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FREE ENERGIES AND ENTROPIES OF TRANSFER FROM WATER TO METHANOL OF CATIONS COMPLEXED BY 18-CROWN-6

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Abstract. Free energies and entropies of transfer from water to methanol have been obtained for $[M^+18C6]$ complexes, where $M^+ = Na^+, K^+, Rb^+, Cs^+$, and Ag^+. The variation of $\Delta G_t°$ and $\Delta S_t°$ with the central metal cation is smaller than with the $[M^+222]$ complexes and it is concluded that 18-crown-6 shields the metal cation from the solvent more effectively than crystal structure determinations would suggest.

Crystal structure determinations of alkali metal ion cryptates such as $[M^+222]$, where M = Na, K, Rb, and Cs, and 222 indicates the ligand cryptand 222, show that the ligand surrounds the ion in a three dimensional arrangement (1), whereas in the analogous complexes of these cations with 18-crown-6, the ligand takes up essentially a two dimensional arrangement to leave co-ordination sites exposed above and below the ligand plane (2,3). It might therefore be expected that the solvation of $[M^+222]$ and $[M^+18C6]$ complexes in solution would differ, perhaps substantially, with the latter complexes forming at least two cation-solvent specific interactions. However, it has recently been suggested (4) that cation hydration numbers in $[M^+18C6]$ complexes in water are only 1.3(Na^+), 0(K^+), and 0.9(Cs^+). Our own studies on enthalpies of transfer of $[M^+18C6]$ and $[M^+222]$ complexes (5,6) show that the behaviour of the two different types of complex is quite similar, supporting the view that there is but limited solvation of the M^+ cation in the $[M^+18C6]$ complexes. The corresponding entropies of transfer of the complexes could provide further evidence on the solvation of the two sets of complexes in solution, and therefore we have determined the free energies of transfer of $[M^+18C6]$ complexes from water to methanol, and have combined these with our previous enthalpic data (6) to obtain the required entropies of transfer.

In the Scheme, below , values of the free energy of complex formation in water ΔG°_W, are known (4,7) as are also (5) the transfer values of the simple cations, $\Delta G^\circ_t(M^+)$. We have now determined the free energy of complex formation of the 18-crown-6 complexes in methanol, ΔG°_M, and the

$$\begin{tikzcd}
\mathrm{M^+(aq)} \arrow[d, "\Delta G^\circ_t(\mathrm{M^+})"'] & + & \mathrm{L(aq)} \arrow[r, "\Delta G^\circ_W"] \arrow[d, "\Delta G^\circ_t(\mathrm{L})"'] & {[\mathrm{M^+L}]\ \mathrm{(aq)}} \arrow[d, "\Delta G^\circ_t([\mathrm{M^+L}])"] \\
\mathrm{M^+(MeOH)} & + & \mathrm{L(MeOH)} \arrow[r, "\Delta G^\circ_M"] & {[\mathrm{M^+L}]\ \mathrm{(MeOH)}}
\end{tikzcd}$$

SCHEME

free energy of transfer of the 18-crown-6 ligand itself, $\Delta G^\circ_t(L)$. Thus all the data necessary to complete the cycle are known, and a summary of the calculations leading to the $\Delta G^\circ_t([M^+18C6])$ values is given in Table 1. The found values of the free energy of transfer of the complexed ions do not depend very much on the central cation, and just as for the cryptates, the most negative ΔG°_t value corresponds to transfer of the most stable complex. We can combine the ΔG°_t values with our previous enthalpy results (6) to obtain the entire set of parameters shown in Table 2.

Table I. Determination of free energies of transfer from water to methanol of the complexes $[M^+18C6]$, molar scale in kcal mol^{-1} at 298K.

Cation	ΔG°_M [a]	ΔG°_W [b]	$\Delta G^\circ_t(M^+)$ [c]	$\Delta G^\circ_t([M^+18C6])$ [d]
Na^+	-6.13	-1.09	2.05	-1.56
K^+	-8.32	-2.77	2.35	-1.77
Rb^+	-7.19	-2.13	2.45	-1.18
Cs^+	-6.40	-1.35	2.30	-1.33
Ag^+	-6.44	-2.05	1.80	-1.16

[a] This work. [b] From log K values in ref. (7).

[c] Ref. (5), based on the Ph_4As^+/Ph_4B^- assumption.

[d] Calculated from $\Delta G^\circ_t([M^+18C6]) = \Delta G^\circ_M - \Delta G^\circ_W + \Delta G^\circ_t(M^+) + \Delta G^\circ_t(18C6)$; the latter value is 1.43 kcal mol^{-1} (this work).

There is a considerable degree of similarity between the three sets of values for $[M^+18C6]$ and for $[M^+222]$ complexes. In general, all the complexes of both series behave as typical hydrophobic cations, compare values with those for Pr_4N^+. The values of ΔS°_t, especially, suggest that in water the $[M^+18C6]$ and the $[M^+222]$ complexes undergo hydrophobic hydration, so that on transfer to a nonaqueous solvent there is a substantial loss of solvation and gain in entropy (8). Furthermore, the behaviour of the $[M^+18C6]$ and $[M^+222]$ complexes is similar enough to suggest that interaction of the central metal atom with the solvent must be at least semi-quantitatively the same in the two sets of complexes. The effect of 18-crown-6 in modifying the properties of the M^+ cations in solutions is thus much nearer that of cryptand 222 than would be expected from the complex crystal structures.

Table 2. Thermodynamics of transfer from water to methanol of complexed and simple ions, and ligands, molar scale at 298 K[a].

Ion	ΔG°_t	ΔH°_t	ΔS°_t
$[Na^+18C6]$	-1.56	3.3	16
$[K^+18C6]$	-1.77	2.3	14
$[Rb^+18C6]$	-1.18	1.5	9
$[Cs^+18C6]$	-1.33	1.8	10
$[Ag^+18C6]$	-1.16	1.1	8
18C6	1.43	13.6	41
$[Na^+222]$	-2.23	5.5	26
$[K^+222]$	-3.53	4.1	26
$[Rb^+222]$	-2.89	4.1	23
$[Cs^+222]$	-0.60	3.9	15
$[Ag^+222]$	-0.61	1.2	6
222	1.13	13.9	43
Na^+	2.05	-4.9	-23
K^+	2.35	-4.5	-23
Rb^+	2.45	-3.7	-21
Cs^+	2.30	-3.3	-19
Ag^+	1.80	-5.0	-23
Me_4N^+	1.70	0.3	-5
Et_4N^+	0.25	2.2	7
Pr_4N^+	-2.05	3.8	20

[a] ΔG°_t and ΔH°_t in kcal mol^{-1}, and ΔS°_t in cal K^{-1} mol^{-1}, using the Ph_4As^+/Ph_4B^- assumption. Values of $\Delta H^\circ_t([M^+18C6])$ from ref. (6), and all values for $[M^+222]$ and for the simple ions from ref. (5).

Also given in Table 2 are transfer values for the two ligands, 18-crown-6 and cryptand 222, themselves; the two sets of values are surprisingly close to each other in all three thermodynamic parameters, G, H, and S. The very large entropies of transfer are probably due to large hydrogen-bond interactions between water and the ligands. Other solutes that can interact in this way also give rise to positive ΔS°_t values, for example the entropy of transfer of triethylamine from water to methanol is +26 cal K^{-1} mol^{-1} on the molar scale (8).

It should be noted that the transfer values for the complexed ions are not simply intermediate between those for the ligand and those for the uncomplexed ion. Thus whereas ΔG°_t is positive for the ligands and positive for the five uncomplexed ions considered, the ΔG°_t values for the complexed ions are all negative in value.

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References

1. B. Metz, D. Moras, and R. Weiss, J. Chem. Soc. Chem. Comm., 217 (1970); J. Chem. Soc. Chem. Comm., 444 (1971); Acta Cryst., B29, 388 (1973).
2. P. Seiller, M. Dobler, and J. D. Dunitz, Acta Cryst., B30, 2744 (1974); M. Dobler and R. P. Phizackerley, Acta. Cryst., B30, 2746, 2748 (1974).
3. D. L. Ward, H. S. Brown, and L. R. Sousa, Acta Cryst., B33, 3537 (1977).
4. H. Hoiland, J. A. Ringseth, and T. S. Brun, J. Solution Chem., 8, 779 (1979).
5. M. H. Abraham, A. F. Danil de Namor, and R. A. Schulz, J. Chem. Soc. Faraday Trans. I, 76, 869 (1980).
6. M. H. Abraham, A. F. Danil de Namor, H. C. Ling, and R. A. Schulz, Tetrahedron Letters 21, 961 (1980).
7. R. M. Izatt, R. E. Terry, B. L. Haymore, L. D. Hansen, N. K. Dailey, A. G. Avondet, and J. J. Christensen, J. Amer. Chem. Soc., 98, 7620 (1976).
8. M. H. Abraham, J. Chem. Soc. Faraday Trans. I, 69, 1375 (1973).
9. M. H. Abraham and A. Nazehzadeh, J. Chem. Thermodynamics, 13, 549 (1981).

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