paraffin chains as a result of film compression we expect the second condensed state at a = 40 Å^2 (π = 20 dyn/cm), as found. This fact is not well understood. The model for the molecular arrangement depicted in Figure 9A is indeed consistent with the experimental data but must be considered as suggestive. Only a weak indication of a second phase transition is shown by the π-a curves of N_{VI} = 0.75, 0.5, and 0.25, whereas the π-a curve of N_{VI} = 0.35 rises straightly. This latter behavior may be related to an "eutectic mixture" for which the cross-sectional area of the close-packed chromophores is just equal to the average cross-sectional area of the close-packed paraffin chains (for a_{12} = 30 Å^2/molecule at π = 10 dyn/cm we calculate 18.2 Å^2 for one paraffin chain). The molecules in this close-packed state (Figure 9C) apparently have enough cohesion, which prevents hydration of the glycerol group and expansion at surface pressures > 4 dyn/cm.

As the geometry of the di- and triglyceride-like dyes predestine the architecture of the two-component monolayer, the interaction of the head groups of I, STOOH, and STNH$_2$ has an important influence on the molecular arrangement of the three-component films. Attraction of the amine group of STNH$_2$ and the carboxyl group of dye I causes an anchoring effect and prevents in this way the squeezing out of dye molecules at high surface pressures. A further effect of the head-group interaction is the dissolution of the aggregates of I in the film into dimers and monomers which lead to an intimately mixed film. Cd ions have a strong condensing effect on fatty acid monolayers and therefore should favor a lateral demixing of the acid and base components. The analysis of the absorbance spectra, however, shows that a lateral demixing occurs only in case of mixed films of STOOH and I on CdCl$_2$ subphases; in case of "neutral films" the interaction between the amino and carboxyl groups predominates. We may conclude our study by saying that CPK molecular models and considerations about intermolecular interactions indicate indeed the direction for designed monolayer assemblies, but the main work is still a play of trial and error.

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Study of Electrolytic Solution Process Using the Scaled-Particle Theory. 2. The Standard Entropy of Solvation

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Abstract: A method has been developed to describe the entropy of solvation of ions and electrolytes at different temperatures using the scaled-particle theory in conjunction with the Born charging equation. The treatment is apparently consistent with the assumption that the effective size of an ion in solution does not change significantly with temperature and the Born relationship can accurately describe the electrical part of the solvation thermodynamic functions. The prediction of entropy of hydration by this unified approach is reasonably good at higher temperatures where the solvent hydrogen bonding becomes considerably weak. The treatment has also been applied to several nonaqueous solvents to predict entropy of solvation of electrolytes in these solvents.

Introduction

It has been of consistent interest for scientists to calculate some thermodynamic properties of ions in solution from the first principles, and this has been one of the important objectives of the theory of electrolytes in solution. Although it is true that Debye–Hückel theory and its various modifications provide a description of the change of some thermodynamic functions with electrolyte concentration, the prediction of the absolute free energy or entropy of an electrolyte from basic parameters has only been partially successful. Many attempts have made use of some type of electrostatic model[1-5] frequently based upon the Born equation,[6] but the results cannot be made quantitative for ions in general without a large number of arbitrary constants. At least one author in an excellent review has concluded that continuum theories of ionic hydration based on the Born equation seem to have reached an asymptotic limit of usefulness or applicability.[7] The two stumbling blocks to use of continuum models are obtaining or even defining the ionic radius in solution to the required degree of accuracy and lack of detailed knowledge of the dielectric constant in the vicinity of an ion in solution. A number of features of electrolyte behavior have been qualitatively correlated with a more structurally based model[8] such as the Frank–Wen proposal,[9] but the attractive features of this approach have not yet been translated into a quantitative theory.

Latimer did explore in detail the ability of the continuum theory to predict the relative order of hydration energies among various ions, and was able to construct a simple model involving one arbitrary constant each for cations and anions.[10] It can, however, be demonstrated that such a single constant cannot apply for all ions. Latimer also proposed that the experimental

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Table I

A. Physical Parameters of Various Solvents at Different Temperatures Used in the Thermodynamic Calculations[a]

t, °C	α_p,[b] deg^{-1} × 10^{-5}	B_0, cal mol^{-1}	B_1, cal mol^{-1} Å^{-1}	B_2, cal mol^{-1} Å^{-2}	D	$-dD/dT$, deg^{-1} × 10^{-2}	$-(1/D^2)(dD/dT)$, deg^{-1} × 10^{-5}
				Water			
0	−6.81	−5	−9.1	−8.73	87.90	40.15	5.196
25	25.71	25	41.8	40.25	78.36	35.62	5.801
50	45.78	50	84.7	80.60	69.88	31.64	6.480
60	52.34	60	100.8	92.84	66.76	30.20	6.776
75	61.30	74	124.0	115.33	62.34	28.21	7.259
100	75.00	98	161.1	145.32	55.58	25.31	8.194
				Methanol			
0	114.2	92	120.1	89.25	37.90	23.04	16.04
25	120.2	103	131.5	92.66	32.63	19.84	18.64
50	126.7	113	141.8	94.93	28.10	17.08	21.63
				Ethanol			
0	104.8	105	126.5	91.45	28.4	17.66	21.89
25	108.8	117	137.8	93.92	24.3	15.10	25.58
50	117.1	133	151.0	97.75	20.8	12.93	29.89
75	130.5	151	167.6	102.30	17.8	11.07	34.93
				Ethylene Glycol			
25	62.09	108	144.4	128.32	37.7	19.44	13.68
50	70.19	135	175.4	149.46	33.1	17.07	15.58
75	74.84	156	198.5	162.27	29.1	15.01	17.72
100	75.82	170	210.4	164.84	25.6	13.21	20.15
				Acetic Acid			
25	107.9	127	152.0	109.14	6.18	−0.80	−20.87
50	111.9	139	162.1	109.97	6.38	−0.82	−20.22
75	117.1	151	171.6	110.09	6.70	−0.86	−19.25
				Acetone			
25	144.1	165	180.7	117.76	20.7	9.77	22.80
50	151.6	179	189.3	115.12	18.4	8.68	25.65
				Nitrobenzene			
0	80.70	143	169.2	139.21	39.63	20.53	13.07
25	82.80	162	185.1	144.24	34.82	18.04	14.88
50	84.98	172	185.6	132.93	30.59	15.85	16.94

$B_3 = K_3/8 = 0.0076$ cal mol^{-1} Å^{-3} for all the solvents at 1 atm pressure

B. Physical Parameters of Various Solvents at 25 °C Used in the Thermodynamic Calculations[c]

		protic solvents[d]				
		1-PrOH	2-PrOH	*n*-BuOH	glycerol	F[e]
mol wt,	g mol^{-1}	60.11	60.11	74.12	92.11	45.04
density,	g cm^{-3}	0.8008	0.78087	0.8066	1.2583	1.12915
$\overline{V}_1$,	cm^3 mol^{-1}	75.06	76.98	91.51	73.20	39.89
α_p × 10^{-5},	deg^{-1}	95.44	105.3	88.64	50.5	74.9
β_T × 10^{-5},	atm^{-1}	11.6	11.2	8.5	2.2	4.11
y		0.4059	0.4125	0.4615	0.5714	0.4506
d_1,	Å	4.5886	4.6522	5.1161	5.0997	3.8484
K_0,	cal mol^{-1}	1552	1629	2324	5239	2147
$-K_1$,	cal mol^{-1} Å^{-1}	1613	1665	2125	4645	2620
K_2,	cal mol^{-1} Å^{-2}	466	473	532	1092	878
B_0,	cal mol^{-1}	115	131	134	119	109
B_1,	cal mol^{-1} Å^{-1}	126.8	143.4	146.1	163.2	154.0
B_2,	cal mol^{-1} Å^{-2}	84.24	95.72	102.00	160.03	138.44
D		20.1	18.3	17.1	42.5	109.03
$-dD/dT$,	deg^{-1}	0.1357	0.1307	0.1320	0.2036	0.4089
$-(1/D^2)dD/dT$ × 10^{-5},	deg^{-1}	33.58	39.02	45.15	11.27	3.44

K_3 and B_3 are 0.0611 and 0.0076 cal mol^{-1} Å^{-3}, respectively, for all the solvents at 1 atm pressure

		dipolar aprotic solvents[f]				
		DMF[g]	Me_2SO[h]	AN	PC[i]	HMPT
mol wt,	g mol^{-1}	73.09	78.10	41.00	102.10	179.40
density,	g cm^{-3}	0.9440	1.0960	0.77682	1.199	1.02
$\overline{V}_1$,	cm^3 mol^{-1}	77.40	71.26	52.78	85.15	175.88
α_p × 10^{-5},	deg^{-1}	100.0	88.0	137.2	100.0	
β_T × 10^{-5},[j]	atm^{-1}	6.5	5.3	10.8	6.0	8.0
y		0.4721	0.4846	0.3745	0.4901	0.5331
d_1,	Å	4.8752	4.7842	3.9721	5.0960	6.6744

Table I (*Continued*)

		dipolar aprotic solvents[f]				
		DMF[g]	Me_2SO[h]	AN	PC	HMPT
K_0,	cal mol^{-1}	2510	2749	1233	2861	3926
$-K_1$,	cal mol^{-1} Å^{-1}	2400	2668	1497	2602	2690
K_2,	cal mol^{-1} Å^{-2}	626	703	512	642	494
B_0,	cal mol^{-1}	158	146	145	170	
B_1,	cal mol^{-1} Å^{-1}	184.2	177.8	175.0	196.0	
B_2,	cal mol^{-1} Å^{-2}	139.11	142.02	123.15	149.37	
D		37.00	46.6	36.01	64.92	30.5
$-\mathrm{d}D/\mathrm{d}T$,	deg^{-1}	0.1902	0.1902	0.1862	0.2402	
$-1/D^2)\mathrm{d}D/\mathrm{d}T$ $\times 10^{-5}$,	deg^{-1}	13.89	8.76	14.36	5.70	

[a] Other necessary physical parameters are listed in ref 15. [b] Reference 20. [c] Reference 20. [d] For physical parameters of other protic solvents see Table IA. [e] L. A. Dunn and R. H. Stokes, *Trans. Faraday Soc.*, **65,** 2906 (1969). [f] Solvent abbreviations: F, formamide; DMF, dimethylformamide; Me_2SO, dimethyl sulfoxide; AN, acetonitrile; PC, propylene carbonate; HMPT, hexamethylphosphoric triamide. [g] J. Julliard, *Pure Appl. Chem.*, **49,** 878 (1977). [h] G. J. Janz and R. P. T. Tomkins, "Nonaqueous Handbook", Vol. 1, Academic Press, New York, 1972, p 1024. [i] W. H. Lee, "The Chemistry of Nonaqueous Solvents", Vol. 4, J. J. Lagowski, Ed., Academic Press, New York, 1976, p 188. [j] M. R. J. Dack, K. J. Bird, and A. J. Parker, *Aust. J. Chem.*, **28,** 955 (1975).

free energy of hydration itself might be used to define the effective size of an ion in solution. Such a suggestion requires the assignment of an arbitrary constant to every ion (or electrolyte) and at the time could not be tested independently nor used to predict any new information on a given electrolyte. Goldman and Bates[11] claimed prediction of hydration thermodynamic functions within 5% of the corresponding experimental values. An off-centered dipole is used to characterize the permanent electrostatic properties of water in the primary hydration shell and a Born continuum treatment used to calculate the secondary solvation effect. Values of their model parameters are obtained by fitting the model to experimental gas-phase single ion hydration data. The calculations are by no means simple. Approximate calculations of the heats and entropies of hydration according to the various models proposed by Bockris and Saluja[12] are also complicated. Recent proposals of a supermolecule-continuum model[13] and also of discrete, continuum, and discrete-continuum models[14] did not simplify the procedures of theoretical calculations and it has been wished that a comparison of the various methods might reveal their respective shortcomings, and simultaneous use of such different models will finally lead to an optimum methodology to deal successfully with various problems involving electrolytic solution process.[14] Without repeating the much familiar line of efforts to modify the Born equation to suit the experimental results a somewhat different approach has, however, been reported recently.[15] The scaled-particle theory (SPT), which so far has been used with success to describe the solution process of neutral gases in aqueous and other solvents, has been extended to study such problems of electrolytes (i.e., ions) in solution. The striking success of this simple unified approach consisting of the SPT (to account for the free energy of solution associated with the size of the solute ionic species) in conjunction with the Born charging free energy equation (to treat the electrostatic part) in accurate prediction of the temperature effect on standard electrolyte free energy is obviously interesting and encourages one to explore the capability of similar treatment for the theoretical prediction of other thermodynamic functions of electrolytes in solution. In the present paper an equation has been constructed on the basis of the above considerations to calculate the standard entropy of solvation ($\Delta S_s°$) and hence the partial molal entropies ($\overline{S}_2°$) of electrolytes in solution. The proposed unified model seems to be consistent with most previous concepts of electrolytes and capable of providing thermodynamic predictions at different temperatures without introducing any arbitrary constant at any stage.

Theory

In the scaled-particle approach dissolution of solute species has been assumed to consist of two steps: (1) the formation of a cavity of appropriate size to accommodate the solute species into the solvent and (2) the introduction of the solute species into the cavity which intereacts with the solvent.[16] The free energy of solution ($\Delta G_s°$) is given by

$$\Delta G_s° = \overline{G}_c° + \overline{G}_i° + RT \ln RT/\overline{V}_1 \qquad (1)$$

where $\overline{G}_c°$ and $\overline{G}_i°$ are the free energies of cavity formation and of interactions, respectively, and the last term in the right-hand side accounts for the change of the standard states—1 atm gas to hypothetical unit mole fraction—$\overline{V}_1$ being the molar volume of the solvent. In the case of neutral solutes the contribution $\overline{G}_i°$ is comparatively less than that of $\overline{G}_c°$. But when the solute species is an ion gas $\overline{G}_i°$ predominates in $\Delta\overline{G}_s°$ (which becomes the free energy of solvation) unless the solute ion is very large with small surface charge density. An attempt to calculate $\overline{G}_i°$ for ions as the solute using the Born charging equation shows that an additional term ($\Delta\overline{G}^*$) is necessary, apparently to represent the free energy associated with the specific interactions in solution such as the formation of different solvation zones around the solute ion, which obviously is not included in the free energy calculated by the Born equation ($\overline{G}°_{\mathrm{Born}}$) in its simplest form. In other words, the overall interaction free energy, $\overline{G}_i°$, becomes the sum of $\overline{G}°_{\mathrm{Born}}$ and ΔG^* ($\overline{G}_i° = \overline{G}°_{\mathrm{Born}} + \Delta G^*$). Thus the free energy of solvation of an ion can be expressed as

$$\Delta G_s° = \overline{G}_c° + (\overline{G}°_{\mathrm{Born}} + \Delta G^*) + RT \ln RT/\overline{V}_1 \qquad (2)$$

It has also been found that ΔG^* is relatively insensitive to temperature.[15] By differentiating both sides of eq 2 with respect to temperature at constant pressure one would get the expression for the entropy of solvation ($\Delta S_s°$) where the unknown ΔG^* term, if independent of temperature, would not interfere. Thus

$$\Delta S_s° = \overline{S}_c° + \overline{S}°_{\mathrm{Born}} + \alpha_p RT - R - R \ln RT/\overline{V}_1 \qquad (3)$$

where $\overline{S}_c°$ is the entropy of cavity formation and α_p ($=(1/\overline{V}_1)$ $\mathrm{d}\overline{V}_1/\mathrm{d}T$) is the thermal expansivity of the solvent.

Method of Calculation

$\overline{S}_c°$ of eq 3 for different electrolytes can be calculated using the SPT and by assuming both the solute and the solvent species to be hard spheres. The expression for $\overline{S}_c°$ may be illustrated[17] as

Table II. Cavity, Interactions, and Standard State Entropy Contributions in the Calculated Entropy of Hydration (ΔS_h°) of Typical 1:1, 2:1, and 3:1 Electrolytes at Different Temperatures (cal mol^{-1} deg^{-1}) (Molal Scale) (1 cal = 4.184 J)

t, °C	$-\bar{S}_c^\circ$	$-\bar{S}_i^\circ$	$-S_x$[a]	$-\Delta S_h^\circ$ (calcd)[b]	$-\Delta S_h^\circ$ (calcd)[c]	$-\Delta S_h^\circ$ (exptl)
			NaCl			
0	21.9	13.9	16.4	52.2	50.7	41.0
25	18.2	15.4	16.4	50.0	48.5	44.4
50	15.1	17.2	16.4	48.7	47.1	46.4
60	13.9	18.0	16.4	48.3	46.6	47.1
75	11.9	19.4	16.3	47.6	45.8	48.4
100	9.1	21.8	16.3	47.2	45.2	50.2
			$BaCl_2$			
0	41.6	35.2	24.6	101.4	97.8	75.0
25	34.6	39.1	24.5	98.2	95.6	83.9
50	28.5	43.7	24.5	96.7	94.9	90.4
60	26.2	45.7	24.5	96.4	95.0	92.8
75	22.5	49.1	24.5	96.1	95.1	96.0
100	17.0	55.3	24.4	96.7	96.5	101.4
			$GdCl_3$			
0	54.1	90.5	32.8	177.4	172.0	152.3
25	47.0	100.9	32.7	178.5	174.6	163.8
50	36.8	112.6	32.7	182.4	179.7	173.5
60	34.0	117.9	32.7	184.6	182.5	177.1
75	29.3	126.4	32.7	188.4	186.9	182.7
100	22.1	142.5	32.6	197.2	196.9	192.0

[a] $S_x = \alpha_p RT - R - R \ln RTM_1/1000\bar{V}_1$ (see eq 13). [b] Calculated using Pauling's radii. [c] Calculated using Gourary and Adrian radii.

Table III. Comparison of Calculated and Experimental Values of Entropy of Hydration (ΔS_h°) (cal deg^{-1} mol^{-1}) of Electrolytes at Different Temperatures (Molal Scale)

	25 °C		60 °C		100 °C	
salts	$-\Delta S_h^\circ$ (calcd)	$-\Delta S_h^\circ$ (exptl)	$-\Delta S_h^\circ$ (calcd)	$-\Delta S_h^\circ$ (exptl)	$-\Delta S_h^\circ$ (calcd)	$-S_h^\circ$ (exptl)
LiCl	53.8	51.5	53.7	54.5	54.7	57.1
NaCl	50.1	44.4	48.3	47.2	47.3	50.1
KCl	50.2	35.5	47.2	40.0	44.7	43.4
RbCl	50.9	33.0	47.4	34.6	44.3	33.9
CsCl	52.3	31.9	48.1	36.2	44.1	40.5
TlCl	50.5	35.0	47.2	42.1	44.4	50.6
AgCl	50.0	45.7	47.2	49.4	44.8	53.0
$MgCl_2$	118.2	114.7	128.6	117.9	137.8	125.0
$CaCl_2$	102.6	95.9	106.4	105.1	110.1	113.0
$SrCl_2$	99.6	93.3	101.6	104.0	103.8	112.3
$BaCl_2$	96.9	83.9	96.5	92.8	96.9	101.4
$CdCl_2$	103.1	103.8	107.2		111.2	111.9
$MnCl_2$	109.3	101.7	116.2	113.5	122.6	121.6
$PbCl_2$	98.5	85.6	99.7	89.5	101.3	89.4

$$\bar{S}_c^\circ = -\bar{G}_c^\circ/T + [RT\alpha_p y/(1-y)]\{[6/(1-y)][2(d_{12}/d_1)^2 - (d_{12}/d_1)] + [36y/(1-y)^2][(d_{12}/d_1)^2 - (d_{12}/d_1) + 1/4] + 1\} \quad (4)$$

where y ($=\pi N d_1/6\bar{V}_1$) 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, and $d_{12} = (d_1 + d_2)/2$. Equation 4 may be simplified by writing as

$$\bar{S}_c^\circ = -\bar{G}_c^\circ/T + \bar{H}_c^\circ/T \quad (5)$$

$\bar{G}_c^\circ$ and $\bar{H}_c^\circ$, the enthalpy of cavity formation, can be expressed as

$$\bar{G}_c^\circ = K_0 + K_1 d_{12} + K_2 d_{12}^2 + K_3 d_{12}^3 \quad (6)$$

and

$$\bar{H}_c^\circ = B_0 + B_1 d_2 + B_2 d_2^2 + B_3 d_2^3 \quad (7)$$

where

$$B_0 = \alpha_p RT^2 y/(1-y) \quad (8)$$

$$B_1 = 3\alpha_p RT^2[y/(1-y)^2]/d_1 \quad (9)$$

$$B_2 = 3\alpha_p RT^2 y[(1+2y)/(1-y)^3]/d_1^2 \quad (10)$$

$$B_3 = \pi PN/6 \quad (11)$$

P and N being the pressure and Avogadro's number, respectively. Equations representing K_0, K_1, K_2, and K_3 are given elsewhere.[15] Values of d_1 and d_2 have been determined[15] from solvent isothermal compressibility (β_T) at different temperatures using Mayer's method,[18] and from the Pauling's crystal radius,[19] respectively. Some of the physical parameters used in the above equations and also used in other thermodynamic calculations are listed in Table I. The rest of the necessary parameters are given elsewhere.[15,20] The interaction entropy contribution which is assumed to be given by the Born entropy equation

$$\bar{S}_i^\circ = \bar{S}^\circ_{\text{Born}} = [N(ze)^2/2rD^2](\mathrm{d}D/\mathrm{d}T) \quad (12)$$

where D is the static dielectric constant of the solvent and r ($=d_2/2$) is the Pauling crystal radius of the solute ion. A term $R \ln (1000/M_1)$, where M_1 is the molecular weight of the solvent, has to be added to convert the entropy of solvation in mole fraction scale (as given by eq 3) to the more commonly used molal scale. Thus

$$\Delta S_s^\circ = \bar{S}_c^\circ + \bar{S}^\circ_{\text{Born}} + \alpha_p RT - R - R \ln (RTM_1/1000\bar{V}_1) \quad (13)$$

From the known values of ΔS_s° the corresponding standard partial molal entropy of the solute ions ($\bar{S}_2^\circ$) in different solvents can be calculated using the equation

$$\Delta S_s^\circ = \bar{S}_2^\circ - S_g^\circ \quad (14)$$

where S_g° is the standard molar entropy of the ion in the gas phase. S_g° for ions can be calculated from the Sackur-Tetrode equation[21] which may be expressed at 1 atm pressure and 25 °C (for monatomic ion gases) as

$$S^\circ_{298} = (3/2)R \ln M + 25.996 \quad (15)$$

where S° is cal deg^{-1} mol^{-1} and M is the atomic weight of the gas. S_g° at some other temperatures can be obtained in cal deg^{-1} mol^{-1} by the relationship

$$S^\circ_T = S^\circ_{298} + (5/2)R \ln T/298 \quad (16)$$

It has been assumed throughout the paper that d_2 does not change significantly with temperature.

Results

The different (cavity, interactions, and change of standard state) contributions and the net values of the standard entropy of hydration (ΔS_h°) of NaCl, $BaCl_2$, and $GdCl_3$ as the typical representatives of 1:1, 2:1, and 3:1 electrolytes, respectively, at different temperatures from 0 to 100 °C, calculated by eq 13, are listed in Table II along with the corresponding experimental data.[22,23] Two sets of calculated values of ΔS_h° obtained by using Pauling's crystal radius[20] and the experimental radius reported by Gourary and Adrian[24] for the solute ions are included in Table II for comparison. Radii for Ba^{2+} and Gd^{3+} ions on the Gourary and Adrian scale are not available. Hence ΔS_h° values for $BaCl_2$ and $GdCl_3$ reported in column 6 of Table II are calculated using Pauling's radii for Ba^{2+} and Gd^{3+} ions but the Gourary-Adrian radius for the Cl^- ion. Table III shows the comparison between the calculated (using Pauling's radii) and the experimental values of ΔS_h° for some other electrolytes at 25, 60, and 100 °C. The experimental values for ΔS_h° have been obtained from the partial molal entropy ($\bar{S}_2°$) data compiled in the literature[25-27] using eq 15 and 16. The uncertainties in the values of experimental $\bar{S}_2°$ of various ions at higher temperatures reported in ref 27 are different for different ions and in general are large when the sources are other than accurate heat capacity ($\bar{C}_p°$) data. To avoid extrathermodynamic division of the entropies of hydration into the cationic and the anionic contributions, the neutral ensemble of ions (i.e., the electrolyte form) has been used for the comparison. It may be noted from Tables II and III that the agreement between the calculated and the experimental values of $\Delta S_h°$ is in general better at higher temperatures.

Discussion

Criss and Cobble[27] showed an excellent linear relationship between the partial molal entropies of ions ($\bar{S}_2°$) in aqueous solution at 25 °C and those at higher temperatures, and proposed the correspondence principle as

$$\bar{S}_{t_2}° = a_{t_2} + b_{t_2}\bar{S}_{t_1}° \ldots \tag{17}$$

where $\bar{S}_{t_2}°$ and $\bar{S}_{t_1}°$ are partial molal entropies of ions at temperatures t_2 and t_1, respectively, and a and b are constants for a particular pair of temperatures. a and b are, however, different for different kinds of ions at the same temperature. The correspondence principle has apparently been proposed in response to the growing need for accurate thermodynamic data for solutes in aqueous solutions at elevated temperatures such as those already existing at 25 °C. Its prediction, therefore, is essentially associated with the known experimental values of entropy at 25 °C or any other temperature. It also takes the help of at least two arbitrary constants (a and b), prior evaluation of which also needs at least a few experimental values of $\bar{S}_2°$ at the higher temperature in question. Morss and Cobble[28] also developed a semiempirical equation which correlates the entropies of monatomic aqueous ions at 25 °C with their charges and radii. But like many other such empirical or semiempirical equations[26,29] it also takes the help of several arbitrary constants and correction terms to suit the known experimental entropy data. On the other hand, the present approach has been derived from some simple basic considerations assuming that the entropy of an ion in solution is more or less given by some functions of some essential physical properties of solute and of the solvent, the nature of which may not play a significant part. This unified theory can predict entropies at different temperatures without the help of any arbitrary constants and one does not have to know any experimental thermodynamic data at any temperature either.

Although it is well recognized that the values of the predicted entropy of hydration for various ions largely depend upon the accuracy of various physical parameters, such as the values of y, d_1, d_2, dD/dT, etc., at different temperatures used in various stages in the theoretical thermodynamic calculations, the trend apparent in Tables II and III (i.e., the prediction is in general more accurate at higher temperatures) seems to be informative and may lead to some interesting speculations. It is customary to envision some kind of electrostatically induced collapse of the solvent molecules taking place due to the presence of the incorporated solute ion. Our present-day knowledge of electrolytes in water also suggests that such processes eventually form a more or less rigid so-called primary hydration sheath of water molecules around the ionic species in solution and that the primary hydration sheath of water molecules is perhaps followed by a so-called secondary region of water differing from the bulk solvent. The effects of these specific interactions in solution are not covered by the simple Born equation when the crystal radius of the ion and the bulk dielectric constant are used, but are supposed to be taken care of by the term ΔG^*, as assumed in the theory. Though the behavior of this rigid primary hydration shell is believed to be unaffected by changes in temperature, the following secondary hydration region may not necessarily be so rigid to be independent of temperature. On the contrary, it is often believed that solvent molecules in the so-called secondary solvation region are in general more free to move in comparison to the hydrogen-bonded solvent molecules in the bulk region. At higher temperature ranges due to increased thermal agitation the water molecules in the secondary hydration zone increasingly cease to be much different from the molecules in the bulk solvent, making the specific interactions of the secondary hydration region progressively insignificant. Thus at some point and maybe thereafter ΔG^* becomes truly the measure of the contribution of the primary hydration effect alone and as such independent of temperature, making the prediction of the hydration entropies according to the theory proposed more accurate. However, the behavior of the various hydration regions at different temperatures may also depend upon the nature of the solute ion involved in the process. This may be one of the reasons why the prediction of $\Delta S_h°$ for some electrolytes is more accurate than of others at lower temperatures (see Tables II and III). On the basis of the above consideration one might be tempted to define water as approaching "ideal" solvent behavior at higher temperatures—the exact temperature probably being a function of the electrolyte—although above 75 °C appears to suffice for many.

Nonaqueous Solvents

One of the important aspects of the present unified theory is that both of its constituents, viz., (1) the scaled-particle approach and (2) the solvent continuum model, do not depend upon the nature of the solute or the solvent involved. Earlier the success of the SPT with different types of solvents has been attributed to the fact that the structure of the solvent (other than its pressure, density, and diameter, and their temperature derivatives) are not explicitly considered, and hence water, the so-called most nonideal solvent, and other nonaqueous solvents are equally well handled.[16] The solvent continuum theory also involves the static dielectric constant of the bulk solvent and nothing else. Thus there seems to be enough scope of optimism that the above unified approach will work reasonably for the prediction of entropy of solvation of electrolytes in different nonaqueous solvents at different temperatures. The difficulties, however, lie somewhere else. Although thermodynamic data of electrolytes in different nonaqueous solvents are nowadays more frequently available in the literature[30-36] than they had been any time in the past, most of these data vary considerably from one group of authors to another, often depending upon the sources from which these data are derived. A revealing illustration of this discrepancy has recently been presented by Padova.[30] This problem obviously presents a very difficult hurdle in testing the validity of the proposed theory in various nonaqueous solvents by comparing the predicted values of entropy of solvation ($\Delta S_s°$) of electrolytes with the corresponding experimental data.

The term ΔG^* in eq 2 according to the proposed theory is a measure of the specific solute–solvent interaction effects. When the values of the experimental free energy of solvation ($\Delta G_s°$) for ions are known at 25 °C or at any other temperature, the corresponding values for ΔG^* can be calculated using eq 2. Such calculations have been made for several ions in various solvents and the resulting ΔG^* values are presented in Tables IVA (for protic solvents) and IVB (for dipolar aprotic solvents). The free energy of transfer ($\Delta G_{tr}°$) of ions from water to other different solvents, reported by various workers,[30-36] have been utilized to calculate the experimental values of $\Delta G_s°$ of ions in these solvents using the real free energy of hydration ($\Delta G_h°$) of ions given by Case and Parsons.[33] The data presented in Tables IVA and IVB might give an ap-

Table IV

A. Values of the Specific Interaction Term ΔG^* ($=\Delta G_h{}^\circ{}_{(\text{exptl})} - \Delta G_h{}^\circ{}_{(\text{calcd})}$) for Ions in Various Protic Solvents at 25 °C

	ΔG^*, kcal mol^{-1} (molal scale)							
ion	H_2O[a]	MeOH[a]	MeOH[b]	EtOH[a]	1-PrOH[c]	*n*-BuOH[a]	F[a]	F[b]
Li^+	148.2	137.0	144.7	135.7	140.9	130.3		146.6
Na^+	70.7	62.4	70.4	62.6	68.8	59.9		69.1
K^+	37.9	31.4	39.4	29.4	38.5	31.7	35.8	36.6
Rb^+	30.0	24.2	32.0	23.0	31.7	28.4	27.9	28.9
Cs^+	23.2	14.5	25.6	17.2	25.7	17.8		21.5
Tl^+	30.1	24.2		22.7			26.6	
Cu^+	30.8							
Ag^+	10.1	2.5	11.8	1.2	6.4			6.6
Zn^{2+}	398.2	372.5		368.6			394.2	
Cd^{2+}	241.7	217.9		213.8			236.5	
Cu^{2+}	385.6	360.0		344.5			378.6	
Ca^{2+}	277.7							
Pb^{2+}	184.1	160.7		158.0			175.5	
F^-	16.6		19.7					21.8
Cl^-	13.3	24.9	16.8	25.1	12.8	22.9	17.5	16.8
Br^-	12.0	23.4	15.6	23.6	8.6	19.3		14.9
I^-	10.6	21.7	13.7	21.6	10.8	21.5		12.6

B. Values of the Specific Interaction Term ΔG^* ($\Delta G_h{}^\circ{}_{(\text{exptl})} - \Delta G_h{}^\circ{}_{(\text{calcd})}$) for Ions in Various Dipolar Aprotic Solvents at 25 °C

	ΔG^*, kcal mol^{-1} (molal scale)								
ion	DMF[d]	DMF[e]	DMF[f]	Me_2SO[e]	Me_2SO[f]	AN[e]	AN[g]	PC[e]	PC[f]
Li^+	137.2	142.0	144.0	142.1	143.7	151.5	145.4	152.9	154.8
Na^+	64.1	65.9	68.5	65.9	67.7	72.0	68.1	73.8	75.5
K^+	32.3	34.6	36.1	34.1	35.4	39.0	34.7	39.3	40.8
Rb^+		26.7	29.2	26.8	28.6	31.2	26.9	29.4	33.6
Cs^+	19.0	20.5	22.9	19.8	22.0	24.5	20.8	20.6	22.8
Tl^+		26.3	26.6	24.5	25.0	31.7			33.7
Ag^+		4.6	5.6	1.2	2.2	4.0	−0.9	13.7	15.1
Cl^-	19.5	24.1	22.0	22.4	20.0	23.9	28.8	22.8	21.2
Br^-	15.8	19.2	17.9	18.1	17.0	20.5	23.6	19.8	17.3
I^-	11.8	15.5	13.1	13.1	11.9	16.5	19.7	15.7	12.2

[a] $\Delta G_h{}^\circ{}_{(\text{exptl})}$ obtained from ref 33. [b] $\Delta G_h{}^\circ{}_{(\text{exptl})}$ obtained from the data in ref 31 and 33. [c] $\Delta G_h{}^\circ{}_{(\text{exptl})}$ obtained from ref 36. [d] $\Delta G_h{}^\circ{}_{(\text{exptl})}$ obtained from ref 34. [e] $\Delta G_h{}^\circ{}_{(\text{exptl})}$ obtained from the data in ref 31–33. [f] $\Delta G_h{}^\circ{}_{(\text{exptl})}$ obtained from the data in ref 33 and 34. [g] $\Delta G_h{}^\circ{}_{(\text{exptl})}$ obtained from ref 33.

Table V. Comparison of Calculated and Experimental Entropy of Solvation of Electrolytes in Various Protic Solvents at 25 °C

	$-\Delta S_s{}^\circ$, cal mol^{-1} deg^{-1} (molal scale)												
	MeOH				EtOH				1-PrOH		F		
		exptl				exptl				exptl		exptl	
salt	calcd	*a*	*b*	*c*	calcd	*a*	*c*	*d*	calcd	*d*	calcd	*a*	*b*
LiCl	86.2	61.4	76.5	86.2	113.2	73.1	89.8	83.2	143.5	90.5	38.2	47.6	56.0
LiBr	86.3	58.8	74.9	80.2	111.9	71.0	83.1	81.0	141.6	88.6	38.8	45.0	54.3
LiI	85.2	55.0	71.1	76.5	110.2	66.3	82.4	75.8	139.4	84.1	39.8	40.9	50.6
NaCl	68.7	58.2	71.8	75.3	87.6	70.2	81.2	79.2	109.8	84.1	35.8	46.5	59.0
NaBr	67.8	55.6	69.8	69.9	86.2	68.1	74.4	77.0	107.9	82.2	36.4	43.9	56.9
NaI	66.7	51.8	66.0	65.6	84.6	63.4	73.7	71.8	105.7	77.7	37.4	39.8	53.2
KCl	60.0	51.9	62.6	58.5	75.5	64.1	73.6	71.4	93.1	79.4	35.6	39.2	51.8
KBr	59.1	49.3	60.9	54.5	74.1	62.0	66.8	69.2	91.2	77.5	36.2	36.6	50.1
KI	58.1	45.5	57.2		72.5	57.3	66.1	64.0	89.0	73.0	37.2	32.5	46.4
RbCl	57.9	48.7	57.9		72.5			66.6	89.9	75.8	35.9	38.0	49.9
RbBr	57.0	46.1	56.1		71.1			64.4	88.0	73.9	35.6	35.4	48.6
RbI	56.0	42.3	52.3		69.4			59.2	85.8	69.4	37.4	31.3	44.9
CsCl	55.8	47.5	53.2		69.4			62.7	85.7	71.1	36.5	36.9	47.4
CsBr	54.9	44.9	51.6		68.0			60.5	83.8	69.2	37.0	34.3	45.8
CsI	53.8	41.1	47.8		66.3			55.3	81.6	64.7	38.0	30.2	42.0

[a] C. M. Criss, R. P. Held, and E. Luksha, *J. Phys. Chem.*, **72,** 2970 (1968). [b] Reference 31. [c] G. A. Krestov, *Zh. Strukt. Khim.*, **3,** 516 (1962); see ref 30. [d] Reference 36.

proximate idea about the relative order of solvation of different ions in various solvents. It may also be mentioned here that, because of its near independence of temperature,[15] ΔG^*, once fixed with the help of some known experimental values of $\Delta G_s{}^\circ$ at any single temperature, can be useful for the prediction of the absolute value of $\Delta G_s{}^\circ$ of electrolytes in various solvents at different temperatures by eq 2. Tables V and VI show the comparison between the calculated and the corresponding experimental values of $\Delta S_s{}^\circ$ of some halides in nonaqueous protic and dipolar aprotic solvents, respectively. Several sets of experimental values of $\Delta S_s{}^\circ$ for electrolytes, which are quite different from one group of authors to another, have been accommodated in these tables. Because of the obvious difficulties in picking the right experimental data for comparison with the

Table VI. Comparison of Calculated and Experimental Values of Entropy of Solvation ($\Delta S_s°$) of Electrolytes in Various Dipolar Aprotic Solvents at 25 °C

	$\Delta S_s°$, cal mol^{-1} deg^{-1} (molal scale)								
	DMF			Me_2SO		AN		PC	
		exptl			exptl		exptl		exptl
salt	calcd	*a*	*b*	calcd	*b*	calcd	*b*	calcd	*b*
LiCl	71.1	77.3	89.1	54.3	76.2	69.6		41.5	74.5
LiBr	70.4	73.7	87.1	54.2	74.6	68.8		41.4	72.9
LiI	69.7	71.0	86.4	54.1	69.5	67.8		41.3	72.5
NaCl	57.4	71.8	82.1	46.1	70.9	55.2		36.1	68.8
NaBr	56.7	68.2	79.7	45.9	68.8	54.4	81.6	36.0	66.8
NaI	56.0	65.5	79.0	45.8	63.7	53.4	78.2	35.9	66.4
KCl	51.0	68.5	78.9	42.5	69.0	48.4		33.7	63.9
KBr	50.4	64.7	76.9	42.3	67.3	47.6	76.1	33.6	62.3
KI	49.6	62.0	76.2	42.2	62.2	46.5	72.7	33.5	61.9
RbCl	49.5		74.3	41.8	66.1	46.7		33.2	56.0
RbBr	48.9		72.7	41.6	64.8	45.9	72.9	33.1	54.7
RbI	48.1		72.0	41.5	59.7	44.9	69.5	33.0	54.4
CsCl	47.9		73.5	41.1	63.0	44.9		32.7	49.9
CsBr	47.3		71.6	40.9	61.3	44.0		32.6	48.2
CsI	46.5		70.8	40.8	56.2	43.0		32.5	47.8

[a] Reference 34. [b] Reference 31.

Table VII. Conversion Factors for Different Concentration Scales of the Thermodynamic Functions in Various Solvents at 25 °C

solvent	$-RT \ln \rho_1$[a]	$(-RT \ln M_1)/1000$[a]	$(-RT \ln M_1)/1000\rho_1$[a]	$-R \ln \rho_1$[b]	$(-R \ln M_1)/1000$[b]	$(-R \ln M_1)/1000\rho_1$[b]
H_2O	2	2380	2378	0.01	7.98	7.97
MeOH	142	2038	1896	0.48	6.84	6.37
EtOH	143	1823	1680	0.48	6.11	5.63
1-PrOH	132	1666	1534	0.44	5.59	5.15
2-PrOH	147	1666	1519	0.49	5.59	5.10
n-BuOH	128	1542	1414	0.43	5.17	4.74
ethylene glycol	−62	1647	1709	−0.21	5.52	5.73
glycerol	−136	1413	1549	−0.46	7.74	5.20
formamide	−72	1837	1909	−0.24	6.16	6.40
DMF	34	1550	1516	0.11	5.20	5.09
Me_2SO	−51	1511	1562	−0.17	5.07	5.24
PC	108	1352	1460	−0.36	4.53	4.89
AN	150	1892	1742	0.50	6.35	5.85
acetone	144	1686	1542	0.48	5.65	5.17
acetic acid	−26	1666	1692	−0.09	5.59	5.68
HMPT	−12	1018	1030	−0.04	3.41	3.45
nitrobenzene	−107	1241	1348	−0.36	4.16	4.52

[a] cal mol^{-1}. [b] cal mol^{-1} deg^{-1}.

corresponding theoretically predicted values, it might not be possible at this stage to form a clear idea of the accuracy of the entropy predictions in different solvents. Nevertheless, it appears from Table V that in many nonaqueous protic solvents the general agreement between the experimental and the predicted values of $\Delta S_s°$ at 25 °C may be more encouraging in comparison to the case in aqueous solution at 25 °C. Unfortunately, higher temperature thermodynamic data of electrolytes in nonaqueous solvents are practically nonexistent to this date. So the obvious speculation that at higher temperatures the proposed theory would work comparatively even better in other protic solvents (because most of them are comparatively less strongly hydrogen bonded than water) could not be tested at this stage.

Dipolar Aprotic Solvents

Solvation of ions in dipolar aprotic solvents is in general considered to be altogether a different proposition, and often much more complicated.[37] Many of the dipolar aprotic solvents, such as hexamethylphosphoric triamide (HMPT) and propylene carbonate (PC), have large molar volumes, and according to the nature of the localization of the positive and negative charge centers distributed in the solvent molecules some of the solute cations or anions may be sometimes less easily available to be solvated than the other type of the solute ions, owing to the volume bulk effect or the steric effect. So solvation of the ions in these solvents obviously will not be quite independent of the charge on the solute ion, the fact which the proposed theory as such cannot visualize easily. Moreover, some of the aprotic solvents may be self-associated (somewhat similar to hydrogen bonding in the protic solvents), e.g., dimethyl sulfoxide (Me_2SO), which may involve chains of sulfur and oxygen atoms of variable size.[37] On the other hand, there is little scope of such self-association among molecules of solvents such as acetonitrile (AN), acetone, and nitrobenzene. Thus it is quite likely that the solvation of ions in dipolar aprotic solvents may not follow a general pattern as is often the case with many protic solvents. Nevertheless, it might be of interest to apply eq 13 for the theoretical calculations of $\Delta S_s°$ of electrolytes in various dipolar aprotic solvents and have a comparison with the corresponding experimental data whenever available. Table VI shows such a comparison for some dipolar aprotic solvents. In these cases also the same difficulty regarding the discrepancies in the experimental results reported by various workers persists. It may be, however, evident from Table VI that the agreement between the calculated and the experimental results is somewhat encouraging, at least in DMF (dimethylformamide). It would be no doubt interesting to compare the entropy predictions at some higher temperatures when the necessary experimental data in these solvents at different temperatures would become available.

Conclusion

The attractive features of the unified theory which has been developed in the present work utilizing the scaled-particle approach in conjunction with the Born charging equation are its extreme simplicity and its noninvolvement with any arbitrary adjustable parameter at any stage. Another additional advantage of this simple theory is that, even though it makes use of the simple and primitive model of Born, it seems to avoid the usual source of error associated with the assumption of symmetry between positive and negative charged ions.[38] The main important assumption of the proposed theory is that the specific interaction term, ΔG^*, which includes the free-energy changes associated with the formation of the multilayer solvation zones among the solvent molecules in the vicinity of the dissolved ion (the fact which the Born equation cannot recognize), is temperature independent. The correctness of this assumption has already been demonstrated elsewhere.[15] Different orientation of the solvent molecules around the dissolved positive and negative ions may make the magnitude of ΔG^* different for the cation and the anion of same size but apparently this does not seem to interfere significantly with ΔG^* becoming temperature independent.

It must, however, be mentioned that, although the proposed theory seems to predict the entropy of hydration for electrolytes in aqueous solution with some accuracy at higher temperatures where the hydrogen bonding among the solvent molecules themselves is known to be progressively weakening due to increased thermal agitation, this simple approach apparently does not work well at lower temperatures around 25 °C where the solvent hydrogen bonding remains sufficiently strong.

Moreover, even though some encouraging results can occasionally be found when the proposed theory is applied in the nonaqueous solvents, particularly in the protic solvents, lack of sufficient experimental data with undisputed accuracy at different temperature does not allow us at this stage to provide a clear picture about the performance of the theory in the case of ions in various nonaqueous solvents at 25 °C and also at other temperatures.

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Appendix

Thermodynamic functions of electrolytes in various solvents are available in the literature in three different scales, viz., molality (m), molarity (c), and mole fraction (x) scales. Prior conversion of such data into one particular scale of these three is necessary in order to make any comparative study of results from various sources. The following are the relationships among themselves which may be used for such conversions from one particular scale into the other. Table VII shows the corresponding conversion factors in different solvents at 25 °C.

$$\Delta G_m{}^\circ = \Delta G_x{}^\circ + RT \ln M_1/1000 \tag{18}$$

$$\Delta G_m{}^\circ = \Delta G_c{}^\circ + RT \ln \rho_1 \tag{19}$$

$$\Delta G_c{}^\circ = \Delta G_x{}^\circ + RT \ln M_1/1000\rho_1 \tag{20}$$

$$\Delta S_m{}^\circ = \Delta S_x{}^\circ - R \ln M_1/1000 \tag{21}$$

$$\Delta S_m{}^\circ = \Delta S_c{}^\circ - R \ln \rho_1 \tag{22}$$

$$\Delta S_c{}^\circ = \Delta S_x{}^\circ - R \ln M_1/1000\rho_1 \tag{23}$$

ρ_1 is the density of the solvent.

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