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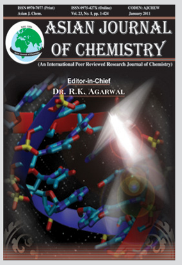

A Model Describing the Osmotic Coefficients and the Activities of Water for Electrolyte Solutions

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This work presents a model for thermodynamic properties of the uni-univalent electrolytic solutions based on the linear relation between the constructed dimensionless-thermodynamic potential for solvent and the newly defined probability-distribution function of water molecules. The model allows quantitative reproduction of the osmotic coefficients for the uni-univalent electrolytic solutions, especially for some hydroxides of alkali metals and monoacids such as NaOH, KOH, LiOH, HF, HCl, HBr, HI, HNO_3 and $H(HSO_4)$, within experimental accuracy. A comparison is made of the results of the presented model with the Pitzer's equation.

Key Words: Osmotic coefficients, Activity of water, Electrolytic solution model, Inorganic monobasic acid, Alkali.

INTRODUCTION

Since Debye and Hückel published their interionic-attraction theory for electrolytic solution in 1923[1], there have been a lot of studies on the thermodynamic properties for aqueous solutions of electrolytes[1-12]. Some of them are modified models[3-5], some of them are theoretical approaches such as the ion-interaction[2], ion-pairing or ion-association[6] and ion-hydration[7] to describe the electrolyte solutions. The new concept and the inherent deficiency introduced by these theories and models had been critically reviewed by Bassett and Melchior[13]. The field of modeling of electrolyte solutions has advanced greatly and some physically based approaches have been presented[14]. However, the most noteworthy and most frequently used model for depicting the thermodynamic properties of the aqueous solution of electrolyte is well known to be the ion interaction or the virial coefficient approach developed by Pitzer[15,16]. The virial coefficient expansion equation based on the Debye-Hückel ionic distribution function and the effect of short-range interaction proposed by Guggenheim is used for activities of species in high ionic strength solutions[15], up to 6 molalities for single electrolytic solutions. The equation works well for much more electrolytes, but many parameters such as b, α (though they are the empirical constant) and the ion-interaction parameters $\beta^{(0)}$, $\beta^{(1)}$ and C^{Φ}, are engaged. Additionally, the predicting accuracy for some monoacids (including $H(HSO_4)$) and hydrate of alkali metals is not too high[2,16], especially such as HNO_3, LiOH, KOH and $H(HSO_4)$. This reason could impute to that the change in the arrangement of solvent molecule in the course of ion solvation was ignored, though the short-range interaction and the interionic-attraction were taken into considered in his equation. It is well known that the acids have many properties in common with other electrolytes, but their dissociation into H_3O^+ ions and their ability to act as solvents. This may be a reason to make their thermodynamic properties differ from salts. This paper tries to reproduce the osmotic coefficients and the activities of water in the uni-univalent electrolytic solutions, especially for the hydroxides of alkali metals and monoacids such as NaOH, KOH, LiOH, HF, HCl, HBr, HI, HNO_3 and $H(HSO_4)$ or H_2SO_4 by constructing a potential function and a probability-distribution function for water molecules and giving a pertinent model based on a newly discovered regular pattern on the experimental data.

Creation of model: Consider the aqueous solution system of an electrolyte. Let a_w and x_w be the activity of water on the basis of mole fraction and the mole fraction for water in the studied solution, respectively. When the dissociation of the electrolyte is full, the mole fraction of water can be expressed as:

$$x_w = \frac{n_w}{(\nu m + n_w)} \quad (1)$$

where n_w is the number of moles of water, being 1000/18 on molal scale, ν is the number of ions into which a molecule of solute dissociates, which equals to 2 for both ions uni-univalent and m is molality of electrolyte. Define a dimensionless-thermodynamic potential for solvent as (see Appendix):

$$\omega=\frac{v\ln\left(\frac{a_w}{a_w^o}\right)}{(1-x_w)^{k_1}} \tag{2}$$

where a_w^0 is the activity of water at $x_w = 1$, in general specified as 1 and k_1 is a parameter close to 2. The dimensionless-thermodynamic potential, apparently, is related to the activity of water, which can broadly reveal a whole effect of the various interactions in the electrolyte solution. They involve the short-range interaction between solvent and ions, the long-range interionic attraction and the interaction between solvent species due to the change of solution structure in development of solvation of ions. The first two interactions have been respectively described by Born and Debye-Hückel equations. For the third interaction, in Born's approach[17] and Onsager self-consistent reaction field theory[18], the solvent at all was assumed to be a continuous medium of structureless in the course of ion hydration, that is to say, the solvent was never considered to be change in structure or arrangement and the effects of change in the arrangement of solvent molecules are omitted wholly. In fact, during dissolution of an ionic crystal by the action of a continuum solvent, the structure of the continuous medium (or the arrangement of solvent molecules) would be also influenced by solutes[19].

Based on some quantum mechanical calculations[20,21], we could get a simplified picture for the structure altering of solution. Suppose that the distribution of the water molecules around a positive ion is shown in Fig. 1. The center ion is close surround by a hydration shell, outside which is enveloped by the negative ionic atmosphere. Each negative ion in the ionic atmosphere is randomly adsorbed by various groups of water molecules such as H_2OH^+, OH^-, H^+, even $H_5O_2^+$, $H_9O_4^+$ [22,23], which link together by the electrostatic force or hydrogen bond, thereupon forming a water molecular cluster containing the ion. The arrangement of the water molecules around an ion was varied until the minimum energy configuration was found[19]. At equilibrium, the number of the water molecules in the cluster is n, which is directly proportional to x_w. And the number of the water molecular clusters that emerge around the center ion is k_2 ($k_2 > 0$). The probability of k_2 water molecular clusters that simultaneously congregate around the hydration layer of the center ion is n^{k_2} or is allowed to express as $x_w^{k_2}$. Apparently, the water molecule number n in a cluster and the value of k_2 all would be changed with the solute concentration. It could be imaged that the smaller the concentration is, the bigger the value of k_2. Although the water molecule number for a cluster would be approximately the same, its congregated form or the congregated mode might be dissimilar. The dissimilar congregated modes could not influence the chemical potentials (or activity) of water and they could be considered as a kind of degenerate form of the water molecular clusters with the same energy configuration. Therefore they should be removed from the total probability, $x_w^{k_2}$. As a simplified treatment, assuming that the degenerate degree is g and it can approximately be replaced by $\ln(n^{k_2})$, then one obtains a function $x_w^{k_2}/\ln(n^{k_2})$. If taking $-\ln(x_w^{k_2})$ to replace $\ln(n^{k_2})$, we can construct a new function h′ as:

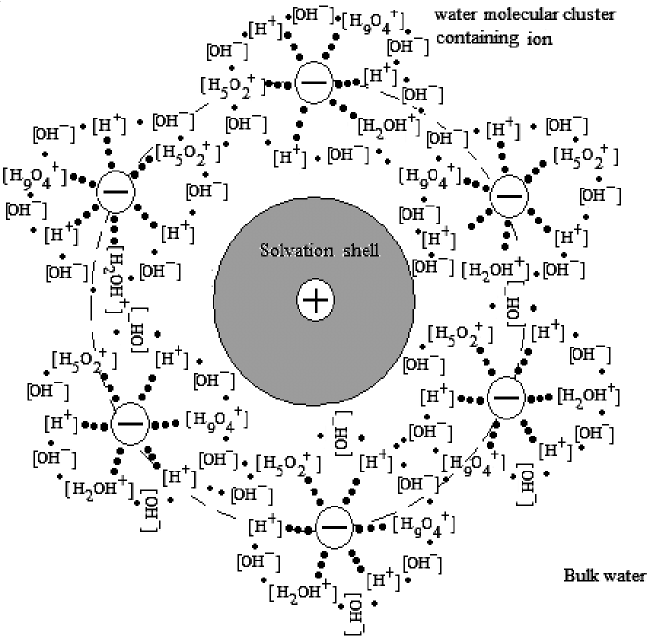


Fig. 1. Schematic picture for the water molecules cluster around a positive ion. The positive center ion close surround by a hydration shell, outside, as shown by dashed line, enveloped by an ionic atmosphere where each negative ion is adsorbed by various groups such as H_2OH^+, OH^-, H^+, $H_5O_2^+$, $H_9O_4^+$, which link together by the electrostatic force or hydrogen bond, shown by little black circle, forming a water molecular cluster. The k_2 clusters simultaneously emerge around the hydration layer of the center ion

$$h'=-\frac{(x_w)^{k_2}}{\ln(x_w^{k_2})} \tag{3}$$

which could be considered as a probability-distribution function of water molecules around the center ions. The ω function that contains the term "ln (a_w)" is related to the chemical potential of water and also linked with the water distribution function as follows,

$$\omega = f(h') \tag{4}$$

The experimental data show that ω against h′ has the good linear relationship for many inorganic monoacid, alkali and some type of salts when the parameters k_1 and k_2 are appropriately chosen. For simplifying, the h′ function would be replaced by $h = (x_w)^{k_2}/\ln(x_w)$, and the results of model do not be affected. There is still the good linear relationship between ω and h. The examples of the linear relations of ω and h for 1-1 type of acid, alkali and salt solution are shown in Fig. 2. Table-1 gives the values of the parameters k_1, k_2, the slope α_1, the intercept α_2 and the linearly related coefficient r for HF, HCl, HBr, HI, HNO_3, $H(HSO_4)$, LiOH, NaOH, KOH, NaCl and KCl systems. The parameters for both HF and LiOH in Table-1 are given on the different concentration sections. The reason might be attributed to the structure entropies of ions. In alkali metals and halogen elements, only the ions of fluorine and lithium have the negative structure entropies[24].

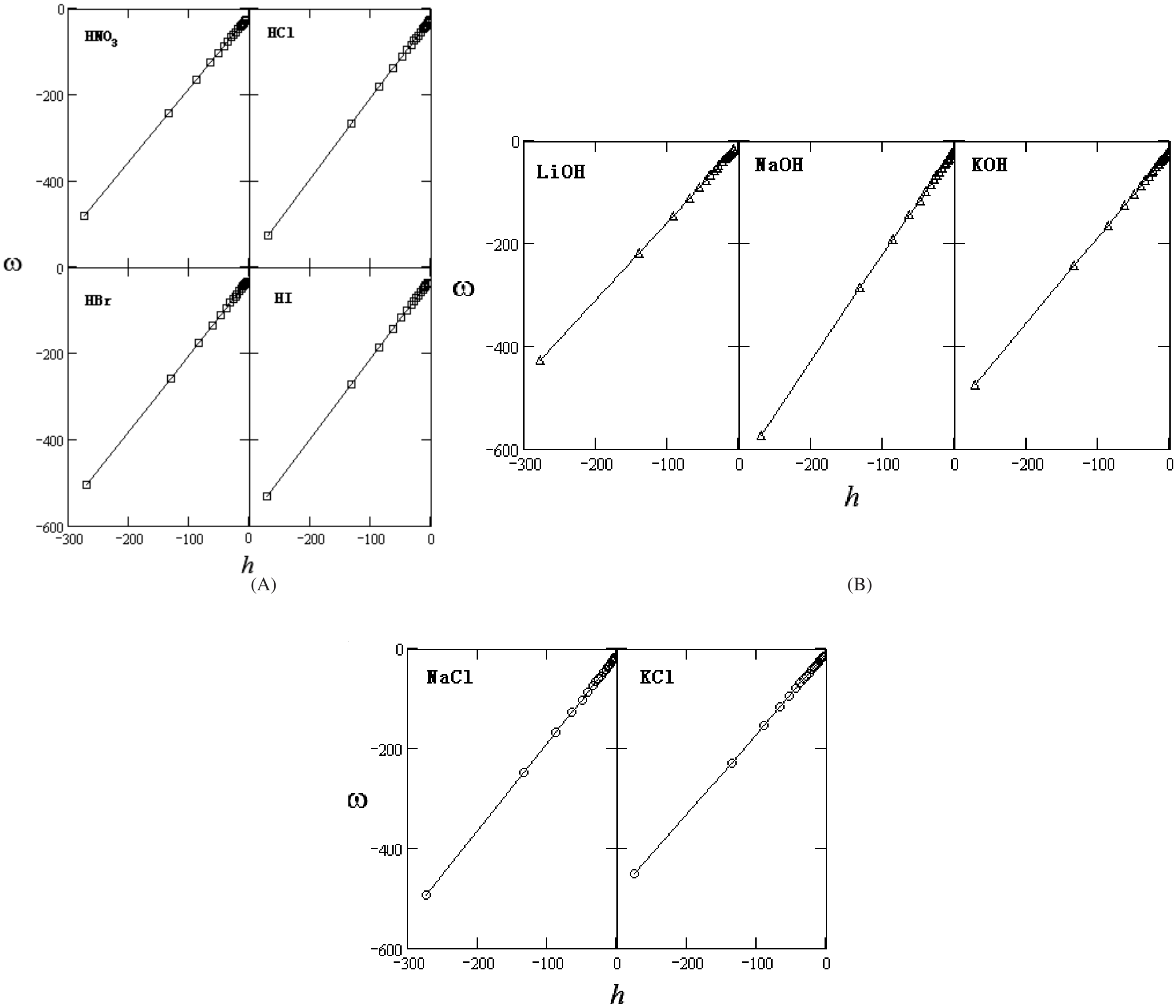
According to the defined molal osmotic coefficient, Φ as follows[25]

$$\Phi=-\frac{n_w\ln\left(\frac{a_w}{a_w^o}\right)}{vm} \tag{5}$$

TABLE-1
PARAMETERS k_1 AND k_2 AND SLOPE α_1, INTERCEPT α_2 AND LINEARLY RELATED COEFFICIENT r OF ω *VERSUS* h FOR SOME INORGANIC ACIDS, ALKALIS AND SALTS WITH BOTH IONS UNIVALENT AND THE COMPARISON OF THE ERRORS

Aqueous system [Ref]	k_1	k_2	r	α_1	α_1	σ(Φ) × 10^{-3} This model	σ(Φ) × 10^{-3} Pitzer model	ARD(Φ) × 10^{-3} This model	ARD(Φ) × 10^{-3} Pitzer model	Concentration (m)
HF[11]	1.98086	2.3411	0.999999	0.96921	-3.2500	0.35	–	0.53	–	0.1-4.0
	2.6165	5.4000	0.999980	6.2316	-9.2655	1.60	–	2.2	–	4.0 -20
HCl[25]	1.9907	8.5939	0.999998	1.7694	-22.9631	4.40	4.9	2.2	1.8	0.1-6.0
HBr[25]	1.9899	9.6240	0.999999	1.766	-26.2561	1.70	1.6	1.1	1.3	0.1-3.0
HI[25]	1.9997	8.5799	0.999999	1.8721	-27.1979	1.60	2.2	0.89	1.8	0.1-3.0
HNO_3[11]	1.98106	2.7967	0.999999	1.6739	-12.0025	0.65	1.3	0.51	0.97	0.1-6.0
	1.9817	2.9490	0.999999	1.6803	-12.1784	1.50	–	0.93	–	0.1-15.0
	1.0946	0.8210	0.999928	-1.2281	-7.2094	0.99	–	0.56	–	15-28
$H(HSO_4)$[25]	1.98805	14.0844	0.999984	1.2695	-18.985	4.20	–	2.6	–	0.1-21
LiOH[25]	2.0048	10.3540	0.999999	1.8597	-15.4721	0.61	–	0.46	–	0.1-1.0
	2.0208	1.0010	0.999999	1.8206	-5.0861	0.52	–	0.45	–	1.0-4.0
KOH[25]	1.9833	7.4290	0.999998	1.6794	-19.8696	5.50	9.5*	3.0	7.2*	0.1-6.0
NaOH[25]	2.0185	9.2125	0.999991	2.0615	-18.3374	6.60	8.8	5.0	7.7	0.1-6.0
NaCl[25]	1.9894	6.7400	0.999999	1.7544	-14.6119	2.10	0.89	1.8	0.62	0.1-6.0
KCl[25]	1.9753	3.8809	0.999999	1.6092	-9.5669	0.22	0.76	0.19	0.74	0.1-4.8

*The error is corresponding to maximum concentration of 5.5 m.



(A)

(B)

(C)

Fig. 2. Some examples of the linear relation of ω *versus h* for the aqueous systems of acid (A), alkali (B) and salt (C) solution of some 1-1 type. Symbols □, Δ, O are experimental data; straight lines are the calculated by best-fit of ω *versus h*

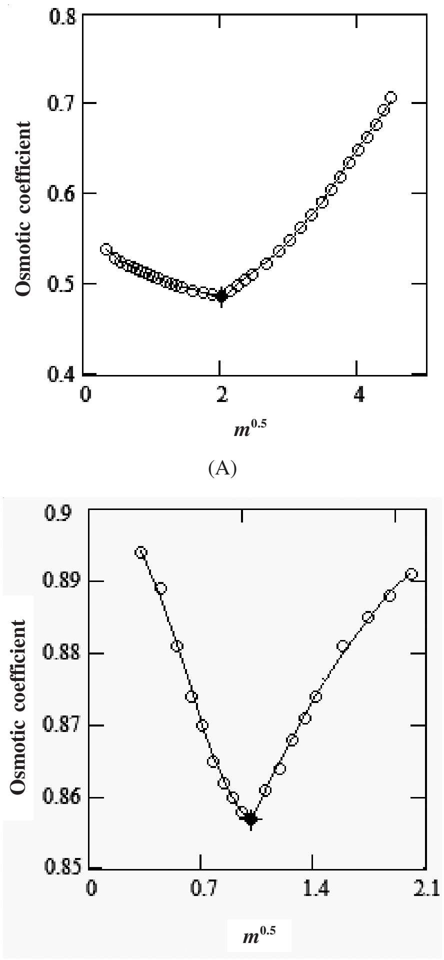
and noting the linear relation of ω against h, we have

$$\Phi = -\frac{(\alpha_2 + \alpha_1 h)(1 - x_w)^{k_1} n_w}{\nu^2 m} \tag{6}$$

Eqn. 6 indicates that the molal osmotic coefficients can be determined by means of the slope α_1 and interception α_2 which are derived by the least square best-fit to experimental data of ω *versus* h.

Application of the model

HF-H_2O system: The investigation on the aqueous solution for this single solute has been summarized by Hamer and Wu[11]. The experimental data of the osmotic coefficients are shown by small circle in Fig. 3(A). The data came from different methods, such as EMF measurements, freezing-point depressions, apparent molar heat capacity and recalculated dissociation constants. Up to now, we did not find the parameters of the pitzer model for this system. Because it is difficult to describe them in a unique equation well, Hamer *et al.*[11] have fitted the experimental data to a quadrinomial expression, as shown by eqn. 7, to describe the osmotic coefficients of the HF solution.



(A)

(B)

Fig. 3. Osmotic coefficients against $m^{0.5}$ for the aqueous systems of HF(A) and LiOH (B). Small circles are the experimental data of the osmotic coefficients, and solid lines are calculated values of them. In the datum points of osmotic coefficients, the point marked by a cross divides the whole concentration range into two continuous sub-concentration sections

$$\Phi = a + bm^{-1.5} + cm^{0.5} + dm \tag{7}$$

The whole concentration region from 0.001 to 20.0 in molality was divided into 4 sections, *i.e.*, from 0.001 to 0.05, 0.05 to 0.5, 0.5 to 4.0 and 4.0 to 20.0 for individual fitting. They gave the four sets of differently polynomial parameters, separately.

However, from Fig. 3(A) it can be seen that there appears a turning point at $m^{0.5}$ =2.0, as shown by a cross mark, in the whole data points. Considering the particularity of this set data (as stated above that exists the negative structure entropy of fluorine ions, which maybe converts to positive at this concentration), an approach of concentration-sectional district is also used to describe the thermodynamic properties of this acidic aqueous solution. The whole concentration range is divided into 2 parts from 0.1 to 4.0 and 4.0 to 20.0 on molality scale. In these divisions, one constructs the ω potential and h function, respectively. The values of x_w in the two functions are calculated by eqn. 1 on the experimental data[11]. The relation of ω *versus* h is linear under available k_1 and k_2. The slope α_1 and the intercept α_2 and the excellent related coefficient r for two sub-concentration ranges are listed in Table-1. The osmotic coefficients calculated on these parameters are represented by the solid lines in Fig. 3(A), where it can be seen that only two parameters, k_1 and k_2 are chosen so that the calculated values are well in agreement with the experimental data.

In order to evaluate the model, one defines the average relative deviation [ARD (Q)]:

$$\mathrm{ARD}(Q) = \frac{\sum_{i=1}^{N} \left| \frac{(Q - Q_{cal})}{Q} \right|}{N} \tag{8a}$$

and the variance [σ(Q)]

$$\sigma(Q) = \sqrt{\frac{\sum_{i=1}^{N} (Q - Q_{cal})^2}{N}} \tag{8b}$$

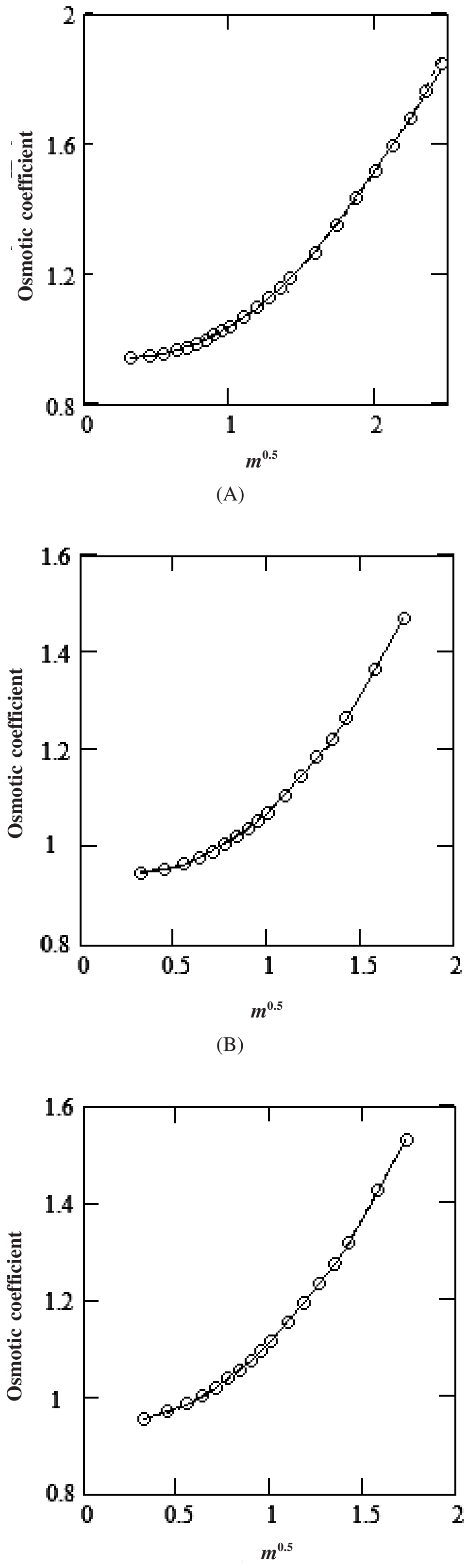
where N is number of data points, Q and Q_{cal} are, respectively, the osmotic coefficients determined experimentally and calculated by the models such as the present model and Pitzer equation. The ARD(Φ) and σ(Φ) for the HF-H_2O system are listed in Table-1, where the Pitzer eqn. 9 and the present model (eqn. 6) are, respectively, as the reference.

LiOH-H_2O system: The two sets of data with obvious difference are given in literature[11,25], respectively. Pitzer used his model with the parameters listed in Table-2 to calculate the osmotic coefficients of this system on the data of literature[25]. However, the errors of the predicting results are noticeable [not given in Table-1 and Fig. 3(B)].

Similar to HF-H_2O system, the osmotic coefficients, as shown by small circles in Fig. 3(B), have an apparent turning point at $m^{0.5}$ =1.0, as shown by a cross mark, in the concentration range from 0.1-4.0 molalities. The concentration-sectional approach, like the used in HF-H_2O system, is also applied here. The whole concentration range is divided into 2 parts from 0.1-1.0 and 1.0-4.0 molalities. Similarly, the

TABLE-2
PARAMETERS IN PITZER'S EQUATION FOR SOME UNI-UNIVALENT ELECTROLYTES

Electrolyte	$\beta^{(0)}$	$\beta^{(1)}$	C^{Φ}	Max m	Ref.
HCl	0.1775	0.2945	0.00080	6.0	[16]
HBr	0.1960	0.3564	0.00827	3.0	[2]
HI	0.2362	0.392	0.0011	3.0	[2]
HNO_3	0.1168	0.3456	-0.00539	6.0	[16]
$H(HSO_4)$	0.2103	0.4711	0.0027	6.0	[26]
LiOH	0.015	0.14	–	4.0	[16]
NaOH	0.0864	0.253	0.0044	6.0	[16]
KOH	0.1298	0.320	0.0041	5.5	[16]
CsOH	0.150	0.30	–	–	[16]
NaCl	0.00765	0.2664	0.00127	6.0	[16]
KCl	0.04835	0.2122	-0.00084	4.8	[16]



(A)

(B)

(C)

Fig. 4. Osmotic coefficients against $m^{0.5}$ for the aqueous systems of HCl (A), HBr (B) and HI (C). Small circles are the experimental points and solid and dot lines are the calculated by the present model as well as Pitzer eqn., respectively

relations of ω *versus* h for the two concentration ranges are all linear. The values of the slope α_1, the intercept α_2, parameters k_1, k_2 and the linearly related coefficient r for two sub-concentration ranges are listed in Table-1, respectively. The calculated osmotic coefficients are represented by the solid lines in Fig. 3(B), where it can be seen that the predicting values are quite well in agreement with the experimental data. The errors are listed in Table-1.

HCl (HBr, HI)-H_2O system: The HCl-H_2O system has been investigated a lot. Hamer and Wu have made excellent summaries for earlier investigations on thermodynamic properties of HCl[11] and given the osmotic coefficients of HCl up to 16 molality. The comprehensive data differ from those in literature[25] by a few units in the third place over 0.1 to 6.0 molalities, which may make the parameters in model different slightly to acquire the best reproduction of the original data. Pitzer's equation gives the best fit to the data[25] up to 6 molalities. The equation is as follows[16]:

$$\Phi = 1 + |X_M Z_X| f^{\Phi} + m\left(\frac{2\nu_M \nu_X}{\nu}\right) B_{MX}^{\Phi} + m^2\left[\frac{2(\nu_M \nu_X)^{1.5}}{\nu}\right] C_{MX}^{\Phi} \quad (9)$$

with

$$f^{\Phi} = -\frac{A_{\Phi} I^{0.5}}{(1 + bI^{0.5})} \quad (9a)$$

$$B_{Mx}^{\Phi} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} \exp(-\alpha I^{0.5}) \quad (9b)$$

where ν_M and ν_X are the numbers of cation M and anion X in electrolyte, respectively, Z_M and Z_X the respective charges, $\nu = \nu_M + \nu_X$, m = molality, I = ionic strength and A_{Φ} = the D-H parameter that is 0.3915 $kg^{1/2}$ $mol^{-1/2}$ for water at 298.15 K. The empirical constants b =1.2 $kg^{1/2}$ $mol^{-1/2}$ and α = 2.0 $kg^{1/2}$ $mol^{-1/2}$ and the ion-interaction parameters $\beta^{(0)}$, $\beta^{(1)}$ and C^{Φ} which are taken from literature[15] and are listed in Table-2. According to the Pitzer's equation, the osmotic coefficients for HCl are calculated. The calculated and measured data[25] are shown by dot line and little circle in Fig. 4(A), respectively. Obviously, the pitzer equation is very good in agreement with the data points.

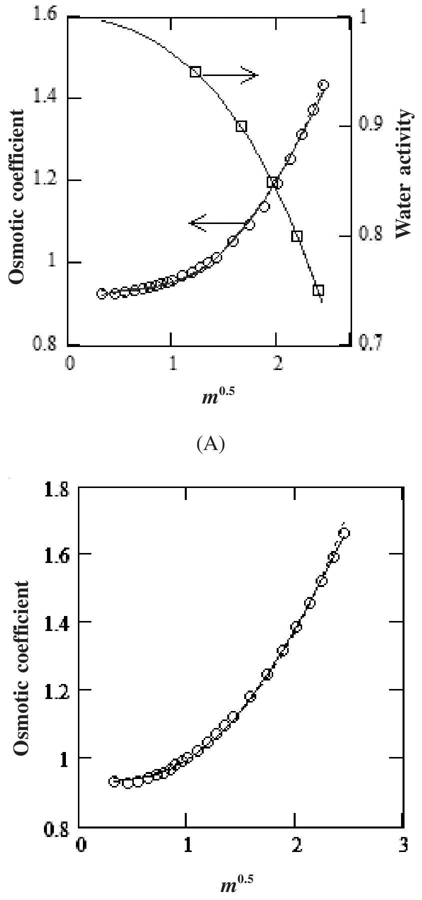
When using the present model, it is found that ω *versus* h is linear with α_1 = 1.7694 and α_2 = -22.9631 at k_1 =1.9907, k_2 = 8.5939 and the linearly related coefficient is 0.999998. Substituting the parameters for eqn. 6, we have

$$\Phi = -\frac{(-22.9631 + 1.7694h)(1 - x_w)^{1.9907} n_w}{\nu^2 m} \quad (10)$$

where $\nu = 2$ and h is the quantity in which $k_2 = 8.5939$. From eqn. 10, the osmotic coefficients are evaluated. They are shown by the solid line in Fig. 4(A), where it can be seen that both solid line and dot line are almost complete overlapping, indicating that eqn. 10 can describe the osmotic coefficients of HCl solution well.

For the HBr-H_2O and HI-H_2O systems, Pitzer respectively gave two sets of parameters for each[16,26]. One is for the data in literature[25] where the maximum concentration is 3 molalities and another for those in literatures[26] where the maximum of the concentration up to 6 molalities. The calculated parameters for the former set of HBr and HI are listed in Table-1. Fig. 4(B-C) give the experimental and calculated results of the osmotic coefficients for these systems, respectively. The ARDs and σ for Φ of these two systems are all listed in Table-1.

NaOH (KOH)-H_2O system: Two sets of the osmotic coefficients are given by previous workers[11,25]. The difference for most of them is by a few units in the third place. Pitzer used the data[25] to obtain the parameters, listed in Table-2, for calculating the osmotic coefficients. We used the same data for best-fitting to acquire a set of parameters, as listed in Table-1. Fig. 5(A-B) give the calculated results of the osmotic coefficients for the two systems. The experimental data[25] of water activities and their calculated values by eqn. 5 are given in Fig. 5A at same time. The errors are listed in Table-1.

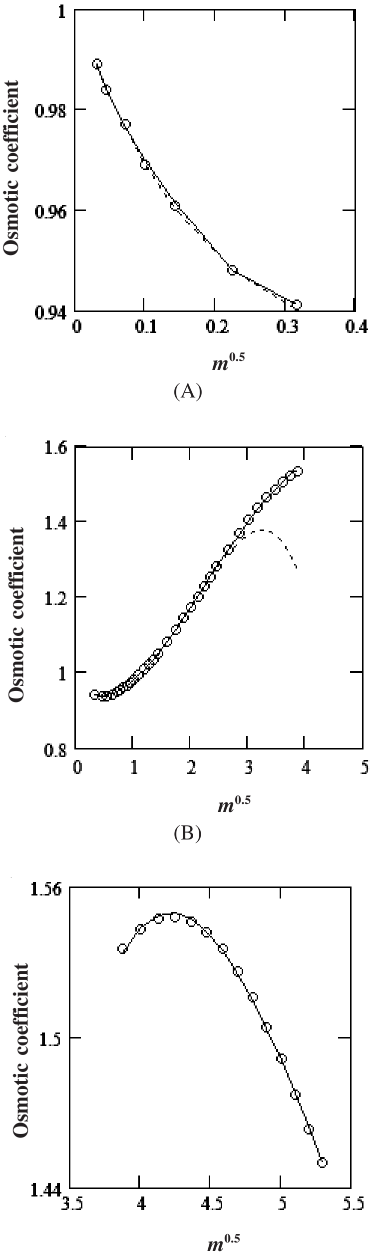


(A)

(B)

Fig. 5. Osmotic coefficients and the water activities against $m^{0.5}$ for the aqueous systems of NaOH (A) and KOH (B). Small circles and squares are the experimental points and solid and dot lines are the calculated by the present model as well as Pitzer eqn., respectively

HNO_3-H_2O system: Literature[11] gave the osmotic coefficients of the system up to 28 molalities. Clegg and Brimblecombe have given the equations[27] to calculate the thermodynamic properties in the system. From Table-1 we can see that the errors on the present model are observably lower than those on Pitzer's in the concentration range of 0.1-6.0 molalities. The present model is also used to compute the osmotic coefficients in the wider range of concentration from 0.1-15 and 15-28 molalities. The errors for these two concentration ranges are also very small and given in Table-1. This means that the present model is more suited to the high concentration range. The comparison of the calculated with experimental data in the two concentration ranges is given in Fig. 6B and 6C, respectively.



(A)

(B)

(C)

Fig. 6. Osmotic coefficients against $m^{0.5}$ for the HNO_3-H_2O system. Small circles are experimental points and solid and dot lines are the calculated by the present model as well as Pitzer eqn., respectively. (A), (B) and (C) are respectively for 0.001-0.1, 0.1-15.0 and 15-28 *m*

$H(HSO_4)$-H_2O system: The $H(HSO_4)$ is just H_2SO_4 in which the ionization of it is supposed to be completely primary, *i.e.*, $H_2SO_4 + H_2O = HSO_4^- + H_3O^+$ and ν in eqn. 6 equals to 2. The osmotic coefficients of the system have given in literature[25,26]. Pitzer *et al.*[26] treated the solution on a mixed electrolyte basis with different anions of HSO_4^- and SO_4^{2-} because actually exists the partial dissociation of HSO_4^-. However, this needs to know the dissociation fraction from HSO_4^- to SO_4^{2-} to calculate the osmotic coefficients. They calculated the thermodynamic properties of the system within 0.1 to 6.0 molalities, but the results are not quite satisfactorily. We have calculated the osmotic coefficients over 0.1 to 21 molalities, as shown in Fig. 7 where it can be seen that the results are excellent in agreement with the experimental data. The parameters for calculation and errors are listed in Table-1. Nevertheless, the water activities calculated by eqn. 5 based on the obtained osmotic coefficients are not good in agreement with the experiment results although the predicting osmotic coefficients are very well. If taking $\nu = 3.0053$, the calculated results of water activities are improved a lot, as shown in Fig. 7. The ν value is different from 2 which represent ion number of ionization of the solute. This should ascribe to this special electrolyte uni-univalent. Firstly, the sulphuric acid is not just primary ionization to HSO_4^-, part of which is further ionized to SO_4^{2-}, making the ion number increase to more than 2. Secondly, also importantly this electrolyte, especially at high concentrations, has the powerful moisture absorption, making the water activities lower than normal. According to eqn. 5, it needs to gain the ν value to remain unchanged of the Φ value. Therefore, the ν value would be equal a value more than 2 at this case.

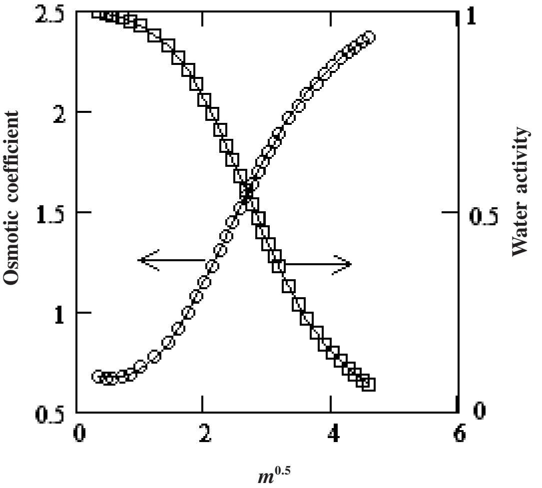
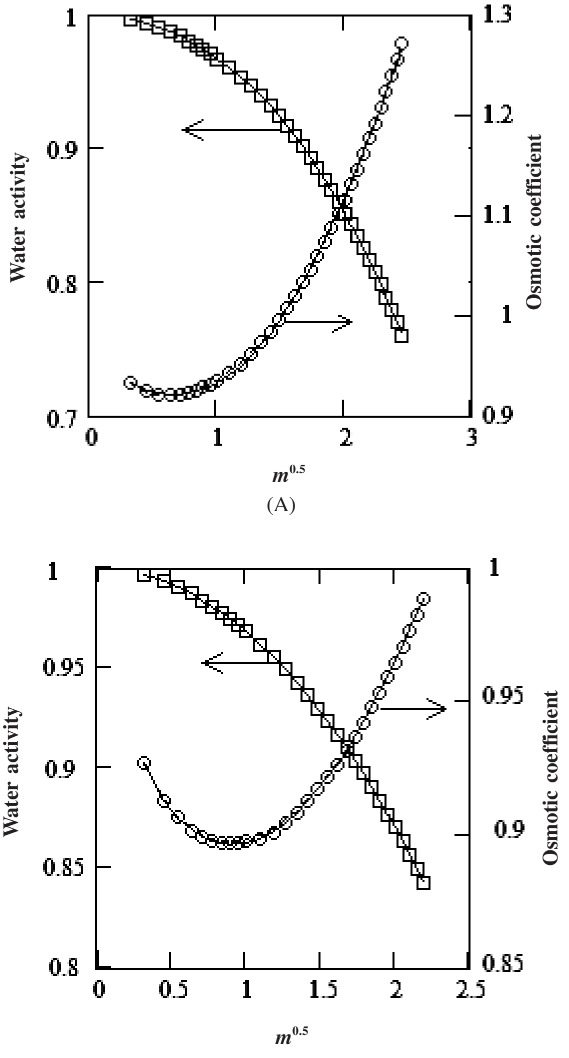


Fig. 7. Water activities and osmotic coefficients against $m^{0.5}$ for the $H(HSO_4)$-H_2O system. Small squares and circles are the experimental points of them, respectively, and solid lines are the calculated by the present model

Some 1-1 type salts-H_2O systems: Although the main intent discussed in this paper is aimed at some hydroxides of alkali metals and monoacids, we are still planning to extend the model to some salts to understand its suitability.

Take the most common two salts, NaCl and KCl, as the example. Literature[25] gave the considerably accurate data of the osmotic coefficients and water activities for their aqueous solution. The present model can also describe the aqueous systems of NaCl and KCl. The model parameters and the errors are listed in Table-1. The calculated results are shown in Fig. 8(A-B) where it can be seen that the results on both the present and Pitzer's models almost coincide and also agree with the experimental data well.



(A)

(B)

Fig. 8. Water activities and osmotic coefficients against $m^{0.5}$ for the NaCl-H_2O (A) and KCl-H_2O (B) systems. Small squares and circles are the experimental points of them, respectively, and solid and dot lines are the calculated by the present model as well as Pitzer eqn., respectively

Although a good prediction of the water activities for these systems has been obtained by eqn. 5 based on the achieved osmotic coefficients, the results can be still improved. Combining eqns. 5 and 6, and noting $a_w^0 = 1$ one can obtain a formula for calculation of water activity as follows,

$$\ln(a_w) = \frac{(\alpha_2 + \alpha_1 h)(1 - x_w)^{k_1}}{\nu} \quad (11)$$

The value of ν in eqn. 11 is assumed to be 2 for uni-univalent electrolyte. Obviously, this assumption is only suitable to the case that the electrolytic molecule completely ionizes in the dilute solution. Nevertheless, the electrolytic molecules may partially associate in the higher concentrations. Considering an "apparent association degree" and letting it be equal to ε, then eqn. 11 can rewrite to be

$$\ln(a_w) = \frac{(\alpha_2 + \alpha_1 h)(1 - x_w)^{k_1}}{\nu(1-\varepsilon)} \qquad (12)$$

For these two systems where the maximum concentrations are up to 6.0 and 4.8 molalities, respectively, the association of ions must exist. When letting ε be 0.00021 and 0.00065 for the solutions of NaCl and KCl, respectively, the predicting values of the water activities are much more close to the experimental data [Fig. 8(A and B)]. Since ε is very small, usually it can be ignored. In order to attain the more accurate water activities, the effect of association of ions should be considered sometimes.

The ε value is a mean in the given concentration range, because the ionic association degree is increasing with the concentration increasing. Take NaCl as an example. When taking the same parameters including k_1, k_2, α_2 and α_1 and computing the ε value in the concentration ranges of 0.1-6.0, 0.1-5.6 and 0.1-5.0 molalitites, respectively, the value drops from 0.00021 to 0.00019 and 0 as the concentration shifts down.

RESULTS AND DISCUSSION

Differing the concepts of ion-interaction, ion-association and ion-hydration, the present model is based on a dimensionless-thermodynamic potential function ω that contains a term of ln (a_w), which can broadly reveal various interactions in the electrolyte solution such as ion and ion, ion and solvent and interacting energy due to change in the permutation of solvent molecules as well. The ω function is related with the microcosmic distribution of water and the macroscopic thermodynamic properties of solution. As mentioned above, in the dimensionless-thermodynamic potential function ω, k_1 in general is a number close to 2. From the Tables 1 and 3 it can be seen that this is true.

In the modern quantitative theories of electrolytic solution, a fundamental ideal is the distribution function that is a probability of finding an ion or ion-pair in a giving position. Differing from the Debye-Hückel ionic distribution function, here the constructed probability-distribution function is for solvent molecules or the probability of finding the water molecule clusters around the some center ion at a giving concentration. As the solution concentration increases, the arrangement of solvent molecules near the solute will be changed. This probability is dependent on the solvent concentration, x_w. We can use the function $x_w^{k_2}$ to describe the probability of finding the water molecule clusters around the center ion. The bigger the value is, the larger the probability of finding it. When $x_w \rightarrow 1$, the probability of finding the water molecule clusters is close to unit and $x_w \rightarrow 0$, the probability to zero. It should be pointed out that k_2 is allowed to be not an integer because some water groups in an ionic atmosphere attached to a center ion could be shared by other center ions. However, as stated above, the change in structure of solvent basically was not referred to in some previous models.

In the function h, the constant k_2 represents a probability distribution of the water molecule clusters that congregate around the hydration layer of the center ion at same time. This quantity is changeable as the concentration of solution changes. Strictly speaking, there is a definite k_2 value at each concentration. The given value here only is a mean result in a given range of concentration. If a concentration range is divided into some sub-concentration sections and one chooses more suitable k_2 (or h) for each, the model will describe the osmotic coefficients more better. Take HNO_3-H_2O system as an example. The osmotic coefficients in the concentration range from 0.001 to 28 molalities are given[11]. If divided the range into three sub-concentration sections of 0.001 to 0.1, 0.1 to 15 and 15 to 28 molalities, the described results of the present model for each concentration section are all better and more close to measured values. The calculated parameters and the errors are listed in Table-1, where it can be seen that the value of k_2 is increasing with the solute concentration decreasing. In Table-3, we calculate the model parameters and the errors for 11 electrolytes in the concentration range from 0.001 to 0.1 molalities. As seen in Table-3, although the value of k_1 basically remain unchanged, k_2 evidently increases in the high-dilute concentration range, *i.e.*, the probability of finding the water molecule clusters around the center ion increases.

In eqn. 12, we propose a concept, "apparent association degree". It should be pointed that the apparent association degree is not the real fraction of association of ions. It only reminds the fact that there exists the association of ions.

TABLE-3
CALCULATED PARAMETERS AND THE ERRORS FOR SOME ELECTROLYTES WITH BOTH IONS UNIVALENT IN THE CONCENTRATION RANGE OF 0.001-0.1 MOLALITIES*

Aqueous system	k_1	k_2	r	α_1	α_2	$\sigma(\Phi) \times 10^{-3}$	ARD $(\Phi) \times 10^{-3}$
HCl	1.9931	64.665	0.999999	1.844	-101.365	0.57	0.32
HBr	1.9933	64.0172	0.999999	1.8479	-102.812	0.65	049
HI	1.99364	63.90755	0.999999	1.8541	-107.12	0.62	0.39
HNO_3	1.9932	68.9087	0.999999	1.846	-105.754	0.43	0.31
$H(HSO_4)$	1.93459	64.921	0.999993	0.9480	-52.8177	6.5	6.4
LiOH	1.99307	78.6754	0.999999	1.8426	-101.621	0.82	0.61
NaOH	1.99393	75.999	0.999999	1.8585	-109.89	0.78	0.60
KOH	1.993603	70.774	0.999999	1.852	-104.467	0.92	0.66
CsOH	1.99326	60.6369	0.999999	1.847	-96.251	1.4	0.55
NaCl	1.99376	71.2321	0.999999	1.8551	-104.3871	0.68	0.48
KCl	1.9940	80.3255	0.999999	1.860	-113.6612	0.82	0.62

*All of experimental data are taken from literature[11].

Macroscopically, if considered this effect, eqn. 12 can describe the water activity more accurate.

Finally, it should be pointed that the model, in principle, is also opposite to the electrolytes with other valent type and the mixed electrolytes but a likely function form selected to eq. 4. This will be discussed in another paper.

Conclusion

This paper presents a model for thermodynamic properties of the solutions of uni-univalent electrolytes based on the constructed a dimensionless-thermodynamic potential for solvent and a probability-distribution function of water molecules near the solute ion. The model can reproduce the osmotic coefficients well for the uni-univalent electrolytic solutions, especially for some hydroxides of alkali metals and monoacids, such as NaOH, KOH, LiOH, HF, HCl, HBr, HI, HNO_3 and $H(HSO_4)$. Compared with Pitzer's, the present model can be opposite to the higher concentrations where the various interactions such as between ions, ions and solvent, especially, the effect of the structure of solvent molecules are prominently revealed.

Appendix

For an aqueous electrolyte solution, the Gibbs-Duhem equation can be given by

$$-m_w \, d\ln(a_w) = \nu m \, d\ln(\gamma_{\pm} m) \qquad (1')$$

where m_w is moles of solvent per kilogram of solvent, $\gamma_{\pm}$ is mean activity coefficients and the meaning of other symbols is the same as text. When m approaches zero or the solution remains high-diluted, the integration of eqn. (1') would have the difficulty. To overcome this problem, there are two ways. One is by use of the expression of the osmotic coefficient Φ:

$$\nu m\Phi = -n_w \ln\left(\frac{a_w}{a_w^0}\right) \qquad (2')$$

Eqn. (1') can be changed into:

$$d\ln(\gamma_{\pm}) = (\Phi - 1)\left(\frac{dm}{m}\right) + d\Phi \qquad (3')$$

Only remembering that the value of Φ at infinite dilution is unity, the integration of eqn. (3') can be completed without any difficulty. Another is to define a function as:

$$\omega' = \frac{\nu \ln\left(\frac{a_w}{a_w^0}\right)}{\tau^{(u+1)}} \qquad (4')$$

where $\tau = (1 - x_w)^{1/u}$ and $u \geq 1$. Noting that $m_w/m = x_w/x$ and $d\ln(a_w) = d\ln(a_w/a^0_w)$, eqn. 1' can be transformed into:

$$\nu d\ln(\gamma_{\pm} m) = \left(\frac{-x_w}{x}\right) d\left(\ln\left(\frac{a_w}{a_w^0}\right)\right) \qquad (5')$$

where x is the mole fraction of solute. Replacing the function ω' to eqn. 5' and rearranging, one obtains:

$$\nu^2 d\ln(\gamma_{\pm} m) = d(\tau(\tau^u - 1)\omega') - u\omega' d\tau \qquad (6')$$

It has been proved that the function ω' is bounded under the condition that the value of u ≥ 1, and eqn. 6' can be integrated in the whole concentration range with any difficulty [K.-C. Chou, Science in China (Series A) 5 A (1978) 312 or Zheng Fang, *Acta Metall. Sin.*, **22**, A352 (1986)]. Letting $(u + 1)/u = k_1$, then $\omega' = \omega = \nu \ln(a_w/a_w^0)/(1 - x_w)^{k_1}$, which is just the dimensionless-thermodynamic potential defined in the text and k_1 in general is a number close to 2. When $u = 1$, *i.e.*, $k_1 = 2$, and activity is substituted by activity coefficient the ω' function is reduced to the well known α function used generally in non-electrolyte solution ($\nu = 1$) for the complete integration of the Gibbs-Duhem equation.

In substance, both *Φ* (*i.e.*, molal osmotic coefficient) and ω function is equivalent, except the later is a dimensionless quantity on the molar scale.

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