Single-ion Gibbs Energies, Enthalpies and Entropies of Transfer from Water to Aqueous Methanol based on the $(Ph_4P^+, Ph_4As^+) = Ph_4B^-$ Assumption

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Enthalpies of solution of 298 K of the electrolytes NaCl, Ph₄PCl and NaBPh₄ in water and aqueous methanol mixtures are reported. These measurements lead to single-ion enthalpies of transfer based on the assumption that $\Delta H_t^{\ominus}(Ph_4P^+) = \Delta H_t^{\ominus}(Ph_4B^-)$. Together with literature values for enthalpies of transfer of electrolytes and additional measurements made in the present work, a set of single-ion $\Delta H_t^{\ominus}$ values for 14 ions is constructed. Literature values for Gibbs energies are used to construct a similar set of $\Delta G_t^{\ominus}$ values based on $\Delta G_t^{\ominus}(Ph_4P^+) = \Delta G_t^{\ominus}(Ph_4B^-)$; the corresponding entropies of transfer are also reported. It is shown that for transfer from water to pure methanol transfer values for Ph_4P^+ are, within experimental error, the same as those for Ph_4As^+.

On the $(Ph_4P^+, Ph_4As^+) = Ph_4B^-$ assumption it is found that $\Delta G_t^{\ominus}(H^+)$ is slightly negative for transfer to most aqueous methanol mixtures but is very positive (2.49 kcal mol⁻¹) for transfer to pure methanol. Enthalpies and entropies of transfer of ions do not vary monotonically with solvent composition but reflect changes in solvent structure. There is quite good agreement between the single-ion entropies of transfer and those obtained by the correspondence-plot method for transfer from water to up to 80 wt% methanol mixtures, but not for transfers to 90 wt% methanol mixtures and to pure methanol.

Discussions on the thermodynamic parameters for the transfer of electrolytes from one solvent to another are often greatly facilitated by the use of assumptions that enable single-ion values to be deduced from the experimental data. Of these assumptions the one based on the equality of transfer values for Ph_4As^+ (or Ph_4P^+) and Ph_4B^- is now by far the most commonly used and it has been applied by several workers to transfer from water to many of the more common pure organic solvents.[1-6] Much less work has been carried out on the application of the Ph_4As^+, Ph_4P^+/Ph_4B^- assumption to transfer from water to aqueous organic solvents. Although Gibbs energies of transfer based on this assumption have been obtained for transfer to a number of aqueous organic solvents,[7-10] there have been very few studies in which single-ion $\Delta G_t^{\ominus}$, $\Delta H_t^{\ominus}$ and $\Delta S_t^{\ominus}$ values based on the Ph_4As^+, Ph_4P^+/Ph_4B^- assumption have been determined for transfer from water to aqueous organic solvents.[10-12] Rather surprisingly, there are no sets of single-ion transfer values based on the Ph_4As^+, Ph_4P^+/Ph_4B^- assumption available for the aqueous methanol solvent system, although this is one of the most frequently used solvent systems for thermodynamic and kinetic studies of electrolytes. Popovych *et al.*[13] have determined Gibbs energies of transfer of KPic, Ph₄PPic and KBPh₄ (Pic = picrate ion) from water to aqueous methanol, so that it is possible to construct a set of single-ion $\Delta G_t^{\ominus}$ values based on the Ph_4P^+/Ph_4B^- assumption. In the present work, we use literature values of $\Delta G_t^{\ominus}$ for

a number of electrolytes to obtain such a set of single-ion $\Delta G_t^{\ominus}$ values and we determine enthalpies of solution of the electrolytes Ph_4PCl, $NaBPh_4$ and $NaCl$ in aqueous methanol solvents in order to construct a similar set of single-ion values in terms of enthalpy and hence also in terms of entropy. Finally we compare single-ion values of transfer from the above assumption with values obtained using other single-ion assumptions.

EXPERIMENTAL

Water was doubly distilled and deionised. Methanol (James Burrough Ltd) was distilled under nitrogen and the middle fraction collected and used immediately. The water + methanol solvents were made up by weight on a large scale. Sodium chloride (Alfa, ultrapure grade) was dried in a vacuum oven at 383 K overnight and used at once. Sodium tetraphenylborate (B.D.H., laboratory reagent) was dissolved in acetone and added to an excess of toluene. Slight cloudiness developed slowly on standing and the mixture was then filtered. The clear filtrate was evaporated at room temperature to small bulk and again filtered. The filtrate was then warmed to 323–333 K when crystals were slowly deposited. After standing at this temperature for a further 10 min the hot mixture was filtered rapidly through a pre-heated Büchner funnel and the crystals collected and dried in a vacuum dessicator at room temperature for 3 days [analysis (%): found: C, 84.28; H, 5.84; calculated for $C_{24}H_{20}NaB$: C, 84.22; H, 5.89]. Tetraphenylphosphonium chloride (Fluka, purum p.a. > 98%) was recrystallised from a mixture of 1, 1- and 1,2-dichloroethane (70 + 30), the solvents having previously been dried over anhydrous potassium carbonate. The purified salt was dried at room temperature under vacuum for 3 days and then at 343 K under vacuum for a further 3 days [analysis (%): found: C, 76.89; H, 5.40; calculated for $C_{24}H_{20}PCl$: C, 76.90; H, 5.38]. The salt is extremely hygroscopic, and ampoules for the calorimetric experiments were charged with the salt and then sealed in a dry box. Ammonium iodide (Alfa, ultrapure grade), sodium perchlorate (B.D.H., AnalaR grade) and silver perchlorate (B.D.H., AnalaR grade) were all stored in a dessicator and used as such. Tetramethylammonium iodide (B.D.H.) was recrystallised twice from water, tetra-ethylammonium iodide (B.D.H.) was recrystallised twice from aqueous acetone, tetra-n-propylammonium iodide (prepared from tri-n-propylamine and n-propyl iodide using acetone solvent) was recrystallised twice from aqueous acetone and tetra-n-butylammonium iodide (B.D.H.) was recrystallised from aqueous methanol. All the tetra-alkylammonium iodides were dried at 323 K in a vacuum oven and stored over P_2O_5.

Enthalpies of solution were obtained using an LKB-8700 solution calorimeter. The enthalpy of solution of 0.1–0.4 g samples of tris(hydroxymethyl)aminomethane in 100 cm³ of 0.1 mol dm⁻³ hydrochloric acid was determined as a check and found to be 7111 ± 7 cal mol⁻¹ (average of 5 runs), in good agreement with our recently reported[14] value of 7104 ± 8 cal mol⁻¹ and with the originally reported[15] value of 7107 ± 4 cal mol⁻¹. Enthalpies of solution of the salts were usually determined over a range of final concentrations between ca. 5×10^{-4} and 1×10^{-2} mol dm⁻³. In all cases, separate experiments were carried out to obtain the heat of breaking of empty ampoules in the various solvents, and the enthalpies of solution were corrected for this heat of breaking. Values of the enthalpy of solution at zero concentration, $\Delta H_s^{\ominus}$, were then obtained through linear plots of the corrected ΔH_s values against the square root of the final electrolyte concentration.

RESULTS

GIBBS ENERGIES OF TRANSFER

The results of Popovych et al.[13] enable single-ion $\Delta G_t^{\ominus}$ values on the molar scale to be obtained for transfer of the ions $Ph_4P^+ = Ph_4B^-$, K^+ and Pic^- from water to various wt % aqueous methanol mixtures. We have constructed large-scale plots of these $\Delta G_t^{\ominus}$ values against wt % methanol to yield results at various rounded-off weight percentages. These are in table 1 and represent the prime set of data on which

Table 1. Single-ion Gibbs energies of transfer from water to aqueous methanol, on the molar scale in kcal mol⁻¹ at 298 K[a]

MeOH (wt %)	$Ph_4P^+ = Ph_4B^-$	H^+	Li^+	Na^+	K^+	Rb^+	Cs^+	Ag^+	Me_4N^+	Pr_4N^+	Bu_4N^+	OH^-	F^-	Cl^-	Br^-	I^-	SCN^-[b]	CN^-	OMe^-	ClO_4^-	Pic^-
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
10	−0.60	0.08	0.21	0.33	0.33	0.33	0.29	0.18	0.21	−0.22	−0.35	−0.02	0.19	0.10	0.03	−0.04	−0.13	−0.26	−0.01	−0.01	−0.05
20	−1.17	0.10	0.37	0.63	0.63	0.61	0.55	0.33	0.21	−0.70	−0.75	−0.04	0.47	0.25	0.11	−0.03	−0.17	−0.42	−0.02	0.02	−0.18
30	−1.86	0.11	0.53	0.93	0.96	0.89	0.81	0.54	0.28	−0.78	−1.15	−0.02	0.75	0.40	0.21	−0.01	−0.25	−0.63	0.00	0.00	−0.44
40	−2.68	0.04	0.65	1.17	1.19	1.13	1.03	0.79	0.43	−0.93	−1.57	0.04	1.09	0.62	0.38	0.09	−0.26	−0.63	0.10	−0.05	−0.62
50	−3.33	−0.07	0.73	1.38	1.39	1.36	1.23	0.99	0.51	−1.18	−2.10	0.25	1.51	0.91	0.62	0.24	—	−0.48	0.24	0.02	−0.77
60	−3.95	−0.15	0.79	1.57	1.65	1.59	1.46	1.16	0.65	−1.40	−2.64	0.64	1.99	1.22	0.86	0.37	—	−0.27	0.36	0.14	−0.85
70	−4.45	−0.18	0.82	1.77	1.90	1.88	1.75	1.35	0.87	−1.58	−3.16	1.15	2.49	1.58	1.18	0.51	—	0.04	0.57	0.30	−0.90
80	−4.90	−0.13	0.83	1.89	2.16	2.15	2.02	1.53	1.15	−1.80	−3.73	1.78	3.04	2.01	1.66	0.93	—	0.43	0.58	0.55	−0.87
90	−5.17	0.18	0.83	1.97	2.24	2.33	2.18	1.65	1.37	−2.17	−4.52	2.35	3.79	2.57	2.12	1.37	—	1.12	1.18	1.04	−0.86
100	−5.41	2.45	0.81	2.01	2.31	2.41	2.26	1.76	1.66	−2.09	−5.24	2.98	4.97	3.19	2.67	1.64	—	2.07	1.54	1.50	−0.74
100[c]	−5.56	2.49	0.85	2.05	2.35	2.45	2.30	1.80	1.70	−2.05	−5.20	2.94	4.93	3.15	2.63	1.60	1.30	2.03	1.50	1.46	−0.78

[a] From references given in the text. [b] From values of $\Delta G_t^{\ominus}(H^+ + SCN^-)$ given in ref. (66), after correction to the molar scale. The value for transfer to pure methanol is from results given in ref. (2). [c] Based on the assumption $Ph_4As^+ = Ph_4B^-$ (−5.56 kcal mol⁻¹), the value for Ph_4P^+ being −5.35 on this assumption.

all the following results depend. The most extensive set of $\Delta G_t^\ominus$ values of electrolytes is that of Feakins and Voice,[16] and by use of values of $\Delta G_t^\ominus(K^+)$ from the determinations of Popovych et al. (table 1) corresponding $\Delta G_t^\ominus$ values may then be obtained for the ions Li^+, Na^+, Rb^+, Cs^+, Cl^-, Br^- and I^- at rounded-off wt % methanol mixtures, again with interpolation of results where necessary. Elsemongy[17] has recently reported data for HCl, HBr and HI from which the relevant $\Delta G_t^\ominus$ values may be obtained. Then using the values of Cl^- from the work of Feakins and Voice[16] and Popvych et al.[13] it is possible to obtain $\Delta G_t^\ominus$ values for H^+, Br^- and I^-. Agreement between the Feakins and Voice values and those of Elsemongy is reasonably good and we give in table 1 the most recent values of the latter author for H^+, Br^- and I^- and those of Feakins and Voice for Li^+, Na^+, Rb^+, Cs^+ and Cl^-. In a number of cases the $\Delta G_t^\ominus$ values for transfer from water to methanol are not available from the above workers and in these cases the values given by Abraham and Danil de Namor[4] have been used, after a very slight correction from the Ph_4As^+ scale to the Ph_4P^+ scale.

Several workers[18-20] have reported solubility products for the silver halides in water and aqueous methanol mixtures, from which $\Delta G_t^\ominus$ values may be calculated. Those of Feakins et al.[18] and Anderson et al.[20] on AgCl are in good agreement, and by use of large-scale plots against wt % methanol values of $\Delta G_t^\ominus(Ag^+ + Cl^-)$ were obtained and combined with the Cl^- values in table 1 to obtain values of $\Delta G_t^\ominus(Ag^+)$. In a similar way, using the values of Anderson et al. for AgBr and AgI at the low wt % methanol compositions and Nedoma's values for AgBr and AgI at the high wt % methanol region $\Delta G_t^\ominus(Ag^+ + X^-)$ may be evaluated. Then use of the halide ion results in table 1 enables two further sets of data for Ag^+ to be constructed. Unfortunately, there is only poor agreement between values of $\Delta G_t^\ominus(Ag^+)$ calculated from the three silver halide solubility products and we list in table 1 those obtained from the results of Feakins et al.[18] and Anderson et al.[20] for silver chloride.

De Ligny et al.[21] have reported $\Delta G_t^\ominus$ values for transfer of perchlorates of K^+, Rb^+, Cs^+ and R_4N^+ ions. Using values in table 1 for $\Delta G_t^\ominus$ of K^+, Rb^+ and Cs^+, it is possible to obtain the single-ion values for ClO_4^- and then those for the R_4N^+ ions. These are in table 1, again with interpolation through large-scale plots against wt % methanol. In a similar way, values for the CN^- ion may by calculated from the $\Delta G_t^\ominus(K^+ + CN^-)$ results recently reported by Blandamer et al.[22]

Very recently, Tissier[23] obtained $\Delta G_t^\ominus$ values for transfer of $(K^+ + F^-)$ from water to aqueous methanol through careful measurements using ion-selective electrodes. Subtraction of the $\Delta G_t^\ominus(K^+)$ values in table 1 leads to $\Delta G_t^\ominus(F^-)$, as recorded also in table 1 (values at 30 and 50 wt % methanol have been estimated through large-scale plots).

Villermaux and Delpuech[24] have obtained values of $\Delta G_t^\ominus$ for H^+ and for OH^- by use of the Ph_4As^+/BPh_4^- assumption based on their own determinations of values of $\Delta G_t^\ominus$ for the series of electrolytes Ph_4AsCl, $NaBPh_4$ and NaCl. Although the obtained single-ion values differ from those in table 1 it is possible to recombine those for H^+ and HO^- and then to dissect the total value using $\Delta G_t^\ominus(H^+)$ from table 1 to deduce $\Delta G_t^\ominus(OH^-)$. Wells[25] has also listed results from which further values at low methanol content may be obtained and rounded-off values of $\Delta G_t^\ominus(OH^-)$ are given in table 1.

Another set of values of $\Delta G_t^\ominus(OH^-)$ may be obtained from results given by Rochester;[26] although the numerical values are different to those given in table 1 the general trend is the same. Rochester[26] also lists values for $\Delta G_t^\ominus(OMe^-)$ and these are given in table 1 after conversion from the molal to the molar scale and after correction to the new single-ion convention.

A number of $\Delta G_t^\ominus$ values for bivalent metal chlorides have been reported[27] and table 2 gives values of $\Delta G_t^\ominus$ for Sr^{2+}, Ba^{2+} and Cd^{2+} calculated using the Cl^- values in table 1.

Table 2. Single-ion Gibbs energies of transfer for bivalent cations from water to aqueous methanol, on the molar scale in kcal mol⁻¹ at 298 K[a]

methanol (wt %)	Zn^{2+}	Cd^{2+}	Sr^{2+}	Ba^{2+}
0	0	0	0	0
10	0.40	0.40	0.56[b]	0.58
20	0.83	0.77	1.04	1.07
30	1.41	1.10[b]	1.46[b]	1.50[b]
40	1.87[b]	1.42	—	1.96
50	2.27	—	—	—
60	2.67[b]	—	—	—
70	3.21	—	—	—
80	—	—	—	—
90	—	—	—	—
100	6.60	7.79	—	4.40

[a] Data from ref. (27)–(29), all based on $Ph_4P^+ = Ph_4B^-$ [b] Interpolated values.

More recently, an extensive set of results for $ZnCl_2$ was published by Lewandowski;[28] there is very good agreement with the results given previously at 10 and 20 wt % methanol, and table 2 gives values of $\Delta G_t^{\ominus}(Zn^{2+})$ from Lewandowski's set, together with values for transfer to pure methanol obtained by Hedwig *et al.*[29]

Burgess *et al.*[30–33] have determined the solubilities of several complex salts in water and in methanol + water mixtures. If corrections for activity coefficients and ion association are neglected, approximate $\Delta G_t^{\ominus}$ values may be calculated through the relationship $\Delta G_t^{\ominus} = nRT \ln (S^w/S^s)$, where S^w and S^s are the molar solubilities of an electrolyte in water and in a given solvent and n is the number of ions contained in the electrolyte. For these electrolytes, where n is 3, 4 and even 6, any experimental error in S^w or S^s leads to very large errors in the calculated $\Delta G_t^{\ominus}$ values. However, the general trend in $\Delta G_t^{\ominus}$ for the electrolytes, and hence in the calculated single-ion values, will probably be realistic, and table 3 gives single-ion values for a number of complex ions.

ENTHALPIES OF TRANSFER

Because of the insolubility of $KBPh_4$ the set of electrolytes used by Popovych *et al.*[13] for the Gibbs energies of transfer is not suitable for measurements of enthalpies of solution. We therefore used the electrolytes NaCl, $NaBPh_4$ and Ph_4PCl to obtain $\Delta H_s^{\ominus}$ values and thence $\Delta H_t^{\ominus}$ values for single ions. Our values of $\Delta H_s^{\ominus}$ are summarised in table 4. Enthalpies of solution of NaCl in water were discussed by Parker[34] in 1965. There have been several further determinations[35–39] (table 5) and our value of 933 ± 16 cal mol⁻¹ is in good agreement with the value of 928 ± 1 cal mol⁻¹ obtained by Bury *et al.*[37] Previous work on $\Delta H_s^{\ominus}$ values of NaCl in methanol + water mixtures has been carried out by Slansky,[40] by Dadgar and Taherian[38] and by Feakins *et al.*[41] There is very good agreement between our values and those of Feakins *et al.*[41] and we have therefore obtained $\Delta H_t^{\ominus}$ values for transfer of NaCl from water to the methanol + water mixtures from smoothed plots of $\Delta H_t^{\ominus}(NaCl)$ against wt % methanol, using our results, those of Feakins *et al.*[41] and the value of -2910 cal mol⁻¹ for transfer from water to pure methanol recommended by Krishnan and Friedman[42]

Table 3. Approximate single-ion Gibbs energies of transfer from water to aqueous methanol, on the molar scale in kcal mol^{-1} at 298 K^a

methanol (wt %)	0	10	20	30	40	50	60	70	80	90	100
$[Cr(en)_3]^{3+}$	0	0.1	0.2	0.5	0.7	0.8	1.3	1.8	2.9	—	—
$[Cr(NH_3)_5Cl]^{2+}$	0	0.2	0.6	1.2	1.4	—	—	—	—	—	—
$[Fe(phen)_3]^{2+}$	0	−0.5	−1.1	−2.1	−3.1	—	—	—	—	—	−4.4^b
$[ReO_4]^-$	0	−0.1	−0.2	−0.3	−0.4	—	—	—	—	—	—
$[IrCl_6]^{2-}$	0	0.6	1.1	1.5	2.0	—	—	—	—	—	—
$[ReCl_6]^{2-}$	0	0.0	0.3	0.6	1.2	—	—	—	—	—	—
$[ReBr_6]^{2-}$	0	−0.2	0.0	0.4	1.1	—	—	—	—	—	—
$[S_2O_8]^{2-}$	0	0.1	0.3	0.4	0.7	—	—	—	—	—	—
$[IrCl_6]^{3-}$	0	1.2	2.8	4.8	—	—	—	—	—	—	—
$[Fe(CN)_6]^{3-}$	0	−0.6	−0.9	−1.1	0.0	0.0	0.7	2.0	3.8	6.6	10.6
$[CoW_{12}O_{40}]^{5-}$	0	−1.5	−2.8	−4.2	—	—	—	—	—	—	—

^{a} From ref. (30)–(33) based on the single-ion values in table 1. ^{b} From solubility products given by F. M. Van Meter and H. M. Neumann, *J. Am. Chem. Soc.*, 1976, **68**, 1382.

(see table 6). Recorded values for $\Delta H_s^{\ominus}(NaBPh_4)$ in water range from -4500^{43} to -4805^{44} cal mol^{-1}, the value due to Krishnan and Friedman^{42} being -4770 cal mol^{-1}. Our value of -4780 ± 20 cal mol^{-1} is in good agreement with the latter. There has been considerable controversy over $\Delta H_s^{\ominus}(NaBPh_4)$ values in pure methanol, with reported values of $-3900,^{45}$ -8000 (at 303 K),^{46} -10000^2 and -10060^{47} cal mol^{-1}. We found it very difficult to obtain reliable $\Delta H_s^{\ominus}$ values for $NaBPh_4$ especially in solvents with a methanol content > 70 wt %. Although for a given sample of $NaBPh_4$ values of $\Delta H_s^{\ominus}$ were fairly reproducible, different samples yielded different values of $\Delta H_s^{\ominus}$. We traced, at least in part, the origin of this irreproducibility to drying of the recrystallised $NaBPh_4$ *in vacuo* at temperatures around 323 K and found that if the recrystallised material was dried *in vacuo* at room temperature much more reproducible results were obtained. Even then, the error in the $\Delta H_s^{\ominus}$ values increases markedly as the solvent approaches pure methanol. However, our value for $\Delta H_s^{\ominus}$ in pure methanol, -9990 ± 250 cal mol^{-1}, compares quite well with the approximate value given by Parker *et al.*^{2} and with the generally accepted value of Krishnan and Friedman,^{47} -10060 cal mol^{-1}.* Values of $\Delta H_t^{\ominus}(NaBPh_4)$ obtained from our own data in table 4 are given in table 6. Although Ph_4PCl is very hygroscopic and must be handled in a completely dry atmosphere, two literature values for $\Delta H_s^{\ominus}$ in water agree exactly, -2190^{48} and -2194^{49} cal mol^{-1}. Our own value of -2130 ± 30 cal mol^{-1} is in reasonable agreement with these values and table 6 gives $\Delta H_t^{\ominus}(Ph_4PCl)$ values based on our own data from table 4. Also in table 6 are the calculated single-ion values for Na^+, Cl^- and $Ph_4P^+ = Ph_4B^-$, together with single-ion vaues given by Krishan and Friedman^{42} for transfer from water to methanol based on the Ph_4As^+/Ph_4B^- assumption.

Our single-ion values for transfer to methanol based on $\Delta H_t^{\ominus}(Ph_4P^+) = \Delta H_t^{\ominus}(Ph_4B^-)$ are very close to those of Krishnan and Friedman^{42} based on $\Delta H_t^{\ominus}(Ph_4As^+) = \Delta H_t^{\ominus}(Ph_4B^-)$, the differences being within experimental error (< 0.1 kcal per mol of ion). There is a considerable simplification to be made if these

* No error limits were given for this measurement.

Table 4. Enthalpies of solution of electrolytes, in cal mol^{-1} at 298 K

electrolyte	solvent (wt %)	$\Delta H_s^{\ominus a}$	n^b	concentration range^c
NaCl	water	933 ± 16	8	1.0×10^{-3} to 1.0×10^{-2}
NaCl	15% methanol	1560 ± 90	4	6.4×10^{-4} to 2.3×10^{-3}
NaCl	25% methanol	1730 ± 50	4	6.2×10^{-4} to 2.3×10^{-3}
NaCl	40% methanol	1680 ± 70	6	3.3×10^{-4} to 1.7×10^{-3}
NaCl	70% methanol	625 ± 20	4	2.2×10^{-4} to 1.7×10^{-3}
Ph$_4$PCl	water	-2130 ± 30	6	8.3×10^{-4} to 1.7×10^{-3}
Ph$_4$PCl	15% methanol	3170 ± 30	3	3.3×10^{-4} to 6.6×10^{-4}
Ph$_4$PCl	25% methanol	4240 ± 30	4	2.5×10^{-4} to 7.5×10^{-4}
Ph$_4$PCl	40% methanol	3345 ± 10	4	2.0×10^{-4} to 7.4×10^{-4}
Ph$_4$PCl	70% methanol	45 ± 2	4	3.1×10^{-4} to 7.4×10^{-4}
Ph$_4$PCl	85% methanol	-560 ± 50	4	2.4×10^{-4} to 9.4×10^{-4}
Ph$_4$PCl	methanol	-505 ± 20	3	4.8×10^{-4} to 9.3×10^{-4}
NaBPh$_4$	water	-4780 ± 17	5	1.0×10^{-3} to 4.4×10^{-3}
NaBPh$_4$	10% methanol	-1600 ± 60	5	4.1×10^{-4} to 1.3×10^{-3}
NaBPh$_4$	15% methanol	120	2	1.2×10^{-3} to 2.2×10^{-3}
NaBPh$_4$	20% methanol	1530 ± 30	6	1.4×10^{-4} to 9.3×10^{-4}
NaBPh$_4$	25% methanol	2620 ± 20	5	2.6×10^{-4} to 1.7×10^{-3}
NaBPh$_4$	30% methanol	3030 ± 50	3	3.2×10^{-4} to 8.0×10^{-4}
NaBPh$_4$	40% methanol	2750 ± 30	4	2.0×10^{-4} to 9.6×10^{-4}
NaBPh$_4$	70% methanol	-1900 ± 70	5	1.7×10^{-4} to 1.0×10^{-3}
NaBPh$_4$	80% methanol	-3510 ± 50	7	5.8×10^{-4} to 4.8×10^{-3}
NaBPh$_4$	90% methanol	-6890 ± 100	6	1.1×10^{-3} to 4.4×10^{-3}
NaBPh$_4$	methanol	-9985 ± 250	7	1.3×10^{-3} to 7.6×10^{-3}
NaClO$_4$	70% methanol	2240 ± 30	5	7.0×10^{-4} to 3.8×10^{-3}
AgClO$_4$	70% methanol	50 ± 10	4	2.8×10^{-3} to 5.9×10^{-3}
NH$_4$I	70% methanol	890 ± 30	7	1.5×10^{-4} to 3.0×10^{-3}
Me$_4$NI	70% methanol	8000 ± 340	8	8.0×10^{-4} to 2.2×10^{-3}
Et$_4$NI	70% methanol	7510 ± 200	7	1.2×10^{-3} to 1.0×10^{-2}
Pr$_4$NI	70% methanol	5730 ± 30	5	1.9×10^{-3} to 8.5×10^{-3}
Bu$_4$NI	70% methanol	10130 ± 90	7	5.2×10^{-4} to 1.0×10^{-2}
Me$_4$NPic	methanol	6990 ± 200	5	1.7×10^{-4} to 7.6×10^{-4}
Et$_4$NPic	methanol	8890 ± 80	4	4.3×10^{-4} to 1.6×10^{-3}

^{a} After correction of all observed enthalpies of solution for the heat of breaking of empty ampoules in the solvent concerned, followed by extrapolation of the corrected enthalpies of solution to zero concentration through linear plots against $\sqrt{c}$. The given errors, s, are calculated from the deviations of the experimental points from those of the linear regression through $s = [(y - \bar{y})^2/(n-2)]^{\frac{1}{2}}$. ^{b} Number of experimental points. ^{c} Range of concentration of electrolyte in the final solution.

two scales are taken as equivalent for enthalpies of transfer to methanol, and we shall use the division of Krishnan and Friedman for this particular transfer.

The prime set of single-ion $\Delta H^{\ominus}$ values in table 6 may now be combined with literature data for values of $\Delta H_f^{\ominus}(M^+ + X^-)$ to obtain further single-ion values. Enthalpies of transfer of the alkali-metal halides have been reported by Slansky,[40] Dadgar and Taherian[38] and Feakins *et al.*[41] Those of Slansky are not internally consistent at high methanol solvent content, and since our own values for NaCl agree very well with these of Feakins *et al.*[41] we have used the latter workers' values for

Table 5. Enthalpies of solution of sodium chloride in water, in cal mol^{-1} at 298 K

$\Delta H_s^{\ominus}$	date	ref.
928	1965	34
930	1971	35
990 ± 30	1972	36
928 ± 1	1976	37
907	1977	38
908	1980	39
933 ± 16	—	this work

Table 6. Enthalpies of transfer of electrolytes and ions from water to aqueous methanol, in kcal mol^{-1} at 298 K

methanol (wt %)	NaCl[a]	NaBPh$_4$[b]	Ph$_4$PCl[b]	Na$^+$	Cl$^-$	Ph$_4$P$^+$ = Ph$_4$B$^-$
0	0	0	0	0	0	0
10	0.45	3.18	4.10	-0.23	0.68	3.42
20	0.76	6.31	6.06	0.50	0.26	5.80
30	0.83	7.81	6.32	1.16	-0.33	6.65
40	0.75	7.53	5.47	1.40	-0.65	6.12
50	0.58	6.20	4.36	1.21	-0.63	4.99
60	0.32	4.61	3.14	0.90	-0.58	3.72
70	-0.30	2.88	2.18	0.20	-0.50	2.68
80	-0.66	1.27	1.70	-0.55	-0.11	1.82
90	-1.55	-2.11	1.52	-2.59	1.04	0.48
100	-2.91[c]	-5.21	1.62	-4.87	1.96	-0.34
100	-2.91[c]	-5.34[c]	2.07[c]	-4.92[d]	2.01[d]	-0.42[d]

[a] Smoothed values from table 4 and ref. (41). [b] Values from table 4. [c] Ref. (42). [d] Single-ion values based on Ph$_4$As$^+$ = Ph$_4$B$^-$. The value for Ph$_4$P$^+$ is 0.06 kcal mol^{-1}, according to ref. (42), on this assumption.

transfer from water to aqueous methanol and Krishnan and Friedman's data for transfers to pure methanol. Single-ion values obtained in this way are in table 7. Values of $\Delta H_t^{\ominus}(H^+ + X^-)$ derived from the temperature dependence of Gibbs energies of transfer have been reported[17] and surveyed.[50] Those of Feakins et al.[51] are the most self-consistent and values of $\Delta H_t^{\ominus}(H^+)$ obtained from results of Feakins et al.[51] are in table 7.

Lewandowski[28] has determined $\Delta H_t^{\ominus}(Zn^{2+} + 2Cl^-)$, and using the single-ion values for Cl$^-$ corresponding single-ion values for Zn^{2+} were deduced (table 7). Both $\Delta H_s^{\ominus}$ and $\Delta H_t^{\ominus}$ values for (Sr^{2+} + 2Cl$^-$) and (Ba^{2+} + 2Cl$^-$) have been listed by Dadgar and Taherian;[38] there are numerical discrepancies between some of these values, but we have used the recorded[38] $\Delta H_s^{\ominus}$ values to recalculate $\Delta H_t^{\ominus}$ for the electrolytes and thence for Sr^{2+} and Ba^{2+} (table 7).

For transfer from water to methanol, $\Delta H_t^{\ominus}$ values for a range of univalent[2, 42, 52] and bivalent[53-55] ions may be set out using the Ph$_4$P$^+$, Ph$_4$As$^+$ = Ph$_4$B$^-$ assumption and these are collected in table 8. It is convenient to collect the corresponding $\Delta G_t^{\ominus}$

Table 7. Single-ion enthalpies of transfer from water to aqueous methanol, in kcal mol⁻¹ at 298 K[a]

methanol (wt %)	Ph₄P⁺ = Ph₄B⁻	H⁺	Li⁺	Na⁺	K⁺	Rb⁺	Cs⁺	Cl⁻	Br⁻	I⁻	Zn²⁺	Sr²⁺	Ba²⁺
0	0	0	0	0	0	0	0	0	0	0	0	0	0
10	3.42	0.38	−0.39	−0.23	−0.29	−0.29	−0.27	0.68	0.74	0.78	−1.00	−0.53	−0.62
20	5.80	0.28	0.13	0.50	0.33	0.30	0.28	0.26	0.25	0.26	0.11	0.54	0.10
30	6.65	1.04	0.58	1.16	0.89	0.84	0.76	−0.33	−0.46	−0.61	1.39	1.22	0.82
40	6.12	1.50	0.80	1.40	1.18	1.08	0.95	−0.65	−0.95	−1.25	1.95	1.70	1.42
50	4.99	1.50	0.58	1.21	1.12	1.03	0.81	−0.63	−1.16	−1.64	1.71	—	—
60	3.72	1.00	−0.02	0.90	0.76	0.65	0.48	−0.58	−1.15	−1.87	1.26	—	—
70	2.68	0.46	−0.82	0.20	0.20	0.18	0.09	−0.50	−1.06	−2.15	0.60	—	—
80	1.82	−0.63	−1.94	−0.55	−0.55	−0.41	−0.38	−0.11	−0.84	−2.27	—	—	—
90	0.48	−2.29	−3.71	−2.59	−2.37	−1.97	−1.83	1.04	0.25	−1.57	—	—	—
100[b]	−0.42	−3.80	−5.31	−4.92	−4.52	−3.71	−3.28	2.01	1.10	−0.48	−11.1	−13.7	−14.2

[a] Using the prime set of values in table 6 and literature values[28,38,41,47,48] for neutral combinations of ions as explained in the text. Values for transfer to pure methanol from ref. (42) except for Zn²⁺ [ref. (28)], Sr²⁺ and Ba²⁺ [ref. (29) and (52)]. [b] Based on the assumption Ph₄As⁺ = Ph₄B⁻ (−0.42 kcal mol⁻¹), the value for Ph₄P⁺ being −0.39 kcal mol⁻¹ on this assumption (from our own value of 1.62 kcal mol⁻¹ for $\Delta H_t^\ominus$ for Ph₄PCl and the single-ion value of 2.01 kcal mol⁻¹ for Cl⁻).

Table 8. Thermodynamics of transfer of single ions from water to methanol, molar scale at 298 K[a]

ion	$\Delta G_t^{\ominus}$	$\Delta H_t^{\ominus}$	$\Delta S_t^{\ominus}$	ion	$\Delta G_t^{\ominus}$	$\Delta H_t^{\ominus}$	$\Delta S_t^{\ominus}$
H^+	2.49	-3.80	-21.1	HO^-	2.94	—	—
Li^+	0.85	-5.31	-20.7	F^-	4.93	—	—
Na^+	2.05	-4.92	-23.4	Cl^-	3.15	2.01	-3.8
K^+	2.35	-4.52	-23.0	Br^-	2.63	1.10	-5.1
Rb^+	2.45	-3.71	-20.7	I^-	1.60	-0.48	-7.0
Cs^+	2.30	-3.28	-18.7	CN^-	2.03	—	—
—	—	—	—	SCN^-	1.30	-0.79	-7.0
—	—	—	—	OMe^-	1.50	—	—
—	—	—	—	I_3^-	-3.00	—	—
Tl^+	0.95	—	—	ClO_4^-	1.46	-0.57	-6.8
Ag^+	1.80	-5.0	-22.8	N_3^-	2.60	0.1	-8.4
NH_4^+	1.17	-4.50	-19.0	NO_3^-	3.00	1.0	-6.7
Me_4N^+	1.70	0.28	-4.8	Pic^-	-0.78	-0.92^b	-0.5
Et_4N^+	0.25	2.18	6.5	Ph_4B^-	-5.56	-0.42	17.2
Pr_4N^+	-2.05	3.82	19.7	$CF_3SO_3^-$	—	1.17	—
Bu_4N^+	-5.2	4.92	33.9	$CF_3CO_2^-$	—	2.16	—
Pe_4N^+	—	4.82	—	$CH_3CO_2^-$	3.82	—	—
Ph_4P^+	-5.35	-0.34	16.8	$PhCO_2^-$	1.77	—	—
Ph_4As^+	-5.56	-0.42	17.2	—	—	—	—
Mg^{2+}	—	-7.2	—	Zn^{2+}	6.68	-11.1	-59.6
Ca^{2+}	—	-11.5	—	Cd^{2+}	7.87	-9.9	-59.6
Sr^{2+}	—	-13.7	—	Cu^{2+}	6.3^c	—	—
Ba^{2+}	4.48	-14.2	-62.7	Ni^{2+}	—	-17.2^d	—
Pb^{2+}	—	-13.4	—	Mn^{2+}	—	-9.4^d	—

[a] Values of $\Delta G_t^{\ominus}$/kcal mol^{-1} and $\Delta H_t^{\ominus}$/kcal mol^{-1} from tables 1, 2 and 7 (with slight adjustments to make $Ph_4As^+ = Ph_4B^-$) or from references in the text, unless shown otherwise. The given $\Delta G_t^{\ominus}$ values are in good agreement with those recently listed by Y. Marcus, *Pure Appl. Chem.*, 1983, **55**, 977, from which the value of $\Delta G_t^{\ominus}(I_3^-)$ was taken. [b] From the $\Delta H_t^{\ominus}(R_4N^+ + Pic^-)$ values in table 9 and the $\Delta H_t^{\ominus}(R_4N^+)$ values in this table; -0.90 from $(Me_4N^+ + Pic^-)$ and -0.94 from $(Et_4N^+ + Pic^-)$. [c] J. F. Coetzee and W. K. Istone, *Anal. Chem.*, 1980, **52**, 53. [d] Ref. (55).

values, from tables 1 and 2, and then to calculate $\Delta S_t^{\ominus}$ for these ions also. All the single-ion values in table 8 have been adjusted so that values for Ph_4As^+ equal those for Ph_4B^-; within any realistic experimental error the resulting values are identical to those in tables 1 and 7.

Values of $\Delta H_t^{\ominus}$ for transfer from water to 70 wt % methanol can be obtained for an extended series of electrolytes using the $\Delta H_s^{\ominus}$ values in table 4, together with known $\Delta H_s^{\ominus}$ values in water[34, 56] (see table 9). All the available $\Delta H_t^{\ominus}$ values are collected in table 10, together with the corresponding $\Delta G_t^{\ominus}$ values from tables 1 and 2 and the deduced $\Delta S_t^{\ominus}$ values.

DISCUSSION

The single-ion values based on $Ph_4P^+ = Ph_4B^-$ are set out in tables 1, 7 and 11. For transfers from water to pure methanol this assumption is equal, within experimental error, to the assumption that $Ph_4As^+ = Ph_4B^-$, and for convenience we shall use the numerical values of the latter assumption for transfer to pure methanol. There have

Table 9. Calculation of $\Delta H_t^\ominus$ for transfer of electrolytes from water to 70 wt % methanol, in kcal mol^{-1} at 298 K

electrolyte	$\Delta H_s^\ominus$ in water	$\Delta H_s^\ominus$ in 70 wt % methanol[a]	$\Delta H_t^\ominus$
NaClO$_4$	3.32[b]	2.24	−1.08
AgClO$_4$	1.76[c]	0.05	−1.71
NH$_4$I	3.28[d]	0.89	−2.39
Me$_4$NI	10.08[e]	8.00	−2.08
Et$_4$NI	6.67[e]	7.51	0.84
Pr$_4$NI	2.76[e]	5.73	2.97
Bu$_4$NI	4.13[f]	10.13	6.00
Me$_4$NPic	7.61[g]	6.99[h]	−0.62[i]
Et$_4$NPic	7.65[g]	8.89[h]	1.24[i]

[a] All values from table 4, this work. [b] Average of 3.302 (M. Mastroianni and C. M. Criss, *J. Chem. Eng. Data*, 1972, **17**, 222), 3.317 [ref. (34)] and 3.55 (C. V. Krishnan and H. L. Freidman, *J. Phys. Chem.*, 1970, **74**, 2356). [c] *Natl Bur. Stand. (U.S.), Circ.* 270–1 and 270–3. [d] Ref. (34). [e] Ref. (56). [f] Calculated from $\Delta H_s^\ominus$ in methanol (8.57 kcal mol^{-1})[47] and $\Delta H_t^\ominus$ from water to methanol (4.44 kcal mol^{-1}, table 8). [g] A. Finch and A. E. Smith, *Thermochim. Acta*, 1982, **53**, 349. [h] Solution in methanol, table 4. [i] For transfer from water to methanol.

Table 10. Thermodynamics of transfer of single ions from water to 70 wt % methanol, molar scale at 298 K[a]

ion	$\Delta G_t^\ominus$	$\Delta H_t^\ominus$	$\Delta S_t^\ominus$	ion	$\Delta G_t^\ominus$	$\Delta H_t^\ominus$	$\Delta S_t^\ominus$
H$^+$	−0.18	0.46	2.1	HO$^-$	1.15	—	—
Li$^+$	0.82	−0.82	−5.5	F$^-$	2.49	—	—
Na$^+$	1.77	0.20	−5.3	Cl$^-$	1.58	−0.50	−7.0
K$^+$	1.90	0.20	−5.7	Br$^-$	1.18	−1.06	−7.5
Rb$^+$	1.88	0.18	−5.7	I$^-$	0.51	−2.15	−8.9
Cs$^+$	1.75	0.09	−5.6	CN$^-$	0.04	—	—
				OMe$^-$	0.57	—	—
Ag$^+$	1.35	−0.43	−6.0	ClO$_4^-$	0.30	−1.28	−5.3
NH$_4^+$	—	−0.24	—	Pic$^-$	−0.90	—	—
Me$_4$N$^+$	0.87	0.07	−2.7	Ph$_4$B$^-$	−4.45	2.68	23.9
Et$_4$N$^+$	—	2.99	—	—	—	—	—
Pr$_4$N$^+$	−1.58	5.12	22.5	—	—	—	—
Bu$_4$N$^+$	−3.16	8.15	37.9	Zn^{2+}	3.21	0.60	−12.8
Ph$_4$P$^+$	−4.45	2.68	23.9	—	—	—	—

[a] From results in tables 1, 2, 7 and 9.

been no previous reports of single-ion enthalpies of transfer in the water + methanol system based on these assumptions, but Tissier has obtained single-ion Gibbs energies of transfer based on Ph$_4$As$^+$ = Ph$_4$B$^-$ from solubility measurements on KPi, Ph$_4$AsPic and KBPh$_4$.[57] These single-ion values are almost exactly the same as those we have calculated (table 1) from the similar measurements of Popovych *et al.*[13] Villermaux and Delpeuch[24] have also constructed a set of single-ion $\Delta G_t^\ominus$ values using the Ph$_4$As$^+$ = Ph$_4$B$^-$ assumption based on vapour-pressure measurements, but their single-ion values are quite different to those of Popovych *et al.*[13] and of Tissier.[57, 58]

Table 11. Single-ion entropies of transfer from water to aqueous methanol, on the molar scale in cal K^{-1} mol^{-1} at 298 K [a]

methanol (wt %)	$Ph_4P^+ = Ph_4B^-$	H^+	Li^+	Na^+	K^+	Rb^+	Cs^+	Cl^-	Br^-	I^-	Zn^{2+}	Sr^{2+}	Ba^{2+}
0	0	0	0	0	0	0	0	0	0	0	0	0	0
10	13.5	1.0	−2.0	−1.9	−2.1	−2.1	−1.9	−1.9	2.4	2.7	−4.7	−3.7	−4.0
20	23.4	0.6	−0.8	−0.4	−1.0	−1.0	−0.9	0.0	0.5	1.0	−2.4	−1.7	−3.2
30	28.5	3.1	0.2	0.8	−0.2	−0.2	0.2	−2.4	−2.2	−2.0	−0.1	−0.8	−2.3
40	29.5	4.9	0.5	0.8	0.0	−0.2	−0.3	−4.3	−4.5	−4.5	0.3	—	−1.8
50	27.9	5.3	−0.5	−0.6	−0.9	−1.1	−1.4	−5.2	−6.0	−6.3	−1.9	—	—
60	25.7	3.9	−2.7	−2.2	−3.0	−3.1	−3.3	−6.0	−6.7	−7.5	−4.7	—	—
70	23.9	2.1	−5.5	−5.3	−5.7	−5.7	−5.6	−7.0	−7.5	−8.9	−8.8	—	—
80	22.5	−1.7	−9.3	−8.2	−9.1	−8.6	−8.0	−7.1	−8.4	−10.7	—	—	—
90	19.0	−8.3	−15.2	−15.3	−15.5	−14.4	−13.4	−5.1	−6.6	−9.9	—	—	—
100[b]	17.2	−21.1	−20.7	−23.4	−23.0	−20.7	−18.7	−3.8	−5.1	−7.0	−59.6	—	−62.7

[a] From $\Delta G_t^\ominus$ and $\Delta H_t^\ominus$ values in tables 1 and 7. [b] Based on the assumption $Ph_4As^+ = Ph_4B^-$ (17.2 cal K^{-1} mol^{-1}).

Table 12. Comparison of Gibbs energies of transfer of H^+ from water to aqueous methanol, on the molar scale in kcal mol^{-1} at 298 K

methanol (wt %)	de Ligny *et al.*[59]	Wells[60]	Kalidas *et al.*[61]	table 1
0	0	0	0[a]	0
10	−0.2	−0.16	—	0.08
20	—	−0.37	0.00	0.10
30	—	—	—	0.11
40	−0.7[b]	−0.98	−0.59	0.04
50	—	−1.41	—	−0.07
60	—	—	−1.93	−0.15
70	—	—	—	−0.18
80	—	—	−2.49	−0.13
90	−1.0[c]	—	−2.83	0.18
100	0.8	—	−1.68	2.49

[a] At 303 K, probably on the molal scale.   [b] 43.12%.   [c] 87.68%.

We have no explanation for this lack of agreement but recommend the values of Popovych *et al.* and of Tissier (table 1).

Numerous workers have obtained single-ion $\Delta G_t^\ominus$ values for transfer of univalent ions from water to aqueous methanol based on some particular extra-thermodynamic assumption. We illustrate in table 12 the quite different single-ion values that may thus be obtained[59-61] with reference to $\Delta G_t^\ominus(H^+)$. Such differences are magnified for the M^{2+} ions and on Wells' division,[60] for example, $\Delta G_t^\ominus$ for Zn^{2+}, Cd^{2+} and Ba^{2+} is negative for transfers from water to aqueous methanol whereas the corresponding values in table 2 are all positive.

Although there is no objective method of selecting one or other set of single-ion values, we thought that results of experiments based on n.m.r. relaxation of individual ions might be of use in this context. Mishustin[62] has reported $\Delta G_t^\ominus(Li^+)$ values from n.m.r. relaxation of $^7Li^+$, but for transfer from water to methanol this value (and hence that of H^+) is even more positive than that given in table 1 and certainly does not support the less positive[59, 61] values shown in table 12. Covington and Newman,[63] using n.m.r. methods, suggest that both Na^+ and Cl^- are selectively solvated by water, whereas Hertz *et al.*[64] deduce that Na^+ is selectively solvated by water and Cl^- selectively solvated by methanol. More recent results[65] indicate either that Na^+ is weakly solvated by methanol and Cl^- strongly solvated by methanol,[65a] or that at 5 wt % methanol the alkali-metal halide cations are rather weakly selectively solvated by water and the anions slightly preferentially solvated by methanol.[65b] Since there is no general agreement on the selective solvation of ions in the aqueous methanol system, there is no possibility of using these results to assess the various assumptions employed to obtain single-ion $\Delta G_t^\ominus$ values.

Having assembled results for $\Delta G_t^\ominus$, $\Delta H_t^\ominus$ and $\Delta S_t^\ominus$ for numerous single ions, literature values for ionic combinations $(M^+ + X^-)$ may now be dissected into single-ion quantities and values for other ions may be included. Patra and Das[66] have determined $\Delta G_t^\ominus(H^+ + SCN^-)$ and the values of $\Delta G_t^\ominus(SCN^-)$ we have derived are in table 1. Results for $\Delta G_t^\ominus(H^+ + Cl^-)$ and $\Delta G_t^\ominus(Rb^+ + Cl^-)$ are available and agree well with those in table 1.[67] Malahias and Popovych[68] have redetermined $\Delta G_t^\ominus(K^+ + Cl^-)$; the revised values agree well with those in table 1 for transfer to aqueous methanol above

Table 13. Single-ion $\Delta G_t^{\ominus}$ values for acid anions and base conjugate acids, molar scale in kcal mol^{-1} at 298 K

methanol (wt %)	0	20	40	60	80	100
p-nitrobenzoate[a]	0	−0.16	−0.27	−0.10	0.30	1.07
p-methylbenzoate[a]	0	−0.17	−0.30	−0.29	0.10	0.96
2,4-dinitrophenolate[a]	0	−0.15	−0.36	−0.56	−0.49	−0.21
2,4,6-trinitrophenolate[b]	0	−0.18	−0.62	−0.85	−0.87	−0.78
2,6-dibromo-4-nitrophenolate[a]	0	−0.57	−1.38	−2.01	−2.31	−2.14

methanol (wt %)	0	30	50	70	90	
BH^{+c}	0	0.54	0.73	0.94	1.06	
Me$_4$N^{+d}	0	0.28	0.51	0.87	1.37	

[a] Ref. (69) and (70) using values of $\Delta G_t^{\ominus}(H^+)$ in table 1. [b] Values for the picrate ion from table 1. [c] B = tris(hydroxymethyl)aminomethane; values from ref. (71) using $\Delta G_t^{\ominus}(Cl^-)$ from table 1. [d] From table 1.

ca. 40 wt %, but for transfers to lower wt % methanol mixtures the new values are lower than those in table 1. We have also included in the table for transfer to pure methanol a few results from a number of literature surveys.[1, 2, 42]

Values of $\Delta G_t^{\ominus}(H^+ + A^-)$ may be obtained from transfer values of the undissociated acids, $\Delta G_t^{\ominus}(HA)$, and pK values of the acids in water and in aqueous methanol. Juillard and Simonet[69] applied this method to a number of acids and then calculated $\Delta G_t^{\ominus}(A^-)$ using the $\Delta G_t^{\ominus}(H^+)$ values of de Ligny et al.[69] We have taken the original values of Juillard and Simonet[69, 70] and recalculated $\Delta G_t^{\ominus}(A^-)$ using our $\Delta G_t^{\ominus}(H^+)$ values; results are in table 13 together with values for the picrate ion from table 1. In a similar way, $\Delta G_t^{\ominus}(BH^+ + X^-)$ values for the conjugate acid of a base, BH^+, may be obtained from pK values and $\Delta G_t^{\ominus}(B)$, and knowing $\Delta G_t^{\ominus}(X^-)$ it is possible to calculate $\Delta G_t^{\ominus}(BH^+)$. Bates et al.[71] have determined $\Delta G_t^{\ominus}(BH^+ + Cl^-)$, where B = tris-(hydroxymethyl) aminomethane, and in table 13 are given values for $\Delta G_t^{\ominus}(BH^+)$ using our values of $\Delta G_t^{\ominus}(Cl^-)$ from table 1. As expected, the $\Delta G_t^{\ominus}$ values for the acid anions become more negative as the anion becomes larger and the (negative) non-electrostatic effect larger. The values for the picrate ion from table 1 are entirely compatible with those for the other phenolate ions obtained by Juillard and Simonet.[69, 70]

Although values of $\Delta G_t^{\ominus}$ for the simple alkali-metal halide ions (table 1) generally increase monotonically from water to methanol, the corresponding $\Delta H_t^{\ominus}$ and $\Delta S_t^{\ominus}$ values show marked fluctuations. The single-ion $\Delta H_t^{\ominus}$ values, table 7, exhibit a minimum (M^+) or maximum (X^-) at 10 wt % methanol, a maximum (M^+) or minimum (X^-) at ca. 50 wt % methanol and then a steady decrease (M^+) or increase (X^-) in value up to 100 wt % methanol. Such fluctuations are not unexpected in view of the well known variations with composition of a number of physical and thermodynamic properties of aqueous methanol mixtures,[72–75] as well as variations with composition of kinetic parameters.[75–77] As usual, the entropy fluctuations (as $-T\Delta S_t^{\ominus}$) mirror the fluctuations in $\Delta H_t^{\ominus}$ for single ions.

Criss et al.[78, 79] and Abraham[56] have discussed in detail entropies of transfer of single ions from water to a variety of pure solvents. Criss et al. showed that the standard partial molal entropies of single ions in a given solvent and in water were related through

$$\bar{S}^{\circ}(\text{in solvent}) = a + b\,\bar{S}^{\circ}(\text{in water}) \qquad (1)$$

where a and b are constants characteristic of the solvent. It follows from eqn (1) that single-ion entropies of transfer from water to the solvent will be given by

$$\Delta S_t^{\ominus} = a + (b-1)\, \bar{S}^{\ominus} \text{ (in water)}. \tag{2}$$

In eqn (1) and (2) 'absolute' values of $\bar{S}^{\ominus}$ were assigned with $\bar{S}^{\ominus}$ (H^+, aq) equal to -13 cal K^{-1} mol^{-1} on the mole fraction scale, equivalent to $\bar{S}^{\ominus}(H^+,$ aq$) = -5$ cal K^{-1} mol^{-1} on the molar scale used in the present work. With the latter value for $\bar{S}^{\ominus}(H^+,$ aq$)$,[80] $\bar{S}^{\ominus}(K^+,$ aq, 1 mol dm$^{-3}) = 19.2$ cal K^{-1} mol^{-1} and $\bar{S}^{\ominus}(Cl^-,$ aq, 1 mol dm$^{-3}) = 18.6$ cal K^{-1} mol^{-1}, so that from eqn (2) $\Delta S_t^{\ominus}(K^+) \approx \Delta S_t^{\ominus}(Cl^-)$. Single-ion entropies of transfer assigned according to the correspondence-plot method[78, 79] have been shown to agree well with those assigned according to $\Delta S_t^{\ominus}(Ph_4As^+,$ $Ph_4P^+) = \Delta S_t^{\ominus}(Ph_4B^-)$ for transfers from water to pure aprotic solvents, but not for transfers from water to pure alcohols.[4, 56] The approximation $\Delta S_t^{\ominus}(K^+) = \Delta S_t^{\ominus}(Cl^-)$ is a simplification of the correspondence-plot method but is quite sufficient to check the single-ion values of $\Delta S_t^{\ominus}$ given in table 11. For transfers from water to the aqueous methanol solvents containing up to 80 wt % methanol there is agreement between the $Ph_4P^+ = Ph_4B^-$ method of assignment and the correspondence-plot method to within *ca.* ± 2 cal K^{-1} mol^{-1}. Only for transfer to 90 wt % methanol and to methanol itself (as shown before[56]) do the two methods differ substantially. The cause of these differences must be due either to some peculiar solvation of Ph_4As^+, Ph_4P^+ or Ph_4B^- in the highly methanolic region or to a very large experimental error in the $\Delta G_t^{\ominus}$ or $\Delta H_t^{\ominus}$ values. Since the same type of discrepancy between the two single-ion assignment methods occurs also for transfers to pure ethanol and pure n-propanol, random experimental error seems unlikely. Judging from the values of $\Delta H_t^{\ominus}(NaBPh_4)$ in table 6 it is possible that the Ph_4B^- ion undergoes some specific interaction with methanol in the highly methanolic region.

Not only did Criss *et al.*[78, 79] apply the correspondence-plot method to entropies of transfer, but they also observed that for the alkali-metal halides values of $\Delta S_t^{\ominus}(M^+ + X^-)$ for transfers between water and pure solvents were largely independent of M^+ and X^-. That is, no matter what division into cation and anion values is used, $\Delta S_t^{\ominus}(M^+)$ will be the same for all the M^+ ions and $\Delta S_t^{\ominus}(X^-)$ will be the same for all the X^- ions, for a given transfer. Inspection of the results in table 11 shows that this is also the case for transfers from water to the various aqueous methanol solvents. Abraham[56] has shown that for transfers from water the constancy of the $\Delta S_t^{\ominus}(M^+ + X^-)$ values can not be extended to hydrophobic ions such as R_4N^+ or Ph_4P^+ or Ph_4B^-. For transfer to 70 wt % methanol we have results for an extended series of ions, table 10, that show the constancy of $\Delta S_t^{\ominus}(M^+ + X^-)$ not only for the alkali-metal halide ions but also for Ag^+ and ClO_4^-. As found by Abraham for transfer to pure methanol, values of $\Delta S_t^{\ominus}$ for the hydrophobic ions (above) are all more positive than for the simple ions. From the extended set of results for transfer to pure methanol, table 8, the SCN^- ion behaves as a simple anion and the picrate ion as a weakly hydrophobic ion, with $\Delta S_t^{\ominus}$ only 6 cal K^{-1} mol^{-1} more positive than for the simple anions as compared with a more positive $\Delta S_t^{\ominus}$ value of 24 cal K^{-1} mol^{-1} for the Ph_4B^- ion. From the few results[54] for M^{2+} ions it is possible that $\Delta S_t^{\ominus}(M^{2+})$ is constant at -60 cal K^{-1} mol^{-1} (compare the constant value of -21 ± 2 cal K^{-1} mol^{-1} for the seven simple M^+ ions in table 8), but more results are needed before a definite conclusion can be drawn.

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