

# Chemical Transfer Energetics of the $-\text{CH}_2-$ Group: A Possible Probe for the Solvent Effect on Hydrophobic Hydration and the 3D-Structuredness of Solvents

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Transfer Gibbs energies  $\Delta G^\circ_t$ , and entropies,  $\Delta S^\circ_t$ , of  $-\text{CH}_2-$  have been evolved in aqueous mixtures of methanol (MeOH), ethanol (EtOH), 2-propanol (2-PrOH), *tert*-butyl alcohol (t-BuOH), and acetonitrile (ACN) by determining the solubilities of Ag salts of acetate ( $\text{OAc}^-$ ), propionate ( $\text{OPr}^-$ ), *n*-butyrate ( $\text{OBU}^-$ ), as well as picrate ( $\text{Pi}^-$ ) ions from 15 to 35 °C by spectrophotometric measurements. The chemical contributions of these energetics of the ions (i),  $\Delta G^\circ_{t,\text{ch}}(\text{i})$  and  $T\Delta S^\circ_{t,\text{ch}}(\text{i})$ , at  $T = 298.15$  K have been evolved by subtracting the cavity effect and Born-type and ion–dipole-type electrostatic interaction effects.  $\Delta G^\circ_{t,\text{ch}}(\text{i})$  values of carboxylates ( $\text{RCOO}^-$ ) are guided by solvent acidity induced hydrophilic hydration ( $\text{H}_\text{b}\text{H}$ ) of the  $\text{COO}^-$  ion and cosolvent induced hydrophobic hydration ( $\text{H}_\text{h}\text{H}$ ) of the R group and the back-bonding interaction of  $d^{10}$  electrons in the case of  $\text{Ag}^+$  ion, while  $T\Delta S^\circ_{t,\text{ch}}(\text{i})$  values are partly guided by structural effects as well.  $\Delta G^\circ_{t,\text{ch}}$  and  $T\Delta S^\circ_{t,\text{ch}}$  values of  $-\text{CH}_2-$  are found to be more or less same, indicating their additivity. The increase in  $\Delta G^\circ_{t,\text{ch}}(-\text{CH}_2-)$ –composition profiles and the “characteristic maximum” of  $T\Delta S^\circ_{t,\text{ch}}(-\text{CH}_2-)$ –composition profiles indicate the effect of increasingly reduced  $\text{H}_\text{b}\text{H}$  caused by increasing 3D-structure promotion of these alkanols. The decrease in  $\Delta G^\circ_{t,\text{ch}}(-\text{CH}_2-)$  and the broad minimum in  $\Delta S^\circ_{t,\text{ch}}(-\text{CH}_2-)$  in aqueous ACN indicate the effect of increased  $\text{H}_\text{b}\text{H}$  caused by 3D structure breaking of ACN. Thus the chemical transfer energetics and especially entropies of  $-\text{CH}_2-$  reflect not only the solvent effect on  $\text{H}_\text{b}\text{H}$  but also the 3D-structuredness of aquo-organic cosolvents.

## Introduction

It is well known that genesis of the unique properties of water lies in the three-dimensional (3D) tetrahedral structure of water molecules.<sup>1–3</sup> These “bulky” 3D water clusters along with some “dense” monomeric water molecules in the interstitial spaces are distributed in space giving rise to the “structuredness” of water. Numerous studies<sup>3–7</sup> on thermodynamic, kinetic, transport, and spectroscopic properties reflect the existence of structuredness of aquo-organic solvents as well. Kundu and co-workers’ comprehensive studies<sup>7</sup> on transfer energetics  $\Delta P^\circ_t(\text{i})$ , where  $P = G, S$ , and  $H$  and especially  $P = S$  and  $i =$  hydrogen halides (HX),<sup>7b</sup> benzoic acid (HBz),<sup>7c</sup> *p*-nitroaniline (pNA),<sup>7d</sup>  $\text{H}_2\text{O}$ ,<sup>7e</sup> and also tetraalkylammonium ions ( $\text{R}_4\text{N}^+$ ),<sup>7f</sup> from water to aquo-ionic and nonionic cosolvents, transpired that the structuring and destructuring ability of a cosolvent depends on the ratio of hydrophobic to hydrophilic propensity of the cosolvents. An increase in the hydrophobic groups in the cosolvents increases the promotion of 3D bulky water structure, while an increase in the hydrophilicity of H-bonding sites of organic cosolvents or hydration of ions in ionic cosolvents decreases the same.

Kundu and co-workers’ recent studies<sup>8</sup> on  $\Delta S^\circ_t(\text{i})$  of individual ions as based on the TATB method,<sup>9</sup> i.e.,  $\Delta S^\circ_t(\text{Ph}_4\text{As}^+) = \Delta S^\circ_t(\text{Ph}_4\text{B}^-) = \frac{1}{2}\Delta S^\circ_t(\text{Ph}_4\text{As} \text{ Ph}_4\text{B})$  in various aquo-cosolvents indicate that while small hydrophilic cations such as  $\text{H}^+$  and  $\text{K}^+$  pass through a maximum, relatively larger anions such as  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  pass through a minimum at water-rich compositions reflecting mirror-image relations. This unique observation was explained in the light of Kundu *et al.*’ four-step transfer process<sup>7,8,10</sup> and the ion-induced perturbation of the relative 3D-structuredness of aqueous cosolvents.

Since HBz,<sup>7c</sup> pNA,<sup>7d</sup> and  $\text{R}_4\text{N}^+$  ions<sup>7f</sup> contain both hydrophobic and hydrophilic moieties, they exhibit the so-called “buffer bonds”.<sup>7c,d</sup> These arise from the combined dispersion and H-bonding interaction with cosolvent molecules in the surrounding hydrophobic hydration sphere<sup>11,12</sup> around these nonelectrolyte/ions. And since the combined solvent effect on the “buffer bonds” may confuse the issue to some extent, one may wonder about the real efficacy of the  $\Delta S^\circ_t$  of these species as structural probes. But hydrophobic solutes induce hydrophobic hydration<sup>11–16</sup> alone and result in an increase of free energy and a decrease of entropy of the system.<sup>15</sup> So, transfer energetics and entropies of hydrophobic solutes would give a better view of the 3D-structuredness of aqueous mixtures of ionic and nonionic cosolvents.

Since the  $-\text{CH}_2-$  group induces “hydrophobic” hydration alone, it would be of particular interest and utility to study the behavior of transfer energetics and especially  $\Delta S^\circ_t(-\text{CH}_2-)$  as a function of cosolvent composition in aqueous alkanols such as MeOH, EtOH, 2-PrOH, and t-BuOH, which have increasing 3D structure-making propensity<sup>2a</sup> and then in structure breaking cosolvents<sup>7a,f,17</sup> such as ACN and the like. It is hoped that “standardization” of the relative behavior of the  $-\text{CH}_2-$  group in two different types of cosolvent systems will help decide its utility as a useful probe for the 3D-structuredness and hydrophobic hydration.

Preliminary attempts for finding out  $\Delta S^\circ_t(-\text{CH}_2-)$  from  $\Delta S^\circ_t$  of phenylacetic acid (PhAc) and benzoic acid from additional solubility measurement of PhAc in aqueous alkanols are found unfeasible because of an additional phase separation. The Ag salts of acetic (HOAc), propionic (HOPr), and butyric (HOBu) acids are found to be sparingly soluble in all the aquo-cosolvent

systems referred to above. So,  $\Delta S^\circ_t$  values of the Ag salts ( $\text{RCOO}^- \text{Ag}^+$ ) ( $\text{R} = \text{Me}, \text{Et}, \text{or Pr}$ ) were determined by measuring their solubility at five equidistant temperatures ranging from 15 to 35 °C. The required  $\Delta S^\circ_t$  values of  $\text{Ag}^+$  were obtained by measuring the solubility of sparingly soluble silver picrate ( $\text{AgPi}$ ), the  $\Delta S^\circ_t(\text{Pi}^-)$  values being known for these solvent systems from our previous studies.<sup>8c</sup> The  $\Delta S^\circ_t(\text{RCOO}^-)$  values helped determine  $\Delta S^\circ_t(-\text{CH}_2-)$  values on subtracting the corresponding values of acetate from propionate and of propionate from butyrate.

## Material and Methods

Methods of purification of the cosolvents, preparation of the salts, and measurement by spectrophotometry were similar to those adopted earlier.<sup>7,8,18–20</sup> Constancy of absorbance to within  $\pm 1\%$  was taken as the criterion of the attainment of equilibrium. At least two sets of measurements were made and the results were found to agree within  $\pm 1\%$ . Molar extinction coefficients and  $\lambda_{\text{max}}$  values of  $\text{AgPi}$  were taken from literature.<sup>8a,20</sup> Corresponding extinction coefficients for  $\text{AgOAc}$ ,  $\text{AgOPr}$ , and  $\text{AgOBu}$  were found to be  $1.17 \times 10^3$ , and  $1.18 \times 10^3$ ,  $1.3 \times 10^3$ , respectively, at  $\lambda = 200 \text{ nm}$ .

## Results

$\text{pK}^\circ_{\text{sp}}$  values and free energies of solution  $\Delta G^\circ_s$  on molar scale of all the salts at five temperatures in water and aqueous alkanols and ACN were computed using the relations

$$\text{pK}^\circ_{\text{sp}} = -2 \log (s y_{\pm}) \quad (1)$$

$$\Delta G^\circ_s = 2.303RT \text{pK}^\circ_{\text{sp}} \quad (2)$$

where  $s$  is the observed saturated solubility in  $\text{mol dm}^{-3}$  listed in Table 1 and  $y_{\pm}$  is the mean molar activity coefficient of the salts as computed by the use of the extended Debye–Huckel equation.<sup>21</sup> Values of density ( $d_s$ ) and dielectric constant ( $\epsilon_s$ ) are taken from the literature.<sup>21–24</sup> Ion-size parameters of the ions are taken to be  $0.3 \text{ nm}$ .<sup>22</sup> The estimated uncertainties in  $\Delta G^\circ_s$  are about  $\pm 0.025 \text{ kJ mol}^{-1}$ . All the salts are assumed to be completely ionized as  $\epsilon$  values of most of the solvents lie above 35 and the salts have low solubility.  $\Delta G^\circ_s$  values at different temperatures were fitted by least squares to the equation

$$\Delta G^\circ_s = a + bT + cT \ln T \quad (3)$$

The values of the coefficient  $a$ ,  $b$ , and  $c$  are in Table 2. These values reproduce the experimental value to within  $\pm 0.03 \text{ kJ mol}^{-1}$ . Transfer energetics  $\Delta G^\circ_t$  and  $T\Delta S^\circ_t$  from water to aquo-cosolvents at 25 °C were calculated on the mole fraction scale using (4) and (5) and are listed in Table 2.

$$\Delta G^\circ_t = {}_s\Delta G^\circ_s - {}_w\Delta G^\circ_s = 2.303RT[\text{p}_s K^\circ_{\text{sp}} - \text{p}_w K^\circ_{\text{sp}}] - 2RT \ln (M_s d_w / M_w d_s) = (a_s - a_w) + (b_s - b_w)T + (c_s - c_w)T \ln T - 2RT \ln (M_s d_w / M_w d_s) \quad (4)$$

$$\Delta S^\circ_t = (b_w - b_s) + (c_w - c_s)(1 + \ln T) + 2R \ln (M_s d_w / M_w d_s) - 2RT (d \ln d_s / dT - d \ln d_w / dT) \quad (5)$$

Subscripts  $s$  and  $w$  refer to the cosolvents and water, respectively, and  $M$  is the molar or mean molar mass of pure and mixed solvents. As in previous works,<sup>7,8</sup> the estimated uncertainties in  $\Delta G^\circ_t$  and  $\Delta S^\circ_t$  are about  $\pm 0.05 \text{ kJ mol}^{-1}$  and  $\pm 2 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively.  $\Delta G^\circ_t(i)$  values can be divided into

cavity, electrostatic, and chemical contributions

$$\Delta G^\circ_t(i) = \Delta G^\circ_{t,\text{cav}}(i) + \Delta G^\circ_{t,\text{el}}(i) + \Delta G^\circ_{t,\text{ch}}(i) \quad (6)$$

where  $\Delta G^\circ_{t,\text{cav}}(i)$  is the difference in free energy change involved to create cavities for the ion in water and aquo-cosolvents from scaled particle theory (SPT),<sup>7,8,22a,25</sup> and  $\Delta G^\circ_{t,\text{el}}(i)$  is the electrostatic term associated chiefly with a Born-type interaction<sup>26</sup> and ion–dipole interaction term.<sup>27</sup> Corresponding ion-induced dipole ( $i$ – $d$ ) and ion–quadrupolar ( $i$ – $q$ ) interaction terms are likely to be negligibly small<sup>19,28</sup> and are not included in  $\Delta G^\circ_{t,\text{el}}(i)$ . The values of  $\Delta G^\circ_{t,\text{ch}}(i)$  in Table 3, and illustrated in Figure 1a–d, include all other effects such as those arising from acid–base or short range interaction, hydrophilic/hydrophobic hydration, and structural effects. Similarly  $T\Delta S^\circ_{t,\text{ch}}(i)$  values were calculated by subtracting  $T\Delta S^\circ_{t,\text{B}}(i)$  and  $T\Delta S^\circ_{t,\text{cav}}(i)$  from total  $T\Delta S^\circ_t(i)$  values and are listed in Table 3 and illustrated in Figure 1a–d. The terms involved in  $\Delta G^\circ_{t,i-d}(i)$  are not temperature dependent, and hence the  $i$ – $d$  term for  $\Delta S^\circ_t(i)$  is taken to be zero.

## Discussion

**Free Energies of Transfer.** The data in Table 3 and Figure 1a show that  $\text{Ag}^+$  is stabilized in the order  $t\text{-BuOH} > 2\text{-PrOH} > \text{EtOH} > \text{MeOH}$ . The negative magnitudes of  $\Delta G^\circ_{t,\text{ch}}(i)$  values arise from the increased “basicity” of the media, and d-electron back-bonding.<sup>8a</sup>

Figure 1b–d shows that increased destabilization of  $\text{OAc}^-$ ,  $\text{OPr}^-$ , and  $\text{OBu}^-$  is in the order  $t\text{-BuOH} > 2\text{-PrOH} > \text{EtOH} > \text{MeOH}$ . Destabilization of the ions follows the order  $\text{OBu}^- > \text{OPr}^- > \text{OAc}^-$ .  $\Delta G^\circ_{t,\text{ch}}(\text{RCOO}^-)$  values are guided by both “hydrophilic hydration” ( $\text{H}_b\text{H}$ )<sup>11,12,15</sup> of  $\text{COO}^-$  through the acidity of the solvents and “hydrophobic hydration” ( $\text{H}_b\text{H}$ )<sup>11,12,15</sup> induced by R groups. Had the effect of superimposed dispersion interaction of the R group of  $\text{RCOO}^-$  and R' groups of R'OH solvents been dominant, increased solvation of the R group of the ions would have resulted in reverse order of  $\Delta G^\circ_{t,\text{ch}}(i)$ . It has been observed for  $\text{R}_4\text{N}^+$  ions in aqueous  $t\text{-BuOH}$  and ACN.<sup>7f</sup>

This e-donating inductive ( $I$ ) effect of the alkyl group of the alcohols follows the order  $t\text{-BuOH} > 2\text{-PrOH} > \text{EtOH} > \text{MeOH}$ .<sup>8e</sup> The proticity of the  $-\text{OH}$  group and hence acidity of the cosolvents would decrease in the reverse order. As a result the  $\text{RCOO}^-$  ions would be destabilized due to the “acidity” effect of the solvents in the same order, as has been observed (Figure 1a–d). Moreover, since the e-donating ( $I$ ) effect of alkyl groups of  $\text{RCOO}^-$  ions would increase in the order  $\text{OAc}^- < \text{OPr}^- < \text{OBu}^-$ , it is expected that their desolvation due to decreased acidity of the solvents would also follow same order, as observed (Figure 1e).

Since  $(\text{RCOO}^-)$  ions induce monomeric  $\text{H}_2\text{O}$  molecules around them to organize similarly to clathrate hydrates causing  $\text{H}_b\text{H}$ , resulting in a significant “increase” of free energy and “decrease” of entropy of the system,<sup>11–16</sup> these anions are likely to get hydrophobically hydrated in water in the order  $\text{OAc}^- < \text{OPr}^- < \text{OBu}^-$ . The structure inducing propensity of the aqueous alkanols decreases the number of monomeric  $\text{H}_2\text{O}$  molecules in the aqueous mixtures in the order  $t\text{-BuOH} > 2\text{-PrOH} > \text{EtOH} > \text{MeOH}$ . So it will reduce the  $\text{H}_b\text{H}$  in the same order. The observed destabilization of  $\text{RCOO}^-$  ions in these aqueous alkanols is guided by increased hydrophilic hydration ( $\text{H}_b\text{H}$ ) of  $-\text{COO}^-$  and decreased hydrophobic hydration ( $\text{H}_b\text{H}$ ) of R as compared to water.

$\Delta G^\circ_{t,\text{ch}}(i)$  values of  $\text{Ag}^+$  in Table 3 and Figure 2 decrease in aqueous ACN, whereas in aqueous 2-PrOH they decrease at

**TABLE 1: Solubility  $S$  (in mol dm<sup>-3</sup>) of AgPi, AgOAc, AgOPr, and AgOBu in Water and Aqueous MeOH, EtOH, 2-PrOH, t-BuOH, and ACN at Different Temperatures**

solutes	$S$	15°	20°	25°	30°	35°	solutes	$S$	15°	20°	25°	30°	35°
H <sub>2</sub> O													
AgPi	×10	0.382	0.427	0.472	0.525	0.592	AgOPr	×10	0.455	0.478	0.501	0.526	0.551
AgOAc	×10	0.586	0.624	0.667	0.710	0.752	AgOBu	×10	0.208	0.215	0.220	0.227	0.238
10 wt % MeOH													
AgPi	×10	0.356	0.391	0.424	0.459	0.502	AgOPr	×10	0.373	0.380	0.399	0.407	0.421
AgOAc	×10	0.496	0.520	0.542	0.566	0.589	AgOBu	×10	0.164	0.165	0.172	0.176	0.177
30 wt % MeOH													
AgPi	×10	0.361	0.403	0.457	0.519	0.576	AgOPr	×10	0.215	0.226	0.237	0.251	0.266
AgOAc	×10	0.247	0.265	0.282	0.301	0.321	AgOBu	×10	0.096	0.101	0.104	0.109	0.115
50 wt % MeOH													
AgPi	×10	0.375	0.427	0.507	0.569	0.659	AgOPr	×10	0.116	0.124	0.133	0.142	0.151
AgOAc	×10	0.129	0.140	0.152	0.164	0.177	AgOBu	×100	0.745	0.785	0.804	0.865	0.903
70 wt % MeOH													
AgPi	×10	0.433	0.473	0.519	0.571	0.629	AgOPr	×100	0.777	0.815	0.872	0.918	0.957
AgOAc	×100	0.741	0.796	0.855	0.908	0.960	AgOBu	×100	0.504	0.525	0.540	0.562	0.594
10 wt % EtOH													
AgPi	×10	0.340	0.367	0.417	0.489	0.567	AgOPr	×10	0.328	0.351	0.373	0.396	0.419
AgOAc	×10	0.439	0.468	0.502	0.537	0.589	AgOBu	×10	0.157	0.164	0.173	0.183	0.189
20 wt % EtOH													
AgPi	×10	0.347	0.405	0.465	0.535	0.631	AgOPr	×10	0.252	0.270	0.289	0.313	0.338
AgOAc	×10	0.349	0.378	0.409	0.436	0.477	AgOBu	×10	0.128	0.137	0.146	0.155	0.165
30 wt % EtOH													
AgPi	×10	0.383	0.449	0.486	0.571	0.662	AgOPr	×10	0.201	0.217	0.233	0.252	0.271
AgOAc	×10	0.263	0.285	0.308	0.332	0.358	AgOBu	×10	0.103	0.111	0.115	0.123	0.131
50 wt % EtOH													
AgPi	×10	0.636	0.716	0.792	0.891	1.042	AgOPr	×10	0.148	0.158	0.169	0.179	0.189
AgOAc	×10	0.159	0.172	0.186	0.199	0.214	AgOBu	×100	0.883	0.924	0.979	1.029	1.081
70 wt % EtOH													
AgPi	×10	0.805	0.871	0.933	1.023	1.175	AgOPr	×10	0.117	0.124	0.131	0.138	0.144
AgOAc	×10	0.083	0.089	0.095	0.102	0.109	AgOBu	×100	0.676	0.707	0.739	0.770	0.801
10 wt % 2-PrOH													
AgPi	×10	0.321	0.355	0.409	0.479	0.590	AgOPr	×10	0.339	0.364	0.391	0.416	0.443
AgOAc	×10	0.440	0.473	0.513	0.549	0.587	AgOBu	×10	0.159	0.168	0.178	0.190	0.202
20 wt % 2-PrOH													
AgPi	×10	0.452	0.499	0.572	0.706	0.794	AgOPr	×10	0.256	0.276	0.299	0.324	0.349
AgOAc	×10	0.354	0.388	0.417	0.447	0.484	AgOBu	×10	0.133	0.144	0.155	0.167	0.179
30 wt % 2-PrOH													
AgPi	×10	0.634	0.722	0.809	0.954	1.096	AgOPr	×10	0.226	0.242	0.259	0.277	0.298
AgOAc	×10	0.262	0.284	0.307	0.331	0.356	AgOBu	×10	0.113	0.120	0.128	0.136	0.143
50 wt % 2-PrOH													
AgPi	×10	1.077	1.180	1.288	1.403	1.517	AgOPr	×10	0.157	0.167	0.178	0.189	0.202
AgOAc	×10	0.166	0.179	0.193	0.208	0.223	AgOBu	×10	0.109	0.113	0.118	0.125	0.132
70 wt % 2-PrOH													
AgPi	×10	1.036	1.148	1.247	1.365	1.486	AgOPr	×10	0.135	0.145	0.157	0.169	0.181
AgOAc	×10	0.098	0.107	0.116	0.126	0.136	AgOBu	×100	0.819	0.874	0.937	0.999	1.061
10 wt % t-BuOH													
AgPi	×10	0.390	0.422	0.500	0.572	0.654	AgOPr	×10	0.378	0.406	0.433	0.467	0.491
AgOAc	×10	0.541	0.578	0.615	0.663	0.710	AgOBu	×10	0.168	0.178	0.189	0.201	0.214
20 wt % t-BuOH													
AgPi	×10	0.559	0.650	0.751	0.851	0.979	AgOPr	×10	0.244	0.266	0.288	0.314	0.343
AgOAc	×10	0.429	0.469	0.508	0.545	0.585	AgOBu	×10	0.139	0.150	0.163	0.177	0.192
30 wt % t-BuOH													
AgPi	×10	0.828	0.944	1.097	1.202	1.417	AgOPr	×10	0.215	0.236	0.258	0.283	0.309
AgOAc	×10	0.385	0.407	0.444	0.496	0.547	AgOBu	×10	0.117	0.127	0.138	0.149	0.162
40 wt % t-BuOH													
AgPi	×10	1.125	1.202	1.328	1.462	1.708	AgOPr	×10	0.183	0.198	0.214	0.230	0.247
AgOAc	×10	0.316	0.342	0.368	0.396	0.425	AgOBu	×10	0.101	0.109	0.117	0.125	0.133
20 wt % ACN													
AgOAc		0.365	0.392	0.402	0.421	0.450	AgOBu		0.135	0.136	0.137	0.138	0.140
AgOPr		0.289	0.298	0.305	0.313	0.321							
40 wt % ACN													
AgOAc		0.371	0.383	0.397	0.412	0.424	AgOBu		0.149	0.150	0.151	0.152	0.153
AgOPr		0.322	0.328	0.336	0.343	0.350							
60 wt % ACN													
AgOAc		0.243	0.249	0.254	0.259	0.265	AgOBu		0.128	0.131	0.132	0.133	0.136
AgOPr		0.237	0.243	0.248	0.252	0.254							

**TABLE 2: Coefficients  $a$ ,  $b$ , and  $c$  in the Equation  $\Delta G^\circ_s = a + bT + cT \ln T$  for AgPi, AgOAc, AgOPr, and AgOBu in Water and Aqueous MeOH, EtOH, 2-PrOH, t-BuOH, and ACN and Transfer Energetics  $\Delta G^\circ_t$  and  $T\Delta S^\circ_t$  from Water to Aqueous Cosolvents at 25 °C (in Mole Fraction Scale)**

solutes	$a$ (kJ mol <sup>-1</sup> )	$b$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )	$c$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G^\circ_t$ (kJ mol <sup>-1</sup> )	$T\Delta S^\circ_t$ (kJ mol <sup>-1</sup> )	solutes	$a$ (kJ mol <sup>-1</sup> )	$b$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )	$c$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G^\circ_t$ (kJ mol <sup>-1</sup> )	$T\Delta S^\circ_t$ (kJ mol <sup>-1</sup> )
H <sub>2</sub> O											
AgPi	-99.72	2.9043	-0.442 10			AgOPr	-11.37	0.5753	-0.085 51		
AgOAc	22.53	-0.1074	0.013 50			AgOBu	-105.96	2.6275	-0.387 61		
10 wt % MeOH											
AgPi	-8.88	0.7295	-0.113 55	0.27	-7.33	AgOPr	-19.92	0.6768	-0.097 60	0.80	-5.60
AgOAc	19.08	-0.1389	0.021 69	0.78	-6.56	AgOBu	43.19	-0.7868	0.124 57	0.81	-4.47
30 wt % MeOH											
AgPi	-6.88	0.8739	-0.140 28	-0.70	3.87	AgOPr	-64.78	1.8135	-0.269 22	2.81	-1.04
AgOAc	12.26	0.1553	-0.024 02	3.32	-2.86	AgOBu	-40.85	1.2442	-0.180 97	2.73	0.98
50 wt % MeOH											
AgPi	8.16	0.6632	-0.112 41	-1.81	12.13	AgOPr	14.67	0.1125	-0.015 72	5.04	0.80
AgOAc	27.80	-0.1099	0.015 20	5.69	-0.59	AgOBu	-85.71	2.2774	-0.335 18	3.55	2.38
70 wt % MeOH											
AgPi	-70.89	2.1663	-0.329 77	-2.77	-0.86	AgOPr	64.77	-1.0749	0.164 44	6.35	-3.90
AgOAc	91.24	-1.6055	0.242 03	7.88	-6.26	AgOBu	-120.25	3.0124	-0.442 60	4.66	-1.58
10 wt % EtOH											
AgPi	-470.27	11.3588	-1.707 50	-0.67	6.62	AgOPr	34.51	-0.3765	0.055 40	1.07	2.68
AgOAc	-158.54	4.0198	-0.603 41	1.11	1.82	AgOBu	3.90	0.2515	-0.034 57	0.87	3.73
20 wt % EtOH											
AgPi	-93.56	2.9816	-0.459 23	-0.69	12.42	AgOPr	-100.08	2.7177	-0.407 69	1.62	5.36
AgOAc	-35.60	1.2866	-0.195 50	1.65	2.89	AgOBu	9.09	0.2169	-0.031 07	1.43	7.86
30 wt % EtOH											
AgPi	-178.92	4.8207	-0.731 96	-1.45	9.33	AgOPr	-33.64	1.2116	-0.181 84	2.50	4.20
AgOAc	9.00	0.2908	-0.046 14	2.65	2.24	AgOBu	-49.07	1.5029	-0.221 84	2.43	6.26
50 wt % EtOH											
AgPi	-270.19	6.7908	-1.025 30	-4.67	9.00	AgOPr	24.24	-0.1235	0.019 41	3.30	2.02
AgOAc	11.81	0.2163	-0.033 21	4.20	-0.06	AgOBu	-12.74	0.6493	-0.092 90	2.01	4.32
70 wt % EtOH											
AgPi	-394.89	9.4268	-1.415 00	-6.66	2.65	AgOPr	71.65	-1.2446	0.188 99	3.27	-0.70
AgOAc	37.43	-0.3718	0.056 89	6.28	-3.22	AgOBu	28.08	-0.3096	0.052 22	1.96	1.91
10 wt % 2-PrOH											
AgPi	-630.75	15.0840	-2.266 71	-0.12	12.67	AgOPr	31.71	-0.2829	0.040 49	0.92	4.71
AgOAc	40.04	-0.4424	0.062 79	0.93	1.97	AgOBu	-55.72	1.6607	-0.246 87	0.61	7.69
20 wt % 2-PrOH											
AgPi	-301.88	7.6610	-1.158 55	-1.82	13.83	AgOPr	1.47	0.4613	-0.071 54	1.50	7.45
AgOAc	42.34	-0.4673	0.066 40	1.68	3.16	AgOBu	0.62	0.4782	-0.072 09	1.11	11.98
30 wt % 2-PrOH											
AgPi	-210.88	5.5529	-0.843 11	-4.09	13.12	AgOPr	-57.41	1.7398	-0.260 84	1.89	4.77
AgOAc	15.04	0.1526	-0.025 42	2.50	2.34	AgOBu	19.08	-0.0229	0.005 55	1.37	7.30
50 wt % 2-PrOH											
AgPi	46.92	-0.5394	0.073 10	-7.33	1.55	AgOPr	13.88	0.1131	-0.016 22	2.56	3.01
AgOAc	15.94	0.1237	-0.019 51	3.62	0.59	AgOBu	-150.75	3.7420	-0.555 00	0.80	5.57
70 wt % 2-PrOH											
AgPi	42.72	-0.4268	0.055 92	-8.83	3.93	AgOPr	18.99	0.0562	-0.008 82	2.01	6.16
AgOAc	17.32	0.1453	-0.022 59	4.70	1.97	AgOBu	19.22	0.0103	0.000 61	0.78	10.34
10 wt % t-BuOH											
AgPi	-133.39	3.7767	-0.575 55	-0.64	6.86	AgOPr	28.24	-0.2149	0.030 29	0.27	4.74
AgOAc	-50.28	1.5589	-0.235 84	-0.04	1.67	AgOBu	-49.02	1.5010	-0.222 96	0.59	7.75
20 wt % t-BuOH											
AgPi	50.74	-0.3165	0.033 31	-3.20	12.60	AgOPr	-58.55	1.8516	-0.280 12	0.79	9.48
AgOAc	84.30	-1.4128	0.207 07	0.48	4.17	AgOBu	-17.61	0.9243	-0.139 79	0.91	14.92
30 wt % t-BuOH											
AgPi	-58.73	2.0946	-0.326 50	-4.04	12.88	AgOPr	-3.87	0.6573	-0.102 36	0.86	11.27
AgOAc	-288.39	7.0389	-1.056 51	0.57	8.35	AgOBu	8.85	0.3333	-0.051 16	0.93	14.31
40 wt % t-BuOH											
AgPi	-466.28	11.0889	-1.665 81	-7.23	6.41	AgOPr	15.85	0.1311	-0.021 05	1.49	6.85
AgOAc	18.74	0.0433	-0.008 99	1.08	2.98	AgOBu	48.33	-0.6269	0.094 64	1.61	10.73
20 wt % ACN											
AgOAc	-51.87	1.4246	-0.216 78	-9.59	3.85	AgOBu	-43.86	1.0655	-0.155 33	-9.82	2.67
AgOPr	7.47	0.0006	-0.000 97	-9.66	3.29						
40 wt % ACN											
AgOAc	3.52	0.1268	-0.021 53	-10.39	1.83	AgOBu	-4.88	0.1787	-0.022 89	-11.16	3.53
AgOPr	-8.49	0.3270	-0.049 12	-11.03	2.85						
60 wt % ACN											
AgOAc	8.71	-0.0537	0.008 40	-9.22	-3.10	AgOBu	1.72	0.0679	-0.006 95	-11.57	5.80
AgOPr	82.62	-1.7344	0.259 90	-10.56	1.55						



**TABLE 3: Free Energies of Transfer  $\Delta G^\circ_{\text{t}}(\text{i})$  and  $\Delta G^\circ_{\text{t, ch}}(\text{i})$  and Entropies of Transfer  $T\Delta S^\circ_{\text{t}}(\text{i})$  and  $T\Delta S^\circ_{\text{t, ch}}(\text{i})$  of Individual Ions from Water to Aqueous MeOH, EtOH, 2-PrOH, t-BuOH, and ACN at 25 °C (on Mole Fraction Scale in kJ mol<sup>-1</sup>)**

ions	$\Delta G^\circ_{\text{t}}(\text{i})$	$\Delta G^\circ_{\text{t, ch}}(\text{i})^a$	$T\Delta S^\circ_{\text{t}}(\text{i})$	$T\Delta S^\circ_{\text{t, ch}}(\text{i})^a$	$\Delta G^\circ_{\text{t}}(\text{i})$	$\Delta G^\circ_{\text{t, ch}}(\text{i})^a$	$T\Delta S^\circ_{\text{t}}(\text{i})$	$T\Delta S^\circ_{\text{t, ch}}(\text{i})^a$
10 wt % MeOH					30 wt % MeOH			
Ag <sup>+</sup>	-0.05	-1.01	0.59	1.81	0.97	-2.84	7.02	7.65
OAc <sup>-</sup>	0.83	0.69	-7.15	-6.59	2.35	0.88	-9.88	-13.58
OPr <sup>-</sup>	0.85	0.88	-6.19	-5.69	1.84	1.11	-8.06	-12.83
OBu <sup>-</sup>	0.86	1.14	-5.06	-4.66	1.76	1.43	-6.04	-12.20
50 wt % MeOH					70 wt % MeOH			
Ag <sup>+</sup>	1.57	-5.50	4.58	7.51	1.73	-9.60	3.97	10.05
OAc <sup>-</sup>	4.12	1.11	-5.17	-11.18	6.15	1.29	-10.23	-15.15
OPr <sup>-</sup>	3.47	1.77	-3.78	-11.58	4.62	2.44	-7.87	-16.44
OBu <sup>-</sup>	1.98	2.29	-2.20	-11.89	2.93	3.38	-5.55	-17.81
10 wt % EtOH					20 wt % EtOH			
Ag <sup>+</sup>	-0.10	-0.80	5.97	6.44	0.36	-1.29	13.78	13.75
OAc <sup>-</sup>	1.21	1.66	-4.15	-5.53	1.29	1.72	-10.89	-15.07
OPr <sup>-</sup>	1.17	1.86	-3.29	-5.10	1.26	2.12	-8.42	-13.82
OBu <sup>-</sup>	0.97	1.99	-2.24	-4.63	1.07	2.49	-5.92	-12.53
30 wt % EtOH					50 wt % EtOH			
Ag <sup>+</sup>	1.29	-1.63	10.07	10.22	-0.06	-6.16	2.68	5.76
OAc <sup>-</sup>	1.36	1.78	-7.83	-14.47	4.26	4.32	-2.74	-10.86
OPr <sup>-</sup>	1.31	2.24	-5.87	-13.85	3.36	4.70	-0.66	-11.63
OBu <sup>-</sup>	1.14	2.68	-3.81	-13.33	2.07	5.10	1.64	-12.23
70 wt % EtOH					10 wt % 2-PrOH			
Ag <sup>+</sup>	-0.66	-11.62	1.79	9.03	-0.32	-0.88	12.40	13.03
OAc <sup>-</sup>	6.94	4.38	-5.01	-10.98	1.25	1.84	-10.43	-11.73
OPr <sup>-</sup>	3.93	5.21	-2.49	-12.06	1.24	2.03	-7.69	-9.44
OBu <sup>-</sup>	2.62	6.21	0.12	-13.22	0.93	2.16	-4.71	-7.08
20 wt % 2-PrOH					30 wt % 2-PrOH			
Ag <sup>+</sup>	-0.83	-2.31	18.93	19.67	-1.26	-3.70	9.82	10.58
OAc <sup>-</sup>	2.51	3.40	-15.77	-21.13	3.76	5.36	-7.48	-15.14
OPr <sup>-</sup>	2.33	3.82	-11.48	-18.51	3.15	5.85	-5.05	-14.42
OBu <sup>-</sup>	1.94	4.18	-6.95	-15.78	2.63	6.30	-2.52	-13.70
50 wt % 2-PrOH					70 wt % 2-PrOH			
Ag <sup>+</sup>	-2.53	-8.59	2.06	7.12	-2.78	-16.10	-5.23	11.44
OAc <sup>-</sup>	6.15	6.86	-1.47	-6.64	7.48	7.11	7.20	3.26
OPr <sup>-</sup>	5.09	7.82	0.95	-7.15	4.79	8.17	11.39	3.60
OBu <sup>-</sup>	3.33	8.71	3.51	-7.75	3.56	9.19	15.57	3.89
10 wt % t-BuOH					20 wt % t-BuOH			
Ag <sup>+</sup>	-1.13	-2.13	14.29	15.45	-2.91	-4.51	22.03	22.97
OAc <sup>-</sup>	1.09	1.68	-12.62	-14.19	3.39	4.44	-17.86	-23.68
OPr <sup>-</sup>	1.40	2.31	-9.55	-11.78	3.70	5.30	-12.55	-20.24
OBu <sup>-</sup>	1.72	2.91	-6.54	-9.37	3.82	6.04	-7.11	-16.75
30 wt % t-BuOH					40 wt % t-BuOH			
Ag <sup>+</sup>	-3.10	-5.95	11.37	14.76	-3.16	-8.37	-1.90	6.41
OAc <sup>-</sup>	3.67	5.17	-3.02	-9.80	4.24	5.60	4.88	0.09
OPr <sup>-</sup>	3.96	6.35	-0.10	-9.01	4.65	7.36	8.75	0.83
OBu <sup>-</sup>	4.03	7.42	2.94	-8.30	4.77	9.05	12.63	1.60
20 wt % ACN					40 wt % ACN			
Ag <sup>+</sup> b	-10.43	-7.43	-28.06	-29.89	-15.97	-9.55	-29.01	-30.41
OAc <sup>-</sup>	0.84	4.59	31.91	24.88	5.58	13.48	30.84	21.09
OPr <sup>-</sup>	0.77	4.70	31.35	23.34	4.94	13.59	31.86	19.81
OBu <sup>-</sup>	0.61	4.77	30.73	21.79	4.81	13.72	32.54	18.51
60 wt % ACN								
Ag <sup>+</sup> b	-21.19	-9.93	-30.27	-30.67				
OAc <sup>-</sup>	11.97	26.45	27.17	14.60				
OPr <sup>-</sup>	10.63	26.05	31.82	15.60				
OBu <sup>-</sup>	9.62	25.67	36.07	16.53				

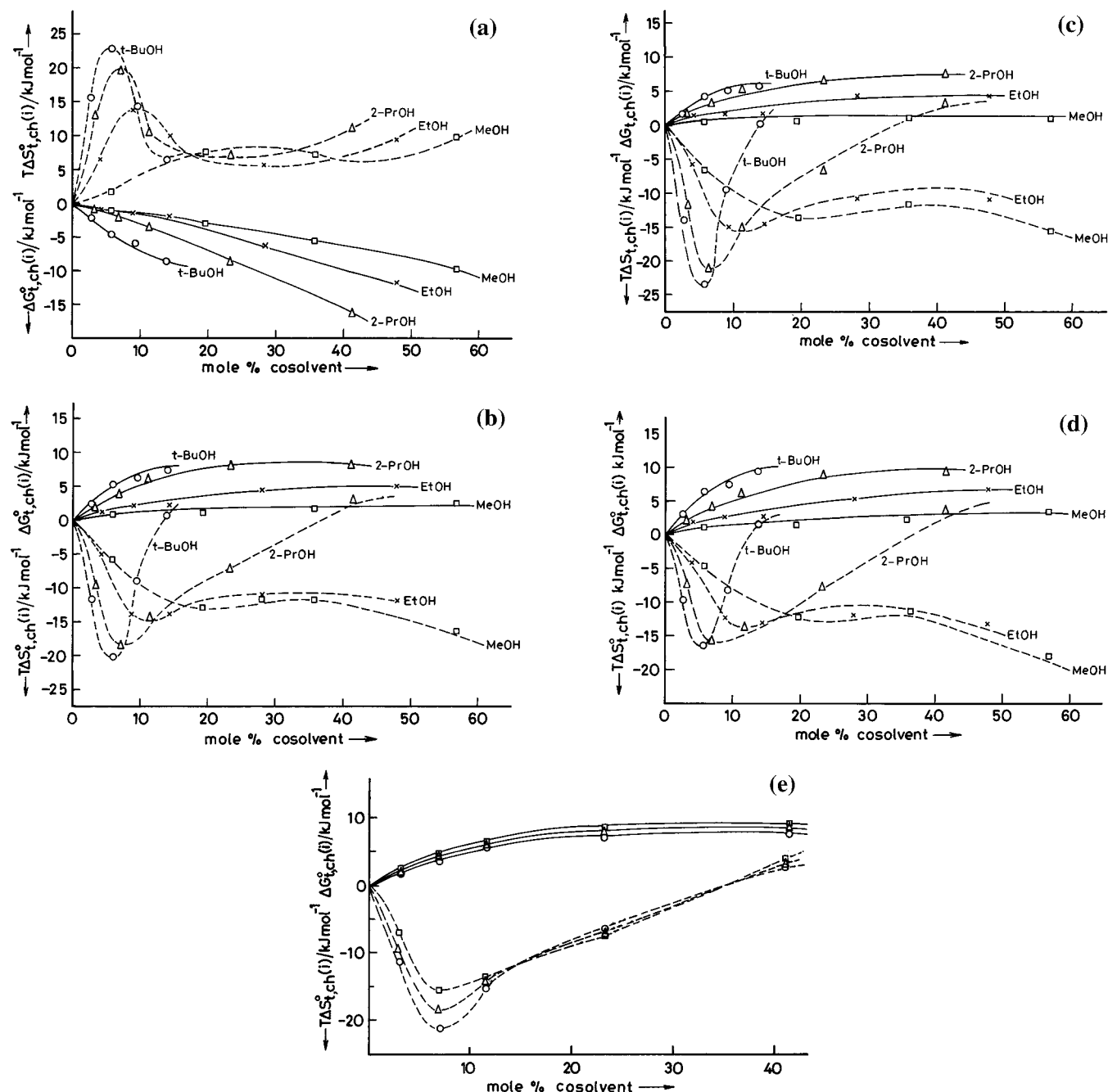
<sup>a</sup> For computing  $\Delta P^\circ_{\text{t, cav}}(\text{i})$ ,  $\Delta P^\circ_{\text{t, B}}(\text{i})$ , and  $\Delta G^\circ_{\text{t, i-d}}(\text{i})$  values, the required diameter of the solvent constituents and the value of dipole moment of aquo-alkanols and the ACN are taken as given in ref 22a and the required diameter of the ionic species are obtained from ref 8a, 19a, and 31.<sup>b</sup>  $\Delta G^\circ_{\text{t}}$  and  $T\Delta S^\circ_{\text{t}}$  values of Ag<sup>+</sup> in aqueous ACN are obtained from ref 28b.

higher composition of 2-PrOH compared to aqueous ACN. Ag<sup>+</sup> in both the solvents is stabilized due to its back-bonding ability from its filled d<sup>10</sup> orbital. The extent of stabilization at higher cosolvent composition is less in aquo-ACN solvent compared to aqueous 2-PrOH due to cationophilicity of ACN molecules<sup>7f,8e,28</sup> and cationophobicity of 2-PrOH as dictated by "cation-O-center"-type acid-base interactions.<sup>7,8,29</sup> Comparison of these results with  $\Delta G^\circ_{\text{t, ch}}(\text{K}^+)$  shows that the latter is less negative in aquo-2-PrOH, compared to that for Ag<sup>+</sup> ion, indicating the effect of superimposed back-bonding interaction of Ag<sup>+</sup>. While K<sup>+</sup> is destabilized in ACN due to cationo-

phobicity of ACN molecules, the Ag<sup>+</sup> ion is stabilized through its back-bonding capacity from the filled d<sup>10</sup> orbital.

The observed highly positive magnitudes of  $\Delta G^\circ_{\text{t, ch}}(\text{RCOO}^-)$  and their reverse order (OAc<sup>-</sup> > OPr<sup>-</sup> > OBU<sup>-</sup>) in ACN-water mixtures compared to those in aqueous alkanols at high mole percent signify that the combined effect of decreased acidity and increased H<sub>b</sub>H in aquo-ACN due to its structure breaking propensity<sup>7f,8e,17</sup> is responsible.

**Entropies of Transfer.**  $T\Delta S^\circ_{\text{t, ch}}(\text{i})$  values for RCOO<sup>-</sup> and Ag<sup>+</sup> ion in Table 3 and Figure 1b-d reveal that like other small cations, viz. K<sup>+</sup>, H<sup>+</sup>, etc.,<sup>8e</sup> the profiles for cation Ag<sup>+</sup> pass



**Figure 1.** (a) Variation of  $\Delta G^\circ_{t, ch(i)}$  (—) and  $T\Delta S^\circ_{t, ch(i)}$  (---) of  $\text{Ag}^+$  at 25 °C in aqueous MeOH [□], EtOH[×], 2-PrOH[Δ], and t-BuOH [○]. (b) Variation of  $\Delta G^\circ_{t, ch(i)}$  (—) and  $T\Delta S^\circ_{t, ch(i)}$  (---) of  $\text{OAc}^-$  at 25 °C in aqueous MeOH [□], EtOH[×], 2-PrOH [Δ], and t-BuOH [○]. (c) Variation of  $\Delta G^\circ_{t, ch(i)}$  (—) and  $T\Delta S^\circ_{t, ch(i)}$  (---) of  $\text{OPr}^-$  at 25 °C in aqueous MeOH [□], EtOH[×], 2-PrOH [Δ], and t-BuOH [○]. (d) Variation of  $\Delta G^\circ_{t, ch(i)}$  (—) and  $T\Delta S^\circ_{t, ch(i)}$  (---) of  $\text{OBU}^-$  at 25 °C in aqueous MeOH [□], EtOH[×], 2-PrOH[Δ], and t-BuOH [○]. (e) Variation of  $\Delta G^\circ_{t, ch(i)}$  (—) and  $T\Delta S^\circ_{t, ch(i)}$  (---) of  $\text{OAc}^-$  [○],  $\text{OPr}^-$  [Δ], and  $\text{OBU}^-$  [□] in aqueous 2-PrOH at 25 °C.

through a maximum while those of anions  $\text{RCOO}^-$  like  $\text{Cl}^-$ ,  $\text{Br}^-$ , etc.,<sup>8c</sup> pass through a minimum at water-rich compositions. And these peaks shift toward lower cosolvent compositions in the order t-BuOH (5–6 mol %) < 2-PrOH (6–8 mol %) < EtOH (8–11 mol %) < MeOH as the 3D water structure promoting propensity of aqueous alkanols increases in the reverse order.

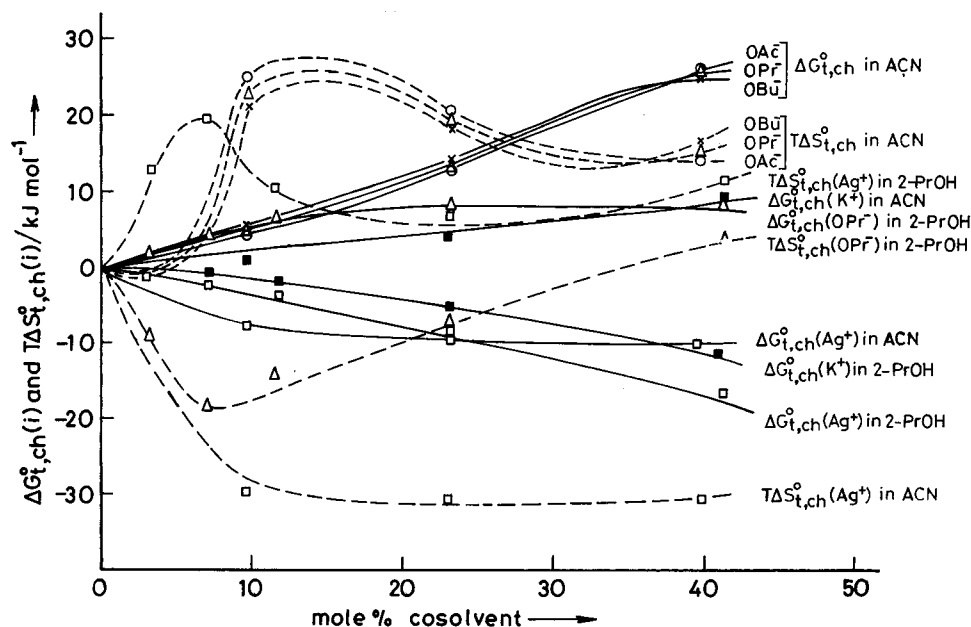
This behavior has been discussed relative to a four-step<sup>7,8,10</sup> transfer process:

$$\Delta S^\circ_{t, ch(i)} = (\Delta S^\circ_1 - \Delta S^\circ_2) + (\Delta S^\circ_3 - \Delta S^\circ_4) \quad (7)$$

$\Delta S^\circ_1$  is the entropy change to release the ion/solute (i) from its hydration cosphere,  $\Delta S^\circ_2$  is that for formation of the 3D water

structure released from step 1,  $\Delta S^\circ_3$  is that for disruption of structuredness of cosolvents, to release the water/cosolvent molecules, and  $\Delta S^\circ_4$  is that for solvating the transferred ion. The composite term  $(\Delta S^\circ_1 - \Delta S^\circ_2)$  is related to water molecules and remains constant for an ion/solute (i). It is positive or negative, depending upon the relative extent of the primary solvation zone (psz)<sup>11b</sup> resulting from  $\text{H}_b\text{H}$  or that of the secondary solvation zone (ssz)<sup>11b</sup> for anions such as  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ , etc., or  $\text{H}_b\text{H}$  of  $\text{RCOO}^-$ . The other composite term  $(\Delta S^\circ_3 - \Delta S^\circ_4)$  being related to solvents changes with cosolvent composition until the effect of packing imbalance sets in.

The values of  $(\Delta S^\circ_1 - \Delta S^\circ_2)$  will be a constant and positive because  $\text{Ag}^+$  is likely to be hydrated with  $\text{H}_2\text{O}$ . This is because



**Figure 2.** Variation of  $\Delta G^\circ_{t, ch(i)}$  (—) and  $T\Delta S^\circ_{t, ch(i)}$  (---) of  $Ag^+$  [□],  $K^+$  [■],  $OAc^-$  [○],  $OPr^-$  [△], and  $OBu^-$  [×] in aqueous ACN and 2-PrOH at 25 °C.

in step 1 we have to dismantle larger order around  $Ag^+$ , while in step 2 ordering is involved by weak H-bonding interactions forming 3D water clusters. Since promotion of 3D water structure takes place in aquo-alkanols in the order  $t\text{-BuOH} > 2\text{-PrOH} > \text{EtOH} > \text{MeOH}$ , it is expected that  $\Delta S^\circ_3$  will be increasingly positive in the same order.  $-\Delta S^\circ_4$  will also increase in the same order, because of increased basicity of these alkanols. Evidently  $(\Delta S^\circ_3 - \Delta S^\circ_4)$  and  $\Delta S^\circ_{t, ch}(Ag^+)$  will be increasingly positive at first followed by a decrease due to increased  $-\Delta S^\circ_4$  to overcome the initial increasing magnitudes of  $(\Delta S^\circ_1 - \Delta S^\circ_2) + \Delta S^\circ_3$ . The “magic composition” of the maxima will be guided by the effect of gradual blending of 3D structure promoting effect of alkanols by the onset of packing imbalance of the cosolvent molecules. This will occur earlier the larger is the size of alkanols.

In Figure 1b–d we see that the observed downward trend of  $T\Delta S^\circ_{t, ch(i)}$  was followed by upward trends after a minimum; their relative order in the alkanol series and also the characteristic composition of the minima are similar to those observed for  $Cl^-$ ,  $Br^-$ , and  $I^-$  in these aquo-alkanols<sup>8c</sup> and  $\Delta H^\circ_t$  of  $RCOO^-$  ion in aquo- $t\text{-BuOH}$ .<sup>30</sup>

As the molecular anions  $RCOO^-$  with both hydrophilic and hydrophobic sites<sup>20a</sup> are likely to involve ssz, the composite term  $(\Delta S^\circ_1 - \Delta S^\circ_2)$  should be a constant negative quantity depending on the size of  $RCOO^-$  ions. But  $\Delta S^\circ_3 > 0$ , since the 3D water structure should be broken to solvate the incoming ion. Also,  $RCOO^-$  anions are likely to induce less order due to less  $H_bH$  and less  $H_iH$  compared to that of pure water. This may also be partially opposed by dispersion interaction. Therefore,  $-\Delta S^\circ_4$  would be less negative, thus resulting in increasing positive magnitudes of  $(\Delta S^\circ_3 - \Delta S^\circ_4)$  that oppose the constant negative magnitude of  $(\Delta S^\circ_1 - \Delta S^\circ_2)$  and thus result in the observed minima in  $\Delta S^\circ_{t, ch(i)}$ –composition profiles. The characteristic compositions where minima appear in aquo-alkanols are likely to be guided by packing imbalance induced by the cosolvents. At higher mole percent, the nature and relative position of the profiles are seemingly the result of relative complexity of solvation of  $RCOO^-$  and the structuredness of aqueous cosolvents.

The absence of characteristic “maxima” in Figure 2 for  $\Delta S^\circ_{t, ch}(Ag^+)$  in ACN–water mixtures is indicative of the fact

that the structural effect of water in ssz, rather than in psz, gives negative  $(\Delta S^\circ_1 - \Delta S^\circ_2)$ . Also, increasing solvation of  $Ag^+$  by back-bonding of  $d^{10}$  electrons imparts larger  $-\Delta S^\circ_4$ , and the 3D structure breaking propensity of ACN makes  $\Delta S^\circ_3 \approx 0$  or their possible formation of ACN–water complexes<sup>7f,28</sup> makes  $\Delta S^\circ_3 > 0$ .

The  $\Delta S^\circ_t(RCOO^-)$ –composition profiles in ACN–water mixtures [vide Figure 2] after exhibiting an initial downward trend pass through a maximum at higher mole percent. These are indicative of the fact that the constant negative values of  $(\Delta S^\circ_1 - \Delta S^\circ_2)$  are overcome by the increased positive values of  $(\Delta S^\circ_3 - \Delta S^\circ_4)$ . Here also  $\Delta S^\circ_3 \approx 0$  or  $\Delta S^\circ_3 > 0$ , and the well-known anion desolvation effect of ACN<sup>28</sup> results in positive  $\Delta S^\circ_4$ . The downward trend past the broad maxima is likely to be the effect of packing imbalance of ACN molecules causing an increased  $H_bH$  effect.

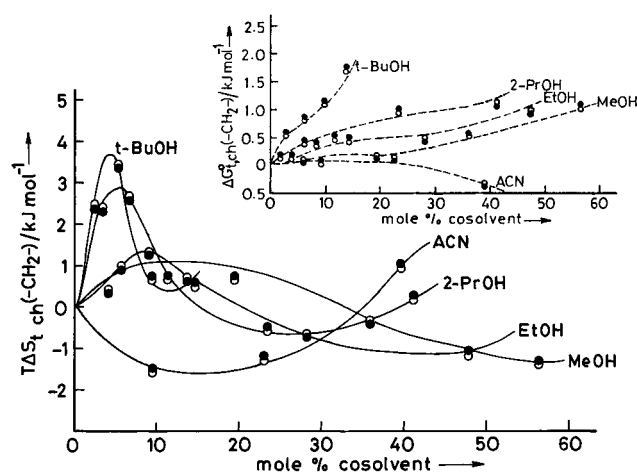
The solvent effect on hydrophilic and hydrophobic hydration dictating  $\Delta S^\circ_{t, ch}(RCOO^-)$ –composition profiles are somewhat involved. To facilitate understanding them, the values of  $\Delta G^\circ_{t, ch}(-CH_2-)$  and  $\Delta S^\circ_{t, ch}(-CH_2-)$ , obtained by subtracting  $\Delta G^\circ_{t, ch(i)}$  and  $\Delta S^\circ_{t, ch(i)}$  values of  $OAc^-$  from those of  $OPr^-$  and those of  $OPr^-$  from the corresponding values of  $OBu^-$  are plotted in Figure 3.  $\Delta G^\circ_{t, ch}(-CH_2-)$  and  $\Delta S^\circ_{t, ch}(-CH_2-)$  are nearly equal [vide Table 4] which shows their additive nature, at least in these lower series of aliphatic  $RCOO^-$  ions.

$\Delta G^\circ_{t, ch}(-CH_2-)$ –composition profiles in Figure 3 gradually increase with cosolvent composition for aqueous alkanols in the order  $t\text{-BuOH} > 2\text{-PrOH} > \text{EtOH} > \text{MeOH}$  while in ACN–water mixtures the plot shows a decrease. Since dispersion is likely to have the reverse effect, the observed trends are evidently the result of a reduced  $H_bH$  effect that results from less availability of  $H_2O$  molecules in aqueous alkanols due to 3D structure promotion and the larger availability of  $H_2O$  molecules in the aqueous mixtures of structure breaking ACN.

It is interesting to note that the profiles in Figure 3 are similar to those for pNA and HBz despite the fact that in the latter two cases  $\Delta S^\circ_{t, ch(i)}$  values are guided by the effect of “buffer” bond entailing both  $H_bH$  and  $H_iH$  effects, rather than  $H_bH$  alone dictating  $\Delta S^\circ_{t, ch}(-CH_2-)$ .  $\Delta S^\circ_{t, ch}(-CH_2-)$ –composition profiles in the aqueous alkanols pass through a maxima at their “magic composition” and a broad minima in aquo-ACN

**TABLE 4: Values of Free Energies of Transfer  $\Delta G^\circ_{\text{t, ch}}$  and Entropies of Transfer  $T\Delta S^\circ_{\text{t, ch}}$  for  $(-\text{CH}_2-)$  Group at 25 °C (on Mole Fraction Scale in  $\text{kJ mol}^{-1}$ ) from Water to Aqueous MeOH, EtOH, 2-PrOH, t-BuOH, and ACN**

wt % solvent	10		20		30		40		50		60		70	
	$\Delta G^\circ_{\text{t, ch}}$	$T\Delta S^\circ_{\text{t, ch}}$	$\Delta G^\circ_{\text{t, ch}}$	$T\Delta S^\circ_{\text{t, ch}}$	$\Delta G^\circ_{\text{t, ch}}$	$T\Delta S^\circ_{\text{t, ch}}$	$\Delta G^\circ_{\text{t, ch}}$	$T\Delta S^\circ_{\text{t, ch}}$	$\Delta G^\circ_{\text{t, ch}}$	$T\Delta S^\circ_{\text{t, ch}}$	$\Delta G^\circ_{\text{t, ch}}$	$T\Delta S^\circ_{\text{t, ch}}$	$\Delta G^\circ_{\text{t, ch}}$	$T\Delta S^\circ_{\text{t, ch}}$
MeOH														
OPr <sup>-</sup> -OAc <sup>-</sup>	0.19	0.90			0.23	0.75			0.66	-0.40			1.15	-1.29
OBu <sup>-</sup> -OPr <sup>-</sup>	0.26	1.03			0.32	0.63			0.52	-0.31			0.94	-1.37
EtOH														
OPr <sup>-</sup> -OAc <sup>-</sup>	0.20	0.43	0.40	1.25	0.46	0.62			0.38	-0.77			0.83	-1.08
OBu <sup>-</sup> -OPr <sup>-</sup>	0.13	0.47	0.37	1.29	0.44	0.52			0.40	-0.60			1.00	-1.16
2-PrOH														
OPr <sup>-</sup> -OAc <sup>-</sup>	0.19	2.29	0.42	2.62	0.49	0.72			0.96	-0.51			1.06	0.34
OBu <sup>-</sup> -OPr <sup>-</sup>	0.13	2.36	0.36	2.73	0.45	0.72			0.89	-0.60			1.02	0.29
t-BuOH														
OPr <sup>-</sup> -OAc <sup>-</sup>	0.63	2.41	0.86	3.44	1.18	0.79	1.76	0.74						
OBu <sup>-</sup> -OPr <sup>-</sup>	0.60	2.41	0.74	3.49	1.07	0.71	1.69	0.77						
ACN														
OPr <sup>-</sup> -OAc <sup>-</sup>			0.11	-1.54			0.11	-1.28			-0.40	1.00		
OBu <sup>-</sup> -OPr <sup>-</sup>			0.07	-1.55			0.13	-1.30			-0.38	0.93		

**Figure 3.** Variation of  $T\Delta S^\circ_{\text{t, ch}}(-\text{CH}_2-)$  at 25 °C with composition of cosolvents MeOH, EtOH, 2-PrOH, t-BuOH, and ACN obtained by subtracting  $T\Delta S^\circ_{\text{t, ch}}$  values of OPr<sup>-</sup> from that of OBU<sup>-</sup> (○) and that of OAc<sup>-</sup> from that of OPr<sup>-</sup> (●). Inset is that for  $\Delta G^\circ_{\text{t, ch}}(-\text{CH}_2-)$ .

mixtures. Evidently, the sharp upward trend of the profiles in aqueous alkanols is the effect of reduced  $H_bH$  of alkanols resulting from the 3D structure promoting effect of alkanols followed by a decrease due to an increased  $H_bH$  effect with the onset of packing imbalance at high mole percent of aquo-alkanols.

In the case of ACN–water mixtures the observed initial decrease followed by an increase at higher compositions can be caused by the initial larger  $H_bH$  effect than that in water due to the 3D structure breaking propensity of ACN molecules, which, however, gets reduced due to the possible formation of H-bonded ACN–H<sub>2</sub>O complexes.<sup>7f,28</sup>

Thus it appears that  $\Delta S^\circ_{\text{t, ch}}(-\text{CH}_2-)$ -composition profiles serve as a probe not only for the solvation effect of  $H_bH$  but also for the 3D-structuredness of aqueous mixtures of various cosolvents. Furthermore,  $\Delta S^\circ_{\text{t, ch}}$ -composition profiles of  $(-\text{CH}_2-)$  lead us to conclude that despite the uncertain effects of “buffer bond”,  $\Delta S^\circ_{\text{t, ch}}$ -composition profiles of HBz and pNA are chiefly guided by the effect of  $H_bH$ . Thus they are an effective probe for the solvent effect of  $H_bH$  as well as the 3D-structuredness of aqueous cosolvents.

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