

Ion-Solvent Interactions in Aqueous 1,2-Dimethoxyethane

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Standard free energies of transfer, ΔG_t° of alkali metal chlorides have been determined in aqueous mixtures of 10, 30 and 50 wt % of 1,2-dimethoxyethane (DME) at 25°C using the double cells comprising metal amalgam and Ag-AgCl electrodes. These values have been apportioned into individual ionic contributions using the tetraphenylarsonium tetraphenylboride reference electrolyte method. The increased destabilisation of Cl^- as well as of Br^- and I^- (as obtained from literature values of HBr and HI) reflects the expected decreased acidity of the mixed solvents resulting from the aprotic character of the cosolvent DME. However, the increased stabilization of H^+ and alkali metal cations is indicative of pronounced basicity effects as well as the possible formation of bidentate $\text{M}^+(\text{DME})_2$ complex with the cosolvent in the case of alkali metal cations. Also, the observed relative order of stabilization of alkali cations: $\text{Li}^+ \gg \text{Na}^+ < \text{K}^+ < \text{Rb}^+ \sim \text{Cs}^+$ is the result of decreased short range interaction and the increased soft-soft interactions down the group. Moreover, while tetraphenyl ions are increasingly stabilized due to the combined effects of dispersion and "cavity-forming" interactions, picrate ions are relatively less stabilized due to the opposing effects of decreased acidity and increased dispersion interactions. A comparison of the relative behaviour of some selected ions, viz. H^+ , K^+ , Cl^- and Ph_4B^- in aqueous mixtures of the closely related cosolvents like ethanediol, 2-methoxyethanol and 1,2-dimethoxyethane also conforms to the characteristic solvating effects of the protic, quasi-aprotic and aprotic nature of the cosolvents respectively.

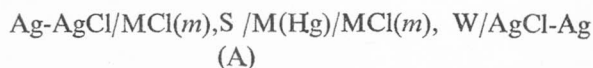
AS an extension of our previous studies¹⁻³ on free energies of transfer (ΔG_t°) of alkali metal halides and of the individual ions^{1,3} in aqueous mixtures of ethyleneglycol (EG)^{2,3} and 2-methoxyethanol (ME)¹, we now report the results of such studies in aqueous mixtures of 1,2-dimethoxyethane (DME). This solvent has very little, if any, hydrogen-bond donating ability, but due to the presence of two O-linked methyl groups it has a high tendency to accept hydrogen bonds. The two basic centres (O-atoms) are thus expected to be very much active due to the electron repelling inductive effect of CH_3 groups.

Materials and Methods

1,2-Dimethoxyethane (Riedel-De-Haenag) was first shaken with FeSO_4 (AR, BDH) for 1-2 hr, decanted and then distilled. The distillate was then successively refluxed (~ 12 hr) and distilled over sodium metal and LiAlH_4 . The finally distilled sample was preserved in a desiccator and freshly distilled after refluxing with LiAlH_4 before use. The b.p., density and refractive index compared fairly well with the corresponding values in the literature⁵. Other chemicals used were of similar grade as in earlier studies^{3,6-9}. The experimental procedures including the preparation of the solvent, cell solutions and the electrodes have been described^{1,7-9}. The behaviour of the electrodes in the systems was also essentially similar to that in previous studies^{1,7-9}.

The ΔG_t° values of alkali metal chlorides MCl [$\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}$ and Cs] have been computed

from the e.m.f. data of the double cell (A), as described earlier¹.



where S, W and m denote solvents containing 10, 30 and 50 wt % of DME, water and the molality of MCl respectively. These ΔG_t° values have been apportioned into individual ion contributions by the reference electrolyte (RE) method⁴ using tetraphenylarsonium tetraphenylboride ($\text{Ph}_4\text{AsBPh}_4$) as the RE.

Results

The emf's (ΔE) of the double cell (A) for different molalities (m) of MCl in the different DME + water mixtures were measured[†]. The ΔE_m° values were evaluated from these values as described in the preceding paper¹. The uncertainties in ΔE_m° values were within ± 0.5 mV. The required solvent parameters at 25°C were taken from literature¹⁰. Standard free energies of transfer (ΔG_t°) of MCl from water to the mixed solvents on mole fraction scale were also evaluated as before¹ and are listed in Table 1. Solubility, pK_{sp} and ΔG_t° values of the reference electrolyte salts, namely Ph_4AsPi , KBPh_4 and KPi determined in a manner indicated earlier¹ are given in Tables 2 and 3. Transfer free energies of individual ions ΔG_i° (i) were also estimated as before¹ and are presented in Tables 3 and 4. The maximum uncertainties in ΔG_i° (i) values of MCl, salts of RE and of the individual ions are also

[†]Detailed data can be had from the authors on request.

of the same order as in aqueous EG^{3,3} and ME¹ systems, namely $\pm 0.05 \text{ kJ mol}^{-1}$, $\pm 0.1 \text{ kJ mol}^{-1}$ and 0.3 kJ mol^{-1} respectively.

Discussion

The variations of ΔG_i° values of some salts with wt % cosolvent, depicted in Fig. 1, show that as in aqueous ME¹ and EG^{2,3} while the alkali metal chlorides are increasingly destabilized by the addition of the cosolvent DME, the reference electrolyte salts are increasingly stabilized, the salts of tetraphenyl ions being much more stabilized than the picrate (Pi⁻) salts. Expectedly, as in ME and EG co-solvent systems, the behaviour of alkali chlorides in DME is dictated by the Born-type destabilization. The increased destabilization of Cl⁻ due to decreased proticity is likely to be opposed by the increased stabilization of the cations due to the increased basicity of the mixed solvents. But the behaviour of the RE salts containing organic ions is seemingly governed by the increased dispersion interactions and partially by the cavity effect in the cases of large-sized tetraphenyl boride or arsonium ions.

However, to facilitate better understanding of the ion-solvent interactions, ΔG_i° (i)-composition pro-

files are illustrated in Fig. 2. The values for H⁺, Br⁻ and I⁻ were obtained from ΔG_i° (HBr)¹⁰ and ΔG_i° (HI)¹¹ values reported earlier. The values of Rb⁺ and Cs⁺ being only slightly different from those of K⁺, the ΔG_i° (K⁺)-composition profile is representative of Rb⁺ and Cs⁺ as well.

It is interesting to note that ΔG_i° (H⁺) composition profile decreases monotonically instead of showing an initial hump followed by a minimum at higher cosolvent composition as in aqueous ME¹ (also see Fig. 4). This suggests that unlike ME, DME shifts the bulky $\leftrightarrow$ dense water equilibrium to the right freeing more monomeric water molecules right from the beginning. This is supported by the observed non-appearance of any hump in ΔS_i° (HI)-composition profile in these mixtures¹¹ contrary to what has been observed in aqueous mixtures of aliphatic alcohols¹²—the well-known structure-inducing cosolvents¹³. The non-appearance of the usual minimum within the range of composition studied, apparently indicates that the effect of the pronounced basicity of the mixed solvents caused partly by the increased more basic monomeric water molecules and partly by the influence of more basic DME, has not yet been overcome by the effect of Born-type destabilization.

TABLE 1 — STANDARD TRANSFER FREE ENERGIES ΔG_i° OF MX FROM WATER TO 1,2-DIMETHOXYETHANE (DME) + WATER MIXTURES AT 25°C

Wt % DME	[ΔG_i° (MX) values in kJmol ⁻¹]				
	LiCl	NaCl	KCl	RbCl	CsCl
10	1.37	1.61	1.60	1.26	1.44
30	3.59	4.60	4.29	3.97	4.21
50	5.72	7.32	7.08	6.98	6.78

TABLE 3 — STANDARD FREE ENERGIES OF TRANSFER OF REFERENCE ELECTROLYTES AND OF THE IONS Ph₄B⁻ and Pi⁻ IN AQUO 1,2-DIMETHOXYETHANE (DME)

Wt %	[ΔG_i° values in kJmol ⁻¹]				
	KBPh ₄	Ph ₄ AsPi	KPi	Ph ₄ B ⁻	Pi ⁻
10	-6.55	-5.23	-0.10	-5.8	0.6
30	-15.40	-12.38	-2.28	-12.8	0.4
50	-27.91	-23.11	-6.51	-22.7	-0.9

TABLE 2 — SOLUBILITIES (S), MEAN ACTIVITY COEFFICIENTS ($\gamma_{\pm}$) AND SOLUBILITY PRODUCTS K_{sp}^c (MOLAR SCALES) IN AQUO-1,2-DIMETHOXYETHANE

Wt % DME	S(mol dm ⁻³)			$\gamma_{\pm}$			pK_{sp}^c		
	KPh ₄ B	Ph ₄ AsPi	KPi	KPh ₄ B	Ph ₄ AsPi	KPi	KBPh ₄	Ph ₄ AsPi	KPi
0*	—	—	—	—	—	—	7.53	8.92	3.41
10	0.60×10^{-3}	0.92×10^{-4}	2.09×10^{-2}	0.979	0.991	0.885	6.46	8.08	3.47
30	3.03×10^{-3}	3.20×10^{-4}	2.67×10^{-2}	0.954	0.985	0.875	5.08	7.00	3.26
50	39.98×10^{-3}	23.18×10^{-4}	6.75×10^{-2}	0.700	0.900	0.629	3.11	5.34	2.76

*Ref. Das, A. K. & Kundu, K. K., *Indian J. Chem.*, **16A** (1978), 467.

TABLE 4 — STANDARD FREE ENERGIES OF TRANSFER OF SOME INDIVIDUAL IONS FROM WATER TO AQUO-1,2 DIMETHOXYETHANE MIXTURES AT 25°C

Wt %	[ΔG_i° values in kJ mol ⁻¹]								
	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	H ⁺ (a)	Cl ⁻	Br ⁻ (a)	I ⁻ (b)
10	-0.9	-0.7	-0.7	-1.1	-0.9	-2.0	2.3	1.3	0.7
30	-3.4	-2.3	-2.7	-3.0	-2.7	-6.3	6.9	4.8	2.8
50	-7.0	-5.4	-5.7	-6.0	-6.2	10.4	12.7	10.0	5.8

*Ref. 10; *Ref. 11

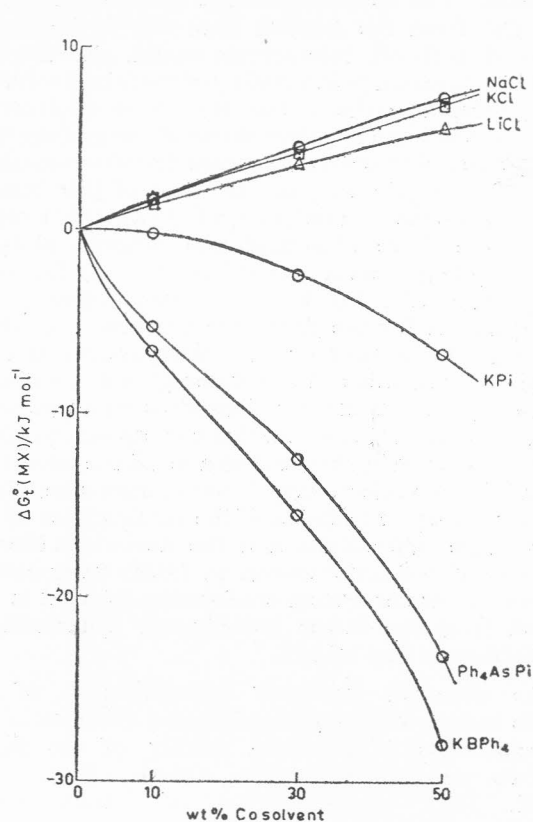


Fig. 1 — Free energies of transfer, ΔG_t^o of some electrolytes in 1,2-dimethoxyethane (DME)-water mixtures as a function of wt % DME at 25°C.

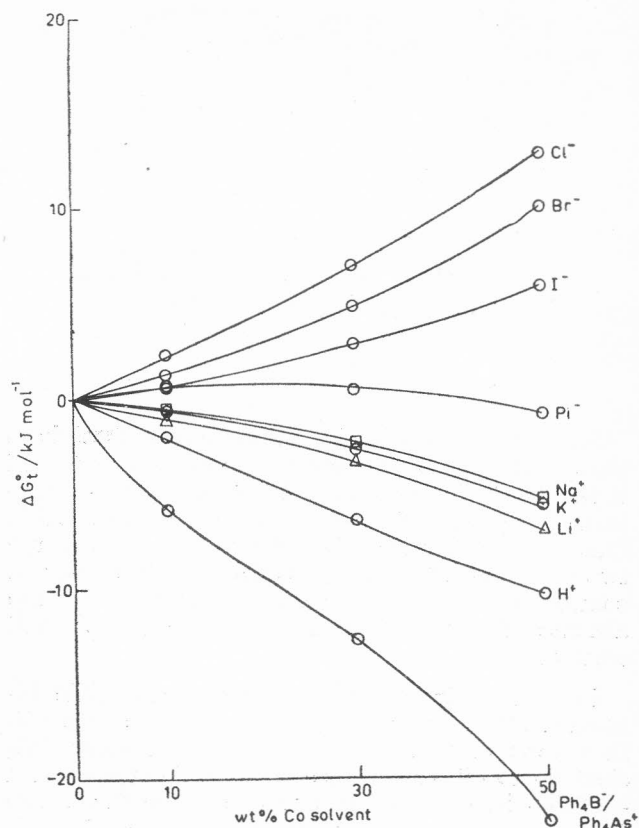


Fig. 2 — Free energies of transfer, ΔG_t^o (i) of some individual ions obtained by use of $\text{Ph}_4\text{AsBPh}_4$ (TATB) assumption in 1,2-dimethoxyethane (DME)-water mixtures as a function of wt % DME at 25°C.

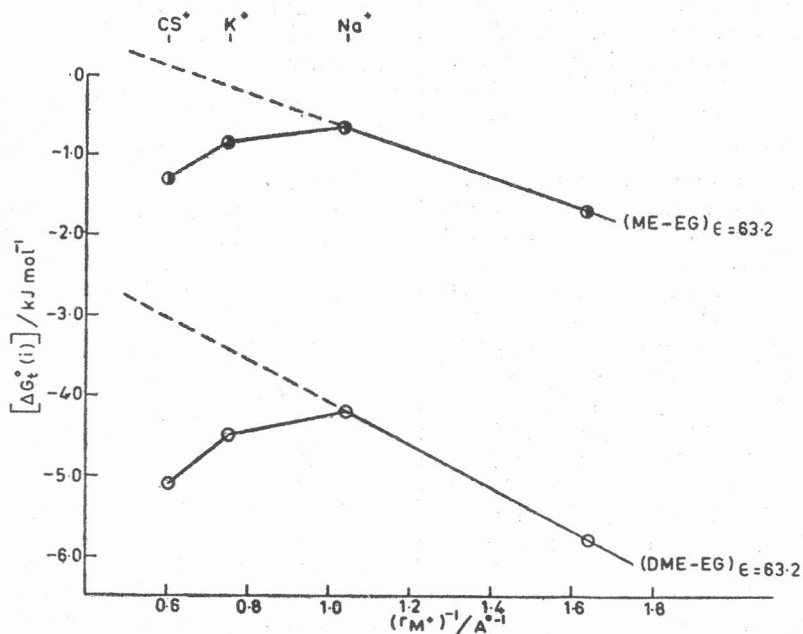
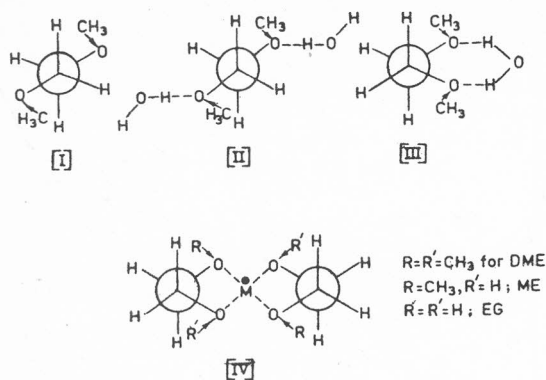


Fig. 3 — Variation of $\delta\Delta G_t^o$ (M^+) [ΔG_t^o (M^+) cosolvent + water — ΔG_t^o (M^+) ethylene glycol (EG) + water] versus $(rM^+)^{-1}$ in aqueous 1,2-dimethoxyethane or 2-methoxyethanol (ME) for some alkali metal ions.



Since no intramolecular H-bonding is feasible in pure DME the predominant configuration of DME is the *trans*-form (I) around $-\text{CH}_2-\text{CH}_2-$ group instead of the *gauche*-form as in ME^{1,14,15} and EG^{7b}. Due to the inductive effect of two CH_3 groups, the two O-centres of DME molecules are more basic as compared to that of water, EG and ME. But the absence of any acidic hydrogen atom makes DME wholly aprotic.

In DME-water system however, the possible H-bonded DME-water complexes are of the type (II) in water-rich compositions and (III) in water deficient compositions. Since a *gauche*-form around a $-\text{CH}_2-\text{CH}_2-$ group is likely to be more favourable for association, it may influence the equilibrium between *trans* and *gauche* forms in favour of *gauche*-form as in (III). Thus, in aqueous solutions of DME, both (II) and (III) are more basic and less acidic than water. Moreover, since the basicity and acidity of the cosolvent are likely to be relayed through cooperative structure of H-bonding^{1,6,16,17} between the cosolvent and H_2O molecules in the aqueous solution the possible H-bonded cosolvent-water complexes and hence the mixed solvents as a whole are likely to be increasingly more basic and at the same time less acidic than water. This increased basicity is partly responsible for the pronounced stabilization of H^+ in the solvent system.

On the other hand, the observed increased stabilization of the alkali metal cations may be caused partly by the more basic O-centres of H-bonded aquo-complexes (II) and (III) and partly by the formation of electrostatically bound M^+ -bidentate complexes (IV)¹⁸ as suggested for EG³ and ME¹.

The order of stabilization of the cations: $\text{Li}^+ \gg \text{Na}^+ < \text{K}^+ \leq \text{Rb}^+ \approx \text{Cs}^+$ is essentially similar to that in aqueous ME solutions¹ and other cationophilic cosolvent systems^{1,9a,b,19}. This order, therefore, is the result of the decreasing effect of basicity and the increasing effect of superimposed soft-soft interactions^{9,19,20} with the increasing size of the cations. Moreover, as explained in those cases, the negative slopes of the guiding lines joining the data points of Li^+ and Na^+ in $\Delta G_i^\circ (\text{M}^+)$ versus $(r_{\text{M}^+})^{-1}$ profiles, dictated by short-range interactions of acid-base type^{16,17} and bidentate complexation, would increase with the increased cationophilicity of the mixed

solvents. The deviations of the data points of Rb^+ and Cs^+ from the guiding lines due to the superimposed soft-soft interactions would also increase with the increased polarizability of the mixed solvents. As indicated earlier¹, the Born-type electrostatic effect opposes the negative slopes of the guiding lines and hence influences the observed deviations masking the soft-soft interactions. In view of this, instead of showing the simple plots of $\Delta G_i^\circ (\text{M}^+)$ versus $(r_{\text{M}^+})^{-1}$ we have illustrated the rational plots of $\delta[\Delta G_i^\circ (\text{M}^+)]$ versus $(r_{\text{M}^+})^{-1}$ in Fig. 3, for both DME-water and ME-water systems. Here $\delta[\Delta G_i^\circ (\text{M}^+)]$ stands for the difference between $\Delta G_i^\circ (\text{M}^+)$ value in DME-water or ME-water system and the corresponding value in EG-water system, all of such compositions so that their dielectric constant remains constant (namely $\epsilon \approx 63.2$ which corresponds to 50 wt % EG-water system^{6,11}) and as a result the Born-type destabilization effects cancels out in each case. Significantly enough, the slopes of the guiding lines of the short-range interactions and the deviations thereof due to soft-soft interactions in DME-water exceed that in ME-water system conforming to what is expected from the larger basicity and polarizability of DME than that of ME.

The observed increased destabilization of the halide ions provides thermodynamic evidence of the expected effect of decreased acidity of the mixed solvents, as induced by the aprotic character of DME. The relative order of destabilization: $\text{Cl}^- > \text{Br}^- > \text{I}^-$ is the result of decreased acid-base stabilization and increased soft-soft interactions down the group. Moreover, as in ME-water system¹, the pronounced stabilization of the large-sized hydrophobic solute, $\text{Ph}_4\text{B}^-/\text{Ph}_4\text{As}^+$ in DME-water system is also clearly indicative of the combined effects of increased dispersion interactions of the highly polarizable Ph-groups with the more polarizable cosolvent molecules and the possible increased cavity-forming interactions in the mixed solvents compared to that in water.

For Pi^- ion, however, the observed initial destabilization followed by increased stabilization at higher cosolvent composition suggest that the two opposing effects are in operation. Also, while the acid-base type interactions on the hydrophilic substituents of Pi^- is dominating at lower range, the dispersion interactions on the hydrophobic benzenoid ring overcomes the former effect at higher cosolvent composition, which is likely to be the case especially for the cosolvents with larger hydrophobic character.

Finally, a comparison (Fig. 4) of the behaviour of some selected ions, viz. H^+ , K^+ , Cl^- and Ph_4B^- in the aqueous mixtures of EG, ME and DME should be rewarding.

The analysis of the structural features of the three cosolvents^{1,3,6,7b} appears to suggest that the basicity measured by the intensity of partial negative charge on the O-centres in the cosolvents or the H-bonded complexes in aqueous cosolvents increase in the order: water < EG < ME < DME. Also, the relative acidities measured by the intensity of partial positive

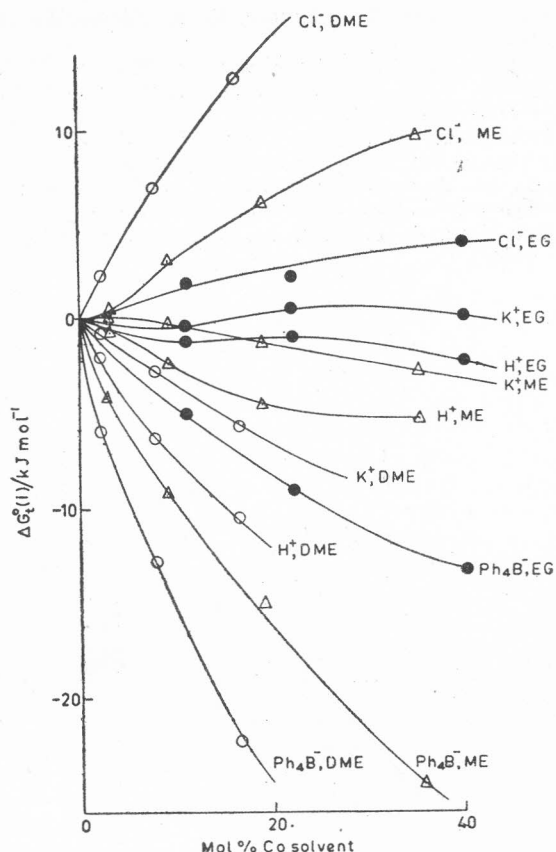


Fig. 4 — Comparison of ΔG_i° (i) for some ions : H^+ , K^+ , Cl^- and Ph_4B^- as obtained from TATB assumption in aqueous mixtures of ethylene glycol (EG), 2-methoxyethanol (ME) and 1,2-dimethoxyethane (DME) at 25°C.

charges on the hydroxylic H-atoms of the cosolvents or of the H-bonded complexes in aqueous cosolvent increase in the reverse order. Consequently, despite increasing effects of Born-type destabilization, the increased stabilization of H^+ and their relative order $EG < ME < DME$ is indicative of the effects of pronounced basicity of the cosolvents and of their aqueous mixtures.

Similarly, the increased destabilization of Cl^- in these cosolvent systems are also in accordance with the effects of decreasing acidity and decreasing dielectric constant of the cosolvent systems.

Again, in view of the fact that Born-type interactions are likely to induce pronounced destabilization on the small-sized alkali metal cations, the observed relative stabilization of K^+ in the order $EG < ME < DME$ implies that non-Born type short range stabilization would be fairly pronounced. This is in accordance with what is expected from the increased basicity of the mixed solvents as well as of the increasing propensity for bidentate complex formation of the cosolvents referred to elsewhere in this paper.

As indicated earlier¹, the Born-type electrostatic interactions of the large-sized hydrophobic solute Ph_4B^-/Ph_4As^+ being nearly same in these aqueous cosolvents, ΔG_i° values of these ions are dictated

partly by dispersion interaction and partly by cavity forming interactions. The observed increased stabilization of these ions in all these cosolvent systems and their relative order at any cosolvent composition $EG < ME < DME$ are in conformity with what is expected from the relative polarizability dictating the 'dispersion' interactions and the relative extent of hydrogen-bonded association dictating the 'cavity-forming' interactions in these cosolvent systems. Since DME is the most polarizable cosolvent, EG the least and quasi-aprotic ME intermediate of the other two, it is expected that the dispersive effect in these aquo-cosolvent systems will also increase in the sequence $EG < ME < DME$. Moreover, it may be reasonable to assume, that the cavity-forming interactions will be less associated are the aqueous mixtures of these cosolvents^{1,19}. As the extent of association arising from intermolecular hydrogen bonding is likely to decrease in the order: $EG > ME > DME$, it is expected that ΔG_i° associated with cavity-forming interactions will be increasingly negative in the order: $EG < ME < DME$. Thus it appears that both these effects together render the ΔG_i° values increasingly negative in the order $EG < ME < DME$, as observed.

An estimate of ΔG_i° (cav) say by the scaled-particle theory (SPT)²² method, would have been more informative from quantitative point of view¹⁹. But the intrinsic approximations of the theory^{23,24} and uncertainties in various parameters involved²⁵ in such calculations does not at all preclude the possibility of introducing more confusion instead.

Acknowledgement

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