

Ion-Solvent Interactions in Aqueous 2-Propanol & *t*-Butanol: Free Energies of Transfer of Some Ions from Water to Aqueous Mono-ols

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Transfer free energies ΔG_t^0 (i) of H^+ , K^+ , Cl^- , picrate (Pi^-) and tetraphenylboride (Ph_4B^-) ions have been obtained in several aqueous mixtures of 2-propanol and *t*-butanol by dissecting ΔG_t^0 values of the appropriate electrolytes using tetraphenylarsonium tetraphenylboride ($Ph_4AsPh_4B/TATB$) reference electrolyte (RE) method. The required ΔG_t^0 values of KPi , $KBPh_4$ and Ph_4AsPi have been obtained by measuring the saturated solubilities of the salts in the solvents. These values have been compared with the corresponding values in aqueous methanol and ethanol available in literature. The ΔG_t^0 (i)-composition profiles for these simple ions reflect that solvation of these ions is chiefly guided by the combined effects of acid-base, structural and Born-type interactions and that for picrate ion by the opposing effects of dispersion and H-bonding interactions, whilst that for Ph_4B^- is guided chiefly by cavity effect and partially by dispersion interactions.

In continuation of our earlier work¹ on transfer free energies of ions like H^+ , K^+ , Cl^- , picrate (Pi^-) and tetraphenylboride (Ph_4B^-) ions from water to aqueous mixtures of ethylene glycol^{1a} and glycerol^{1b} using tetraphenylarsonium tetraphenylboride (TATB) reference electrolyte (RE) method, we report herein the transfer free energies of the same ions from water to aqueous mixtures of 2-propanol and *t*-butanol using the RE method. The results have been compared with the data available in literature in aqueous mixtures of methanol² and ethanol³. Such a comparison will help reveal the relative contributions of different solvent parameters in dictating the relative stability or solvation of these ions in the series of aqueous mono-ols.

Materials and Methods

Purification methods of the alcohols and the salts of the reference electrolytes and the experimental details were essentially the same as described earlier^{1,4,5}. The essential uncertainties lie within $\pm 2\%$.

Results

The saturated solubilities (S) (in mol dm⁻³) of the electrolytes KPi , $KBPh_4$ and Ph_4AsPi at 25°C are presented in Table 1. As the dielectric constants of these water-rich media are fairly high these salts are assumed to be completely dissociated in these media. Hence, the values of the solubility product (K_{sp}) of these salts (CA) were determined by the relation (1)

$$K_{sp}^c(CA) = (S_{\pm}^c)^2 \quad \dots (1)$$

using the observed solubility data (S) and the corresponding mean molar activity coefficient ($\gamma_{\pm}$) values of the salts using the familiar Debye-Hückel relationship, as described earlier^{1,4}. The values of $\gamma_{\pm}$ and pK_{sp}^c (on molar scale) for the salts of RE are given in Table 2.

The ΔG_t^0 values for the salts of the reference electrolyte on mol fraction scale are obtained using the relation (2)

$$\Delta G_t^0(CA) = 2.303 RT [p(sK_{sp}^c) - p(wK_{sp}^c)] + 2.303 RT \log(d_s M_w / d_w M_s) \quad \dots (2)$$

where the subscripts s and w stand for the mixed solvent and water respectively. The ΔG_t^0 values for KPi , $KBPh_4$ and Ph_4AsPi are presented in Table 2.

$\Delta G_t^0(Ph_4AsPh_4B)$ values are obtained using the relation (3) and those for Ph_4B^- by relation (4)

$$\Delta G_t^0(Ph_4AsPh_4B) = \Delta G_t^0(Ph_4AsPi) + \Delta G_t^0(KBPh_4) - \Delta G_t^0(KPi) \quad \dots (3)$$

$$\Delta G_t^0(Ph_4As^+) = \Delta G_t^0(Ph_4B^-) = \frac{1}{2} \Delta G_t^0(Ph_4AsPh_4B) \quad \dots (4)$$

$\Delta G_t^0(K^+)$ values and those of other ions, were obtained by additivity rule using the values of the appropriate electrolytes, collected from literature (vide Table 2). The ΔG_t^0 (i) values for H^+ , Cl^- , K^+ , Pi^- and Ph_4B^- so obtained are presented in Table 3.

Discussion

Figure 1A shows the variation of $\Delta G_t^0(H^+)$ with mol % cosolvent. Except at lower compositions of *t*-butanol, the observed profiles move downward fairly smoothly confirming that H^+ gets increasingly stabilized with increased cosolvent composition and that structural changes in the solvent are not prominently reflected in the free energy function^{6a}.

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Table 1—Solubilities (S), Mean Activity Coefficients ($\gamma_{\pm}$) and Solubility Products (pK_{sp}^c) of KPi, Ph_4AsPi and $KBPh_4$ in Aqueous 2-PrOH and *t*-BuOH at 25°C

Mono-ol Wt %	S/mol dm ⁻³	$\gamma_{\pm}$	pK_{sp}^c
KPi			
<i>t</i> -BuOH			
0	—	—	3.41 ¹
10	0.188×10^{-1}	0.845	3.60
20	0.242×10^{-1}	0.797	3.43
30	0.368×10^{-1}	0.715	3.16
50	0.371×10^{-1}	0.556	3.37
2-PrOH			
10	0.184×10^{-1}	0.851	3.61
30	0.275×10^{-1}	0.767	3.35
50	0.302×10^{-1}	0.659	3.40
Ph_4AsPi			
<i>t</i> -BuOH			
0	—	—	8.92 ¹
10	0.089×10^{-3}	0.989	8.46
20	0.248×10^{-3}	0.974	7.23
30	0.855×10^{-3}	0.942	6.19
50	1.545×10^{-3}	0.867	5.75
<i>t</i> -PrOH			
10	0.060×10^{-3}	0.990	8.47
30	0.738×10^{-3}	0.951	6.31
50	1.634×10^{-3}	0.894	5.67
$KBPh_4$			
<i>t</i> -BuOH			
0	—	—	7.55 ¹
10	0.122×10^{-2}	0.977	7.14
20	0.122×10^{-2}	0.945	7.10
30	0.262×10^{-2}	0.903	5.87
50	0.383×10^{-2}	0.806	5.02
2-PrOH			
10	0.030×10^{-2}	0.976	7.07
30	0.171×10^{-2}	0.928	5.60
50	0.381×10^{-2}	0.848	4.98

Table 2—Standard Free Energies (ΔG_i^0) of KPi, Ph_4AsPi , $KBPh_4$ and KCl from Water to Aqueous 2-PrOH and *t*-BuOH at 25°C[ΔG_i^0 of salts in kJ mol⁻¹ (Mole fraction scale)]

Mono-ol Wt %	Mono-ol mol %	ΔG_i^0 of			
		KPi	Ph ₄ AsPi	KBPh ₄	KCl
<i>t</i> -BuOH					
10	2.63	0.60	− 3.11	− 3.40	1.4 ^a
20	5.78	− 0.87	− 10.66	− 10.45	2.9 ^a
30	9.44	− 2.96	− 17.12	− 14.55	4.6 ^a
50	19.55	− 3.11	− 20.90	− 17.21	7.8 ^a
2-PrOH					
10	3.23	0.69	− 3.02	− 3.07	1.5 ^b
30	11.39	− 1.77	− 16.30	− 12.44	4.2 ^b
50	23.08	− 2.69	− 21.10	− 17.18	7.5 ^b

a Feakins D & Merkethe P J, *J Electroanal Chem*, **84** (1977) 199.

b Basu Mallick I N & Kundu K K (Unpublished work)

Table 3—Standard Transfer Free Energies ΔG_i^0 (i) of Some Ions from Water to Aqueous 2-PrOH and *t*-BuOH at 25°C[ΔG_i^0 (i) values in kJ mol⁻¹]

Mono-ol Wt %	ΔG_i^0 of				
	Ph_4B^-	Pi^-	$H^{+ (a)}$	Cl^-	K^+
<i>t</i> -BuOH					
2.63	-3.6	0.5	0.0	1.2	0.2
5.78	-10.1	-0.6	-1.6	3.3	-0.4
9.44	-14.4	-2.7	-3.2	4.8	-0.2
19.55	-17.0	-3.5	-4.8	7.4	0.4
2-PrOH					
3.23	-3.4	0.4	-0.7	1.2	0.3
11.39	-13.5	-2.8	-2.4	3.2	1.0
23.08	-17.8	-3.4	-4.2	6.8	0.7

^(a)Required ΔG_i^0 (HCl) values were obtained from ref. 8.

Also, as expected from the inductive effect of CH_3 groups of the cosolvents, the observed increased stabilization with cosolvent composition and the relative order of stabilization at any composition follow the sequence: *t*-BuOH > 2-PrOH > EtOH > MeOH. The observed hump at lower compositions is due to the pronounced structural effect of the cosolvent *t*-BuOH⁷.

One of the striking differences in these profiles and those obtained by us earlier⁸ using extrapolation method^{6b}, is that here in each cosolvent system especially at water-rich compositions, $\Delta G_i^0(H^+)$ decreases rather slowly with mol % cosolvent, while in the earlier case a sharp fall has been observed for each cosolvent system. This is possibly the result of the intrinsic limitations of extrapolation technique^{6b} as compared to RE method. Besides, the observed sluggish fall of $\Delta G_i^0(H^+)$ with mol % cosolvents, as obtained by RE method seems to be rather reasonable because, besides the opposing effects of Born-type electrostatic interaction, the predominant cosolvent-induced basicity is also opposed by the effect of cosolvent-induced promotion of three dimensional H-bonded water structures which are formed by engaging basic O-centres of free H_2O molecules⁷. This corroborates Bates' earlier prediction⁹ regarding this type of effect of *t*-BuOH. Considering these two opposing effects it is expected that the basicity of these mixed solvents should decrease at a slower rate in the water-rich regions than that in alcohol-rich regions, where three dimensional water structures are broken down due to packing imbalance⁸. However, Born-type electrostatic contributions are likely to impart an upward trend overcoming the effects of increased basicity due to the larger amount of more basic cosolvent molecules as well as the relatively more free

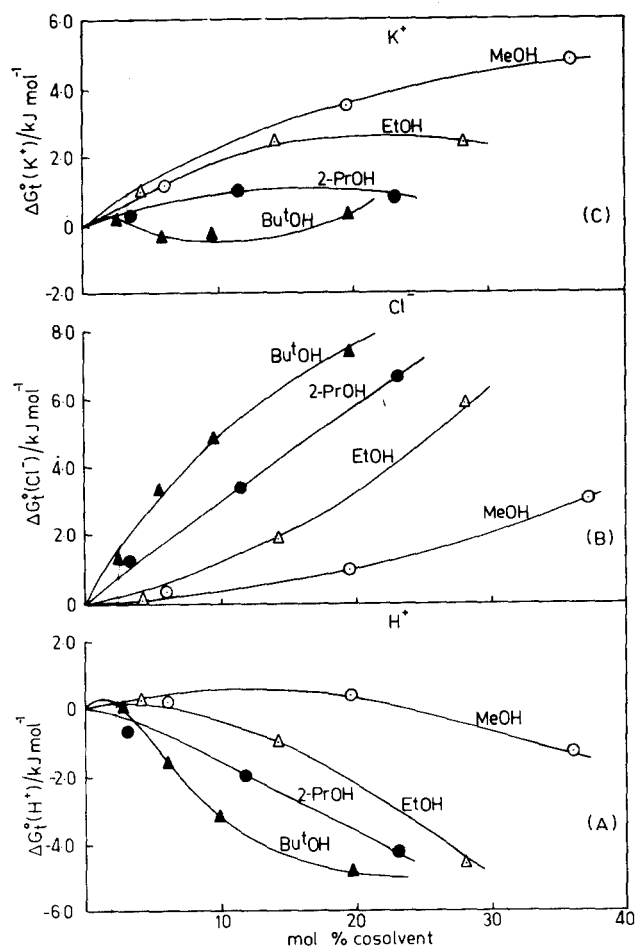


Fig. 1— $\Delta G_i^0(i)$ -composition profiles of (A) H^+ , (B) Cl^- and (C) K^+ in aqueous mixtures of MeOH, EtOH, 2-PrOH and t -BuOH

monomeric water molecules which are more basic than H-bonded water molecules.

ΔG_i^0 -composition profiles for Cl^- (Fig. 1B), unlike those for H^+ , exhibit increasingly positive trends indicating increased destabilization of Cl^- in these cosolvent systems. This and their relative order: t -BuOH > 2-PrOH > EtOH > MeOH suggest that the solvation of Cl^- is dictated by the combined effects of the decreased acidity or anion-H-centre type acid-base interactions^{6,10}, and increased Born-type electrostatic contributions of the respective cosolvent systems.

The $\Delta G_i^0(K^+)$ -composition profiles illustrated in Fig. 1C, show that except in aq. t -BuOH, K^+ ions, unlike H^+ ions, get increasingly destabilized in these media and the sequence of destabilization follows the order: MeOH > EtOH > 2-PrOH > t -BuOH. The decreased dielectric constant of these media on the small-sized K^+ supersedes the stabilizing influence of increased basicity of the media, as dictated by the cation-O-centre type acid-base interactions^{6,10}. Similar $\Delta G_i^0(K^+)$ -composition profiles were also noticed in some other aquo-organic systems^{1,5}. In the case of t -BuOH water mixtures, the initial hump is the

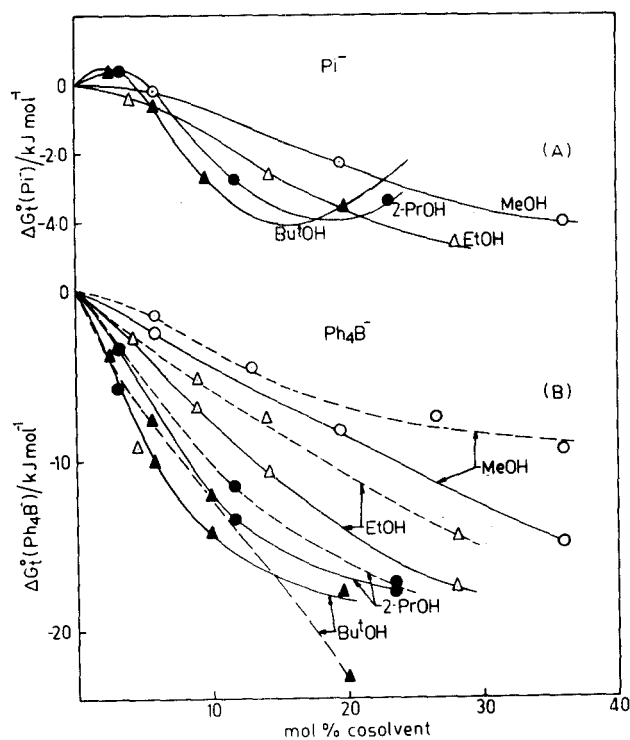


Fig. 2— $\Delta G_i^0(i)$ -composition profiles of (A) picrate ion (Pi^-) and (B) tetraphenyl boride ion (Ph_4B^-) [solid lines] and $\Delta G_i^0(cav)$ for Ph_4B^- [broken lines] in aqueous mixtures of MeOH, EtOH, 2-PrOH and t -BuOH

reflection of the superimposed predominant structural effect of t -BuOH compared to other cosolvents. Thus, as in the case of H^+ and Cl^- ions the relative stability of K^+ in these aqueous mono-ols as well as in other cosolvents is due to the combined effects of different parameters, viz acid-base interactions, Born-type electrostatic effect and structural interactions.

It is worth noting that while $\Delta G_i^0(i)$ -composition profiles for H^+ and K^+ in aq.- t -BuOH system exhibit inflections at water-rich regions due to predominant structural effect of t -BuOH no such inflection is observed for Cl^- . This type of structural interactions may also be explained from Clemente's recent theoretical analysis on water polymers¹¹. In that analysis it has been shown that the most stable geometry of water polymers $(H_2O)_n$ is with $n = 3-8$ and that while the O atoms in water molecules are engaged in forming H-bonds, one of the two H atoms of each water molecule remains free to undergo appropriate interaction. Thus, due to the enhanced water structure only the basic centres of water molecules are possibly perturbed to impart destabilization to H^+ and K^+ so as to exhibit the observed inflections in $\Delta G_i^0(H^+/K^+)$ -composition profiles.

Unlike those for Cl^- , $\Delta G_i^0(Pi^-)$ -composition profiles (Fig. 2A) in aq. MeOH and EtOH exhibit distinct downward trends, while those in aq. 2-PrOH and t -BuOH show roller-coaster type behaviour,

passing first through a maximum and then through a minimum. As is well known^{4,5,12}, the solvation of Pi^- is likely to be dictated by the combined effects of H-bonding interactions through all or some of the seven O-atoms each of which bears the shares of negative charge delocalized in the aromatic nucleus and the dispersion interactions of the π -electron cloud of the phenyl group of Pi^- with the hydrophobic moieties of cosolvent molecules. Moreover, since H-bonding interactions dictated by the acidity of the mixed solvents increase in the order $t\text{-BuOH} < 2\text{-PrOH} < \text{EtOH} < \text{MeOH}$ and the dispersion interactions dictated by the hydrophobicity decrease in the same order, it is likely that the combined effects of these two opposing interactions will partially compensate each other to varying degrees in these aquo-organic cosolvents and thus lead to the observed upward trends at higher compositions of the cosolvents. The upward trend will start earlier the larger the size of the cosolvents. The initial humps for $t\text{-BuOH}$ and 2-PrOH systems may arise partly from the involved structural changes induced by these cosolvents. Similar roller-coaster type behaviour has also been observed in the case of aqueous dimethylformamide^{4b} cosolvent system and aptly ascribed to result from the opposing effects of increased dispersion and decreased H-bonding interactions.

It is interesting to note that $\Delta G_t^0(i)$ values for Ph_4B^- are increasingly negative (Fig. 2B) reflecting that Ph_4B^- gets increasingly stabilized with increasing proportion of the organic cosolvents, and that at any composition the order of increased stabilization is $t\text{-BuOH} > 2\text{-PrOH} > \text{EtOH} > \text{MeOH}$. Since Born-type interactions are likely to be small for this large-sized ion, the observed pronounced stabilization of Ph_4B^- and the relative order in these series of mono-ols can be attributed, as in other pure and aquo-organic cosolvents^{2,5,13,14} to the combined effects of dispersion interactions $\Delta G_t^0(\text{int})$ and the cavity-forming interactions $\Delta G_t^0(\text{cav})$. Since the polarizability of the cosolvents dictating the dispersion interactions and the relative extent of H-bonded association dictating the cavity-forming interactions^{4b} in these series of mono-ols are in the order of the increasing size of the cosolvents, the order of stabilization of Ph_4B^- in these cosolvents should be $t\text{-BuOH} > 2\text{-PrOH} > \text{EtOH} > \text{MeOH}$. This is also found to be the case.

Tentative computation of $\Delta G_t^0(\text{cav})$ values using the scaled-particle theory (SPT) and the relations derived therefrom for mixed solvents^{12,13}, leads to the dotted curves shown in Fig. 2B. The required hard sphere diameters of the cosolvents and the solute molecules have been taken from the papers of Treiner¹³, and Edward and Farrel¹⁴ and the densities of the aqueous mixtures of the cosolvents were taken from

literature^{8,15}. From Fig. 2B it may be easily seen that a large part of $\Delta G_t^0(\text{Ph}_4\text{B}^-)$ is due to $\Delta G_t^0(\text{cav})$ term. But because of the involved approximations and uncertainties¹⁶⁻¹⁸ in SPT computations, particularly the effects of superimposed structural interactions associated with these well known parameters of three dimensional water structure at water-rich compositions and earlier packing imbalance of the large sized cosolvents, the difference of $\Delta G_t^0(\text{Ph}_4\text{B}^-)$ and $\Delta G_t^0(\text{cav})$ i.e. $\Delta G_t^0(\text{int})$ values does not distinctly reflect the dictates of increased relative dispersion effects of the cosolvents in the expected order. In fact the observed reversal of the sign of $\Delta G_t^0(\text{int})$ term at higher compositions of the large sized cosolvents in particular, is indicative of the fact that the repulsive interaction^{13b} involved in $\Delta G_t^0(\text{cav})$ term supersedes the effect of the dispersion term, which is likely to be effective at lower compositions the larger the size of the cosolvents.

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