electron energy.[23] An analyzer voltage scan was used, and a mixture of xenon and argon was used for internal calibration of the energy scale.

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Registry No. 1,10-$C_2B_8H_{10}$, 23653-23-8; 1,12-$C_2B_{10}H_{12}$, 20644-12-6; 1-SB_9H_9, 41646-56-4; 1-$SB_{11}H_{11}$, 56464-75-6; 6-SB_9H_{11}, 12447-77-7; 10-CH_3-1-SB_9H_8, 64173-76-8; 10-Br-1-SB_9H_8, 58568-92-6; 6-Br-1-SB_9H_8, 58575-43-2.

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[23] T. P. Fehlner, *Inorg. Chem.*, **14**, 934 (1975).

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An Experimental Test of Cryptate Assumptions in the Assignment of Single-Ion Enthalpies of Transfer

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Enthalpies of transfer of cryptand 222 between six solvents have been obtained from calorimetric measurements on heats of solution of the cryptand. Combination of these measurements with known enthalpies of complexation and known enthalpies of transfer of cations enables the corresponding enthalpies of transfer of the cryptate cations, $[M^+222]$, to be obtained. It is shown that for transfers between two given solvents values of $\Delta H_t^\circ([M^+222])$ depend on the complexed metal, M^+, and hence that single-ion assumptions such as (a) $\Delta H_t^\circ([M^+222]) = \Delta H_t^\circ(222)$ and (b) $\Delta H_t^\circ([M^+222]) = 0$ are not generally valid.

Introduction

In the first paper that dealt with the thermodynamic parameters for transfer of cryptate electrolytes between solvents, Villermaux and Delpuech[1] showed that the free energy of transfer of $([Na^+221]X^-)$ between water and aqueous methanol was the same as the free energy of transfer of X^- ($X^- = Cl^-, N_3^-$), when the latter was expressed by using the Ph_4As^+/Ph_4B^- assumption. Villermaux and Delpuech[1] tentatively suggested that their results on the water/methanol system could open the way to a new method for the assignment of single-ion free energies of transfer. The implied extra thermodynamic assumption in the above work is that $\Delta G_t^\circ([Na^+221]) = 0$. We use the symbol $[Na^+221]$ to indicate the cryptate[2] formed between Na^+ and the cryptand 221; cryptates formed from metal ions and cryptand 222 are similarly denoted as $[M^+222]$, with the general symbol $[M^+L]$ used for cryptates between any univalent metal ion and any cryptand.

As we have previously shown,[3] thermodynamic parameters for the transfer of cryptates from a reference solvent, A, to another solvent, B, can usefully be discussed in terms of the cycle, shown for the enthalpy function in eq 1. Here, ΔH_A°

$$\begin{tikzcd}
\mathrm{M}^+ \arrow[d, "\Delta H_t^\circ(\mathrm{M}^+)"'] & + & \mathrm{L} \arrow[d, "\Delta H_t^\circ(\mathrm{L})"] \arrow[r, "\Delta H_A^\circ"] & {[\mathrm{M}^+\mathrm{L}]} \arrow[d, "\Delta H_t^\circ([\mathrm{M}^+\mathrm{L}])"] \\
\mathrm{M}^+ & + & \mathrm{L} \arrow[r, "\Delta H_B^\circ"'] & {[\mathrm{M}^+\mathrm{L}]}
\end{tikzcd} \qquad (1)$$

and ΔH_B° are the enthalpies of complexing of M^+ with L in solvents A and B, respectively, and ΔH_t° represents the enthalpy of transfer of a species from solvent A to solvent B. Thus if ΔH_A° and ΔH_B° are known from studies on the complexation in solvents A and B and if $\Delta H_t^\circ(L)$ is obtained by experiments on heats of solution, then knowing $\Delta H_t^\circ(M^+)$, it is possible to obtain experimentally the value of $\Delta H_t^\circ([M^+L])$ from the cycle:

$$\Delta H_t^\circ([M^+L]) = \Delta H_B^\circ - \Delta H_A^\circ + \Delta H_t^\circ(M^+) + \Delta H_t^\circ(L)$$

A similar cycle, of course, can be constructed for any other thermodynamic parameter. Using the cycle, and also using experimental results that yield directly $\Delta H_t^\circ([M^+L])$ from heats of solution of salts $([M^+L]X^-)$ in solvents A and B, we were able[3] to obtain $\Delta H_t^\circ([M^+222])$ values for transfer from water to methanol. We found that $\Delta H_t^\circ([M^+222]) \neq 0$ when values of $\Delta H_t^\circ(M^+)$ were chosen by using the Ph_4As^+/Ph_4B^- assumption and hence that such an extra thermodynamic assumption as $\Delta H_t^\circ([M^+222]) = 0$ could not generally hold for enthalpies of transfer in the water/methanol system.

In spite of these results, two sets of workers[4,5] have recently advocated "cryptate assumptions" in order to obtain single-ion free energies and single-ion enthalpies of transfer between various solvents. Following Schneider and co-workers,[4] we state these assumptions as (a) and (b). As with all extra

$$\Delta G_t^\circ([M^+L]) = \Delta G_t^\circ(L) \qquad \text{(a)}$$
$$\Delta H_t^\circ([M^+L]) = \Delta H_t^\circ(L)$$
$$\Delta G_t^\circ([M^+L]) = 0 \quad \Delta H_t^\circ([M^+L]) = 0 \qquad \text{(b)}$$

thermodynamic assumptions involving single-ions, neither (a) nor (b) can directly be proved or disproved; all that can be done is to determine whether or not one or the other assumption is compatible with some other extrathermodynamic assumption such as the Ph_4As^+/Ph_4B^- assumption. However, both (a) and (b) require that for a given cryptand, L, the identity (2) must hold for different metal ions M_1^+ and M_2^+.

$$\begin{aligned}\Delta G_t^\circ([M_1^+L]) &= \Delta G_t^\circ([M_2^+L]) \\ \Delta H_t^\circ([M_1^+L]) &= \Delta H_t^\circ([M_2^+L])\end{aligned} \qquad (2)$$

It should be noted that assumptions a or b and the identity (2) could be valid in terms of *G* but not in terms of *H* or vice

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[1] Villermaux, S.; Delpuech, J.-J. *J. Chem. Soc., Chem. Commun.* **1975**, 478.

[2] Lehn, J. M. *Struct. Bonding (Berlin)* **1973**, *16*, 1; *Acc. Chem. Res.* **1978**, *11*, 49.

[3] Abraham, M. H.; Danil de Namor, A. F.; Lee, W. H. *J. Chem. Soc., Chem. Commun.* **1977**, 893.

[4] Gutknecht, J.; Schneider, H.; Stroka, J. *Inorg. Chem.* **1978**, *17*, 3326.

[5] Lejaille, M.-F.; Livertoux, M.-H.; Guidon, C.; Bessière, J. *Bull. Soc. Chim. Fr.* **1978**, 1-373.

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Table I. Thermodynamic Parameters for the Transfer of Cryptates, $[M^+222]$, from Water to Methanol at 298 K[a]

species	ΔG_t° [b]/ kcal mol^{-1}	ΔH_t° [c]/ kcal mol^{-1}	ΔS_t°/ cal K^{-1} mol^{-1}
$[Na^+222]$	−2.2	5.5	26
$[K^+222]$	−3.5	4.1	26
$[Ag^+222]$	−0.6	1.2	6
222	1.1	13.9	43

[a] All values are on the molar scale and are based on the Ph_4As^+/Ph_4B^- assumption for single ions. [b] Reference 7. [c] Reference 3.

versa. Now eq 2 can be tested independently of any particular single-ion assumption, and if this identity fails to hold, it can be deduced rigorously that neither (a) nor (b) is generally valid.

It is the purpose of this paper to determine values of $\Delta H_t^\circ([M^+222])$ via the thermodynamic cycle, eq 1, for different metal cations and hence to test the required identity, eq 2; at the same time we can also compare results of using the assumptions (a) and (b) with those from the assumption that $\Delta H_t^\circ(Ph_4As^+) = \Delta H_t^\circ(Ph_4B^-)$.

Experimental Section

Cryptand 222 (from Merck) was used without further purification. Dimethyl sulfoxide (Me_2SO) and dimethylformamide (DMF), both from BDH, were allowed to stand over molecular sieve 4A and then vacuum distilled. Propylene carbonate (PC), from BDH, was similarly treated and then vacuum distilled twice. Acetonitrile (MeCN), from BDH, was stored over P_2O_5, decanted from the discolored residue, and stored over fresh P_2O_5. This was repeated several times, until the residual P_2O_5 was not discolored. The acetonitrile was then distilled from fresh P_2O_5. After the final distillation, the solvents were transferred to the calorimeter vessel under a stream of dry nitrogen, the final distillation being carried out immediately prior to use.

Enthalpies of solution of cryptand 222 were determined by using the apparatus described before;[6] thermochemical functions are expressed in terms of the defined calorie (4.184 J) and refer to the isothermal process at 298.15 K. In all cases, the observed enthalpies of solution were corrected for the (very small) heat of ampoule breaking. For solution of the cryptand 222 in water,[3] experiments were carried out in the presence of OH^- (as $[Na^+222]OH^-$ or $[K^+222]OH^-$) in order to suppress hydrolysis of the cryptand.

Results and Discussion

Before discussing the present results, we give in Table I our results for the water to methanol transfer obtained previously in terms of free energy[7] and enthalpy,[3] and we also now calculate the corresponding entropies of transfer of the ions $[M^+222]$. All the cation values have been assigned by using the Ph_4As^+/Ph_4B^- assumption. Values of $\Delta G_t^\circ(M^+)$ were taken from our own compilation,[8] and values of $\Delta H_t^\circ(M^+)$, from Friedman and Krishnan's recent survey.[9] Schneider and co-workers[4] used transfer parameters for M^+ given by Cox and Parker and co-workers,[10,11] but we prefer the updated values of ΔH_t° given by Friedman and Krishnan.[9] It is clear from the results in Table I that for the transfer of cryptates between water and methanol, the identity, eq 2, is not obeyed and hence that in general for this solvent system neither assumption a nor assumption b will be valid. Furthermore, if assumption a is compared with the Ph_4As^+/Ph_4B^- assumption used to obtain the cation values in Table I, it is evident that, especially for the ΔH_t° and ΔS_t° functions, the two assumptions give rise to quite different values. Assumption b is no better, and we can conclude that for the water to methanol transfer, the cryptate assumptions (a) and (b) cannot in general be valid. It may happen, by chance, that $\Delta G_t^\circ([M^+L]) = 0$ as is apparently the case for $[Na^+221]$ in the experiments of Villermaux and Delpuech,[1] but it is clearly unsound to use such an assumption without experimental evidence. It should be noted that in terms of both G and H, the divergences from the identity (2), shown in Table I, are well outside experimental error. For the free energies of transfer of $[Na^+222]$ and $[K^+222]$, two independent experimental methods, a direct determination through solubility measurements on cryptate salts and the indirect cycle determination, yield ΔG_t° values that differ by 0.4 kcal mol^{-1} for $[Na^+222]$ and by 0.3 kcal mol^{-1} for $[K^+222]$. In the case of the corresponding ΔH_t° values, a direct determination from enthalpies of solution of cryptate salts and the indirect cycle determination differ by 0.4 kcal mol^{-1} for $[Na^+222]$ and by 0.2 kcal mol^{-1} for $[K^+222]$. These differences, around 0.2–0.4 kcal mol^{-1}, can be taken as a measure of the overall random experimental error in the ΔG_t° and ΔH_t° values for transfer of the cryptates from water to methanol.

Table II. Calculation of $\Delta H_t^\circ([M^+222])$ Using the Thermodynamic Cycle, Eq 1 (Values in kcal mol^{-1} at 298 K)

transfer from water to	M^+	ΔH_B° [a]	ΔH_A° [b]	$\Delta H_t^\circ(M^+)$[c]	$\Delta H_t^\circ(222)$[d]	$\Delta H_t^\circ([M^+222])$
DMF	K^+	−12.67	−11.56	−9.44	14.17	3.62
	Ag^+	−13.48	−12.81	−9.87	14.17	3.63
Me_2SO	K^+	−14.53	−11.56	−8.34	14.42	3.11
	Ag^+	−11.42	−12.81	−12.92	14.42	2.89
PC	K^+	−16.54	−11.56	−5.24	13.60	3.38
	Ag^+	−23.78	−12.81	−2.30[e]	13.60	0.33
MeCN	K^+	−17.71	−11.56	−5.53	10.72	−0.96
	Ag^+	−13.03	−12.81	−13.21	10.72	−2.71

[a] Values taken from ref 4. [b] Enthalpies of complexing in water; value for K^+ from ref 3 and value for Ag^+ from: Anderegg, G. *Helv. Chim. Acta* 1975, *58*, 1218. [c] Based on the Ph_4As^+/Ph_4B^- assumption, from ref 9. [d] This work. The standard deviations in the observed $\Delta H_s^\circ(222)$ values are around 0.07 kcal mol^{-1} leading to an estimated error of about 0.10 kcal mol^{-1} in the given $\Delta H_t^\circ(222)$ values. [e] From ref 11.

Schneider and co-workers[4] expressly excluded transfers to methanol in their suggestion that the cryptate assumptions (a) and (b) were useful for single-ion estimations, and they restricted their conclusions to transfers from water to aprotic solvents. In Table II are our calculated values of $\Delta H_t^\circ([K^+222])$ and $\Delta H_t^\circ([Ag^+222])$, since the two cations mostly considered by Schneider and co-workers[4] were K^+ and Ag^+. For transfer from water to the four aprotic solvents in Table II, the identity eq 2 holds in the case of $[K^+222]$ and $[Ag^+222]$ for transfer to DMF and Me_2SO, but for transfer to PC and MeCN we have that $\Delta H_t^\circ([K^+222]) \neq \Delta H_t^\circ([Ag^+222])$ and we can conclude that for the two latter solvents neither assumption a nor assumption b can generally be valid. We can compare hypothesis a, $\Delta H_t^\circ([M^+222]) = \Delta H_t^\circ(222)$, with the values obtained by using the Ph_4As^+/Ph_4B^- assumption; details are in Table III where both water and Me_2SO are used as the reference solvents. If water is the reference solvent, then for transfer to every solvent tested, the hypothesis that $\Delta H_t^\circ([M^+222]) = \Delta H_t^\circ(222)$ would yield values for $\Delta H_t^\circ([M^+222])$ that differ by some 10–14 kcal mol^{-1} from those in Table III obtained by using the Ph_4As^+/Ph_4B^- assumption. When Me_2SO is taken as the reference solvent, then for transfer to DMF it turns out, as required by assumption a, that $\Delta H_t^\circ(222) \simeq \Delta H_t^\circ([K^+222]) \simeq \Delta H_t^\circ([Ag^+222])$; for transfer to PC and MeCN there are discrepancies of about 2 kcal mol^{-1}, however, so that even for transfers between two aprotic solvents as-

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(6) Abraham, M. H.; Irving, R. J.; Johnston, G. F. *J. Chem. Soc. A* **1970**, 199.

(7) Abraham, M. H.; Contreras Viguria, E.; Danil de Namor, A. F. *J. Chem. Soc., Chem. Commun.* **1979**, 374.

(8) Abraham, M. H.; Danil de Namor, A. F. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 2101.

(9) Friedman, H. L.; Krishnan, C. V. In "Solute-Solvent Interactions"; Coetzee, J. F., Ritchie, C. D., Eds.; Marcel Dekker: New York, 1976; Vol. 2.

(10) Cox, B. G. *Annu. Rep. Prog. Chem., Sect. A* **1973**, *70*, 249.

(11) Cox, B. G.; Hedwig, G. R.; Parker, A. J.; Watts, D. W. *Aust. J. Chem.* **1974**, *27*, 477.

Table III. Test of Hypothesis a, $\Delta H_t^\circ([M^+222]) = \Delta H_t^\circ(222)$, and Hypothesis b, $\Delta H_t^\circ([M^+222]) = 0$

	$\Delta H_t^\circ([M^+222])$/kcal mol^{-1}			
	calcd		obsd[a]	
transfer	(a)	(b)	$[K^+222]$	$[Ag^+222]$
water to				
MeOH	13.9	0.0	4.1	1.2
DMF	14.2	0.0	3.6	3.6
Me_2SO	14.4	0.0	3.1	2.9
PC	13.6	0.0	3.4	0.3
MeCN	10.7	0.0	−1.0	−2.7
Me_2SO to				
water	−14.4	0.0	−3.1	−2.9
MeOH	−0.5	0.0	1.0	−1.7
DMF	−0.2	0.0	0.5	0.7
PC	−0.8	0.0	0.3	−2.6
MeCN	−3.7	0.0	−4.1	−5.6

[a] Using the single-ion Ph_4As^+/Ph_4B^- assumption.

sumption a does not agree very well with the Ph_4As^+/Ph_4B^- assumption. In Table III we also test assumption b that $\Delta H_t^\circ([M^+222]) = 0$. Without detailing the arguments again, it is evident that this assumption yields values that are also quite far from those calculated on the Ph_4As^+/Ph_4B^- assumption.

In terms of enthalpies, it therefore seems that the cryptate assumptions (a) and (b) will yield single-ion values that are not the same as those obtained by using the Ph_4As^+/Ph_4B^- assumption. This result by itself does not disprove assumptions a or b but merely indicates that these assumptions are not compatible with another extrathermodynamic assumption. However, if either assumption a or assumption b is applied to the determination of single-ion ΔH_t° values, unless the identity (2) is obeyed, different numerical values will be assigned depending on the actual metal cation used. Thus, as pointed out in the Introduction, if assumptions a and b are to be generally valid, $\Delta H_t^\circ([M_1^+222])$ must equal $\Delta H_t^\circ([M_2^+222])$. As can be seen from Tables II and III, we show that $\Delta H_t^\circ([K^+222])$ may or may not be the same as $\Delta H_t^\circ([Ag^+222])$, depending on the particular solvents studied. The possibility that for any two given cryptates $\Delta H_t^\circ([M_1^+222]) \neq \Delta H_t^\circ([M_2^+222])$ must surely be taken into account in any future application of cryptate assumptions to the assignment of single-ion enthalpies of transfer.

We think that our most important finding is that, generally, values of $\Delta H_t^\circ([M^+222])$ depend on the metal cation, M^+, embedded in the cryptand. Thus the cryptand does not shield the cation from the solvent, and any cryptate hypothesis that depends on the explicit or implicit assumption that $\Delta H_t^\circ([M_1^+L]) = \Delta H_t^\circ([M_2^+L])$ is not likely to be generally valid. The same conclusions can be drawn in terms of free energy for the water to methanol transfer; at the moment we are investigating whether or not cryptate hypotheses may be valid for transfers between other solvents, in terms of free energy.

Registry No. Na^+222, 32611-94-2; K^+222, 32611-95-3; Ag^+222, 57692-62-3; 222, 23978-09-8.

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Dynamics of Boron Acid Complexation Reactions. Formation of 1:1 Boron Acid–Ligand Complexes

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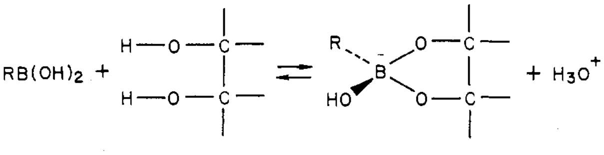
Boron acids form 1:1 complexes with a variety of bidentate chelating ligands according to the equation $RB(OH)_2 + H_2L \rightleftarrows RB(OH)L^- + H_3O^+$. Four boron acids ($m$-$NO_2PhB(OH)_2$, $PhB(OH)_2$, $B(OH)_3$, $CH_3B(OH)_2$) have been studied. Ten different ligands have been examined. Stability constants for the reactions were determined by pH titration methods, and the kinetics were done by temperature jump at $\mu = 0.1$ M (KNO_3) and 25 °C. The stability constants are affected by the acidities of both the boron acid and ligand. The stability constants increase as the ligand and boron acid become more acidic. Various kinetic pathways are possible. Trigonal boron acids, $RB(OH)_2$, can react with either fully protonated ligands or ligand anions. The pattern of reactivity is different for each case. The rate constants for the reactions of fully protonated ligands vary systematically with both ligand acidity and boron substituent. This is discussed in terms of a mechanism which involves proton transfer. The ligand anions do not display a simple correlation with any single ligand parameter, and their reactivities are discussed in terms of a number of ligand-specific effects. Borate anions, $RB(OH)_3^-$, react with high rate constants with fully protonated ligands and with somewhat lower rate constants with ligand anions. Possible reasons for this are discussed.

Trigonal boron acids, $RB(OH)_2$, form anionic four-coordinate complexes with bidentate chelating ligands according to eq 1. Ligands which participate in this type of reaction



(1)

include polyols,[1,2] o-diphenols,[1-3] o-hydroxy acids,[4] α-hydroxycarboxylic acids,[5-7] and dicarboxylic acids.[8-10] For a particular boron acid, the stability constants for reactions with a series of ligands show a general increase as the acidity (pK_{a1}) of the ligand increases. We recently reported[3] in a study of

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(1) G. L. Roy, A. L. Laferriere, and J. O. Edwards, *J. Inorg. Nucl. Chem.*, **4**, 106 (1957), and earlier references therein.

(2) J. P. Lorand and J. O. Edwards, *J. Org. Chem.*, **24**, 769 (1959).

(3) R. Pizer and L. Babcock, *Inorg. Chem.*, **16**, 1677 (1977).

(4) R. Larsson and G. Nunziata, *Acta Chem. Scand.*, **26**, 1503 (1972).

(5) N. Vermaas, *Recl. Trav. Chim. Pays-Bas*, **51**, 955 (1932).

(6) K. Kustin and R. Pizer, *J. Am. Chem. Soc.*, **91**, 317 (1969).

(7) S. Friedman, B. Pace, and R. Pizer, *J. Am. Chem. Soc.*, **96**, 5381 (1974).

(8) J. Boeseken, *Recl. Trav. Chim. Pays-Bas*, **61**, 82 (1942).

(9) S. Friedman and R. Pizer, *J. Am. Chem. Soc.*, **97**, 6059 (1975).

(10) G. Lorber and R. Pizer, *Inorg. Chem.*, **15**, 978 (1976).

0020-1669/80/1319-0056$01.00/0