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FREE ENERGIES OF TRANSFER FROM WATER TO NON-AQUEOUS SOLVENTS OF UNIVALENT (2,2,2) CRYPTAND AND 18-CROWN-6 COMPLEXES

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Abstract: A complexation scheme involving a conformational equilibrium of the ligand is proposed to explain the difference in free energies of transfer between metal complex and ligand from water to non-aqueous solvents.

In a recent paper Abraham and Ling[1] have reported the thermodynamic parameters of transfer (ΔG_{tr}, ΔH_{tr} and ΔS_{tr}) from water to methanol for complexes of alkali and Ag^+ ions with cryptand (2,2,2) and [18]crown-6 (18C6). They suggest that the values of these parameters for $M(2,2,2)^+$ and $M(18C6)^+$ complexes are to a certain extent comparable, thus concluding that the behaviour of these two types of complexes is quite similar. This view is, however, not obvious, and is rather limited, involving as it does only two solvents. In order to give a wider idea of the properties of the two types of complexes, we present a collection of free energy of transfer data from water (W) to several non-aqueous solvents (S) for alkali and Ag^+ ions with (2,2,2) and 18C6.

The difference of free energies of transfer for complex (ML^+) and free ligand (L) has been calculated from the stability constant (K_s) for the complexation equilibrium (1) and the free energy of transfer of the metal ion (M^+), eq. (2).

$$M^+ + L \underset{}{\overset{K_s}{\rightleftharpoons}} ML^+ \qquad (1)$$

$$\Delta G_{tr}(ML^+) - \Delta G_{tr}(L) = -2.303RT \log [K_s(S)/K_s(W)] + \Delta G_{tr}(M^+) \qquad (2)$$

Tables I, II, and III contain the corresponding values of ΔG_{tr}. It can be seen from the data in Tables II and III that the free energy of transfer of the alkali metal complexes with (2,2,2) from water to any of the non-aqueous solvent passes through a clear minimum when $M^+ = K^+$, i.e. the most stable complex. On the other hand, if we consider an experimental accuracy of ± 1 kJ mol^{-1}, no specific dependence of $\Delta G_{tr}(M(18C6)^+)$ on ion size is observable, except for the case of $M^+ = Li^+$ (and to a certain extent Na^+) in propylene carbonate and acetonitrile where the Li^+ metal ion is very poorly solvated. Differences in the solvation of the metal ion complexes with cryptand (2,2,2) and crown ether (dibenzo-18C6) have been demonstrated before more clearly for the aprotic solvent couple dimethylformamide-propylenecarbonate[2]. The results in Table II also show that for complexes of the ions which fit well into the ligand cavity, Na^+, K^+, Rb^+, and Ag^+, $\Delta G_{tr}(M(2,2,2)^+) - \Delta G_{tr}(2,2,2)$ from water to aprotic solvents varies only between -18.6 and -25.8 kJ mol^{-1}. This does not apply for Li^+ (the ion is too small compared with the ligand cavity) or Cs^+ (the ion is too large). The relatively small variation of $\Delta G_{tr}(M(2,2,2)^+) - \Delta G_{tr}(2,2,2)$ with different M^+ and solvents has been noticed previously [3,4].

Table I: ΔG_{tr} in kJ mol^{-1} from water to non-aqueous solvents at 25°C [a)]

	MeOH	EtOH	PC	MeCN	Me_2SO	DMF
Li^+	4.1	8.6	21.7	22.8	-17.5	-9.1
Na^+	9.2	14.0	15.5	13.6	-15.0	-8.7
K^+	10.4	16.3	7.0	7.3	-14.3	-7.8
Rb^+	11.1	18.1	4.6	6.4	-12.4	-7.6
Cs^+	10.6	16.9	3.1	4.0	-15.2	-8.0
Ag^+	7.8	7.1	19.3	-23.0	-34.9	-16.6
I^-	6.7[b)]	11.7[b)]	14.3[b)]	18.8[b)]	13.4[c)]	18.8[c)]

methanol (MeOH), ethanol (EtOH), propylene carbonate (PC), acetonitrile (MeCN), dimethylsulfoxide (Me_2SO), dimethylformamide (DMF)

a) B.G. Cox, J. Garcia-Rosas, and H. Schneider, J.Am.Chem.Soc. 103, 1384 (1981)

b) M.H. Abraham and A.F. Danil de Namor, J.C.S. Faraday I, 2101 (1978)

c) B.G. Cox, Annu.Rep.Prog.Chem., Sect. A, Phys. Inorg. Chem. 70, 249 (1973)

Table II: Differences in free energies of transfer between (2,2,2) cryptates and cryptand (2,2,2), $\Delta G_{tr}(M(2,2,2)^+) - \Delta G_{tr}(2,2,2)$, in kJ mol^{-1} from water to non-aqueous solvents at 25° C [a),b)]

ion	MeOH	EtOH	PC	MeCN	Me_2SO	DMF
Li^+	-5.1	1.5	-11.5	-11.1	-	-
Na^+	-13.6	-12.2	-21.9	-18.6	-22.7	-21.6
K^+	-18.7	-12.4	-25.6	-25.8	-23.7	-22.5
Rb^+	-15.6	-11.6	-22.9	-23.6	-20.9	-21.3
Cs^+	-6.1	1.4	-12.4	-13.7	-15.2	-11.9
Ag^+	-6.5	-3.2	-19.1	-23.4	-21.3	-18.6
δ_{Born} [c)]	2.5	3.9	0.4	2.1	1.2	2.0

a) B.G. Cox, J. Garcia-Rosas, and H. Schneider, J.Am.Chem.Soc. 103, 1384 (1981)

b) Abbreviations for solvents as in Table I

c) $\delta_{Born} = 695\ r_i(\text{Å})^{-1}(\varepsilon_S^{-1} - \varepsilon_W^{-1})$ in kJ mol^{-1}; ε_S, ε_W dielectric constant

Inspection of the free energies of transfer in Tables II and III shows that $\Delta G_{tr}(ML^+) - \Delta G_{tr}(L)$ for a given metal ion varies only by less that 4 kJ mol^{-1} for cryptand complexes and less than 10 kJ mol^{-1} for crown ether complexes in different dipolar aprotic solvents. This result is surprising if we consider the range of variation in $\Delta G_{tr}(M^+)$ values (Table I). A possible explanation would

Table III: Differences in free energies of transfer between 18-crown-6 complexes and 18-crown-6, $\Delta G_{tr}(M(18C6)^+) - \Delta G_{tr}(18C6)$, in kJ mol^{-1} from water to non-aqueous solvents at 25° C a), b)

ion	MeOH	PC	MeCN	Me_2SO	DMF
Li^+	-	~+7.0	~+10.1	-	-
Na^+	-11.1	-9.9	-7.8	-18.6	-17.5
K^+	-12.6	-17.5	-13.7	-21.0	-17.3
Rb^+	-10.4	-16.9	-	-20.1	-18.7
Cs^+	-11.1	-17.1	-	-21.5	-21.5
Ag^+	-10.5	-12.7	-	-	-

a) Abbreviations for solvents as in Table I.

b) The values of the stability constants used in the calculations were taken from the following sources: H_2O: for Li^+ G.W. Liesegang, M.M. Farrow, F.A. Vazquez, N. Purdie, and E. Eyring, J.Am.Chem.Soc. 99, 3240 (1977), for the other ions R.M. Izatt, R.E. Terry, B.L. Haymore, L.D. Hansen, N.K. Dalley, A.G. Avondelt, and J.J. Christensen, J.Am.Chem.Soc. 98, 7620 (1976). MeOH: J.D. Lamb, R.M. Izatt, C.S. Swain, and J.J. Christensen, J.Am.Chem.Soc. 102, 475 (1980). PC: for Li^+ A.J. Smetana and A.I. Popov, J. Solution Chem. 9, 183 (1980), for Na^+, K^+, Cs^+ and Ag^+ I.M. Kolthoff and M.K. Chantooni, Anal. Chem. 52, 1039 (1980), for Rb^+ Y. Takeda, H. Yano, M. Ishibashi, and H. Isazumi, Bull. Chem.Soc. Jap. 53, 72 (1980). MeCN: I.M. Kolthoff and M.K. Chantooni, idem, only for Li^+ A.J. Smetana and A.I. Popov, idem. DMF: K_s obtained from the values of $K_s(M^+)/K_s(Tl^+)$ given by C. Srivanavit, J.I. Zink, and J.L. Dechter, J.Am.Chem.Soc. 99, 5876 (1977) and $K_s(Tl^+)$ reported by M. Shamsipur and A.I. Popov, Inorg.Chim.Acta 43, 243 (1980). Me_2SO: for Na^+ and K^+ I.M. Kolthoff and M.K. Chantooni, idem, for Rb^+ and Cs^+ K_s obtained as described for DMF.

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be provided by assuming a complexation scheme I, which involves the existence

Scheme I:
$$L \overset{K_{conf}}{\rightleftharpoons} L' \qquad (3)$$

$$L' + M \overset{K_s'}{\rightleftharpoons} ML'^+ \qquad (4)$$

of a particular conformation (L') of the ligand in the metal complex. This particular conformation is specific for each metal ion and depends very little on the aprotic solvent. In eq. (3) $K_{conf} = [L']/[L]$, where [L] represents the total number of conformational states of the ligand including the conformation L'. A related scheme involving conformational changes of the ligand has been used in the interpretation of the kinetics of formation of complexes of crown ethers[5,6] and various naturally-occurring macrocyclic antibiotics[7]. In this kinetic scheme the reactive conformation of the ligand is not necessarily the L' of our scheme I. In terms of free energies of transfer we obtain eqs. (5) and (6). Furthermore

$$\Delta G_{tr}(L') = -\ 2.303RT\ \log\ [K_{conf}(S)/K_{conf}(W)] + \Delta G_{tr}(L) \qquad (5)$$

$$\Delta G_{tr}(ML'^{+}) = -\ 2.303RT\ \log\ [K_s'(S)/K_s'(W)] + \Delta G_{tr}(M^{+}) + \Delta G_{tr}(L') \qquad (6)$$

we assume that when the central ion interacts with the solvent only across the barrier of the encapsulating ligand, the solvation free energies of L' and ML'^{+} differ only by a Born term, δ_{Born} (eq. 7). Combining eqs. (2) and (5) - (7),

$$\Delta G_{tr}(ML'^{+}) = \Delta G_{tr}(ML^{+}) = \Delta G_{tr}(L') + \delta_{Born} \qquad (7)$$

we obtain eq. (8). Thus, an almost constant value of $\Delta G_{tr}(ML^{+}) - \Delta G_{tr}(L)$ for a

$$\Delta G_{tr}(ML^{+}) - \Delta G_{tr}(L) = -\ 2.303RT\ \log\ [K_{conf}(S)/K_{conf}(W)] + \delta_{Born} \qquad (8)$$

given complex in different solvents suggests that in these solvents the conformational equilibrium constant has nearly the same value. This condition seems to be fulfilled by cryptates in dipolar aprotic solvents but not in methanol or ethanol. For 18C6 complexes, the above assumptions may not hold completely. The variation of $\Delta G_{tr}(ML^{+}) - \Delta G_{tr}(L)$ is roughly twice as large as for the cryptates. This may be related to the monocyclic structure of the crown ligands. Indeed, Kolthoff and Chantooni[8] have recently shown that for complexes of dibenzo-18C6 there is a linear relationship between $\Delta G_{tr}(ML^{+})$ and $\Delta G_{tr}(M^{+})$, indicating some direct interaction between the solvent and the central metal ion in the complex.

At present we are engaged also in the study of heats of complex formation in order to extend the application of scheme I to ΔH_{tr} and ΔS_{tr} since the thermodynamic parameters of transfer of complexed ions between two media are related to processes such as the extraction of electrolytes from water into non-aqueous media (including phase transfer) by macrocyclic ligands.

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