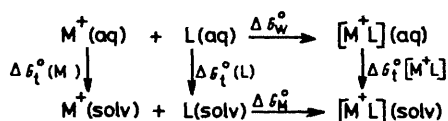


Thermodynamics of 222 Cryptates and the Selective Transfer of Ions in the Water–Methanol System

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Summary Free energies of transfer from water to methanol have been obtained for 222 cryptand and 222 cryptates, and used to calculate partition coefficients for the transfer of cations from the uncomplexed form in water to the cryptated form in methanol; the 222 cryptand alters the cation transfer selectivity by factors of up to 10^7 by comparison with transfer of uncomplexed cation in water to uncomplexed cation in methanol.

CRYPTATES are a novel class of electrolytes, derived from cryptand ligands, whose thermodynamic properties are useful in discussions of cation transfer and of transport by cation carriers. We construct a thermodynamic cycle (Scheme) (*cf.* ref. 1) in which L represents a neutral cation



SCHEME

complexing agent, in this work cryptand 222, and M+L the complexed cation; ΔG_w° and ΔG_M° are the complex formation constants in water and in another medium, the latter being methanol in the present case. We have determined the free energies of transfer from water to methanol, $\Delta G_i^\circ(222)$ and $\Delta G_i^\circ([\text{M}^+222] + \text{ClO}_4^-)$, we know² $\Delta G_i^\circ(\text{M}^+)$ and ³ ΔG_w° and we can then deduce values, in kcal mol⁻¹, † for ΔG_M° of -10.3 (obs. -10.9^4 and -10.8^5) for $\text{M}^+ = \text{Na}^+$ and -14.7 (obs. -14.2^4 and -14.7^5) for $\text{M}^+ = \text{K}^+$.

The cycle is most useful, however, in the determination of values of $\Delta G_i^\circ([\text{M}^+222])$, and details are in Table 1.

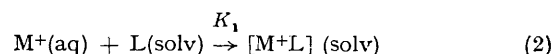
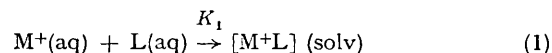
† 1 cal = 4.184 J.

TABLE 1. Calculation of $\Delta G_i^\circ([\text{M}^+222])$ for transfer from water to methanol, molar scale, in kcal mol⁻¹ at 298 K.

M ⁺	ΔG_w° ^a	ΔG_M° ^b	$\Delta G_i^\circ(\text{M}^+)$ ^c	$\Delta G_i^\circ([\text{M}^+222])$ ^d
Li ⁺	-1.7 ^e	-3.5	0.9	0.2
Na ⁺	-5.3	-10.9	2.1	2.4
K ⁺	-7.4	-14.2 ^f	2.4	-3.3
Rb ⁺	-5.9	-12.2	2.5	-2.7
Cs ⁺	-2.0 ^e	-6.0	2.3	-0.6
Tl ⁺	-8.6	-13.8 ^g	1.0	-3.1
Ag ⁺	-13.1 ^h	-16.6 ^h	1.8	-0.6

^a Ref. 3 unless shown otherwise. ^b Ref. 4 unless shown otherwise. ^c Ref. 2, using the Ph₄As⁺/Ph₄B⁻ assumption. ^d Calculated using the values in the previous three columns, together with $\Delta G_i^\circ(222) = 1.1$ kcal mol⁻¹, this work. ^e This work, using a stepwise calorimetric method. Experiments were carried out in presence of OH⁻ to suppress hydrolysis of the cryptand. ^f If the alternative (ref. 5) value of -14.7 kcal mol⁻¹ is used, then $\Delta G_i^\circ([\text{K}^+222])$ is -4.0 kcal mol⁻¹. ^g Ref. 5. ^h From ref. 7.

The error in the final values of $\Delta G_i^\circ([\text{M}^+222])$ is cumulative, and taking the errors in ΔG_w° , ΔG_M° , and $\Delta G_i^\circ(\text{M}^+)$ as *ca.* 0.15 kcal mol⁻¹ (corresponding to an error of 0.1 units in log *K* for the stability constants), the error in $\Delta G_i^\circ([\text{M}^+222])$ will be *ca.* 0.3 kcal mol⁻¹. With the calculated values of $\Delta G_i^\circ([\text{M}^+222])$ (Table 1) we can then obtain ΔG° values and hence equilibrium constants, or partition coefficients, for the extraction processes (1) and (2); these are in Table 2, together with the corresponding partition



coefficients for the uncomplexed ions.

TABLE 2. Partition coefficients for the water \rightarrow methanol system, molar scale, at 298 K.

M ⁺	K(M ⁺) ^a	K ₁	K ₂
Li ⁺	0.238	1.3 \times 10 ¹	8.7 \times 10 ¹
Na ⁺	0.031	4.4 \times 10 ⁵	3.0 \times 10 ⁶
K ⁺	0.019	7.0 \times 10 ⁷	4.7 \times 10 ⁸
Rb ⁺	0.016	2.0 \times 10 ⁶	1.3 \times 10 ⁷
Cs ⁺	0.021	8.1 \times 10 ¹	5.4 \times 10 ²
Tl ⁺	0.201	3.8 \times 10 ⁸	2.6 \times 10 ⁹
Ag ⁺	0.048	1.1 \times 10 ¹⁰	7.4 \times 10 ¹⁰

^a For the equilibrium $M^+(aq) \rightleftharpoons M^+$ (methanol), based on the Ph_4As^+/Ph_4B^- assumption (ref. 2).

Our results show very clearly that cryptand 222 does *not* shield the various cations from the influence of the solvent. On the contrary, there is discrimination between the complexed cations in terms of transfer from water to methanol. We show also that cryptand 222 will selectively transfer ions from water to methanol. Even for a pair of ions such as Na⁺ and K⁺, the selectivity is very large; thus $K(K^+)/K(Na^+)$ for the uncomplexed cations is 0.6 whereas $K_1(K^+)/K_1(Na^+)$ is no less than 1.6×10^2 (and similarly for the K_2 ratio). The largest enhancements of

selectivity, however, involve factors of $>10^7$, for example $K(K^+)/K(Li^+)$ is 0.08 and $K_1(K^+)/K_1(Li^+)$ is 5.4×10^6 , an enhancement of 6.7×10^7 in favour of the potassium ion.

It has been suggested^{6,7} that cryptates might be useful in providing new extrathermodynamic assumptions for the estimation of the thermodynamics of transfer of single ions. Schneider *et al.*⁷ point out two possible extreme cases (L = cryptand): (a) $\Delta G_i^0(ML^+) = \Delta G_i^0(L)$, $\Delta H_i^0(ML^+) = \Delta H_i^0(L)$; (b) $\Delta G_i^0(ML^+) = 0$, $\Delta H_i^0(ML^+) = 0$. We had already shown¹ that for the water-methanol system neither (a) nor (b) is valid in terms of enthalpy, and the present results show that for the same solvent system neither (a) nor (b) is generally valid in terms of free energy. Whether or not (a) or (b) applies to transfers involving dipolar aprotic solvents⁷ can only be determined by experiment; meanwhile we think it unwise to use these cryptate assumptions in order to deduce single ion enthalpies or free energies of transfer.

E.C.V. thanks the University of Zaragoza (Spain) for financial support.

(Received, 28th December 1978; Com. 1380.)

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