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ENTHALPIES OF TRANSFER FROM WATER TO METHANOL OF CATIONS COMPLEXED WITH 18-CROWN-6

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Abstract. Enthalpies of transfer from water to methanol have been obtained via a thermochemical cycle for the [M^+18C6] complexes where $M^+ = Na^+$, K^+, Rb^+, Cs^+, and Ag^+. Variation of the transfer enthalpy with M^+ is small.

Enthalpies of transfer, ΔH°_t, from water to methanol have already been obtained (1) for cations complexed with cryptand 222 both by direct calorimetric measurements on salts of the cryptate complexes, and via the thermochemical cycle (Scheme, L = cryptand 222). In the cycle, the complexed cation is represented as [M^+L], and ΔH°_W and ΔH°_M are the respective enthalpies of complex formation in water and methanol.

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

SCHEME

Even though the cryptand 222 completely surrounds the complexed metal cation (2), our results indicated (1) that the ΔH°_t(M^+222]) values varied considerably with the central metal cation, and therefore that some interaction involving the complexed cation and the surrounding solvent must take place. Unlike the cryptands, the 18-crown-6 ethers do not completely encapsulate the complexed metal cation, judging from X-ray structural determinations (3), and so there would appear to be more scope for cation-solvent interactions in solution. It might thus be expected that $\Delta H^\circ_t([M^+L])$ values, where L is a crown ether, would vary with M^+ even more than the variation in $\Delta H^\circ_t([M^+222])$ values. Since it is not practicable to obtain the ΔH°_t values for crown ether electrolytes directly, we have used the thermochemical cycle (Scheme, L = 18C6) to obtain ΔH°_t values for cations complexed by 18-crown-6. Values of ΔH°_W had already been determined by Izatt and Christensen (4), the necessary $\Delta H^\circ_t(M^+)$ values were known (1, 5, 6), and it therefore remained for us to determine the ΔH°_M values and $\Delta H^\circ_t(18C6)$ by solution calorimetry.

Table 1. Determination of enthalpies of transfer from water to methanol of the crown ether complexes $[M^+18C6]$, in kcal mol^{-1} at 298K

Cation	ΔH°_M [a]	ΔH°_W [b]	$\Delta H^\circ_t(M^+)$ [c]	$\Delta H^\circ_t([M^+18C6])$ [d]
Na^+	-7.7	-2.3	-4.9	3.3
K^+	-13.0	-6.2	-4.5	2.3
Rb^+	-12.2	-3.8	-3.7	1.5
Cs^+	-12.3	-3.8	-3.3	1.8
Ag^+	-9.7	-2.2	-5.0	1.1

[a] This work, each value is the average of at least 12 experiments, standard deviations in ΔH°_M average 0.3 kcal mol^{-1}.

[b] Ref. (4), the given standard deviations in ΔH°_W average only 0.08 kcal mol^{-1}.

[c] Ref. (5) and ref. (6), based on the Ph_4As^+/Ph_4B^- assumption.

[d] Calculated from $\Delta H^\circ_t([M^+18C6]) = \Delta H^\circ_M - \Delta H^\circ_W + \Delta H^\circ_t(M^+) + \Delta H^\circ_t(18C6)$; the latter value is 13.6 kcal mol^{-1}, with a standard deviation of 0.2 kcal mol^{-1}. If the standard deviation in the $\Delta H^\circ_t(M^+)$ values is taken as 0.2 kcal mol^{-1}, the calculated final error in the $\Delta H^\circ_t([M^+18C6])$ values is 0.4 kcal mol^{-1}.

Results, together with the errors associated with the various measurements, are in Table 1. We estimate that the overall error in $\Delta H^\circ_t([M^+18C6])$ is about 0.4 kcal mol^{-1}. This seems a realistic estimate, because in the related cycle (Scheme: L = 222) values of $\Delta H^\circ_t([M^+222])$ for $M^+ = Na^+$ and K^+ agreed with directly determined values to within 0.4 kcal mol^{-1} and 0.2 kcal mol^{-1} respectively (1).

Quite surprisingly, the $\Delta H^\circ_t([M^+18C6])$ values, Table 1, do not vary very much with variation in the central metal cation, M^+. Amongst the alkali metal cations, Na^+ to Cs^+, the total variation is only 1.5 kcal mol^{-1}, and even including the ion $[Ag^+18C6]$ the variation in ΔH°_t with M^+ is but 2.2 kcal mol^{-1}. Since the present results are the first enthalpies of transfer of crown ether cations ever reported, there are no similar data available for comparison. However, the $\Delta H^\circ_t([M^+18C6])$ values may be compared with the corresponding enthalpies of transfer of the cryptate complexes, $[M^+222]$, values of which we have recently obtained (1); details are in Table 2. For a given cation, the ΔH°_t value for the 18-crown-6 complex is not so very different from that for the cryptand 222 complex. The variation of $\Delta H^\circ_t([M^+18C6])$ with variation of M^+ is nearly the same as is the variation of $\Delta H^\circ_t([M^+222])$ with M^+, being about 2.5 kcal mol^{-1} for the Na^+ to Cs^+ series in both cases. It seems as though the enthalpies of transfer of the complexed cations do not just depend on whether the complexed cations have sites available for co-ordination of solvent molecules to the central metal ion, but on other more subtle features such as (possibly) the conformation of the complexed ligand in solution and the interaction of solvent molecules with the complexed ligand. The enthalpies of transfer of the ligands themselves are very large, being 13.6 kcal mol^{-1} for 18-crown-6 and 13.9 kcal mol^{-1} for cryptand 222, so that there are major enthalpic effects associated with the ligand/water and ligand/methanol interactions.

Table 2. Enthalpies of transfer from water to methanol of some simple and complexed ions, in kcal mol^{-1}

Na^+	-4.9[a]	$[Na^+18C6]$	3.3[a]	$[Na^+222]$	5.5[b]	Me_4N^+	0.3[c]
K^+	-4.5	$[K^+18C6]$	2.3	$[K^+222]$	4.1	Et_4N^+	2.2
Rb^+	-3.7	$[Rb^+18C6]$	1.5	$[Kb^+222]$	4.1	Pr_4N^+	3.8
Cs^+	-3.3	$[Cs^+18C6]$	1.8	$[Cs^+222]$	3.9	Bu_4N^+	4.9
Ag^+	-5.0	$[Ag^+18C6]$	1.1	$[Ag^+222]$	1.2	Ph_4As^+	-0.4

[a] Values from Table 1,

[b] From ref. (1).

[c] From ref. (6).

Inspection of Table 2 shows also that the complexed cations with 18-crown-6 or with cryptand 222 all behave as hydrophobic ions (5). The ΔH°_t values for the complexed cations, unlike those for the simple uncomplexed cations, are all positive; compare the values with those for the hydrophobic tetra-alkylammonium ions, Table 2.

Finally, we point out that our results cannot be affected by any ion-pairing in methanol between the $[M^+18C6]$ cation and the counter-anion, usually I^- except for studies with the silver complex. The ΔH°_M values on which our results depend were determined at low concentrations of electrolyte typically $1x10^{-3}$ to $2x10^{-4}$ mol dm^{-3}, and have been extrapolated to zero electrolyte concentration.

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