexes was revealed and their formation constants, reaction enthalpies and entropies were determined. The formation constant increases in the order Ca < Sr < Ba, showing the barium complex to be the most stable in water and dmf. Despite the large difference in the electron-pair donating and accepting abilities of water and dmf, the stability of the $[M(18\text{-crown-}6)]^{2+}$ complexes is very similar in the two solvents. The formation of $[Ca(18\text{-crown-}6)]^{2+}$ is less exothermic, while that of $[Sr(18\text{-crown-}6)]^{2+}$ and $[Ba(18\text{-crown-}6)]^{2+}$ is more exothermic in dmf than in water. The formation entropy is less negative for the calcium complex but more negative for the strontium and barium complexes in dmf than in water. Thus, enthalpy–entropy compensation leads to the similar stability constant of $[M(18\text{-crown-}6)]^{2+}$ in water and dmf. The differences between enthalpies in dmf and in water, ΔH°_1(dmf) − ΔH°_1(water), are 10.9, −6.7 and −11.3 kJ mol^{-1} for the calcium, strontium and barium complexes, respectively. Since dmf has a stronger electron-pair donating ability than water, the solvation of the bivalent cations is expected to be more pronounced in dmf than in water. On the other hand, water has a much stronger electron-pair accepting ability than dmf and the solvation of 18-crown-6 is more enhanced in water than in dmf, *i.e.*, 18-crown-6 is much stabilized in water by forming hydrogen bonds with water molecules. Thus, these two factors compensate and the enthalpic differences change from positive to negative for M^{2+}, *i.e.*, Ca > 0 > Sr > Ba. The decreasing order suggests that the difference between the desolvation energies upon complexation of the metal ions in dmf and in water is more significant for the ion of smaller size.

Complex formation reactions of metal ions in aprotic solvents are markedly different from those in water. Complexation of bi-valent and ter-valent transition metals with halide and thiocyanate ions is pronounced in aprotic solvents regardless of their weaker or stronger electron-pair donating ability relative to water.[1–18] The reaction in aprotic solvents is usually accompanied by a larger entropy change than that in water. These are a result of the more enhanced solvation of anions in water, due to hydrogen bonding of anions with water molecules, than in aprotic solvents, and of the hydrogen-bonded water structure in the bulk.[19,20] Complexation is more endothermic in aprotic solvents having a stronger electron-pair donating ability than water.[8,11,17,18,21–23]

Complexation of 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) with alkali-metal ions has been widely studied in non-aqueous solution as well as in aqueous solution.[24] The stability constants of the 18-crown-6 complexes in non-aqueous solution are generally larger than those in aqueous solution. According to our calorimetric results on the 18-crown-6 complexes with alkali-metal ions in dimethylformamide (dmf),[25] which has a stronger electron-pair donating ability than water,[26] the alkali-metal complexes are all more stable in dmf than in water,[27] similarly to transition-metal complexes. However, the complexation is more exothermic but entropically less favourable in dmf than in water.[25,27] The enthalpic and entropic behaviour of the complexation of 18-crown-6 is much different from that of bi-valent and ter-valent transition metals with halide and thiocyanate ions. The heat of solution of 18-crown-6 in water is negative (−22.1 kJ mol^{-1}), while that in dmf is positive (34.7 kJ mol^{-1}).[28] The macrocycle 18-crown-6 is stabilized in water by forming hydrogen bonds between its oxygen atoms and water molecules. On the other hand, dmf molecules cannot form any hydrogen bonds with 18-crown-6 because dmf has a weak electron-pair accepting ability relative to water.[26] The enthalpy of transfer of 18-crown-6 from dmf to water is −56.8 kJ mol^{-1}; thus 18-crown-6 is much more stable in water than in dmf. The enthalpy of transfer of alkali-metal ions from dmf to water is 32–36 kJ mol^{-1}.[29] Thus, the cationic solvation is less important than the solvation of 18-crown-6. Moreover, as a result of the formation of hydrogen bonds between 18-crown-6 and water molecules, the hydration structure of 18-crown-6 is expected to be quite rigid, similarly to metal complexes. Free 18-crown-6 loses freedom of motion to a considerable extent and, upon complexation with metal ions, 18-crown-6 therefore does not lose much entropy. On the other hand, 18-crown-6 is more flexible in dmf than in water. Much entropy is thus lost upon complexation in dmf and the complexation is not entropically favourable relative to that in water. In the 18-crown-6 complexation with alkali-metal ions, solvation of the ligand plays a crucial role.

The Gibbs energy and enthalpy of hydration from the gas phase range from −250 to −500 kJ mol^{-1} for univalent cations, and −1000 to −2000 kJ mol^{-1} for bivalent cations.[30] Solvation of bivalent metal ions is enhanced as compared with univalent

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ions and solvating molecules around a bivalent central metal ion must be more extensively ordered than those around a univalent cation. Indeed, the enthalpy and entropy of transfer of bivalent cations from dmf to water are larger than those of univalent cations, *e.g.*, the enthalpy and entropy values are 85.5 kJ mol^{-1} and 215 J K^{-1} mol^{-1}, respectively, for the barium ion.[31,32] Thus, different thermodynamic behaviour of 18-crown-6 complexation is expected for bivalent cations. Moreover, no enthalpy and entropy values for the formation of 18-crown-6 complexes with bivalent cations in dmf have been reported so far. In this study, we therefore investigated the complexation of 18-crown-6 with calcium, strontium and barium ions in water and dmf by precise calorimetry.

Experimental

Reagents.—All chemicals used were of reagent grade. The macrocycle 18-crown-6 (Nisso, Japan) was purified as described previously.[25,27] Hydrates of magnesium chloride, calcium chloride, strontium chloride, barium chloride and barium perchlorate were recrystallized once from water. Hydrates of magnesium perchlorate, calcium perchlorate and strontium perchlorate were prepared by dissolving the relevant carbonates in perchloric acid and the crystals obtained were recrystallized once from water. Stock solutions of magnesium chloride, calcium chloride, strontium chloride and barium chloride in water were prepared by dissolving the corresponding hydrates in water. Crystals of dmf solvates of magnesium perchlorate and calcium perchlorate were prepared by dissolving hydrates of the relevant perchlorates in dmf and by repeated evaporation of dmf to remove water, and were finally isolated from dmf. The solvate crystals were dried at room temperature in a vacuum oven for a few days. Stock solutions of strontium perchlorate and barium perchlorate in dmf were prepared by dissolving the corresponding hydrates in dmf and by repeated evaporation of dmf to remove water. The water content in the dmf solutions was checked by the Karl–Fischer method to be < 80 ppm. The content of metal ions in the stock solutions and in the dmf solvates was determined by the ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate titration. Tetraethylammonium chloride was used without further purification. Tetraethylammonium perchlorate was recrystallized once from water. These compounds were dried in a vacuum oven at 50 °C. Dimethylformamide was dried over 4 Å molecular sieves for a few weeks, then distilled under a reduced pressure and stored over 4 Å molecular sieves in a dark bottle. The water content in dmf was < 80 ppm. All dmf solutions were prepared and treated over P_2O_5 in a dry-box under a nitrogen atmosphere.

Measurements.—Calorimetric measurements were performed on a twin-type calorimeter (Tokyo Riko, Japan) at 25 °C and a PC-286VJ computer (EPSON, Japan) was used for the calorimeter control and data acquisition.[33] All aqueous and dmf solutions contained 0.1 mol dm^{-3} NEt_4Cl and NEt_4ClO_4, respectively, as constant ionic media. Two Teflon-coated stainless-steel vessels were inserted in an aluminium block thermostatted at 25 °C (±0.0001 °C) in an air bath. An aqueous metal(II) chloride solution (40 cm^3) was placed in the vessel and titrated with an aqueous 0.1 or 0.2 mol dm^{-3} 18-crown-6 solution by using an APB-118 autoburette (Kyoto Electronics, Japan). Similarly, a metal(II) perchlorate solution in dmf was titrated with a 0.1 or 0.2 mol dm^{-3} 18-crown-6 dmf solution under a dry nitrogen atmosphere. A metal replacement titration, in which a test solution involving strontium ion and 18-crown-6 was titrated with a barium ion solution, was also carried out in water and dmf. Heats of complexation ranging from 0.5 to 3.5 J at each titration point were measured with an error of ±0.02 J. Heats of dilution of titrants were separately measured by titrating a 0.1 mol dm^{-3} medium solution with a titrant solution and used for correction of reaction heats.

Data Analysis.—Only considering the formation of mononuclear species, the overall formation of the 18-crown-6 (L) complex with an alkaline-earth metal ion (M^{2+}) can be defined by equations (1) and (2).

$$M^{2+} + nL \rightleftharpoons [ML_n]^{2+} \qquad (1)$$

$$\beta_n = [ML_n^{2+}]/[M^{2+}][L]^n \qquad (2)$$

The concentrations of free M^{2+} and L in a solution *i* are related to their total concentrations, $c_{M,i}$ and $c_{L,i}$ by the following mass-balance equations (3) and (4), respectively.

$$c_{M,i} = [M^{2+}]_i + \Sigma\beta_n[M^{2+}]_i[L]_i^n \qquad (3)$$

$$c_{L,i} = [L]_i + \Sigma n\beta_n[M^{2+}]_i[L]_i^n \qquad (4)$$

A heat q_i measured at the *i*th titration point is expressed by the overall formation constant β_n and enthalpy $\Delta H^\circ_{\beta n}$ of $[ML_n]^{2+}$ as given by equation (5), where V_i denotes the volume

$$q_i = -(V_i\Sigma\beta_n\Delta H^\circ_{\beta n}[M^{2+}]_i[L]_i^n - V_{i-1}\Sigma\beta_n\Delta H^\circ_{\beta n}[M^{2+}]_{i-1}[L]_{i-1}^n) \qquad (5)$$

of the test solution. Formation constants and enthalpies were simultaneously determined by minimizing the error-square sum $\Sigma(q_{i,\mathrm{calc}} - q_{i,\mathrm{obs}})^2$, using a non-linear least-squares program MQCAL.[34]

Results

Calorimetric titration curves obtained for the calcium and 18-crown-6 systems in water and dmf containing 0.1 mol dm^{-3} NEt_4Cl and NEt_4ClO_4, respectively, are shown in Fig. 1. In the figure, the $-q/(\delta v c_{L,\mathrm{tit}})$ values are plotted against the ratio of the total concentrations of 18-crown-6 to metal ion, c_L/c_M, where q, δv and $c_{L,\mathrm{tit}}$ are the measured heat of complexation, the added volume of the titrant and the concentration of the ligand in the titrant solution, respectively. The calorimetric data were analysed by considering the formation of a plausible set of mononuclear complexes and the Hamilton *R* factor and the σ value (standard deviation of the observed heats) for various sets were compared. By considering the formation of [Ca(18-crown-6)]$^{2+}$, we reproduced well the calorimetric titration curves. The results are given in Tables 1 and 2 for the aqueous and dmf solutions, respectively.

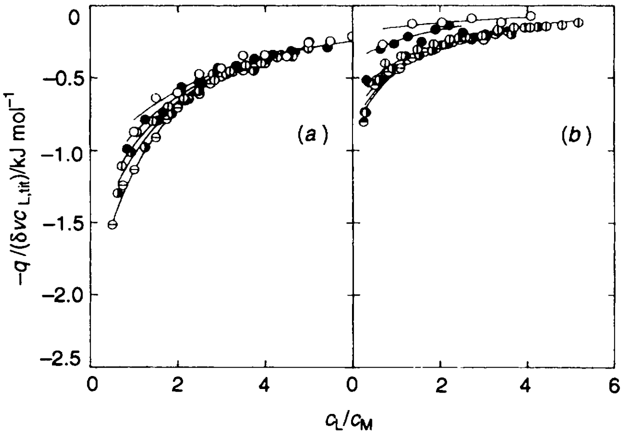

Fig. 1 Calorimetric titration curves for the calcium and 18-crown-6 systems in (*a*) water and (*b*) dmf containing 0.1 mol dm^{-3} NEt_4Cl and NEt_4ClO_4, respectively, at 25 °C. Concentrations of calcium ions in initial test solutions, $c_{M,\mathrm{init}}$/mmol dm^{-3}, are 25.10(○), 29.99(●), 35.18(⦶), 40.17(◑) and 50.02(⊖) in water, 9.246(○), 19.96(●), 33.97(⦶), 41.39(◑), 46.05(⊖) and 49.39(◓) in dmf. Solid lines were calculated by using the constants in Tables 1 and 2

Table 1 Least-squares refinements of formation constants, $\log(\beta_n/\mathrm{dm}^{3n}\ \mathrm{mol}^{-n})$, and enthalpies, $\Delta H^\circ_{\beta n}/\mathrm{kJ\ mol}^{-1}$, of 18-crown-6 complexes in water containing 0.1 mol dm^{-3} NEt_4Cl as constant ionic medium at 25 °C[a]

	Ca	Sr (binary)	Ba (binary)
$\log \beta_1$	0.45 (0.12)	2.77 (0.02)	3.76 (0.03)
$\Delta H^\circ_{\beta 1}$	−15.5 (3.3)	−16.0 (0.2)	−33.2 (0.2)
R[b]	0.051	0.024	0.016
σ[c]/J	0.019	0.018	0.028
N[d]	69	126	105
		Sr (ternary)	Ba (ternary)
$\log \beta_1$		2.80 (0.02)	3.75 (0.02)
$\Delta H^\circ_{\beta 1}$		−15.9 (0.2)	−33.1 (0.1)
R		0.019	
σ/J		0.023	
N		306	

[a] Values in parentheses refer to three standard deviations. [b] Hamilton R factor. [c] Standard deviation of the observed heats. [d] The number of calorimetric data points.

Table 2 Least-squares refinements of formation constants, $\log(\beta_n/\mathrm{dm}^{3n}\ \mathrm{mol}^{-n})$, and enthalpies, $\Delta H^\circ_{\beta n}/\mathrm{kJ\ mol}^{-1}$, of 18-crown-6 complexes in dmf containing 0.1 mol dm^{-3} NEt_4ClO_4 as constant ionic medium at 25 °C

	Ca	Sr (binary)	Ba (binary)
$\log \beta_1$	0.63 (0.18)	2.90 (0.02)	4.10 (0.03)
$\Delta H^\circ_{\beta 1}$	−4.6 (1.4)	−22.6 (0.1)	−44.5 (0.2)
R	0.104	0.013	0.013
σ/J	0.016	0.013	0.025
N	80	106	111
		Sr (ternary)	Ba (ternary)
$\log \beta_1$		2.92 (0.02)	4.10 (0.02)
$\Delta H^\circ_{\beta 1}$		−22.6 (0.2)	−44.4 (0.1)
R		0.015	
σ/J		0.021	
N		283	

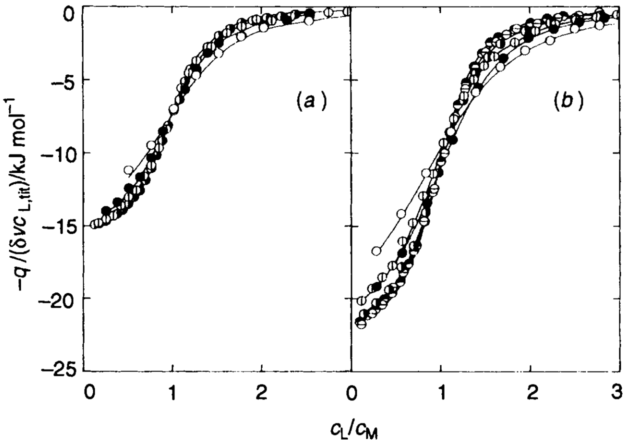

Fig. 2 Calorimetric titration curves for the strontium and 18-crown-6 systems in (*a*) water and (*b*) dmf containing 0.1 mol dm^{-3} NEt_4Cl and NEt_4ClO_4, respectively, at 25 °C. Concentrations of strontium ions in initial test solutions, $c_{\mathrm{M,init}}$/mmol dm^{-3}, are 9.907(○), 19.74(●), 29.64(⦶) and 39.53(◑) in water, 4.520(○), 8.862(●), 10.99(⦶), 18.05(◑), 21.73(⊖) and 27.53(◓) in dmf. Solid lines were calculated by using the constants under 'ternary' in Tables 1 and 2

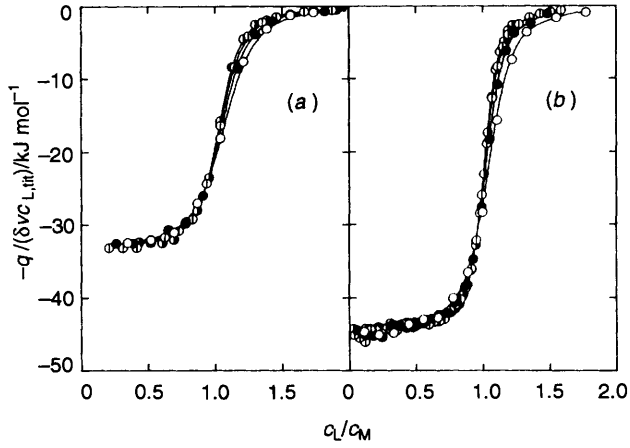

Fig. 3 Calorimetric titration curves for the barium and 18-crown-6 systems in (*a*) water and (*b*) dmf containing 0.1 mol dm^{-3} NEt_4Cl and NEt_4ClO_4, respectively, at 25 °C. Concentrations of barium ions in initial test solutions, $c_{\mathrm{M,init}}$/mmol dm^{-3}, are 15.08(○), 20.11(●), 25.12(⦶) and 30.16(◑) in water, 11.38(○), 20.40(●), 31.78(⦶) and 41.31(◑) in dmf. Solid lines were calculated by using the constants under 'ternary' in Tables 1 and 2

Calorimetric curves obtained by titrating for the strontium and barium ions with 18-crown-6 solutions are depicted in Figs. 2 and 3, respectively. They were similarly analysed as above and best explained in terms of the formation of $[M(18\text{-crown-}6)]^{2+}$ ($M = Sr^{2+}$ or Ba^{2+}). The results are listed under 'binary' in Tables 1 and 2 for the aqueous and dmf solutions, respectively. However, as seen in the Tables, the formation constants for the strontium and barium complexes are relatively large both in water and dmf. In order to check the reliability of the parameter values, calorimetric data titrating various strontium ion and 18-crown-6 solutions with barium ion were measured in water and in dmf (Fig. 4). The whole binary and ternary data in respective solutions were simultaneously analysed. The results are listed under 'ternary' in Tables 1 and 2, and the formation constants and enthalpies are in good agreement with those under 'binary'.

The solid lines, calculated by using the parameter values thus obtained, reproduced well the experimental points over the whole range of c_L/c_M (or c_{Ba}/c_L) examined, as seen in Figs. 1–4.

No significant heat other than heat of dilution of titrant was liberated during the titration of magnesium ion with 18-crown-6 in water and dmf, and thus the formation constants and enthalpies could not be determined.

The thermodynamic quantities for the formation of the $[M(18\text{-crown-}6)]^{2+}$ ($M = Ca^{2+}$, Sr^{2+} or Ba^{2+}) complexes in water and dmf are summarized in Table 3, together with literature values.[35–41] The formation constant obtained for $[Ca(18\text{-crown-}6)]^{2+}$ in water is in good agreement with that obtained by the ion exchange method.[35] However, the formation constants and enthalpies for other systems are appreciably different. The formation constants obtained by the spectrophotometric method in dmf[40] are too large.

Discussion

Origin of Stability Order of Complexes.—As is seen in Table 3, the Gibbs energy varies in the order Ca > Sr > Ba, showing the barium complex to be the most stable in water and dmf. The enthalpy and entropy values similarly change in dmf, Ca > Sr > Ba, while a different variation profile was found in water, Ca ≈ Sr > Ba for ΔH°_1, Sr > Ca ≈ Ba for ΔS°_1. The formation of $[Ba(18\text{-crown-}6)]^{2+}$ is the most exothermic, while the reaction is the most unfavourable entropically.

The metal–oxygen (18-crown-6) interaction energy decreases in the order Ca > Sr > Ba, in parallel with decreasing the hydration energy of the metal ions[30] and increasing their ionic radius.[42] It is thus expected that the stability of $[M(18\text{-crown-}6)]^{2+}$ decreases and the reaction enthalpy becomes less negative in the same order, leading to the most unfavourable and endothermic formation of the barium complex in water and

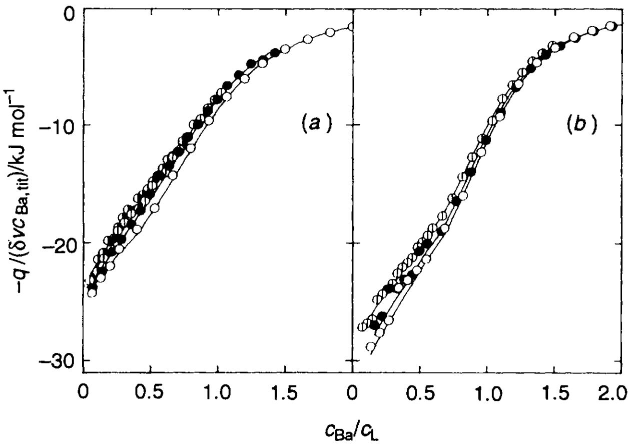

Fig. 4 Calorimetric curves titrating various strontium ion and 18-crown-6 solutions with barium ion in (*a*) water and (*b*) dmf at 25 °C. Concentrations of strontium ions and 18-crown-6 in initial test solutions, $c_{Sr,init}$, $c_{L,init}$/mmol dm^{-3}, are 11.54, 11.29(○), 21.59, 21.13(●), 30.04, 29.31(⦶) and 40.91, 40.66(◑) in water, 16.03, 15.00(○), 20.30, 18.61(●) and 31.62, 27.68(⦶) in dmf. Solid lines were calculated by using the constants under 'ternary' in Tables 1 and 2

Table 3 Thermodynamic quantities, log(K_1/dm^3 mol^{-1}), $\Delta G°_1$/kJ mol^{-1}, $\Delta H°_1$/kJ mol^{-1} and $\Delta S°_1$/J K^{-1} mol^{-1}, for the formation of [M(18-crown-6)]$^{2+}$ (M = Ca^{2+}, Sr^{2+} or Ba^{2+}) in water and dmf at 25 °C[a]

Solvent	Ca	Sr	Ba
Water			
log K_1	0.45(0.12)	2.80(0.02)	3.75(0.02)
	0.48[b]	2.72[e]	3.87[e]
	0.53[c]	2.40[f]	3.67[f]
	1.26[d]		
$\Delta G°_1$	−2.6(0.7)	−16.0(0.1)	−21.4(0.1)
$\Delta H°_1$	−15.5(3.3)	−15.9(0.2)	−33.1(0.1)
	−9.55[c]	−15.1[e]	−31.7[e]
	−2.91[d]		
$\Delta S°_1$	−43.3(13.4)	0.5(1.0)	−39.4(0.8)
	−21.9[c]	1.25[e]	−33.0[e]
	14.4[d]		
dmf			
log K_1	0.63(0.18)	2.92(0.02)	4.10(0.02)
	< 1.30[g]	3.00[g]	4.21[g]
	3.03[h]	4.23[h]	5.29[h]
		2.67[i]	3.81[i]
$\Delta G°_1$	−3.6(1.0)	−16.7(0.1)	−23.4(0.1)
$\Delta H°_1$	−4.6(1.4)	−22.6(0.2)	−44.4(0.1)
$\Delta S°_1$	−3.3(8.2)	−19.9(1.0)	−70.5(0.8)

[a] Values in parentheses refer to three standard deviations. [b] Ref. 35 (ion exchange). [c] Ref. 36 (calorimetry; anion = Cl$^-$). [d] Ref. 36 (calorimetry; anion = NO$_3^-$). [e] Ref. 37 (calorimetry). [f] Ref. 38 (radiopolarography). [g] Ref. 39 (^{23}Na NMR). [h] Ref. 40 (spectrophotometry). [i] Ref. 41 (^{1}H NMR).

dmf. However, the formation of the barium complex is the most favourable and exothermic in the two solvents.

The ionic radius is 149 pm for the barium ion and 152 pm for the potassium ion.[42] The potassium ion is well accommodated in the cavity of 18-crown-6 having D_{3d} conformation within the [K(18-crown-6)]$^+$ complex in water and in the solid state, the potassium–oxygen bond length being 280 pm on average.[43,44] Because of the similar size of the barium and potassium ions, the barium 18-crown-6 complex is expected to have a similar structure. Indeed, the barium 18-crown-6 complex adopts the D_{3d} conformation in the solid state.[45] The metal–oxygen bond lengths within the barium and potassium complexes are comparable to those within the hydrated barium and potassium ions (*ca.* 280 pm).[46] The desolvation energy of the metal ions is thus well compensated upon complexation with 18-crown-6. For the calcium ion (114 pm) having a smaller size than the barium ion,[42] it has been established[47] that the calcium ion is located at the centre of the cavity of 18-crown-6 within [Ca(18-crown-6)]$^{2+}$ in the solid state, similarly to the potassium complex. However, the calcium–oxygen bond distance (256–274 pm) within the complex[47] is much longer than that within the hydrated calcium ion (*ca.* 240 pm).[46] A much weaker calcium–oxygen bond within [Ca(18-crown-6)]$^{2+}$ is formed as compared with that within the solvated calcium ion. The formation of the weak calcium–oxygen bond is not adequate to compensate the desolvation energy of the calcium ion. It is also likely that the calcium complex has a similar structure to that of the sodium complex,[43,48] since calcium and sodium (116 pm) ions have a similar ionic size.[42] The ligand 18-crown-6 adopts a C_1 conformation in the sodium complex in water and in the solid state, the Na–O bond length being 247–254 pm.[43,48] The metal–oxygen bond lengths within the calcium and sodium complexes are similar to those in the hydrated ions[46] and the metal–oxygen bonds are not weakened as in the case of the barium and potassium complexes. According to molecular-mechanics calculations, the C_1 conformation of 18-crown-6 is more unstable by 35 kJ mol^{-1} than the D_{3d} one in the gas phase.[49,50] The intrinsic instability of the C_1 conformation results in the weak calcium–ligand interaction. The same applies for the strontium ion having an ionic radius of 132 pm,[42] which is smaller than the barium ion though larger than the calcium ion. Thus, regardless of which conformation, D_{3d} or C_1, the calcium and strontium complexes adopt in solution (even if the complexes exist as an equilibrium mixture of the two conformations), the formation of [Ca(18-crown-6)]$^{2+}$ and [Sr(18-crown-6)]$^{2+}$ is less favourable and less exothermic than that of [Ba(18-crown-6)]$^{2+}$ both in water and dmf.

The hydration entropy becomes less negative in the order Ca < Sr < Ba,[30] showing the solvating molecules around the barium ion to be the least ordered. Upon complexation with 18-crown-6, the solvent molecules co-ordinating to these metal ions are liberated from the solvation sphere to give an entropy gain. This gain is smallest for the barium ion; the formation of [Ba(18-crown-6)]$^{2+}$ is not entropically as favourable as compared with that of [Ca(18-crown-6)]$^{2+}$ and [Sr(18-crown-6)]$^{2+}$ in water and dmf.

Solvent Effect.—Despite the large difference in the electron-pair donating and accepting abilities of water and dmf, Table 3 shows that the stability of the [M(18-crown-6)]$^{2+}$ (M = Ca^{2+}, Sr^{2+} or Ba^{2+}) complex is very similar in the two solvents. The formation of [Ca(18-crown-6)]$^{2+}$ is less exothermic, while that of [Sr(18-crown-6)]$^{2+}$ and [Ba(18-crown-6)]$^{2+}$ is more exothermic in dmf than in water. The formation entropy is less negative for the calcium complex but more negative for the strontium and barium complexes in dmf than in water. Enthalpy–entropy compensation thus leads to the similar value of the stability constant of [M(18-crown-6)]$^{2+}$ in water and dmf.

The differences between enthalpies in dmf and in water, $\Delta\Delta H°_1 = \Delta H°_1(\text{dmf}) - \Delta H°_1(\text{water})$, are 10.9, −6.7 and −11.3 kJ mol^{-1} for the calcium, strontium and barium complexes, respectively. The Gibbs energy and enthalpy of transfer of the barium ion from water to dmf are negative,[31,51] showing that the barium ion is more stabilized in dmf than in water. Also, the electron-pair donating ability of dmf (*e.g.*, donor number $D_N = 26.6$) is larger than that of water ($D_N = 18.0$).[26] The solvation of alkaline-earth metal ions is expected to be more enhanced in dmf than in water, *i.e.*, more energy is needed for breaking the metal–dmf bonds upon complexation. The cationic solvation positively contributes to the $\Delta\Delta H°_1$ values. On the other hand, water has a much stronger electron-pair accepting ability (*e.g.*, acceptor number $A_N = 54.8$) than dmf ($A_N = 16.0$)[26] and the solvation of 18-crown-6 is expected to be more enhanced in water than in dmf. Indeed, the dissolution of 18-crown-6 in water is exothermic (−22.1 kJ mol^{-1}), while in dmf it is endothermic (34.7 kJ mol^{-1});[28] thus 18-crown-6 is more stable by 56.8 kJ mol^{-1} in water than in dmf. The stabilization is a result of the formation of hydrogen bonds between oxygen atoms of 18-crown-6 and water molecules, as also predicted by Monte Carlo simulation of aqueous 18-crown-6 solutions.[52] By contrast 18-crown-6 is weakly solvated in dmf because dmf molecules cannot form any hydrogen bonds with 18-crown-6, and much less energy is needed for the desolvation of 18-crown-6 in dmf compared with that in water. The different solvation of 18-crown-6 in water and dmf makes a negative contribution to the $\Delta\Delta H^\circ_1$ values. Thus, these two factors compensate and the $\Delta\Delta H^\circ_1$ values change from positive to negative for M^{2+}, *i.e.*, Ca > 0 > Sr > Ba. The decreasing order suggests that the difference between the desolvation energies of the metal ions in dmf and in water is more significant for ions of smaller size. This is also reflected in the differences between reaction entropies in dmf and in water, $\Delta\Delta S_1 = \Delta S^\circ_1$(dmf) − ΔS°_1(water), which are 40, −20 and −30 J K^{-1} mol^{-1} for the calcium, strontium and barium complexes, respectively. Solvating molecules around the ion of smaller size are more ordered and the entropic gain upon complexation is larger in dmf than in water. Also, 18-crown-6 in water has a rigid structure similar to metal complexes, *i.e.*, free 18-crown-6 loses freedom of motion to a considerable extent. Upon complexation with metal ions, 18-crown-6 therefore does not lose much more entropy. On the other hand, 18-crown-6 is more flexible in dmf than in water, and much entropy is lost upon complexation. These lead to the negative $\Delta\Delta S^\circ_1$ values for the strontium and barium complexes.

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