Study of Electrolytic Solution Process Using the Scaled-Particle Theory. 1. The Standard Free Energy of Solvation

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Abstract: The scaled-particle theory has been used in conjunction with the Born charging equation to predict theoretically the standard free energy changes associated with the transfer of various electrolytes in aqueous solution from the reference temperature 25 °C to various other temperatures. The predicted values of free-energy change have been found to be reasonably close to the corresponding experimental data presently available. Assuming that the same treatment can be extended to nonaqueous solvents the values of the standard free energy of transfer of various electrolytes in several nonaqueous solvents such as methanol, ethanol, ethylene glycol, acetic acid, acetone, and nitrobenzene, where the necessary physical parameters are available, have also been calculated theoretically.

Symbols

The following is the list of the principal symbols used in the paper:

β_T	isothermal compressibility coefficient
D	static dielectric constant
d_1, d_2	hard sphere diameters of solvent and solute molecules, respectively
e	electronic charge
$\bar{G}°_c$	partial molal Gibbs free energy of cavity formation
$\bar{G}°_i$	partial molal free energy of interaction
$\Delta G°_h$	molal Gibbs free energy of hydration
$\Delta G°_s$	molal Gibbs free energy of solvation
$\Delta G°_{tr(T_2-T_1)}$	molal free energy of transfer from temperature T_1 to T_2
$(G_T - H_{298})/T$	molal free energy function at temperature T
$\Delta H°_{298}$	molal enthalpy of hydration at 25 °C
K_0, K_1, K_2, K_3	coefficients of equation representing $\bar{G}°_c$
M_1	molecular weight of the solvent
m	molal concentration
N	Avogadro's number
P	pressure
R	universal gas constant
r	radius of the solute ions (= $d_2/2$)
T	temperature, K
t	temperature, °C
V_1	molar volume of the solvent
y	compactness factor or reduced density (= $\pi N d_1^3/6V_1$)
z	number of charge on the ions

Introduction

In the application of the scaled-particle theory (SPT)[1] for describing the thermodynamics of solution process of gases in different solvents the process of introducing the solute species into the solvent is assumed to consist of two steps: (1) the creation of a cavity of a suitable size in the solvent to accommodate the solute species and (2) the introduction into the cavity of a solute species which interacts with the solvent. The reversible work or partial molar Gibbs free energy, $\bar{G}°_c$, required in the first step is identical with that required to introduce 1 mol of hard-sphere solute species of the appropriate radius such as to produce 1 mol of cavities in the solution, whereas the second step is identical with that charging the hard spheres or cavities introduced in the first step ($\bar{G}°_i$). Thus the free energy of solution can be expressed as

$$\Delta G°_s = \bar{G}°_c + \bar{G}°_i + RT \ln RT/V_1 \tag{1}$$

where the last term on the right-hand side accounts for the change in the standard states—hypothetical 1 atm gas to hypothetical unit mole fraction solution.

The process of dissolution of gaseous ions in solvents is called ion solvation. The Born charging equation[2] is often used as the basis for the theoretical description of this solvation process. There are, however, some obvious limitations for using the Born equation and, though many of its modifications sometimes improve the predictions, they are complicated and often contain a number of arbitrary constants.[3] In some approaches[4-7] it has also been assumed that the solvation process has a neutral part in addition to the electrostatic part represented by the Born equation. The solubilities of isoelectronic rare gases related to the dissolved ionic species have been used to estimate the neutral part.[4-7] Pierotti[1] recently showed that the solubilities of inert gases can be accurately estimated using the SPT where the contributions due to the cavity formations predominate. Considering that the solute particle irrespective of being charged or neutral would always need a cavity to be fit into the solvent, it may be assumed that the neutral part of ion solvation is related to the process of cavity formation of appropriate size. It therefore seems reasonable to use the SPT to obtain the neutral term, i.e., the free energy association with the process of cavity formation of the appropriate dimension related to the actual size of the solute ion. The above consideration might tempt one to assume that eq 1 might be applicable for estimation of free energy of solvation of ions where $\bar{G}°_c$, the neutral part, could be calculated by the SPT assuming that both the solute and solvent molecules are hard spheres and $\bar{G}°_i$, the interaction term, by using the Born charging equation.[2]

The prediction of hydration energies of ions at different temperatures using the Born equation has not been very successful in the past.[8] In the present paper eq 1 has been used to estimate the free energy of transfer of various ions between 25 °C and other temperatures in aqueous and some nonaqueous, viz., methanol, ethanol, ethylene glycol, acetic acid, acetone, and nitrobenzene, solvents so that when the ionic solvation energy at 25 °C only is known the same at other temperatures could be estimated.

Calculations and Results

For a hypothetical 1 m standard state eq 1 becomes

0002-7863/79/1501-2530$01.00/0

Table I. Physical Parameters of Various Solvents at Different Temperatures Used in the Thermodynamic Calculations

t, °C	D^a	$\beta_T \times 10^{-5}$/ atm^a	V_1, cm^3/mol	y	d_1, Å	K_0, cal/mol	K_1, cal mol^{-1} Å^{-1}	K_2, cal mol^{-1} (Å^2)$^{-1}$
				Water (mol wt 18.053)				
0	87.90	5.098	18.02	0.3469	2.706	920	−1657	848
25	78.36	4.524	18.07	0.3510	2.719	1036	−1853	941
50	69.88	4.417	18.23	0.3454	2.713	1076	−1929	989
60	66.76	4.450	18.32	0.3415	2.707	1077	−1944	999
75	62.34	4.559	18.48	0.3344	2.696	1067	−1939	1006
100	55.58	4.890	18.80	0.3198	2.671	1023	−1887	999
				Methanol (mol wt 32.04)				
0	37.90	10.78	39.56	0.3513	3.532	951	−1310	512
25	32.63	12.58	40.73	0.3261	3.479	858	−1211	490
50	28.10	14.76	42.01	0.3008	3.422	764	−1109	465
				Ethanol (mol wt 46.07)				
0	28.4	9.87	57.14	0.4037	4.182	1399	−1597	508
25	24.3	11.55	58.68	0.3789	4.131	1274	−1485	486
50	20.8	13.70	60.36	0.3531	4.073	1140	−1360	461
75	17.8	16.67	62.25	0.3246	4.002	919	−1129	398
				Ethylene Glycol (mol wt 62.07)				
25	37.7	3.72	55.92	0.4959	4.447	2986	−3107	875
50	33.1	4.08	56.86	0.4800	4.423	2882	−3030	867
75	29.1	4.50	57.91	0.4640	4.400	2764	−2937	853
100	25.6	5.02	59.01	0.4471	4.374	2621	−2817	832
				Acetic Acid (mol wt 60.05)				
25	6.18	9.40	57.50	0.4000	4.178	1487	−1701	543
50	6.38	11.11	59.10	0.3750	4.127	1341	−1568	515
75	6.70	13.22	60.82	0.3494	4.069	1109	−1327	451
				Acetone (mol wt 58.08)				
25	20.7	12.82	74.04	0.3935	4.521	1418	−1503	445
50	18.4	16.03	76.83	0.3629	4.455	1226	−1333	410
				Nitrobenzene (mol wt 123.11)				
0	39.63	4.41	100.66	0.5449	5.582	4367	−3207	699
25	34.82	5.03	102.74	0.5261	5.555	3726	−3075	681
50	30.59	6.61	104.92	0.4933	5.475	3174	−2684	615

$K_3 = 0.0611$ cal (mol^{-1} Å^3)$^{-1}$ for all the solvents at all temperatures at 1 atm pressure.

[a] Reference 9.

$$\Delta G^\circ_s = \overline{G}^\circ_c + \overline{G}^\circ_i + RT \ln (RT/V_1) + RT \ln (M_1/1000) \qquad (2)$$

$\overline{G}^\circ_c$ can be calculated[1] from the SPT by the equations

$$\overline{G}^\circ_c = K_0 + K_1 d_{12} + K_2 d_{12}^2 + K_3 d_{12}^3 \qquad (3)$$

where $d_{12} = (d_1 + d_2)/2$ and

$$K_0 = RT\{-\ln (1 - y) + 4.5[y/(1 - y)^2\} - PN\pi d_1^3/6 \qquad (4)$$

$$K_1 = -(RT/d_1)\{[6y/(1 - y)] + 18[y/(1 - y)]^2\} + PN\pi d_1^2 \qquad (5)$$

$$K_2 = (RT/d_1^2)\{[12y/(1 - y)] + 18[y/(1 - y)]^2\} - 2PN\pi d_1 \qquad (6)$$

$$K_3 = 4PN\pi/3 \qquad (7)$$

For the calculation of $\overline{G}^\circ_c$ by eq 3 diameters of both solute and solvent molecules, assumed to be hard spheres, are necessary. Solvent molecule diameters at different temperatures have been calculated from the isothermal compressibility data[9] at different temperatures using Mayer's equation[10]

$$d_1 = (6yV_1/\pi N)^{1/3} \qquad (8)$$

where

$$y = (A + 1) - A(A + 3)^{1/2} \qquad (9)$$

and

$$A = (RT\beta_T/V_1)^{1/2} \qquad (10)$$

Twice Pauling's crystal radius[11] has been used for the solute ion diameter, which is assumed to be constant throughout the temperature range used in this work. It may, however, be mentioned that diameters of solvent molecules may also be determined by a number of other methods, and different methods sometimes may lead to slightly different values.[1,10] Because of easy availability of data of various solvents at different temperatures the compressibility method[10] has been used in this work. It has been, however, reported[12] that the change of the values of the solvent diameter (d_1) with respect to temperatures, i.e., $(\partial d_1/\partial T)_P$, does not vary much with the method used for their evaluation. It has therefore been assumed that particularly in the prediction of the transfer functions the method used for the determination of the solvent diameter would not introduce any significant error. Table I lists the relevant physical parameters of various solvents at different temperatures used in the calculation.

The interaction term $\overline{G}^\circ_i$ of eq 1 is assumed to be given by the Born equation:

$$-\overline{G}^\circ_i = N(ze)^2(1 - 1/D)/2r \qquad (11)$$

Table II. Standard Free Energy of Hydration of Electrolytes at Different Temperatures, Calculated $\Delta G^\circ_{h(calcd)}$ and Experimental $\Delta G^\circ_{h(exptl)}$, and the Difference, $\Delta G^\circ_{h(exptl)} - \Delta G^\circ_{h(calcd)}$ (ΔG^*) (kcal/mol) (1 cal = 4.184 J)

t, °C	$\Delta G^\circ_{h(calcd)}$	$\Delta G^\circ_{h(exptl)}$	ΔG^*	$\Delta G^\circ_{h(calcd)}$	$\Delta G^\circ_{h(exptl)}$	ΔG^*
		NaCl			$BaCl_2$	
0	254.31	173.12	81.19	651.67	444.72	206.95
25	252.91	172.08	80.83	648.93	442.90	206.03
50	251.71	170.95	80.76	646.56	440.71	205.85
60	251.31	170.48	80.83	645.76	439.79	205.97
75	250.71	169.77	80.94	644.53	438.37	206.16
100	249.78	168.56	81.22	642.61	435.83	206.78
		$GdCl_3$			CsI	
0	1699.3	1061.9	637.4	160.43	130.04	30.39
25	1694.5	1057.9	636.6	158.77	129.53	29.24
50	1690.1	1053.7	636.4	157.50	128.92	28.58
60	1688.5	1051.9	636.6	157.12	128.66	28.46
75	1685.9	1049.2	636.7	156.58	128.24	28.34
100	1681.7	1044.6	637.1	155.84	127.50	28.34

Table III. Free Energy of Transfer ($\Delta G^\circ_{tr(t-25)}$), Calculated and Experimental, of Electrolytes in Aqueous Solutions at Different Temperatures (cal/mol) (1 cal = 4.184 J)

t, °C	$\Delta G^\circ_{c(tr)}$	$\Delta G^\circ_{i(tr)}$	$\Delta G_x{}^a$	$\Delta G^\circ_{tr(calcd)}$	$\Delta G^\circ_{tr(exptl)}$
			NaCl		
0	−629	−369	−408	−1406	−1040
25	0	0	0	0	0
50	379	413	410	1202	1130
60	432	590	574	1596	1600
75	507	874	818	2199	2310
100	508	1394	1226	3128	3520
			$BaCl_2$		
0	−1195	−935	−612	−2742	−1816
25	0	0	0	0	0
50	710	1046	615	2371	2195
60	815	1496	861	3172	3111
75	955	2215	1227	4397	4530
100	947	3533	1839	6319	7068
			$GdCl_3$		
0	−1554	−2410	−816	−4780	−3956
25	0	0	0	0	0
50	923	2695	820	4438	4225
60	1060	3857	1148	6065	5978
75	1241	5707	1636	8584	8679
100	1231	9102	2452	12785	13332
			CsI		
0	−1010	−242	−408	−1660	−508
25	0	0	0	0	0
50	593	271	410	1274	610
60	686	388	574	1648	874
75	798	574	818	2190	1294
100	786	916	1226	2928	2028

[a] $\Delta G_x = RT_2 \ln (RT_2M_1/1000V_{1(T_2)}) - RT_1 \ln (RT_1M_1/1000V_{1(T_1)})$ and T_1 = 298.15 K (25 °C).

Our present-day knowledge of electrolytes in water insists that there be some type of primary hydration sheath of water molecules around the dissolved ionic species, perhaps followed by a secondary region of water differing from the bulk solvent. Obviously, when the macroscopic dielectric constant and the ionic crystal radius are used, eq 11 is not expected to cover the entire interaction process of ions in solution. A priori calculation of the magnitude of this "left-out" energy term would be no doubt complicated as well as speculative. It would be, however, assumed that the same, which may contain among other things the free energies associated with the necessary process of compressing the radius of the gaseous solute ion to its crystal radius before introduction into the solvent[13,14] and the loss of freedom of movements of the nearest-neighbor solvent molecules which form the solvation shell around the dissolved ion, would be relatively insensitive to temperature, at least within a certain limited range. As the consequence, when the transfer thermodynamic functions between any two temperatures would be considered, this factor would not interfere with the accuracy of the results. To test the validity of the above contention the theoretically calculated values of free energy of hydration of several salts in aqueous solution at different temperatures by eq 2 have been compared with the available experimental data. The results along with the difference, $\Delta G^\circ_{h(exptl)} - \Delta G^\circ_{h(calcd)}$ (say ΔG^*), are listed in Table II. To avoid the presently arbitrary and extrathermodynamic division of thermodynamic functions into the cationic and the anionic contributions, and also the complications associated with surface potential of the solvent,[4,15] the electrolyte form, i.e., the neutral ensemble of positive and negative ions, has been used in the comparison. The process of hydration of 1:1 electrolyte, MX, may be illustrated as

$$\begin{aligned} &M^+(g,1\,atm,T) + X^-(g,1\,atm,T) + aq \\ &\qquad = M^+(aq,1\,m,T) + X^-(aq,1\,m,T) \end{aligned} \tag{12}$$

The experimental standard state free energy of hydration has been obtained by the relationship

$$\begin{aligned} \Delta G^\circ_{h(T)} = {} & [(\overline{G}^\circ_T - \overline{H}^\circ_{298})/T]T_{aq} \\ & - \sum_{\substack{\text{all}\\ \text{gases}}} [(G^\circ_T - H^\circ_{298})/T]T + \Delta H^\circ_{298} \end{aligned} \tag{13}$$

where ΔH°_{298} is the hydration enthalpy at 25 °C. Experimental results reported by Cobble and co-workers[16-19] along with other usual sources of thermodynamic data[20-23] have been used to determine the free energy of hydration at different temperatures.

Free energies of transfer for the above electrolytes in aqueous solution from 25 °C to other temperatures, both theoretically calculated and experimentally observed, are presented in Table III for comparison. For better clarity the calculated values of free energy of hydration have been broken down into the cavity, Born, and standard-state contributions as shown in Table III. Free energy of transfer of different ions can be calculated by the equation

$$\begin{aligned} G^\circ_{tr}(T_2 - T_1) = {} & \overline{G}^\circ_{c(T_2)} - \overline{G}^\circ_{c(T_1)} + N(ze)^2(1/D_{T_2} \\ & - 1/D_{T_1})/2r + RT_2 \ln (RT_2M_1/1000V_{1(T_2)}) \\ & - RT_1 \ln (RT_1M_1/1000V_{1(T_1)}) \end{aligned} \tag{14}$$

in water and other solvents at different temperatures (see Table A-I). T_1 has been taken as 298.15 K, i.e., 25 °C, and $Ne^2/2$

as 166 027 Å·cal/mol.[24] Experimental values of $\Delta G^\circ{}_s$ of several ions, in water, methanol, and ethanol at 25 °C reported by Case and Parsons,[15] when added to the corresponding values of $\Delta G^\circ{}_{tr}$ at different temperatures, calculated by eq 14, give the predicted values of $\Delta G^\circ{}_s$ at other temperatures. These values may be recommended for use when direct experimental data at higher temperatures are not available.

Discussion

The remarkable constancy (approximately within 0.5 kcal) of the difference $\Delta G^\circ{}_{h(\mathrm{exptl})} - \Delta G^\circ{}_{h(\mathrm{calcd})}$ ($=\Delta G^*$) depicted in Table II with respect to temperature variation probably suggests that, if the properly modified Born equation can be used for the determination of the interaction term $\overline{G}^\circ{}_i$, eq 1 can predict the absolute values of $\Delta G^\circ{}_h$ at various temperatures. The comparison in Table III shows that the agreement between the theoretically predicted and the experimentally determined values of $\Delta G^\circ{}_{tr}$ is good for 1:1, 2:1, and 3:1 chlorides. The agreement may be slightly less encouraging in the case of CsI, but there is a possibility that the experimental values of $\Delta G^\circ{}_h$ of CsI at 0 °C, obtained through the help of extrapolated data, may not be as accurate as those at other temperatures.[19] In that case the agreement of the calculated and the experimental data at other temperatures may still be considered as fairly good. Owing to lack of sufficient experimental data at higher temperatures similar comparison could not be made with other different types of electrolytes in solution.

One of the advantages of the present unified approach is that it can be applied universally to all types of solvents irrespective of whether they are protic or dipolar aprotic. Some accurate physical parameters only have to be known. Lack of sufficient data did not permit us at this stage to put forward a comparison of the predicted free energy transfer values of electrolytes with the corresponding experimental data in nonaqueous solutions. The striking success of this simple approach in aqueous solution, however, does encourage one to make use of a similar treatment for prediction of the free energy of transfer of electrolytes in various nonaqueous solvents, particularly because the corresponding experimental values in different solvents are not available to date. The above approach, however, does not distinguish between cationic and anionic solvation. It also cannot predict the free energy transfer of a proton in solution at various temperatures since proton's zero diameter would make $\overline{G}^\circ{}_i$ infinite, which should mean that the free energy of solvation has to be the same at different temperatures. This may cause some apprehension of relatively more uncertainty in the predicted values of $\Delta G^\circ{}_{tr}$ for ions having very small volumes but high charge densities. Only experimental data when available could throw more light on this question. It may also be noted that for ions having comparatively large radius and low charge, i.e., ions with low surface charge densities, $\overline{G}^\circ{}_i$ becomes less significant; on the other hand, $\overline{G}^\circ{}_c$ becomes negligible for ions of smaller radius and higher number of charge, i.e., ions with high surface charge densities.

In conclusion it can be said that without confronting the existing theories of electrolytes in solution or without introducing any arbitrary constants the present unified approach can provide us with a reliable means for accurate prediction of free energy of solvation of electrolytes in various solvents at different temperatures from the known values at any one temperature when the corresponding experimental data are not available.

Acknowledgment. The author thanks Dr. H. V. K. Udupa, Director, CECRI, for his permission to publish this paper.

Supplementary Material Available: Predicted values of free energy transfer for various ions in aqueous solution (Table A-I) (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) R. Pierotti, *Chem. Rev.*, **76,** 717 (1976); *J. Phys. Chem.*, **67**, 1840 (1963); **69**, 281 (1965).
(2) M. Born, *Z. Phys.*, **1,** 45 (1920).
(3) J. E. Desnoyers and C. Jolicoeur, "Modern Aspects of Electrochemistry", Vol. 5, J. O'M Bockris and B. E. Conway, Eds., Butterworths, London, 1969, Chapter 1.
(4) J. I. Padova in ref 3, Vol. 7, 1972, Chapter 1.
(5) C. L. DeLigny and M. Alfenaar, *Recl. Trav. Chim. Pays-Bas*, **84,** 81 (1965).
(6) M. Alfenaar and C. L. DeLigny, *Recl. Trav. Chim. Pays-Bas*, **86,** 929 (1967).
(7) R. M. Noyes, *J. Am. Chem. Soc.*, **86,** 971 (1964); **84,** 513 (1962).
(8) C. M. Criss and J. W. Cobble, *J. Am. Chem. Soc.*, **86,** 5385 (1964).
(9) "Handbook of Chemistry and Physics", 55th ed., CRC Press, Cleveland, Ohio, 1974–1975.
(10) S. W. Mayer, *J. Phys. Chem.*, **67**, 2160 (1963).
(11) L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, N.Y., 1960, pp 514, 518.
(12) E. Wilhelm, *J. Chem. Phys.*, **58**, 3558 (1973).
(13) R. H. Stokes, *J. Am. Chem. Soc.*, **86,** 979 (1964).
(14) S. Goldman and R. G. Bates, *J. Am. Chem. Soc.*, **94,** 1476 (1972).
(15) B. Case and R. Parsons, *Trans. Faraday Soc.*, **63,** 1224 (1967).
(16) W. L. Gardner, R. E. Mitchell, and J. W. Cobble, *J. Phys. Chem.*, **73,** 2025 (1969).
(17) C. M. Criss and J. W. Cobble, *J. Am. Chem. Soc.*, **83,** 3223 (1961).
(18) R. J. Hinchey and J. W. Cobble, *Inorg. Chem.*, **9,** 970 (1970).
(19) R. E. Mitchell and J. W. Cobble, *J. Am. Chem. Soc.*, **86,** 5401 (1964).
(20) D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Schum, *Natl. Bur. Stand.* (*U.S.*), *Tech. Note*, **No. 270-3** (1968).
(21) W. M. Latimer, "Oxidation Potential", 2nd ed., Prentice-Hall, Englewood Cliffs, N.J., 1950.
(22) K. K. Kelley, *U.S.*, *Bur. Mines*, *Bull.*, **No. 584** (1960).
(23) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, *Natl. Bur. Stand.* (*U.S.*), *Circ.*, **No. 500** (1952).
(24) *Natl. Bur. Stand.* (*U.S.*), *Tech. News Bull.* (Oct 1963).