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A Study on the Preferential Solvation of Ions in Mixed Aqueous Binary Solvent Systems Using the Scaled Particle Theory

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The free energies of transfer of electrolytes from water to ethylene glycol (EG)–water, 2-methoxyethanol (ME)–water and 1,2-dimethyoxyethane (DME)–water mixtures have been calculated at 25 °C using the scaled particle theory in conjunction with the Born charging equation. The predicted values of transfer free energies have been compared with the corresponding experimental values in order to gain insight into the preferential solvation of ions by water molecules in these solvent mixtures. The results from the present theoretical analysis indicate that in the cosolvent–water mixtures the ease of preferential solvation of electrolytes by water molecules increase in the order DME–water$<$ME–water$<$EG–water.

Recently there has been an upsurge of interest in the study of thermodynamic transfer functions both from theoretical and experimental points of view. Numerous calculations of various thermodynamic properties of electrolytes in solution from purely theoretical considerations have been reported earlier.[1—9] Many such theoretical approaches are based on several models e.g., the multilayer hydration models of Gurney,[4] Frank and Wen,[5] and Wicke[6] etc.

It is now well established[7] that the solvation process of electrolytes (or ions) can be regarded as carried out in two steps: first the formation of a cavity of suitable size in the solvent to accomodate the solute species and secondly the insertion of the solute ion into the cavity which interacts with the surrounding solvent. The standard free energy of solvation, $\Delta G^\circ_{\mathrm{solv}}$, of an ion can be expressed as

$$\Delta G^\circ_{\mathrm{solv}} = \Delta G^\circ_{\mathrm{c}} + \Delta G^\circ_{\mathrm{i}} + \Delta G^\circ_{\mathrm{x}} \qquad (1)$$

where $\Delta G^\circ_{\mathrm{c}}$ and $\Delta G^\circ_{\mathrm{i}}$ are the free energies of cavity formation and of interaction of the solute with the surrounding solvent respectively and $\Delta G^\circ_{\mathrm{x}}$ represents the free energy change due to standard state conversion.

The interaction process can again be split into two additive parts viz., (i) Born-type electrostatic interaction arising form the presence of an ion of definite size within a uniform dielectric solvent system and (ii) the sum of the other various of specific interactions occurring in the various regions which may result in the formation of so-called multilayer solvation zones around the incorporated ion. These later mentioned specific interactions cannot be obtained by the Born continuum model.

Thus, the free energy of solvation, $\Delta G^\circ_{\mathrm{solv}}$, of an ion can be represented as

$$\Delta G^\circ_{\mathrm{solv}} = \Delta G^\circ_{\mathrm{c}} + (\Delta G^\circ_{\mathrm{Born}} + \Delta G^*) + \Delta G^\circ_{\mathrm{x}} \qquad (2)$$

where $\Delta G^\circ_{\mathrm{Born}}$ and ΔG^* are the respective free energies of Born-type of electrostatic interaction and of specific interaction which is not included in the free energy calculated by the Born equation in its simplest form.

The scaled particle theory (SPT) developed by Reiss and his co-workers[8—11] has often been employed in the investigation of the thermodynamics of solution processes. Several workers[12—16] have used this theory for predicting Gibb's free energies, enthalpies, and entropies of transfer from water to mixed aqueous and other non-aqueous solvent systems. In majority of cases the solutes involved were non polar and it was assumed that the similarity of the solvents for each transfer would cause a cancellation of the interaction terms because of the nonpolar nature of the solute, thus implying a good prediction of the transfer properties of hydrophobic solutes from cavity formation contribution alone, which may be calculated from the SPT. The scaled particle theory, which so far has been used to describe the solution processes of nonpolar gases and hydrocarbons, has been extended to the study of hydrophobic ions e.g., the tetrabutylammonium ion, the charge on which is probably diffuse enough to consider it as an almost neutral entity. Desrosiers[17] applied the original version of the SPT in order to predict the various transfer functions of the tetrabutylammonium ion from water to some mixed aqueous solvent systems from the cavity contribution alone. Sen[7] has further extended this approach to predict the Gibb's free energies of transfer of various electrolytes form water to methanol–water, dimethyl sulfoxide–water, and actonitrile–water solvent systems. Here, unlike earlier occasions involving nonpolar or hydrophobic solutes where all other interaction contributions were ignored, only a part of the overall interaction free energy contribution (viz., the specific interaction term, ΔG^*) has been assumed to be approximately the same in both the aqueous and mixed aqueous solvent systems. It was also pointed out by this author[7] that the results of such theoretical analysis is capable of describing the preferential solvation of ions in binary solvent mixtures.

It is the purpose of the present paper to apply the scaled particle theory to study the changes in solvation behavior of electrolytes resulting form the transfer from water to aqueous mixtures of three chemically related solvents, ethylene glycol (EG), 2-methoxyehtanol (ME), and 1,2-dimethoxyethane (DME).

Table 1. Physical Parameters Used in the Thermodynamic Calculation (at 25 °C)

Mol% of cosolvent	M_{av} g mol^{-1}	ρ g cm^{-3}	y	d_1 Å	D	K_o J mol^{-1}	$-K_1$ J mol^{-1} Å^{-1}	K_2 J mol^{-1} Å^{-2}
EG–H_2O system								
0.00	18.015	0.99707	0.3547	2.729	78.32	4453	7930	4002
6.76	20.993	1.02249	0.3685	2.884	73.40	4934	8273	3910
11.06	22.887	1.03541	0.3764	2.977	70.31	5231	8470	3857
22.49	27.923	1.06165	0.3947	3.205	63.81	5983	8939	3732
30.33	31.376	1.07399	0.4058	3.350	59.78	6488	9237	3661
40.38	35.804	1.08500	0.4182	3.524	55.71	7101	9568	3575
53.72	41.681	1.09475	0.4323	3.737	51.36	7866	9946	3471
64.71	46.522	1.09986	0.4426	3.901	48.27	8476	10231	3398
72.31	49.870	1.10276	0.4490	4.008	46.38	8878	10408	3350
79.58	53.073	1.10505	0.4545	4.106	44.71	9239	10553	3304
89.49	57.439	1.10761	0.4616	4.234	42.57	9727	10749	3249
100.00	62.069	1.10984	0.4686	4.364	40.61	10233	10947	3196
ME–H_2O system								
2.56	19.502	0.99935	0.3632	2.822	74.63	4744	8144	3950
9.21	23.364	1.00473	0.3818	3.042	64.10	5443	8608	3821
19.14	29.132	1.00624	0.4048	3.337	50.25	6441	9209	3667
26.20	33.232	1.00233	0.4184	3.530	42.19	7111	9565	3567
35.58	38.680	0.99627	0.4342	3.767	34.25	7975	9998	3457
48.46	46.161	0.98649	0.4520	4.063	26.52	9073	10482	3322
57.98	51.690	0.98044	0.4715	4.419	22.21	10451	11030	3174
68.06	57.545	0.97466	0.4735	4.459	19.01	10604	11083	3157
82.05	65.670	0.96740	0.4857	4.711	17.20	11588	11419	3055
92.59	71.792	0.96284	0.4939	4.888	17.00	12302	11652	2990
100.00	76.096	0.96002	0.4991	5.006	16.93	12778	11799	2947
DME–water System								
4.76	21.447	0.98800	0.3745	2.954	66.80	5158	8426	3939
11.76	26.495	0.97651	0.3979	3.247	50.00	6125	9022	3710
23.07	34.650	0.95209	0.4276	3.668	35.51	7603	9810	3499
31.81	40.952	0.93351	0.4461	3.959	26.39	8693	10328	3372
44.43	50.035	0.91128	0.4668	4.332	19.48	10101	10891	3207
52.63	55.964	0.90019	0.4781	4.551	16.18	10964	11212	3120
64.27	64.359	0.88752	0.4915	4.835	12.75	12088	11584	3010
72.32	70.161	0.88014	0.4996	5.017	10.94	12825	11814	2943
79.06	75.021	0.87474	0.5058	5.162	9.88	13420	11992	2893
90.01	82.917	0.86767	0.5154	5.382	8.52	14306	12227	2815
100.00	90.123	0.86120	0.5219	5.574	7.07	15108	12439	2753

Methods of Calculation

The standard free energies of transfer of an ion from water (w) to mixed aqueous solvent systems (s) can be expressed as

$$\Delta G^{\circ}_{\mathrm{tr(w\rightarrow s)}} = \Delta G^{\circ}_{\mathrm{c(tr)}} + \Delta G^{\circ}_{\mathrm{Born(tr)}} + \Delta G^{\circ}_{\mathrm{tr}} + \Delta G^{\circ}_{\mathrm{x(tr)}} \quad (3)$$

$$\begin{aligned} \text{i.e.,}\ \Delta G^{\circ}_{\mathrm{s}} - \Delta G^{\circ}_{\mathrm{w}} &= [\Delta G^{\circ}_{\mathrm{c(s)}} - \Delta G^{\circ}_{\mathrm{c(w)}}] \\ &+[\Delta G^{\circ}_{\mathrm{Born(s)}} - \Delta G^{\circ}_{\mathrm{Born(w)}}] \\ &[\Delta G^{*}_{\mathrm{s}} - \Delta G^{*}_{\mathrm{w}}] + [\Delta G^{\circ}_{\mathrm{x(s)}} - \Delta G^{\circ}_{\mathrm{x(w)}}] \end{aligned} \quad (4)$$

The terms $\Delta G^{\circ}_{\mathrm{c(s)}}$ and $\Delta G^{\circ}_{\mathrm{c(w)}}$ can be obtained by calculating the standard free energy of cavity formation for ions in the respective solvents. These can be calculated with the help of the SPT by the following set of equations

$$\Delta G^{\circ}_{\mathrm{c}} = K_{\mathrm{o}} + K_1 d_{12} + K_2 d_{12}^2 + K_3 d_{12}^3 \quad (5)$$

$$K_{\mathrm{o}} = RT[-\ln(1-y) + 4.5\{y/(1-y)\}^2] - PN\pi d_1^3/6 \quad (6)$$

$$K_1 = -(RT/d_1)[\{6y/(1-y)\} + 18\{y/(1-y)\}^2 + PN\pi d_1^2 \quad (7)$$

$$K_2 = (RT/d_1^2)[\{12y/(1-y)\}18\{y/(1-y)\}^2 - 2PN\pi d_1 \quad (8)$$

$$K_3 = 4PN\pi/3 \quad (9)$$

$$d_{12} = (d_1 + d_2)/2 \quad (10)$$

where $y(=N\pi d_1/6V_1$ is the compactness factor of the solvent, d_1 and d_2 are the hard-sphere diameters of the solvent and the solute species, respectively. The mixed solvent systems has been assumed to be a uniform solvent system with an average molecular diameter of d_1 and an average molecular weight M_{av} defined by

$$M_{\mathrm{av}} = (\text{Mol\% of cosolvent}.M_{\mathrm{cosolvent}} + \text{Mol\% of water}.M_{\mathrm{water}})/100 \quad (11)$$

The diameter of the solute ion (d_2) is taken to be twice that of the Pauling ionic crystal radius.[18] The average hard-sphere diameter of the solvent has been obtained using the empirical relationship suggested by Kim.[19]

$$d_1 = 0.9275\sigma_{\mathrm{o}}(V^{\circ}) \times 10^{-8} - 0.8465 \times 10^{-8} \quad (12)$$

where $\sigma_{\circ}(V^{\circ})=(6V^{\circ}/\pi N)^{1/3}$, V° being the molar volume of the mixed solvent.

The Born equation for the free energy of transfer is

$$\Delta G^{\circ}_{\mathrm{Born(tr)}} = N(ze)^2/2r\cdot[1/D_{\mathrm{s}} - 1/D_{\mathrm{w}}] \qquad (13)$$

and the free energy of transfer due to the standard state conversion is

$$\Delta G^{\circ}_{\mathrm{x(tr)}} = RT\ln RTM_{\mathrm{s}}/V_{\mathrm{s}} - RT\ln RTM_{\mathrm{w}}/V_{\mathrm{w}} = RT\ln \rho_{\mathrm{s}}/\rho_{\mathrm{w}} \qquad (14)$$

In Eqs. 13 and 14 D,M, V, and ρ represent the static dielectric constant, molecular weight, molar volume, and density, respectively and the other symbols have their usual significance. Theoretical estimation of the values of the transfer free energies for specific interaction with the help of the present-day knowledge of ion-solvent interactions seems to be difficult. In the attempt made by Sen[7)] to predict the free energies of transfer of the electrolyte it was assumed that the specific interaction term, ΔG^* would be more or less the same in both the aqueous and mixed aqueous solvent systems. Consequently, one can neglect the quantity $(\Delta G^*_{\mathrm{s}} - \Delta G^*_{\mathrm{w}})$ in Eq. 4 and the working formula for the theoretical calculation of the free energy of transfer from water (w) to mixed aqueous binary mixtures (s) can be expressed as

$$\Delta G^{\circ}_{\mathrm{tr(w\rightarrow s)}} = [\Delta G^{\circ}_{\mathrm{c}} + \Delta G^{\circ}_{\mathrm{Born}} + \Delta G^{\circ}_{\mathrm{x}}]_{\mathrm{tr(w\rightarrow s)}} \qquad (15)$$

Results and Discussion

Various physical parameters at 25 °C used in the theoretical calculation of the free energy of transfer for ions form water to different aquo–organic solvent mixtures are listed in Table 1. The coefficient K_3 appearing in Eq. 5 is independent of the solvent systems used and has a value of 0.2556 $\mathrm{J\,mol^{-1}\,Å^{-3}}$.

The experimental values of the free energies of transfer of electrolytes from water to EG–H_2O, ME–H_2O, and DME–H_2O mixtures are still scarce. Only the values for KCl, KBr, and KI are available simultaneously[20—22)] in these three solvent systems and are given in Table 2. In cases where the experimental values were reported in other than the molal scale, these have been converted to the corresponding values in the molal scale. The experimental values of $\Delta G^{\circ}_{\mathrm{tr}}$ are not available for the entire range of the solvent compositions where the components of the binary mixtures would be present from 0 to 100 mol%. In these cases, the available experimental values of $\Delta G^{\circ}_{\mathrm{tr}}$ for different electrolytes are plotted against the solvent composition and the values of $\Delta G^{\circ}_{\mathrm{tr}}$ (expt) at all the desired solvent compositions have been generated from the smooth master curves and are given in Table 2. The values of the free energies of transfer for KBr (as a representative of 1 : 1 electrolyte), calculated by Eq. 15 have been plotted against the corresponding solvent compositions in Fig. 1. To make a comparative study, the experimental values are also given graphically in the same figure.

On passing from EG to DME through ME, the number of $-CH_3$ group increases from zero in EG to two in DME. The electron-donating $-CH_3$ group induces large negative charge density on the oxygen-center to which it is attached and therefore the hydrogen-bond forming capability with water molecules increases in the order EG < ME < DME. Or, in other words, the stability of the cosolvent–water complexes increase in the order EG–H_2O < ME–H_2O < DME–H_2O. Figure 1 shows that in EG–H_2O binary mixtures, the values of ΔG^* is almost similar to that in pure water throughout the entire composition range. This suggests that the solute ions may be getting preferentially solvated by water molecules as they are present in pure water as solvent. This is in agreement with the earlier view[20)] that EG–H_2O complexes are comparatively weaker and hence the water molecules remain available for solvation of the solute ions throughout the entire composition range.

Table 2. $\Delta G^{\circ}_{\mathrm{tr}}$ (exptl) from Water to Mixed Solvents at 25 °C (molal scale)

Mol% of cosolvent	$\Delta G^{\circ}_{\mathrm{tr}}/\mathrm{kJ\ mol^{-4}}$		
	KCl	KBr	KI
EG–water System			
6.76	1.19	0.50	0.45
11.06	2.09	1.39	0.69
22.49	3.69	2.69	1.49
30.33	4.41	3.41	1.92
40.38	5.70	4.32	2.20
53.72	6.57	4.99	2.18
64.71	7.22	5.31	2.01
72.31	7.42	5.32	2.02
79.58	8.01	5.85	2.32
89.49	8.42	6.71	3.84
100.00	9.06	7.36	4.16
ME–water System			
2.56	1.30	0.81	0.60
9.21	3.44	2.34	0.94
19.14	5.99	4.29	1.09
26.20	7.26	5.22	1.22
35.58	8.69	6.29	1.59
48.46	10.80	7.60	2.17
57.98	12.42	8.63	2.83
68.06	14.27	9.87	3.58
82.05	17.22	11.97	4.95
92.59	19.81	14.11	6.26
100.00	21.74	15.94	7.31
DME–water System			
4.76	2.91	1.49	0.41
11.76	6.42	3.50	1.12
23.07	8.85	6.91	2.19
31.81	10.25	9.32	3.16
44.43	16.52	14.00	5.25
52.63	23.83	17.22	7.34
64.27	35.00	22.50	10.76
72.32	43.07	27.23	13.64
79.06	49.84	30.98	16.75
90.01	63.50	38.33	22.23
100.00	78.36	45.35	28.61

For ME–H_2O mixtures, as is evident from Fig. 1, the solute ions would get preferentially solvated by wa-

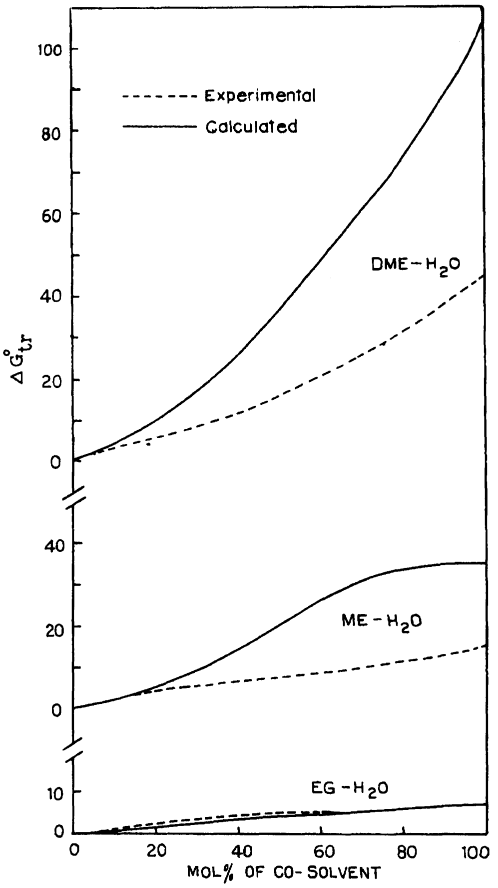

Fig. 1. Comparison of the experimental and calculated values of transfer free energy (ΔG°_{tr}) for a typical 1 : 1 electrolyte (KBr) for different solvent compositions.

ter molecules upto ca. 20 mol% of ME in the solvent mixtures. Here, because of the enhanced stability of the ME–H_2O complex than that of the EG–H_2O complex, the availability of the water molecules in the former mixture towards the solute ions would be obviously somewhat less than that in the later mixture. This is manifested by the fact that the preferential solvation of the solute ions by water molecules vanishes after ca. 20 mol% of ME.

Finally, in the case of DME–H_2O mixtures, the so-called preferential solvation of electrolytes by water molecules may be possible only when the mixtures contain a very low mol% of DME (ca. 8 mol%). Though DME–H_2O complex is the stablest among the three co-solvent–water complexes, the small addition of DME to water possibly does not alter the water structure to a significant extent. Thus making available the water molecules in the mixture for solvation of electrolytes. But at the higher compositions, the solute ions can not compete with the DME molecules which form very stable complexes with water molecules. As a result, the value of ΔG^*, free energy of specific interaction, of electrolytes in DME–H_2O binary solvent systems is different from that in water beyond ca. 8 mol% of DME.

Thus, from the present theoretical analysis it is apparent that in the three aqueous binary solvent systems studied the ease of preferential solvation of the electolytes by water molecules increase in the order DME–water < ME–water < EG–water.

It should be mentioned here that KBr was chosen as a representative system. Similar conclusion can be drawn for other electrolytes also.

Finally, it can be said that the scaled particle theory in conjunction with the Born charging equation constitutes a reliable means for the prediction of the solvational behavior of electrolytes (or ions) in mixed aqueous binary solvent systems.

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