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SINGLE ION FREE ENERGIES OF SOME IONS AND THE HYDROPHOBIC INTERACTIONS OF Ph_4AsBPh_4 AND Ph_4SbBPh_4 IN MIXED ETHANOL–WATER SOLVENTS

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ABSTRACT

Single ion free energies of Cl^-, Br^-, I^-, ClO_4^-, Ph_4B^-, H^+, K^+, Rb^+, Cs^+, Me_4N^+, Et_4N^+, n-Pr_4N^+, n-Bu_4N^+, Ph_4As^+ and Ph_4As^+ were estimated from the experimental solubilities of the corresponding tetraphenyl derivatives in mixed ethanol–water solvents or from the solubility data available in the literature and by applying the asymmetric tetraphenylarsonium-tetraphenylborate assumption at 25 ° C.

The single ion free energies were discussed with reference to the solute–solvent and solvent–solvent interactions. The critical behaviour of the single ion free energy values at low ethanol (EtOH) concentration in mixed $EtOH$–H_2O were discussed from the point of view of the hydrophobic interaction as calculated for the reference Ph_4AsBPh_4 and Ph_4SbBPh_4 electrolytes.

INTRODUCTION

The application of the asymmetric assumption for the reference electrolytes Ph_4AsBPh_4 and Ph_4SbBPh_4, which have cations and anions of similar size and large tetrahedral structures in which the central ion is buried in four phenyl rings, provides the possibility of evaluating single ion thermodynamic quantities in different solvents [1–10]. These reference electrolyte assumptions have been validated both experimentally and theoretically in pure and mixed solvents [11,12]. It has recently been demonstrated that both Ph_4AsBPh_4 and Ph_4SbBPh_4 have small differences between the thermodynamic quantities of their cations and anions [9–12]. This small difference can be important in evaluating the standard free energy of transfer from one solvent to another for small cations. The aim of the present work was to estimate the single ion free energies of transfer for some ions from water to ethanol and their mixtures, and to study the hydrophobic interaction of the

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reference Ph_4AsBPh_4 and Ph_4SbBPh_4 electrolytes in mixed EtOH–H_2O at 25 °C.

EXPERIMENTAL

All the prepared tetraphenyl derivatives, Ph_4AsBPh_4, Ph_4AsBr, Ph_4AsI, $KBPh_4$, $RbBPh_4$, $CsBPh_4$ and Ph_4SbBPh_4 were prepared by the condensation of Ph_4AsCl, $NaBPh_4$ and Ph_4SbBr with the corresponding salts and then filtered, dried, crystallized, recrystallized and stored. BDH ethanol was used. To determine the solubilities in ethanol, water and their mixtures of each of the above salts and the neutral compounds Ph_4C and Ph_4Ge (from Merck), used without purification, several mg of each salt were put into 10 ml of each solvent in a glass vial with an air-tight screw cap and shaken in a thermostat at 25 °C. Neutron activation analysis was used for the determination of the solubilities of Ph_4AsBPh_4 and Ph_4Ge, activating As and Ge to produce ^{76}As ($t_{1/2} = 26.4$ h) and ^{77}Ge ($t_{1/2} = 11.3$ h). Spectrophotometry and gravimetry were used for solubility determination of the other salts in mixed EtOH–H_2O solvents. The density was measured using a digital oscillator densimeter (Heraeus Paar DMA-50) and the dielectric constants were measured using a Dekameter DK 300 (WTW). All measurements were done at 25 ± 0.1 °C.

RESULTS AND DISCUSSION

The measured densities (ρ) and dielectric constants (ϵ) for the mixed ethanol–water solvents which are necessary for many calculations are listed in Table 1. The free energies of transfer of tetraphenylmethane (Ph_4C) and tetraphenylgermanium (Ph_4Ge) from water as a standard solvent to ethanol and their mixtures were evaluated by applying eqn. (1)

$$\Delta_w^s G_f^\ominus = -2.303RT(\log S_s - \log S_w) \tag{1}$$

where S is the solubility and the subscripts s and w denote the mixed solvent and water respectively. The calculated $\Delta_w^s G_t^\ominus$ values for Ph_4C and Ph_4Ge are listed in Table 1. The free energies of transfer for the reference electrolytes, Ph_4AsBPh_4 and Ph_4SbBPh_4, were calculated using eqns. (2)–(4) after correcting the solute–solute interactions by calculating the activity coefficient via the modified Debye–Hückel equation, eqn. (5) [12]

$$\Delta_w^s G_t^\ominus = -2.303RT\,\Delta pK_{sp} \tag{2}$$

$$\Delta pK_{sp} = pK_{sp(w)} - pK_{sp(s)} \tag{3}$$

$$pK_{sp} = -2\log S - 2\log \gamma_\pm \tag{4}$$

$$\log \gamma_\pm = -\frac{1.82 \times 10^6 \times S^{0.5}/(T\epsilon)^{1.5}}{\left[1 + 50.29 \times 10^8/(T\epsilon)^{0.5} a S^{0.5}\right]} \tag{5}$$

TABLE 1

Densities and dielectric constants of mixed EtOH–H_2O solvents and the standard free energies of transfer for Ph_4C, Ph_4Ge, Ph_4AsBPh_4, Ph_4B^- and Ph_4As^+ from water to mixed EtOH–H_2O solvents at 25° C (kJ mol^{-1} in molal scale)

X_s EtOH	d (g cm^{-3})	ϵ	$\Delta^s_w G^\ominus_t$ Ph_4C	$\Delta^s_w G^\ominus_t$ Ph_4Ge	$\Delta^s_w G^\ominus_t$ Ph_4AsBPh_4	$\Delta^s_w G^\ominus_t$ Ph_4B^-	$\Delta^s_w G^\ominus_t$ Ph_4As^+
0	0.99707	78.5	0	0	0	0	0
0.101	0.961	66	−5.439	−6.694	−23.430	−11.088	−12.343
0.200	0.931	54.5	−10.042	−11.506	−32.008	−15.272	−16.736
0.310	0.906	47.2	−14.226	−16.318	−37.447	−17.677	−19.769
0.364	0.886	43.1	−16.108	−17.991	−39.748	−18.933	−20.815
0.417	0.875	40.1	−17.364	−19.246	−41.108	−19.617	−21.497
0.479	0.863	37.4	−18.828	−20.502	−42.258	−20.292	−21.966
0.553	0.848	34.5	−19.874	−21.652	−43.514	−20.869	−22.648
0.636	0.835	32.2	−20.920	−23.012	−44.141	−21.025	−23.117
0.735	0.818	29.5	−22.175	−23.849	−44.559	−21.443	−23.117
0.854	0.802	27	−23.221	−25.104	−44.769	−21.443	−23.326
0.920	0.794	25.7	−23.744	−25.522	−45.083	−21.548	−23.430
1.0	0.784	24.3	−24.058	−26.150	−45.187	−21.548	−23.639

where pK_{sp} is the solubility product, $\gamma_\pm$ is the activity coefficient and a is the solvated radius for the reference electrolyte [10]. The experimental $\Delta^s_w G^\ominus_t$ values for Ph_4AsBPh_4 and Ph_4SbBPh_4 are shown in Tables 1 and 2. The single ion free energies of the reference ions are evaluated by the use of the following equations [11,12]

$$\Delta^s_w G^\ominus_t Ph_4B^- = \Delta^s_w G^\ominus_t Ph_4C + 1/2\big[\Delta^s_w G^\ominus_t Ph_4AsBPh_4 - \big(\Delta^s_w G^\ominus_t Ph_4C + \Delta^s_w G^\ominus_t Ph_4Ge\big)\big] \tag{6}$$

$$\Delta^s_w G^\ominus_t Ph_4As^+ = \Delta^s_w G^\ominus_t Ph_4Ge + 1/2\big[\Delta^s_w G^\ominus_t Ph_4AsBPh_4 - \big(\Delta^s_w G^\ominus_t Ph_4C + \Delta^s_w G^\ominus_t Ph_4Ge\big)\big] \tag{7}$$

$$\Delta^s_w G^\ominus_t Ph_4Sb^+ = \Delta^s_w G^\ominus_t Ph_4SbBPh_4 - \Delta^s_w G^\ominus_t Ph_4B^- \tag{8}$$

and their values are listed in Tables 1 and 2, which also show the asymmetric values for the cations and anions of the Ph_4AsBPh_4 and Ph_4SbBPh_4 electrolytes. From the experimental solubilities of Ph_4AsCl, Ph_4AsBr, Ph_4AsI, $KBPh_4$, $RbBPh_4$ and $CsBPh_4$ in the mixed solvents under consideration (on applying eqns. (2)–(5), and from many literature values [13–17], the single ion free energies for Cl^-, Br^-, I^-, ClO_4^-, H^+, K^+, Rb^+, Cs^+, Me_4N^+, Et_4N^+, n-Pr_4N^+ and n-Bu_4N^+ were calculated by applying the asymmetric Ph_4AsBPh_4 assumption, where the subscripts e and l represent the experimental and literature values respectively

$$\Delta^s_w G^\ominus_t Cl^- = \Delta^s_w G^\ominus_t Ph_4AsCl_{(e)} - \Delta^s_w G^\ominus_t Ph_4As^+ \tag{9}$$

$$\Delta^s_w G^\ominus_t Br^- = \Delta^s_w G^\ominus_t Ph_4AsBr_{(e)} - \Delta^s_w G^\ominus_t Ph_4As^+ \tag{10}$$

TABLE 2

Solubilities (S), solvated radii (a), activity coefficient ($\log \gamma_\pm$), solubility products (pK_{sp}), free energies of transfer ($\Delta^s_w G_t^\ominus$), free energies of making a cavity ($\Delta^s_w G_C^\ominus$), rearrangement free energies of transfer ($\Delta^s_w G_{rgt}^\ominus$) and the hydrophobic free energies ($\Delta^s_w G_{HI}^\ominus$) of transfer for Ph_4SbBPh_4 from water to mixed EtOH–H_2O solvents at 25 °C (kJ mol^{-1} in molal scale)

X_s	S	a (Å$^-$)	$\log \gamma_\pm$	pK_{sp}	$\Delta^s_w G_t^\ominus$ (kJ mol^{-1})	$\Delta^s_w G_t^\ominus$ Ph_4Sb^+ (kJ mol)	$\Delta^s_w G_C^\ominus$ (kJ mol^{-1})	$\Delta^s_w G_{rgt}^\ominus$ (kJ mol^{-1})	$\Delta^s_w G_{HI}^\ominus$ (kJ mol^{-1})
0	2.410×10^{-9}	9.885	-2.733×10^{-5}	17.0776	0	0	0	0	0
0.101	2.087×10^{-6}	9.964	-9.476×10^{-4}	11.363	−32.614	−21.527	−2.335	−30.279	−28.672
0.200	6.691×10^{-6}	10.043	-2.249×10^{-3}	10.354	−38.371	−23.099	−5.468	−32.903	−29.233
0.310	1.213×10^{-5}	10.129	-3.741×10^{-3}	9.839	−41.308	−23.631	−9.029	−32.279	−29.123
0.364	1.517×10^{-5}	10.173	-2.174×10^{-3}	9.642	−42.434	−23.502	−10.703	−31.731	−29.019
0.417	1.720×10^{-5}	10.214	-5.664×10^{-3}	9.540	−43.016	−23.401	−12.372	−29.644	−28.804
0.479	1.918×10^{-5}	10.263	-6.627×10^{-3}	9.447	−43.547	−23.255	−14.677	−28.870	−28.449
0.553	2.126×10^{-5}	10.322	-7.858×10^{-3}	9.361	−44.037	−23.167	−17.523	−26.514	−27.977
0.636	2.458×10^{-5}	10.389	-9.345×10^{-3}	9.238	−44.740	−23.715	−19.313	−25.427	−27.761
0.735	2.723×10^{-5}	10.466	−0.011	9.152	−45.233	−23.790	−21.372	−23.861	−27.472
0.854	3.173×10^{-5}	10.559	−0.014	9.025	−45.957	−24.514	−23.869	−22.088	−27.095
0.920	3.451×10^{-5}	10.612	−0.015	8.954	−46.363	−24.711	−25.347	−21.881	−26.881
1.0	3.618×10^{-5}	10.675	−0.017	8.917	−46.572	−25.025	−27.091	−19.481	−26.573

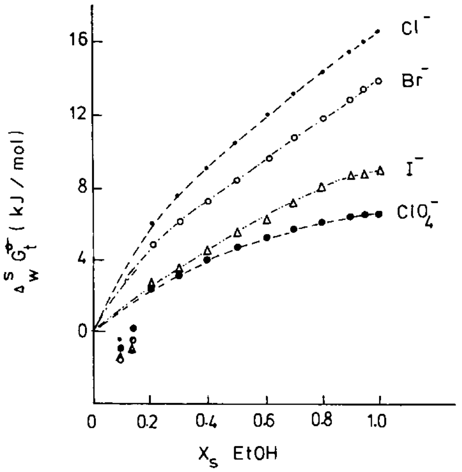


Fig. 1. Plots of single ion free energies of transfer for Cl^-, Br^-, I^- and ClO_4^- versus the mole fraction of ethanol in mixed $EtOH{-}H_2O$ solvents at 25 °C.

$$\Delta^s_w G_t^\ominus I^- = \Delta^s_w G_t^\ominus Ph_4AsI_{(e)} - \Delta^s_w G_t^\ominus Ph_4As^+ \qquad (11)$$

$$\Delta^s_w G_t^\ominus H^+ = \Delta^s_w G_t^\ominus HBr_{(l)} - \Delta^s_w G_t^\ominus Br^- \qquad (12)$$

$$\Delta^s_w G_t^\ominus K^+ = \Delta^s_w G_t^\ominus KBPh_{4(e)} - \Delta^s_w G_t^\ominus Ph_4B^- \qquad (13)$$

$$\Delta^s_w G_t^\ominus ClO_4^- = \Delta^s_w G_t^\ominus KClO_{4(l)} - \Delta^s_w G_t^\ominus K^+ \qquad (14)$$

$$\Delta^s_w G_t^\ominus Rb^+ = \Delta^s_w G_t^\ominus RbBPh_{4(e)} - \Delta^s_w G_t^\ominus Ph_4B^- \qquad (15)$$

$$\Delta^s_w G_t^\ominus Cs^+ = \Delta^s_w G_t^\ominus CsBPh_{4(e)} - \Delta^s_w G_t^\ominus Ph_4B^- \qquad (16)$$

$$\Delta^s_w G_t^\ominus Me_4N^+ = \Delta^s_w G_t^\ominus Me_4NCl_{(l)} - \Delta^s_w G_t^\ominus Cl^- \qquad (17)$$

$$\Delta^s_w G_t^\ominus Et_4N^+ = \Delta^s_w G_t^\ominus Et_4NCl_{(l)} - \Delta^s_w G_t^\ominus Cl^- \qquad (18)$$

$$\Delta^s_w G_t^\ominus n\text{-}Pr_4N^+ = \Delta^s_w G_t^\ominus n\text{-}Pr_4NCl_{(l)} - \Delta^s_w G_t^\ominus Cl^- \qquad (19)$$

$$\Delta^s_w G_t^\ominus n\text{-}Bu_4N^+ = \Delta^s_w G_t^\ominus n\text{-}Bu_4NCl_{(l)} - \Delta^s_w G_t^\ominus Cl^- \qquad (20)$$

The values for single ion free energies obtained from the above equations (eqns. (9)–(20)) are presented graphically in Figs. 1–4. It is observed from these figures that, with the exception of the large n-Pr_4N and n-Bu_4N^+ ions, all the ions have positive $\Delta^s_w G_t^\ominus$ values in mixed $EtOH{-}H_2O$ solvents, indicating the homo-solvatizing nature of these ions. It is also shown in Figs. 1–4 that all the single ion free energy values deviate from the curves at small mole fractions of ethanol (X_s between 0 and 0.2) in the mixed solvents owing to increased solvent–solvent and hydrophobic interactions.

The hydrophobic interactions of Ph_4AsBPh_4 and Ph_4SbBPh_4 in mixed $EtOH{-}H_2O$ was calculated from the empirical equation between the hydrophobic free energies $\Delta^s_w G^\ominus_{HI}$ and $\Delta^s_w G^\ominus_{rgt}$ for transfer from water to mixed

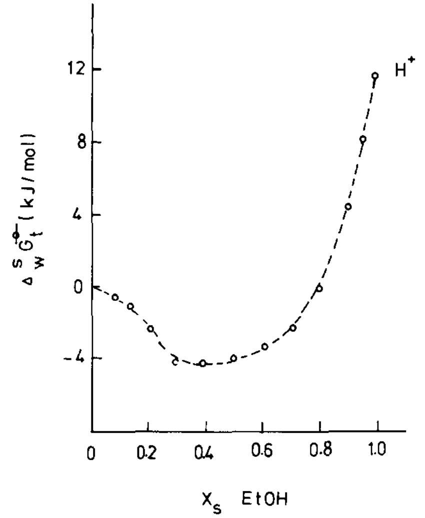


Fig. 2. Plots of single ion free energies for H^+ of transfer from water to mixed EtOH–H_2O solvents versus the mole fraction of ethanol at 25 °C.

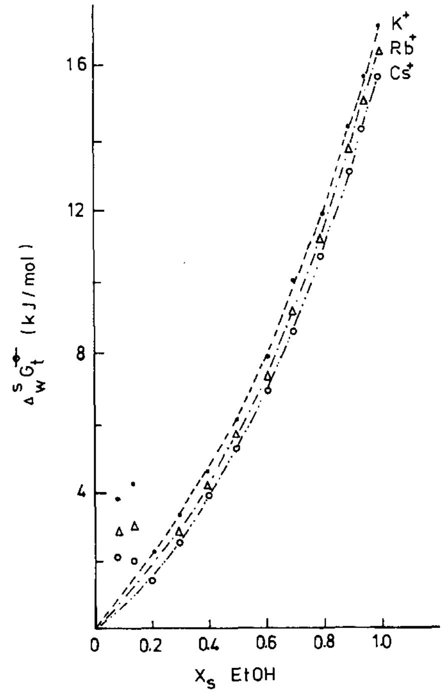


Fig. 3. Plots of single ion free energies of transfer from water to mixed EtOH–H_2O solvents for K^+, Rb^+ and Cs^+ ions versus the mole fraction of ethanol.

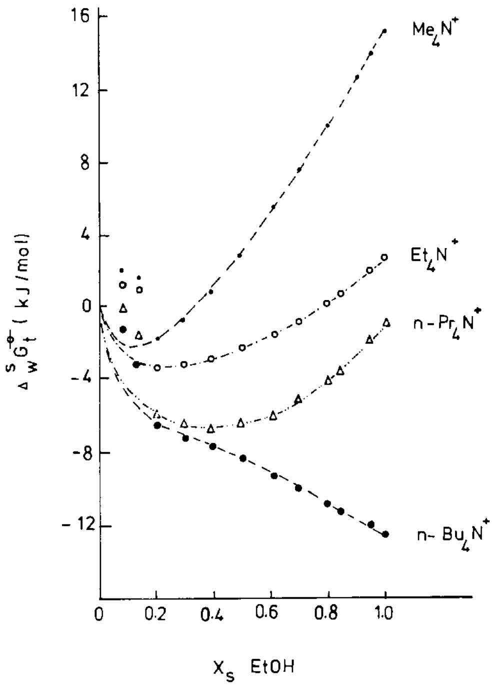


Fig. 4. Plots of single ion free energies of transfer for Me_4N^+, Et_4N^+, n-Pr_4N^+ and n-Bu_4N^+ versus the mole fraction of ethanol in mixed $EtOH-H_2O$ solvents at 25 °C.

$EtOH-H_2O$ solvents for long-chain decyltrimethylammonium carboxylates and some hydrocarbons [18,19] at different ethanol concentrations

$$\Delta^s_w G^\ominus_{HI} = -5.35 + 0.2072\ \Delta^s_w G^\ominus_{rgt} \tag{21}$$

$\Delta^s_w G^\ominus_{rgt}$ can be calculated using eqn. (22) [19]

$$\Delta^s_w G^\ominus_t = \Delta^s_w G^\ominus_C + \Delta^s_w G^\ominus_{rgt} \tag{22}$$

where $\Delta^s_w G^\ominus_t$ is the experimental free energy as calculated, $\Delta^s_w G^\ominus_C$ is the free energy of transfer expended in making a cavity and $\Delta^s_w G^\ominus_{rgt}$ is the free energy released when the solvent molecules rearrange. $\Delta G^\ominus_C$ can be calculated from the scaled particle theory [19–21] by application of eqn. (23). Their values and the transfer values $\Delta^s_w G^\ominus_C$, after subtracting from water, for Ph_4AsBPh_4 and Ph_4SbBPh_4 reference electrolytes are listed in Tables 2 and 3

$$\Delta G^\ominus_C = -RT\left\{\ln(1-Y) + \left(\frac{3Y}{1-Y}\right)R_{1,2} - \left[\left(\frac{3Y}{1-Y}\right) + \frac{9}{2}\left(\frac{Y}{1-Y}\right)^2\right]R^2_{1,2}\right\} + \frac{NYP}{\rho}R^3_{1,2} \tag{23}$$

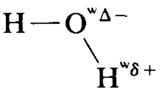
where $Y = (\pi\rho\sigma_1^3)/6$, $\rho = N/V_1^\ominus$, N is Avogadro's number, $V_1^\ominus$ is the molar volume, $P = 1$ atm, $R_{1,2} = \sigma_2/\sigma_1$ and σ_1 and σ_2 are the hard sphere diameters of the solvent and solute respectively [9].

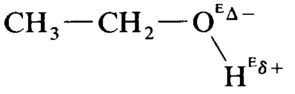
TABLE 3

Cavity free energies ($\Delta G_C^{\ominus}$), cavity free energies of transfer ($\Delta^s_w G_C^{\ominus}$), rearrangement free energies of transfer ($\Delta^s_w G_{rgt}^{\ominus}$) and the hydrophobic interaction for transfer ($\Delta^s_w G_{HI}^{\ominus}$) for Ph_4AsBPh_4 from water to mixed $EtOH-H_2O$ solvents at 25 °C (kJ mol^{-1})

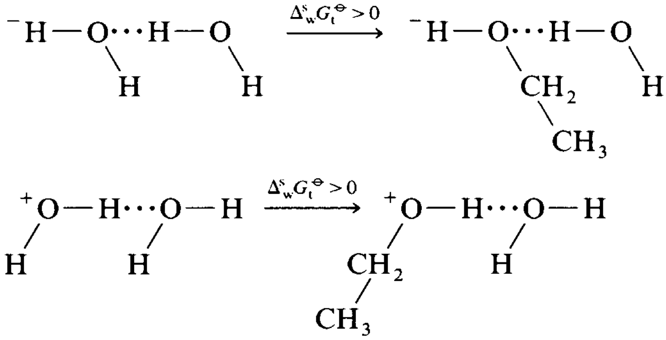
X_s EtOH	$\Delta G_C^{\ominus}$	$\Delta^s_w G_C^{\ominus}$	$\Delta^s_w G_{rgt}^{\ominus}$	$\Delta^s_w G_{HI}^{\ominus}$
0	85.517	0	0	0
0.101	83.249	−2.268	−21.163	−26.769
0.200	80.199	−5.318	−26.689	−27.916
0.310	76.730	−8.786	−28.660	−28.321
0.364	75.107	−10.409	−29.338	−28.464
0.417	73.484	−12.033	−29.075	−28.409
0.479	71.237	−14.279	−27.978	−28.183
0.553	68.471	−17.405	−26.468	−27.869
0.636	66.726	−18.790	−25.351	−27.635
0.735	64.839	−20.677	−23.882	−27.334
0.854	62.296	−23.221	−21.548	−26.849
0.920	60.856	−24.660	−20.422	−26.614
1.0	59.158	−26.359	−18.828	−26.284

The hydrophobic interaction free energies are the continuation or extension of the rearrangement of the solvent molecules which occurred when the non-polar ions (such as tetraphenyl ions) initially dissolved. Thus the hydrophobic interaction is the effect of a net increase in the structure of the solvent, showing maximum values when X_s for ethanol lies between 0 and 0.3 for Ph_4AsBPh_4 and Ph_4SbBPh_4 in mixed $EtOH-H_2O$. The solvation of the charged species is expected to be largely guided by the relative intensities of the positive and negative charge centres of the isolated dipoles and that of the ionic solutes concerned. The following picture may, to a first approximation, represent the isolated dipoles of water and ethanol, as has been indicated by Feakins [22]





Owing to the inductive effect of the ethyl group in ethanol, the negative charge density on the oxygen atom, ${}^{E}\Delta -$, is somewhat larger than the corresponding quantity on the water dipole, ${}^{W}\Delta -$. As a result, the protonic nature of the hydrogen atom of the -OH group in ethanol is enhanced. Furthermore, the ethanol molecule is also expected to induce a negative charge on the hydrogen atom of a water molecule hydrogen-bonded to it. The free energies of transfer of hydrogen ion (Fig. 2) in mixed $EtOH-H_2O$ indicate that these solvent mixtures are more basic in the X_s range 0.3–0.6 than in other proportions. Therefore, the total charge of the bonded mixture is less than that of each solvent alone. The single ion free energies of transfer for cations and anions from water to mixed EtOH–H_2O solvents can be illustrated as follows, giving positive free energy values



Because the larger cations are more solvated by dispersion interactions [23], the solvation of the ions Ph_4B^-, Ph_4As^+, Ph_4Sb^+, n-Pr_4N^+ and n-Bu_4N^+ (large negative transfer free energies) mainly takes place by dispersion processes.

REFERENCES

1 R. Alexander and A.J. Parker, J. Am. Chem. Soc., 89 (1967) 5549.
2 H.L. Friedman, J. Phys. Chem., 71 (1967) 381.
3 F.J. Millero, J. Phys. Chem., 75 (1971) 280.
4 I.M. Kolthoff and M.K. Chantooni, Jr., J. Phys. Chem., 76 (1972) 2024.
5 R. Fuchs and C.P. Hagen, J. Phys. Chem., 77 (1973) 1797.
6 B.G. Cox, G.R. Hedwig, A.J. Parker and D.W. Watts, Aust. J. Chem., 27 (1974) 477.
7 Y. Marcus, Rev. Anal. Chem., 4 (1980) 53.
8 O. Popovych, J. Phys. Chem., 88 (1984) 4167.
9 J.I. Kim, Bull. Soc. Chim. Belg., 95 (1986) 435.
10 E.A. Gomaa, Thermochim. Acta, 140 (1989) 7.
11 J.I. Kim, A. Cecal, H.-J. Born and E.A. Gomaa, Z. Phys. Chem., N.F., 110 (1978) 209.
12 J.I. Kim and E.A. Gomaa, Bull. Soc. Chim. Belg., 90 (1981) 391.
13 O. Popovych and A.J. Dill, Anal. Chem., 41 (1969) 456.
14 D. Bax, C.L. de Ligny and A.G. Remijnse, Recl. Trav. Chim. Pays-Bas, 91 (1972) 965.
15 D. Bax, C.L. de Ligny and M. Alfenaar, Recl. Trav. Chim. Pays-Bas, 91 (1972) 452.
16 R. Alexander, D.A. Owenby, A.J. Parker and W.E. Waghorne, Aust. J. Chem., 27 (1974) 933.
17 B.B. Luff and R.B. Reed, J. Chem. Eng. Data, 24 (1979) 206.
18 A. Ben-Naim, J. Phys. Chem., 79 (1975) 278.
19 D. Oakenfull and D.E. Fenwick, Aust. J. Chem., 30 (1979) 741.
20 R.A. Pierotti, Chem. Rev., 76 (1976) 717.
21 E.A. Gomaa, Thermochim. Acta, 128 (1988) 99.
22 D. Feakins, in F. Franks (Ed.), Physico-Chemical Processes and Mixed Aqueous Solvents, Heinemann, New York, 1967, pp. 71–91.
23 B.G. Cox and W.E. Waghorne, Chem. Soc. Rev., 9 (1980) 381.