Transfer entropies and structuredness of solvents

Kiron K. Kundu

Physical Chemistry Section, Jadavpur University, Calcutta- 700032, India.

Abstract – Standard transfer entropies, $\Delta S^{\circ}_t(i)$, of some ionic and non-ionic solutes from water to aqueous mixtures of some ionic and non-ionic cosolvents, as obtained from emf or solubility measurements at different temperatures, have been analyzed as structural probes in the light of a semiquantitative theory. It transpires that structuring and destructuring ability of a cosolvent depends upon the ratio of hydrophobic to hydrophilic propensities of the cosolvents. Increase in the hydrophobic groups in the cosolvent increases the promotion of 3D structure of water while increase in the hydrophilcity of H-bonding sites of organic cosolvents or hydration of ions of ionic cosolvents decreases the same.

INTRODUCTION

It is wellknown that standard transfer thermodynamic quantities, such as Gibbs free energy (ΔG°_t), enthalpy (ΔH°_t), entropy (ΔS°_t) etc. of any solute (i), which stand for the changes of those quantities accompanying the transfer of one mole of the solute (i) from the standard state in the reference solvent (R) to the standard state in the solvent (s) concerned, i.e. i(R)–i(s), is given by $\Delta P^{\delta}_t(i) = _{s}P^{\circ}(i) - _{R}\bar{P}^{\circ}(i)$, where P = G,H, S etc. Consequently, these quantities are intimately related with the solvent effect in the physico-chemical properties in general and kinetics and equilibria of reactions in particular.

It is also well recognized that composition profiles of $\Delta G^{\circ}_t(i)$ in various aqueous ionic and non-ionic cosolvent systems are usually monotonic, while those for $\Delta H^{\circ}_t(i)$ and $- T\Delta S^{\circ}_t(i)$ exhibit extremum with mirror-image relationship to each other. Since entropy part $(T\Delta S^{\circ})$ of the enthalpy (ΔH°) of reactions gets dissipated.in the surrounding media it is widely believed that the genesis of this lies in the alteration of the "structuredness" of the solvent media, if any.

But the question is what is meant by "structuredness" of aqueous ionic and non-ionic cosolvents. The answer lies in the unique feature of the electron distribution of water molecule itself, which is $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$. This imparts $4sp^3$ hybridized orbitals round the central O-atom of a water molecule, which are almost tetrahedrally spaced with HOH of 104.523°(ref.1a) and with 2 lone pair orbitals – the potential sites for H-bonding with 2 other H_2O molecules and 2 other orbitals bonded with 2 H atoms – the potential sites for H-bonding with lone pair orbitals of 2 other H_2O molecules. Thus, $5 H_2O$ molecules form a unit of three dimensional (3D) tetrahedrala water structure with 1 H_2O molecule at the centre and 4 others at the 4 corners of a tetrahedron H-bonded to the central

molecule (ref.1). These structured clusters are distributed in space giving rise to the 'structuredness' of water. Monomeric H_2O molecules also occupy the interstitial spaces. Thus there exists a statistical equilibrium (ref. 1-2) :

$$(H_2O)_{bulky} \longleftrightarrow (H_2O)_{dense} \qquad\qquad (1)$$

For understanding the solvent effect on the physico-chemical properties in general and equilibrium and kinetics of reactions in particular, in various ionic and non-ionic cosolvents an opt-repeated question is what happens to eqm(1)when different cosolvent are added to water. Kundu and co-workers proposed transfer entropies ΔS^o_t of hydrogen halides(HX) (ref. 3), benzoic acid (HBz) (ref. 4), p-nitroaniline (pNA) (ref. 5) and H_2O (ref. 6) as the fairly effective probes for the structuredness of solvents. The present lecture briefly reviews the said work.

TRANSFER ENTROPIES OF HX

Kundu and co-workers evolved ΔS^o_t(HX) (X = Cl, Br, or l) in a host of aquo-organic solvents by determining standard emf (E^o) values of cells comprising H_2
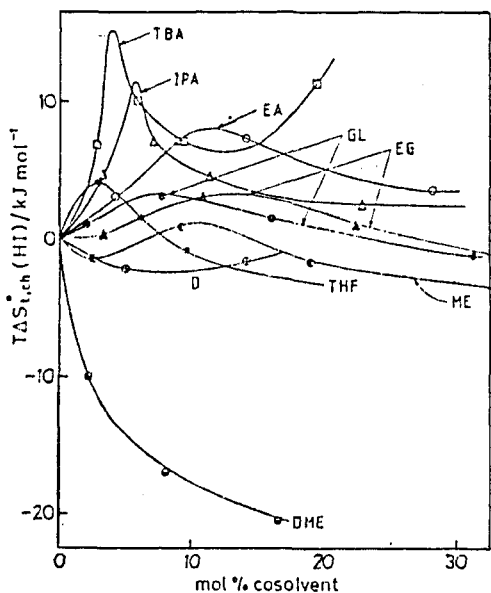

Fig.1. Variation of $T\Delta S^\bullet_{t,ch}$(HI) with mol% co-solvent in aquo-organic solvent systems at 25°C.

and Ag-AgX electrodes with HX (m), HA (m₁) NaA (m₂) NaX (m₃) or NaOH(m₁) NaX (m₂) as electrolytes depending upon thenature of the cosolvent. Fig. 1 illustrates $T\Delta S^o_t$, ch (HX) - composition profiles for aqueous ethyl alcohol (EA), isopropyl alcohol (IPA) and tert-butyl alcohol (TBA), where $T\Delta S^o_{t,ch}$(HX) values were obtained by subtracting the Borth-type electrostatic contributions (ref. 3) for H_3O & I⁻ from the observed $T\Delta S^o_t$ values. Significantly enough, the profiles yield 'characteristic maxima' which appear at lower compositions as the size and hydrophobicity of cosolvent increase. To account for this Kundu et al (ref. 3a) proposed a semi-quantitative theory which is based on 4-step transfer process from water to the mixed solvents as given below :

1. Dismantling of the hydration zones to give the bare ions plus attenuated gas of water molecules, accompanying $\Delta S^o_1 = n^p_w(S^g_w - S^p_w) + n^s_w (S^g_w - S^s_w)$.

2. Condensation of the attenuated gas to give normally structured liquid water, accompanying $\Delta S^o_2 = (n^p_w + n^s_w) (S^b_w - S^g_w)$.

3. Evaporation of liquid solvent molecules required for step·(4) from bulk liquid solvent to give attenuated 'solvent gas' molecules, accompanying $\Delta S^o_3 = (n^p_s + n^s_s) (S^g_s - S^b_s)$,

4. Formation of solvation zone around the bare ion from the 'solvent gas' giving solvated ion, accompanying $\Delta S^o_4 = n^p_s (S^p_s -S^g_w) + n^s_s (S^s_s -S^g_s)$ so that

$$\Delta S^o_{t'ch} = \Delta S^o_1 + \Delta S^o_2 + \Delta S^o_3 + \Delta S^o_4 \qquad (2)$$

Here n_s and S_s respectively denote the number of mole and molar entropy of solvent molecules, while n_w and S_w represent similar quantities for water. Also, the superscripts p,s,b and g respectively signify states of primary solvation zone (psz), secondary solvation zone (ssz), bulk and infinetely dilute gas.

Assuming that psz is composed wholly of water even in mixed solvents we have $n^p_s = n^p_w$, $S^p_s = S^p_w$. Further, as per conservation relations $n^p_{sb} + n^s_s = n^b_s$ and $n^p_w + n^s_w = n^b_w$. It follows that $n^s_s - n^s_w = n^b_s - n^b_w = s$ (say), then eq (2) transforms to

$$\Delta S^o_{t,ch} = n^s_s / S^s_s - S^s_w / + n^b_w / S^b_w - S^b_s /+ \delta / S^s_s - S^b_s / \qquad (3)$$

(a) when solvent structure $>$ pure water structure

$$S^s_s > S^s_w, \quad S^b_w > S^b_s, \quad S^s_s > S^b_s, \quad \delta \text{ small } \therefore \Delta S^o_{t,ch} > 0$$

(b) when solvent structure $<$ pure water structure

$$S^s_s < S^s_w, \quad S^b_w < S^b_s, \quad S^s_s < S^b_s, \delta < 0 \therefore \Delta S^o_{t,ch} < 0$$

Also, since the molar entropies in s and b ought to vary little with changing the size of X ions, and n^s_w, n^b_w and $/\delta/$ decrease i the sequence $I^- > Br^- > Cl^-$, it is expected that in more structured solvents $\Delta S^o_{t,ch}$ should decrease in the sequence $I^- > Br^- > Cl^-$ and reverse is true in the less structured solvents.

The observed $\Delta S^o_{t,ch}$ (HX) - composition profiles show well defined maxima around 3-4, 5-6 and 10-12 mol % TBA, IPA and EA respectively and then sharp decreases at higher cosolvent compositions, which conform to what is expected from the dictates of the structure promoting propensities and the size of the cosolvents (refs. 1,3). This confirms the validity of the above theory, as does the fat that at water-rich compositons $S^o_{t,ch}$ (HX) decreases in the order $I^- > Br^- > Cl^-$, whereas the reverse order is observed at higher cosolvent compositions due to the packing imbalance induced by cosolvents (see papers under ref.3).

Following the dictates of the above-noted semi-quantitative theory it may be concluded from the relative nature and positions of the said profiles for tetrahydrofuran (THF), dioxane (D) and 1,2-dimethoxyethane (DME) (vide fig.1) that THF molecule because of larger hydrophobicity shifts the eqm. (1) towards left and thus acts as structure maker (SM), while D and DME molecules shift the said eqm. (1) towards right and hence act as a weak and strong structure breaker (SB) respectively, as is expected from the relative hydrophobicity and hydrophilicity of the cosolvents.

Similarly, the relative nature and positions of the said profiles for ethylene glycol (EG), glycerol (GL) methoxy ethanol (ME) (vide fig.1) and DME in the same fig.1, lead also to conclude that because of opposing effects of hydrophobicity and hydrophilicity in EG and GL they are neither an SM nor an SB, while increased hydrophilicity of ME and DME, due to increased inductive effect, make them stronger SB's. The observed relative sequence of Cl^-, Br^- or I^- in all these cosolvents are also in accord with the dictates of the theory [vide papers under ref. 3].

TRANSFER ENTROPIES OF NON-ELECTROLYTES LIKE HBz AND pNA

In view of the possible confusion of the issue arising from the uncertainties of Born-type electrostatic contribution to $\Delta S^o_{t,ch}$ (HX) Kundu and co-workers considered it useful to test ΔS^o_t of non-electrolytes like HBz and pNA as the structural probes (refs. 4-5). The required data were obtained from solubility measurements of the solutes at several temperatures (10-40°C) in different aquo-ionic and non-ionic cosolvents including well known SM's like mono-ols and SB's like electrolytes, and the related transfer energetics evaluated by the usual relations.

Significantly enough, as in the case of HX, $T\Delta S^o_t$-composition profiles for both the solutes in these aqueous mono-ols exhibit haracteristic maxima at the respective 'magic' compositions (vide fig. 2) . Evidently the observed maxima are indicative of the effect of promotion of 3D structure by these mono-ols. In order to substantiate this Kundu et al adopted a model of these non-electrolyte solutes (M) with hydrophobic moiety similar to that proposed by Parker (ref. 7), as illustrated in fig. 3.
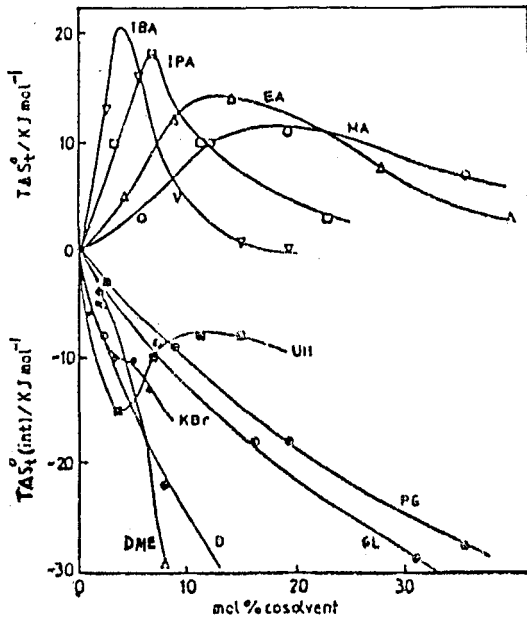
Fig.2. Variation of $T\Delta S_t^o$ & $T\Delta S_t^o$ (int) of p-HA with composition in some aquo-ionic and non-ionic cosolvents of 25°C.
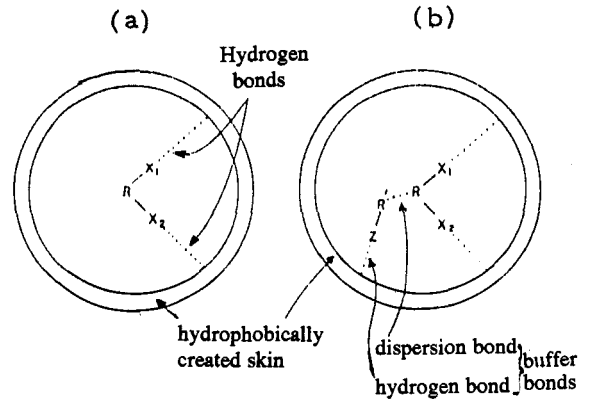

Fig.3. An amphiphilic molecule in (a) water, (b) mixed aqueous solvent. In the transfer process, (a) is the initial state and (b) is the final state.

The transfer of the molecule from water to the mixed solvents comprising water and cosolvent R'Z i.e. from state (a) to state (b) was considered to take place in 4 successive steps :

(1) Rapture of H-bonds (HB) between X_1, X_2 and the skin surface followed by the removal of M from the cavity, accompanying $\Delta S_1^o = -\Delta S_{HB}^w$

(2) Collapse of the skin phase to form normal water structure, accompanying $\Delta S_2^o = S_{bp}^w - S_{sp}^w$.

(3) Creation of a suitable cavity in the mixed solvent, accompanying $\Delta S_3^o = S_{sp}^s - S_{bp}^s$

(4) Introduction of M into the solvent cavity and formation of 'buffer bonds', accompanying $\Delta S_4^o = \Delta S_{HB}^s + \Delta S_{BB}^s$

So, $\Delta S_t^o(i) = \Delta S_1^o + \Delta S_2^o + \Delta S_3^o + \Delta S_4^o$

$$= (S_{sp}^s - S_{sp}^w) + (S_{bp}^w - S_{bp}^s) + (\Delta S_{HB}^s - \Delta S_{HB}^w) + \Delta S_{BB}^s \qquad (4)$$

The subscripts sp and bp denote values on the skin phase and bulk phase respectively and ΔS_{HB} and ΔS_{BB} are entropy changes associated with the formation of H-bonds and buffer bonds respectively.

From a careful analysis of the relative magnitudes of different terms it transpired that the behaviour of ΔS_t^o is chiefly guided by the second term of eq. (4), so that ΔS_t^o exhibits a maxima presumably where the structure is most ordered and falls away sharply as the proportion of cosolvent R'Z increases. Due to the packing imbalance, as has been observed in aqueous mono-ol systems - the well known 3D structure promoters, at initial compositions, and thus establishes ΔS_t^o as a structural probe.

When this probe was applied to the aqueous mixtures of different organic cosolvents like EG, propylene glycol (PG), GL, D, DME, acetonitrile (ACN) and ionic cosolvents like LiCl, KBr etc. (vide ref. 4a), the behaviour of the profiles for organic cosolvents in particular, were found to be at variance not only with those obtained from earlier studies, but also with that expected from

structural and electronic consideration. This led us to consider that as these non-electrolytes are fairly large in size 'cavity forming effect' $\Delta S^{o}_{t,cav}$(i) might significantly contribute to the observed ΔS^{o}_{t} values. Following Desrosiers et al's formulations (ref. 8) based on scaled particle theory (ref. 9) $S^{o}_{t,cav}$(i) values were therefore computed tentatively and subtracted from the corresponding ΔS^{o}_{t} values. The resulting $\Delta S^{o}_{t,int}$(i)-composition profiles for both the non-electrolytes (vite fig.3 for pNA) when examined in the light of the above-noted theory impart the expected structural conclusions regarding these cosolvent systems. Thus, unlike IPA, the polyols, ethers, ACN and the electrolyte cosolvents are found to induce structure breaking of 3D water structures right from initial compositions. Also, the graded reduction of structure promoting effect of IPA in PG and GL cosolvent systems confirm that structuring and destructuring ability of a cosolvent depends on the ratio of hydrophilicity to hydrophobicity of the cosolvents. And the observed roller-coaster type behaviour of the corresponding profiles in aqueous urea is indicative of the effect of 3D structure breaking at initial compositions followed by urea-water aggregation around 4-10 m urea (vide ref. 5,6).

In another attempt , bedises cavity affect, when dipole-dipole and dispersion interactions were computed by appropriate formulations as depicted by Marcus (ref. 10) and used by us (ref.4d) were aslo subtracted from ΔS^{o}_{t} values yielded hydrophobic hydration effect ($\Delta S^{o}_{t,HH}$) for both HBz and pNA, as $S^{o}_{t,HH}$(i) = ΔS^{o}_{t}(i) - $\Delta S^{o}_{t,cav}$(i) - $\Delta S^{o}_{t,dd}$(i) - $\Delta S^{o}_{t,disp}$(i). Significantly enough, the composition profiles of $\Delta S^{o}_{t,HH}$ for both HBz & pNA (fig. 4 for pNA) so resulted in aqueous solutions of IPA, & GL, are also found to be more or less similar to the corresponding $\Delta S^{o}_{t,int}$-composition profiles and thus led us to arrive at the same conclusions regarding the structuredness of the solvents.
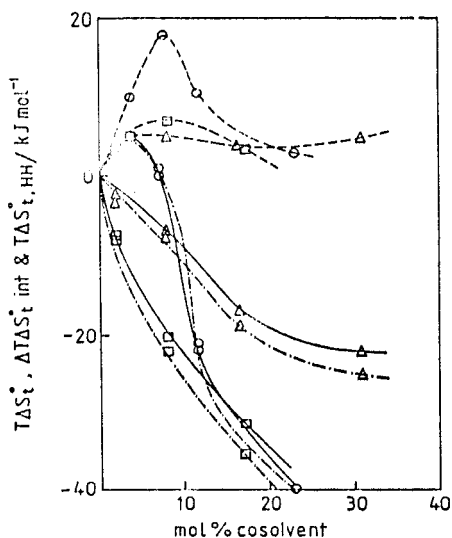

Fig. 4 Variation of $T\Delta S^{o}_{t}$ (---), $T\Delta S^{o}_{t}$ int (-·-·-) & $T\Delta S^{o}_{t,HH}$ (——) of p-NA with composition in different cosolvents (o IPA, Δ GL ▢ D) at 25°C.
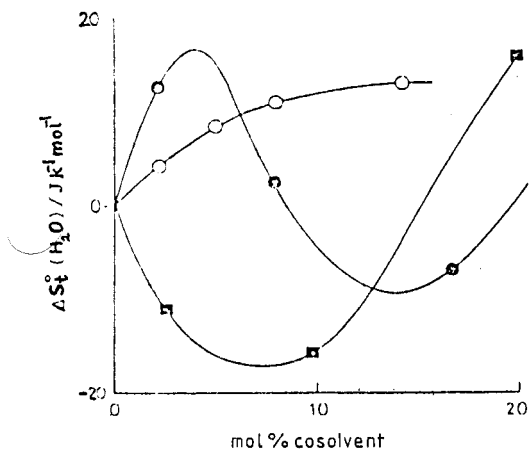

Fig.5 Variation of ΔS^{o}_{t}(H_2O) in aqueous ethers :

▢ THF, ● DME, and o dioxane.

TRANSFER ENTROPIES OF H₂O MOLECULE: ΔS^{o}_{t}(H_2O)

Yet another highly interesting and useful probe for the structuredness of aqueous aprotic cosolvents was arrived at from ΔS^{o}_{t} (H_2O). This was obtained from the autoionization constant $K_{a,ion}$ of H_2O molecules in the aqueous mixtures of some ethers like THF, D and DME (ref.6) at different temperatures, as determined from the measurements of appropriate galvanic cells in the solvents. Since

$$\delta \Delta S^{o}_{a,ion} = \Delta S^{o}_{a,ion} - {}_{w}\Delta S^{o}_{a,ion} = \Delta S^{o}_{t}(H^{+}) + \Delta S^{o}_{t}(OH^{-}) - \Delta S^{o}_{t}(H_2O) \qquad (4)$$

the required [$\Delta S^o_t(H^+)$ +ΔS^o_t (OH$^-$)] values were tentatively obtained by slight extrapolation of the observed smooth plots of the literature values of ΔS^o_t (H$^+$) + ΔS^o_t (X$^-$) [X = Cl, Br & I] against $(r_x)^{-1}$ to $r_x- = r_{OH}- = 0.55$ nm in the respective solvent systems. The resulting ΔS^o_t (H$_2$0)-composition profiles for all the cosolvents are illustrated in fig.5. Simple consideration of order-disorder phenomena indicates that addition of THF initially enhances the 3D structure of water while at higher compositions breaks down the same due to packing imbalance. On the other hand, addition of D to water induces breaking down of 3D structue right from the beginning, while DME induces 3D structure breaking initially, followed by formation of H-bonded DME-water complexes around 4-14 mol % DME and then ultimately packing imbalance at higher compositions.

TRANSFER ENTROPIES OF R₄N⁺ IONS

It is well known that hydrophobic solutes or ions with apolar residues induce water molecules around them to organize in a way similar to clathrate hydrates (ref.1b) causing hydrophobic hydration (HH) and result in a significant increase of free energy and decrease of entropy of the system (ref.11). In a bid to see the salt and solvent effect on hydrophobic hydration, Talukdar and Kundu (ref.12) recently studied transfer free energies and transfer entropies of some R_4N^+ (R = Me, Et, Pr and Bu) ions in aqueous mixtures of NaNO$_3$, TBA and ACN by solubility masurements of R_4N^+ picrate salts in aqueous NaNO$_3$ at different temperatures and using the previously determined ΔP^o_t(Pi) values in the solvents and that of R_4N Ph$_4$B salts in aqueous TBA and ACN solvents at 25°C and using the previously determined ΔG^o_t (Ph$_4$B$^-$) values and coupling the literature values of ΔH^o_t (R$_4$N$^+$) , both based on TATB assumption (ref. 13).

The ΔP^o_t(i) values of R_4N^+ when subtracted from the corresponding cavity and electrostatic effects yielded $\Delta P^o_{t,HH}$ (R$_4$N$^+$) values. The solid lines in fig.6 reflect a comparative view of $\Delta G^o_{t,HH}$ (R$_4$N$^+$)-composition profiles of R_4N in the solvents. This suggests that HH effect in different cosolvent systems as compared to that in pure water decreases in the order : aqueous NaNO$_3$
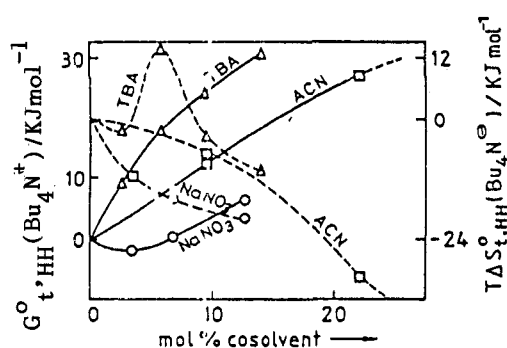

< aqueous ACN < aqueous TBA. This also conforms to what is expected from the relative depletion of free H$_2$0 molecules for undergoing hydrophobic hydration due to the promotion of 3D water structure by TBA, formation of intercomponent H-bonded (H$_2$0)$_x$-ACN complexes (ref. 14) by structure breaker ACN and the hydrophilic hydration of Na$^+$ and NO$_3^-$ ions due to ionic force field round the ions in the NaNO$_3$ cosolvent system.

Fig.6. Variation of $\Delta G^o_{t,HH}$(i) (—) and $T\Delta S^o_{t,HH}$(i)(---) of tetrabutylammonium cation with (mol%) cosolvent ccmpositions of TBA(△) ACN(□) and NaNO₃(o) at 298°K.

The dotted lines in fig.6 reflect the comparison of $T\Delta S^o_{t,HH}$-composition profiles of Bu_4N^+ in these aqueous

ionic and non-ionic cosolvent systems. These follow the dictates of the entropy changes accompanying Kundu et al's four-step transfer process. The minimum at lower compositions of TBA is indicative of the effect of negative entropy effect of ssz molecules over the positive entropy effect of HH for the R_4N^+, contributing an overall constant negative magnitudes of ΔS^o_1 + ΔS^o_2 . These on being combined with increasing positive magnitudes of ΔS^o_3 + ΔS^o_4 cause the minimum. But beyond 6 mol % TBA breaking down of the relevant structure occurs due to hte onset of packing imbalance. Evidently, characteristic maximum implies the 3D structure making effect of TBA, while the absence of the same in both ACN & NaNO$_3$ cosolvent systems implies 3D structure breaking effect of those cosolvents.

It was concluded that although dispersion between the hydrophobic parts of cosolvent molecules and R-groups of R_4N^+ ions are in operation in aqueous TBA and ACN systems, the overall effect of desolvation of R_4N^+ ions is the effect of HH, which is suppressed due to depletion of monomeric water molecules in these as well as in $NaNO_3$ cosolvent systems as compared to pure water. This led to the positive magnitudes of $\Delta G^o_{t,HH}$. Besides, the $T\Delta S^o_t$ (R_4N^+)-compsition profiles reflect the change in solvent structure around the R_4N^+ ions in the present study and thus led to the concept as well as the relative measures of the salt and solvent effect on hydrophobic hydration.

REFERENCES

1. a) B.E.Conway, Ionic Hydration the Chemistry and Biophysics, Elseveyer Scientific Publishing Company, Amsterdam (1981).

    b) F.Franks and D.G.Ives, Q.Rev.Chem.Soc. 20, 1-44 (1966).

    c) W.Y.Wen, Water and Aqueous Solutions, Horne R.A.ed., Wiley Inter Science, New York (1972).

2. J.C. Ahluwalia and T.S.Sarma, Chem.Soc.Rev. 2, 203-232 (1973).

3. a) K.Bose, K.Das, A.K.Das and K.K.Kundu, J.Chem.Soc.Faraday Trans. 1 74 1051-1063 (1978) and the relevant references therein.
    b) I.N.Basu-Mullick and K.K.Kundu,Can.J.Chem. 57 961-967 (1979).
    c) J.Datta and K.K.Kundu, Can.J.Chem. 59, 3149-3156 (1981).
    d) P.Guha and K.K.Kundu, Can.J.Chem. 63, 798-803 (1985).

4. a) K.Das, K.Bose,A.K.Das and K.K.Kundu, J.Phys.Chem. 82, 1242-1248 (1978).
    b) J.Datta and K.K.Kundu, J.Phys.Chem.86,4055-4061 (1982).
    c) S.Rudra , H.Talukdar and K.K.Kundu, Can.J.Chem. 66, 469-475(1988).
    d) S.Sinha and K.K.Kundu, Ind. J.Chem. - Press

5. a) K.Bose and K.K.Kundu, Can.J.Chem. 55, 3961-3966 (1977).
    b) J.Datta and K.K.Kundu, Can.J.Chem. 61, 625-631 (1983).

6. J.Datta and K.K.Kundu, Can.J.Chem. 59, 3141-3148 (1981).

7. A.J.Parker, Electrochim. Acta, 21, 671-679 (1976).

8. N.Desrosiers and J.E. Desroyers, Can.J.Chem.54, 3800-3808 (1976).

9. R.A.Pieorotti, J.Phys. Chem. 67, 1840-1845 (1963); 69, 281-288 (1965); Chem. Rev. 76, 717-726 (1976).

10. Y.Marcus, Ion Solvation, John Wiley & Sons Ltd., Chichester (1985).

11. J.B.F.N. Engberts and J.J.H.Nusselder, Pure Appl. Chem. 62, 47-50 (1990).

12. H.Talukdar and K.K.Kundu, J.Phys.Chem. 95, 3796 --3800(1991) ; 96, 970-975 (1992).

13. B.G.Cox, G.H.Hedwig, A.J.Parker and D.W.Watts, Aust.J.Chem. 27, 477-501 (1974).

14. K.Das, A.K.Das and K.K.Kundu, Electrochim. Acta, 26, 471-478 (1981) and the relevant references therein.