A Note on the Theory of Solution of Hydrated systems

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(Received July 12, 1950)

The Solution of Electrolytes

It is well-known that the Debye-Hückel's theory of solution of strong electrolytes does not hold good any longer for the solutions of the concentration greater than 0.01 mols per litre. But taking the hydration of solute into account we can interpret the experimental results almost up to the concentration of saturation for any sort of solution.

Fundamental Equations.—Now, this theory is based on the following three assumptions:

1. The complete dissociation of electrolyte is assumed for simplicity.

2. The second, the most essential of this theory, is that the hydration water attached to an ion in a co-ordinated position by its strong field can not play the rôle of solvent in an ordinary sense; hence the number of molecules of free solvent in an aqueous solution of the concentration m represented in molality, namely mols of solute per 1000 g. of solvent, may be reduced to

$$55.51-(\nu_+\alpha_++\nu_-\alpha_-)m,$$

where ν_+ and ν_- are the number of positive and negative ions created by the dissociation of one molecule of salt, while α_+ and α_- being the hydration number of positive and negative ions respectively and assumed to be constants at a given temperature characteristic of the sorts of ion and solvent throughout the whole range of concentration.

3. The third is that the water outside of hydration shell, within which the dielectric saturation takes place, behaves normal. Furthermore, for simplicity it is assumed that the interactions between hydrated ion and molecules around it are independent of concentration. In this model, therefore, the solution is composed of the hydrated ions and of the free water molecules bearing themselves quasi-ideal, if the electrostatic interactions were ignored.

Upon taking the hydration into consideration the partial molal free energy of solute, $\overline{F}_1$, can be expressed in the following form:

$$\overline{F}_1=\overline{F}_1{}^\circ+RT\ln f_\pm^{\nu_++\nu_-}\times\frac{(\nu_+m)^{\nu_+}(\nu_-m)^{\nu_-}}{[55.51-(\nu_+\alpha_++\nu_-\alpha_-)m+(\nu_++\nu_-)m]^{\nu_++\nu_-}}$$
$$=\overline{F}_1{}^{\circ\prime}+RT\ln\nu_+^{\nu_+}\nu_-^{\nu_-}(\gamma_\pm m)^{\nu_++\nu_-},\qquad(1)$$

where $\overline{F}_1{}^\circ$ and $\overline{F}_1{}^{\circ\prime}$ are the standard free energies, which differ from the ordinary ones owing to hydration, R, gas constant, T, absolute temperature, $f_\pm$, Debye-Hückel's mean activity coefficient of salt (in which only the interionic attractions are taken into account), and $\gamma_\pm$, stoichiometrical mean activity coefficient of salt (in which both effects of interionic attractions and of hydration are taken into consideration).

Upon introducing into Eq. (1) the usual convention of $f_\pm=\gamma_\pm=1$ at infinite dilution *i. e.*, $m\rightarrow 0$, the relations

$$\overline{F}_1{}^{\circ\prime}=\overline{F}_1{}^\circ-(V_++V_-)RT\ln 55.51$$
$$\ln\gamma_\pm=\ln f_\pm-\ln\left[1-\frac{1}{55.51}\{(\nu_+\alpha_++\nu_-\alpha_-)m-(\nu_++\nu_-)m\}\right]\qquad(2)$$

may be obtained. According to Debye and Hückel,

$$\ln f_\pm=-\frac{z_+z_-e^2}{2DkT}\cdot\frac{\kappa}{1+a\kappa},$$
$$\kappa^2=\frac{8\pi e^2N\omega}{1000DkT},\qquad(3)$$

where z_+ and z_- are the ionic valencies of positive and negative ions respectively, e, the electronic charge, D, the dielectric constant of solvent in solution, k, Boltzmann's constant, a, the mean distance of approach of two hydrated ions, N, Avogadro's number, and ω, the ionic strength.

In a similar way we can define the partial molal free energy $\overline{F}_0$ of free solvent in aqueous solution of a single sort of salt as,

$$\overline{F}_0-\overline{F}_0{}^\circ=RT\ln f_0\times\frac{55.51-(\nu_+\alpha_++\nu_-\alpha_-)m}{55.51-(\nu_+\alpha_++\nu_-\alpha_-)m+(\nu_++\nu_-)m}$$
$$\equiv RT\ln a_0,\qquad(4)$$

where $\overline{F}_0^\circ$ is the standard free energy of solvent, and a_0 is the activity of free solvent. And f_0 is the electrostatic activity coefficient of the free solvent of the following formula

$$\ln f_0 = +\frac{V_0\kappa^3}{24\pi}\cdot\frac{3}{x^3}\left[1+x-\frac{1}{1+x}-2\ln(1+x)\right], \qquad (x=\kappa a) \qquad (5)$$

where V_0 is the molecular volume of solvent. It may easily be shown that the hydration has strictly no effect upon $\overline{F}_0^\circ$.

Now the practical osmotic coefficient, ϕ, may be defined as follows:

$$\begin{aligned}\phi &= -\frac{55.51(\overline{F}_0-\overline{F}_0^\circ)}{(\nu_+ + \nu_-)mRT} = -\frac{55.51}{(\nu_+ + \nu_-)m}\ln a_0 \\ &= -\frac{55.51}{(\nu_+ + \nu_-)m}\ln f_0 \\ &\quad \times\left[\frac{55.51-(\nu_+\alpha_+ + \nu_-\alpha_-)m}{55.51-(\nu_+\alpha_+ + \nu_-\alpha_-)m+(\nu_+ + \nu_-)m}\right].\end{aligned} \qquad (6)$$

Table 1

The Activity Coefficients of Sodium Chloride and the Logarithms of Activity of Water at 25°C.(1), (2), (3)

m	$\gamma\pm$ calc.*	$\gamma\pm$ obs. (1)	$\gamma\pm$ obs. (2)	$1+\log a_0$ calc.**	$1+\log a_0$ obs. (2)	$1+\log a_0$ obs. (3)
0.1	0.780	0.786	0.781	0.9985	0.9985	0.9985
0.2	0.736	0.741	0.737	0.9971	0.9971	0.9971
0.3	0.712	0.717	0.713	0.9956	0.9957	—
0.5	0.686	0.688	0.685	0.9927	0.9928	0.9928
0.7	0.673	0.674	0.671	0.9898	0.9898	—
1.0	0.664	0.664	0.661	0.9853	0.9853	0.9854
1.2	0.663	—	0.651	0.9822	0.9823	—
1.4	0.664	—	0.658	0.9790	0.9792	—
1.6	0.667	—	0.659	0.9758	0.9760	—
1.8	0.670	—	0.662	0.9725	0.9727	—
2.0	0.675	0.672	0.667	0.9691	0.9694	0.9695
2.5	0.691	—	0.686	0.9606	0.9605	—
3.0	0.712	0.713	0.713	0.9515	0.9511	0.9514
3.5	0.737	—	0.746	0.9419	0.9409	—
4.0	0.767	0.772	0.785	0.9319	0.9301	0.9314
4.5	0.801	—	0.832	0.9215	0.9184	—
5.0	0.839	—	0.884	0.9104	0.9061	—
5.2	0.857	0.859	—	—	—	0.9044
6.0	0.935	—	1.007	0.8868	0.8793	—

* $a=4.32$ Å., $\alpha_+ + \alpha^- = 6.0$

** $a=4.32$ Å., $\alpha_+ + \alpha_- = 3$.

If the hydration does not exist, *i.e.*, in the case of $\alpha_+ = \alpha_- = 0$, all the equations cited above may be reduced to the ordinarily known formulae.

However, these equations contain two constants, a and $\nu_+\alpha_+ + \nu_-\alpha_-$, of which exact values are not obtainable at present by purely theoretical bases. Therefore, they must be determined at present as parameters so as to give agreements between the observed and calculated values. It is evident, however, that they are in the closest relation with each other and must be reduced ultimately to one.

The Comparison between the Calculated and Observed Values of $\gamma_\pm$ and ϕ at 25°. —The calculations for about 31 electrolytic aqueous solutions at 25° were made by the writer. Some of these results are compared in Table 1, Fig. 1 and Fig. 2.

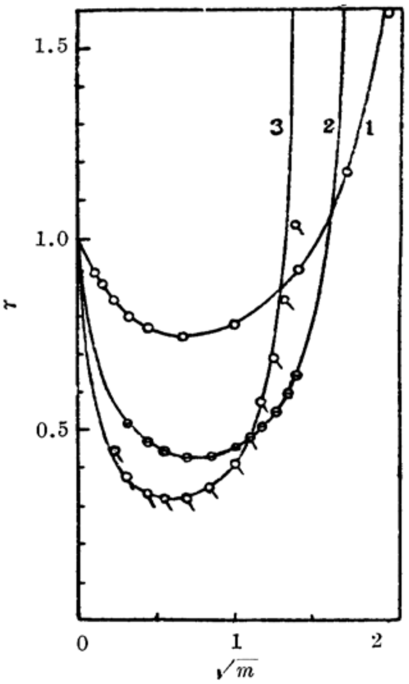

Fig. 1.—The activity coefficients of 1-1, 2-1 and 3-1 electrolytes at 25°C. Observed values: ○, LiCl; ⊖, $SrCl_2$; ɑ, $PrCl_3$. Full line is calculated by Eqs, (2) and (3):
curve 1 (LiCl), $a=5.26$ Å., $\alpha_+ + \alpha_- = 11$;
curve 2 ($SrCl_2$), $a=4.68$ Å., $\alpha_+ + 2\alpha_- = 18$;
curve 3 ($PrCl_3$), $a=6.14$ Å., $\alpha_+ + 3\alpha_- = 28$.

The agreements between calculated and observed values are satisfactorily excellent over the wide range of concentration: the deviations being within 1 % for most uni-uni valent salts of the concentration up to 4 M (but to 3 M in case of HCl and LiCl) and for $CaCl_2$ type

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(1) Landolt, Börnstein, "Physic. Chem. Tabellen," Erg. Bd. III, Berlin, 1936, p. 2153.

(2) G. Scatchard, W. Hamer and S. E. Wood, *ibid.*, **60**, 3061 (1938).

(3) Landolt, Börnstein, "Physik. Chem. Tabellen," Erg. Bd. II, 1931, p. 1126.

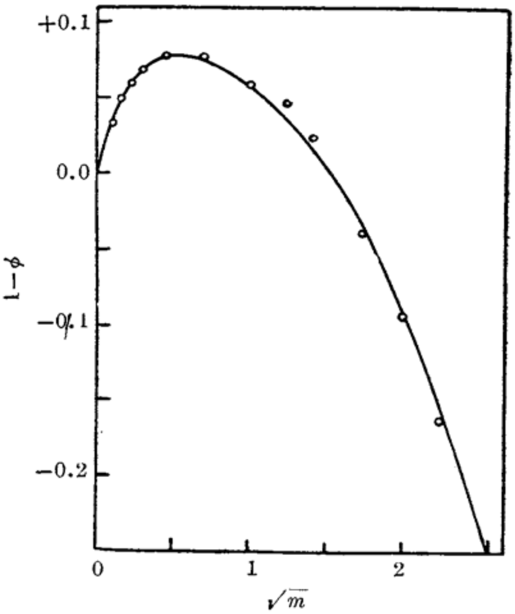

Fig. 2.—The osmotic coefficient of NaCl at 25°C.: ○, observation. Full line is calculated by Eqs. (5) and (6): $a=4.32$ Å., $\alpha_+ + \alpha_- = 3$.

salts of the concentration up to 2 *M* (but to 0.5 *M* in case of $ZnCl_2$), and the deviations being within 2% for $LaCl_3$ type salts of the concentration up to 1.6 *M*. The best fit values of a and $\nu_+\alpha_+ + \nu_-\alpha_-$ for activity coefficients are tabulated in Table 2, in which the fourth row refers to the literatures with which the values are compared.

For all nitrates, sulphates and for a few of chlorides such as $ZnCl_2$ and $CdCl_2$, both the a values and $\nu_+\alpha_+ + \nu_-\alpha_-$ values are either exceedingly small or not satisfactorily obtainable. This probably might be due to the fact the ions of these salts, as compared with the other salts, are so liable to associate or to form the complexes even in the dilute solution that the apparent concentration of these ions becomes small enough to cancel the effects of hydration on the activity coefficients. If these contributions are taken into consideration the values in Table 2 might slightly be altered. And in addition to them the effects of the change of the dielectric constants of solution by varying the concentration⁽⁶⁾ must be taken into consideration in order to make the theory more complete.

Considering the sizes of molecules and ions the hydration number of an ion would probably be less than 12 for most monovalent simple ions. According to Bernal and Fowler⁽⁷⁾, it must be 4 for all the monovalent simple ions, and 6 or 8 for divalent ions. But from the lowering of the dielectric constant of aqueous salt solutions, Hasted, Ritson and Collie⁽⁸⁾ have estimated the minimum hydration number of positive ions at 10 for H^+, 6 for Li^+, 4 for Na^+, K^+ and Rb^+; 14 for Mg^{++} and Ba^{++}; and 22 La^{+++}.

Finally, however, it is not yet understood why the most favorable values of a and $\nu_+\alpha_+ + \nu_-\alpha_-$ for $\gamma_\pm$ and for ϕ do not agree with each other.

Table 2

The Values of the Mean Distance of Approach of Ions, and of the Molecular Hydration Number.⁽⁴⁾⁽⁵⁾

$z_+=1$	HCl	KOH	LiCl	LiBr	LiI	NaCl	KCl	RbCl	CsCl	NH_4Cl	K_2SO_4
a, Å.	5.26	3.51	5.26	5.80	6.86	4.32	3.72	3.14	2.30	3.07	3.00
$\nu_+\alpha_+ + \nu_-\alpha_-$	12	10	11	12	14	6	4	4	4	5	(10)
Lit. No.	(5)	(3)	(3)	(4)	(4)(5)	(1)(2)	(2)(4)	(4)	(4)	(3)	(5)
$z_+=2$	$MgCl_2$	$NiCl_2$	$CoCl_2$	$CaCl_2$	$MnCl_2$	$BaBr_2$	$SrCl_2$	$CuCl_2$	$BaCl_2$	$ZnCl_2$	$MgSO_4$
a, Å.	6.14	5.16	5.00	5.10	5.10	4.93	4.68	4.65	4.42	5.28	2.93
$\nu_+\alpha_+ + \nu_-\alpha_-$	22	22	22	20	18	18	18	14	14	(2)	11
Lit. No.	(4)(5)	(5)	(5)	(5)	(5)	(5)	(5)	(5)	(5)	(5)	(5)
$z_+=3$	$AlCl_3$	$ScCl_3$	YCl_3	$LaCl_3$	$CeCl_3$	$PrCl_3$	$NdCl_3$	$SmCl_3$	$EuCl_3$		
a, Å.	6.60	6.50	6.39	6.22	6.20	6.14	6.14	6.48	6.58		
$\nu_+\alpha_+ + \nu_-\alpha_-$	34	32	30	28	28	28	28	28	28		
Lit. No.	(5)	(5)	(5)	(5)	(5)	(5)	(5)	(5)	(5)		

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(4) Landolt, Börnstein, "Physik. Chem. Tabellen," Erg. Bd. III, 1936, p. 2138.

(5) R. A. Robinson and H. S. Harned, *Chem. Rev.*, **28**, 419 (1941).

(6) E. Hückel, *Physik. Zeits.*, **26**, 93 (1925).

(7) J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

(8) J. B. Hasted, D. M. Ritson and C. H. Collie, *J. Chem. Phys.*, **16**, 1 (1948).

The Solution of Non-Electrolytes

The van't Hoff's theory of dilute solution does not hold good any longer for the concentration higher than 0.1 mol per liter, while the hydration theory is applicable also for the interpretation of the properties of the solutions of non-electrolytes. The mechanism of hydration of non-electrolytes, different from that of electrolytes, is due chiefly to the hydrogen bond formation between solute and water molecules. As the strength of the hydrogen bond between water and hydroxyl radicals of organic compounds is assumed, in many cases, to be somewhat stronger than that of water(9), the function of water as solvent might be somewhat diminished when the hydration occurs. Thus the activity coefficient γ and the osmotic coefficient ϕ of the aqueous solution on the molality (mols of solute per 1000 g. of solvent) scale can be calculated by the following equations (*cf.* Eqs. (2) and (6)),

$$\ln\gamma = -\ln[1-(\alpha-1)m/55.51] \qquad (7)$$

$$\phi = -\frac{55.51}{m}\ln\frac{55.51-\alpha m}{55.51-\alpha m+m} \qquad (8)$$

by adjusting only one parameter α, the number of hydrated water molecules per one molecule of solute.

Some of the results are shown in Fig. 3 and Table 3. The agreements between calculated and observed values are excellent up to 2 M with each characteristic α value, but unsatisfactory in the region of high concentration, as is seen in Fig. 3. It seems here that α value decreases with increasing concentration, suggesting that the association of the solute begins to play some rôles. The behaviors of solutes such as urea,(10) urethane,(10) acetamide,(10) acetone,(11) methyl- and ethyl-alcohols(11) are

Table 3

The Osmotic Coefficients of Aqueous Solution of Sucrose at 25°C.(2)

m	ϕ calc. $\alpha=5$	ϕ obs.	m	ϕ calc. $\alpha=5$	ϕ obs.
0.1	1.008	1.007	1.2	1.108	1.108
0.2	1.016	1.015	1.4	1.128	1.128
0.3	1.024	1.023	1.6	1.149	1.149
0.4	1.033	1.032	1.8	1.170	1.169
0.5	1.042	1.041	2.0	1.195	1.189
0.6	1.051	1.050	2.5	1.255	1.236
0.7	1.059	1.059	3.0	1.322	1.282
0.8	1.069	1.069	3.5	1.397	1.326
0.9	1.078	1.078	4.0	1.482	1.369
1.0	1.088	1.088	5.0	1.686	1.448

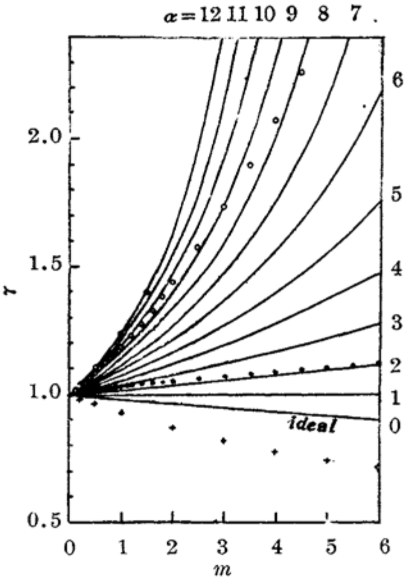

Fig. 3.—The activity coefficients of non-electrolytes at 25°C. ○, Sucrose; ●, Glycerol; +, Urea. Full line is calculated by Eq. (7).

Table 4

The Hydration Numbers of Some Organic Compounds.

Name of solute	No. of free OH radicals	α	Temp., °C.	Obtained from	References
Glycerol	2	3	0	γ(Fr)	(11)
		3	25	γ(p)	(2)
		1	25	ϕ(p)	(2)
Erythrit	4	4	0	γ(Fr)	(11)
Methyl Glucoside	4	3	0	p	(12)
		5	0	P	(13)
Glucose	5	4	0	γ(Fr), P	(11), (13)
Mannit	6	2	20	γ(p)	(11)
Sucrose	8	12	0	γ(Fr)	(11)
		5	0	p, P	(12), (13)
		9∼10	25	γ(p)	(2)
		5	25	ϕ(p)	(2)
		4∼5	25	p	(12), (14)
		5	30	P	(13), (15)
		4	55.7	P	(13), (15)
		4	100	p	(12)

(Fr...Freezing point depression; p...Vapor pressure; P...Osmotic pressure.)

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(9) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, New York, 1940, pp. 284-334.

(10) H. M. Chadwell and F. W. Politi, *J. Am. Chem. Soc.*, **60**, 1292 (1938).

(11) Landolt, Börnstein, "Physik. Chem. Tabellen," Erg. Bd. II, Berlin, 1931, p. 1130.

(12) "International Critical Table," Bd. III, p. 293.

(13) *ibid.*, Bd. IV, p. 429.

(14) Landolt, Börnstein, "Physik. Chem. Tabellen" Erg. Bd. III, 1936, p. 2495.

(15) *ibid.*, Erg. Bd. III, 1936, p. 2664.

exceptional in that their activity coefficients are, even in dilute solution, always below the ideal line. Therefore, such solutes must always be in associated states, because the activity coefficient is diminished by association.

The Hydration Number and the Structure of Solute.—In order to get the most probable value of the hydration number, we must determine it from the activity observed in the solution as dilute as possible, in which the association of the solute can be neglected. The best fit values of α are tabulated in Table 4. Here, it is possible to imagine a certain relation between α and the structural configuration of the solute molecule: a rough correspondence exists between α and the number of hydrogen-bond-forming radicals in the molecule of solute, although some exceptions such as mannit exist.

It is inexplicable in this case too, the reason why some of the values of α estimated from γ are approximately two times of those estimated from ϕ.

Summary

(1) Upon taking the hydration into consideration the thermodynamical properties of solutions of electrolytes and non-electrolytes can be well represented over the wide range of concentration.

(2) The values of hydration number of non-electrolytes seem to be related to the configuration of solute molecules. The hydration number was determined for 37 solutes.

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