

Evaluation of Osmotic Coefficients and the Influence of Temperature on Osmotic Coefficients of NaCl and KBr Electrolyte Solutions

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ABSTRACT

In this study, two things have been done. The first is to evaluate the original data of the osmotic coefficients of NaCl and KBr electrolyte solutions at 25, 60, 70, 80, 90 and 100 °C (Robinson, R. A., Stokes, R.H.: *Electrolyte Solutions*, Butterworths, London 1959 p 480), which originated from the experimental measurements of boiling point evaluation of NaCl (Smith, R.P.: *J. Am. Chem. Soc.* 61, 500–503 1939; Smith, R.P., Hirtle, D.S.: *J. Am. Chem. Soc.* 61, 1123–1126 1939) and KBr solutions (Johnson, G.C., Smith, R.P.: *J. Am. Chem. Soc.* 63, 1351–1353 1942), using a linear rule between a dimensionless-thermodynamic potential of solvent and the probability-distribution of water in single electrolyte solution proposed by one of the authors (Fang, Z.: *Asian J. Chem.* 23, 5384–5392 2011). The second is to investigate the effects of temperature on the osmotic coefficients of these two electrolyte solutions from 60 to 100°C by means of the optimization method of curve fitting to the results from the linear rule mentioned above. Acquire the osmotic coefficients of both of NaCl and KBr solutions as a function of temperature within 60 to 100°C with the satisfying results.

Keywords: Sodium chloride; Potassium bromide; Single electrolyte solution; Activity; Osmotic coefficient; Temperature influence; Dimensionless-thermodynamic potential; Probability-distribution of water; Model for electrolyte solution; Curve fitting

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I. Introduction

The osmotic coefficient related to the activity of water is an important thermodynamic parameter of the aqueous solution of electrolyte. This property varies with temperature and affects the chemical potentials of components of electrolyte solution, then influences the behaviors of the related products, for example, batteries, making their performance do not be able to display better, even damaging the devices sometimes. The osmotic coefficients as a function of temperature are very useful in many fields, such as hydro-metallurgy, metallic corrosion, chemical engineering, electrolysis, even the electrolyte equilibrium in human body, etc. Are the performance of some related products good or bad under given temperature? How are the osmotic coefficients affected by temperature? For answering these questions it is necessary to assess the activity data and to set a system where the osmotic coefficients or activities as the function of temperature can be precisely presented. Although the works in this respect have a considered progress, such as the quasi-random lattice model (QRL) [1], the mean spherical model [2] and its modified form [3], the linear free energy relationship [4], Pitzer model [5, 6], two [7, 8] or three parameter Hückel equation [9], the ion-interaction [10] or its extended form [11-13], etc. In the numerous models either by fitting or by assigning physical meaning to certain parameters, it is hard to apply them accurately. If there is no fitting to experimental data, the accuracy is often not enough, and if fitting, the physical meaning of given parameters is unclear again. Even some of models only are suit for very dilute solution, for example, the well known limiting law [14] and its many modified forms. In a word, it has not been investigated systematically and not exists a theoretical framework currently either. This has resulted in lack of data of activities and osmotic coefficients of electrolyte solutions as a temperature function and effected their application, especially at elevated temperature. Luckily, the water activities and the osmotic coefficients for most inorganic electrolyte solutions have been experimentally measured at the room temperature and higher than 25°C [1–13, 15–25]. This is of great significance to make clear the effects of temperature on the water activities or the osmotic coefficients of electrolyte solutions. Also, this provides a base for investigating the problem that the osmotic coefficients or activities of electrolyte solutions vary with temperature. The solution of NaCl is one of most widespread salts found on the Earth. This paper is trying to apply a new discovered linear rule to assess the original data of the osmotic coefficients of NaCl and KBr electrolyte solutions at 25, 60, 70, 80, 90 and 100°C and to investigate the effect of temperature on the water activity or the osmotic coefficients for these electrolyte solutions.

II. A linear rule about activity of single electrolyte solution

A rule has been determined of the linear relationship between a dimensionless-thermodynamic potential for solvent and the probability-distribution of water molecular cluster in electrolyte solution [26, 27] by a large amount of experimental data for the electrolytes of inorganic salts.

Let a_w and x_w be the activity of water on the basis of mole fraction and mole fraction of water in an electrolyte solution studied, respectively. The mole fraction of water of the system is as follows,

$$x_w = n_w/(vm+n_w) \quad (1)$$

where m is molality of electrolyte, n_w is the number of moles of water, being 1000/18 on molal scale and v is the number of ions into which a molecule of solute completely dissociates. For example, it equals 2 for uni-univalent electrolyte like NaCl.

The dimensionless-thermodynamic potential can be expressed as

$$\omega = v \ln(a_w/a_w^0)/(1-x_w)^{k_1} \quad (2)$$

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 [26]. According to the definition of the osmotic coefficient, Φ [14], the quantitative relation between Φ and water activity a_w is

$$\Phi = -\ln(a_w/a_w^0)n_w/(vm) \quad (3)$$

Combined Eq.(2) and Eq.(3), the relationship between ω and Φ of solution is as follows

$$\Phi = -\omega(1-x_w)^{k_1}n_w/(v^2m) \quad (4)$$

An h function is defined as

$$h = (x_w)^{k_2}/\ln(x_w) \quad (5)$$

where k_2 is a parameter to be determined. The h function could be considered as a probability distribution function when the water molecular is thought as a kind of water clusters containing the ion of electrolyte, and the clusters surround a solvation shell with a center ion as well [26, 27]. Alternative expressions for h are [28]

$$h_1 = (m/m^0)^{k_2(1)} \quad (5-1)$$

or

$$h_2 = (x)^{k_2(2)} \quad (5-2)$$

or

$$h_3 = (m/m^0)^{k_2(3)} \ln(m/m^0) \quad (5-3)$$

or

$$h_4 = x^{k_2(4)} \ln(x) \quad (5-4)$$

where m^0 is unit molality, $x = (1-x_w)$, and $k_2(i)$ ($i = 1, 2, 3$ and 4) are the parameters to be determined. This paper will be only concerned with the h function expressed by Eq. (5).

It has shown that the ω has the excellent linear relationship with h function for many strong electrolyte solutions, when the parameters k_1 and k_2 are suitably chosen [26, 27]. That is

$$\omega = \alpha_2 + \alpha_1 h \quad (6)$$

where α_1 and α_2 are slope and intercept of the straight line, respectively.

It is worth pointing out that there exists this linear relationship not only at the room temperature but also at other temperature. The difference is that the values of k_1 and k_2 change as temperature varies. That is, k_1 and k_2 are the temperature function, respectively. Certainly, the slope and the intercept of the straight line are also varying with temperature. It is only discussed that the osmotic coefficient Φ varies with temperature here, because the activities of solution follow the same regularity.

III. Results

3.1 The corrected osmotic coefficients of NaCl solution

NaCl is often used as a reference electrolyte [10]. Its osmotic coefficients at 25, 60, 70, 80, 90 and 100°C have been experimentally determined [15–19] and recorded in a monograph[14] as a public reference. However, there always have been the experimental errors for any data obtained by experiments. The data of osmotic coefficients of NaCl solution are no exception. The experimental errors are retained more or less and

recorded down as well. But, if these measured data follow a particular rule within a certain scope, they could be corrected according to the regularity to eliminate these errors as far as possible, making the experimental data be smoother and closer to the true. As shown above, the linear relationship between a dimensionless thermodynamic potential of solvent (ω) and the probability distribution of water molecules (h) in single electrolyte solution has been determined. Applying this rule to the experimental data of NaCl electrolyte solutions[14], we will obtain the six sets of straight lines of ω against h corresponding to 25, 60, 70, 80, 90 and 100°C, respectively. The statistics in all cases $Q^2 > 0.9999999$, showing the excellent linear correlation of ω against h . The parameters k_1 , k_2 , the corresponding slope α_1 and intercept α_2 for these straight lines as listed in Table 1, and the fitted straight lines at different temperature are shown in Fig. 1.

Table 1. The parameters k_1 , k_2 , slope α_1 and intercept α_2 of straight lines of ω against h for NaCl solution at 25, 60, 70, 80, 90 and 100°C

	25	60	70	80	90	100°C
k_1	1.983590405	1.977444589	1.975615580	1.975760371	1.975838219	1.975461431
k_2	5.946771110	4.346219711	3.977575989	4.026877671	3.977031889	4.115288759
α_1	1.694194118	1.624254992	1.603187737	1.603126378	1.600555861	1.595347988
α_2	-13.932738655	-12.779532866	-12.392256411	-12.371213124	-12.229938951	-12.280318064

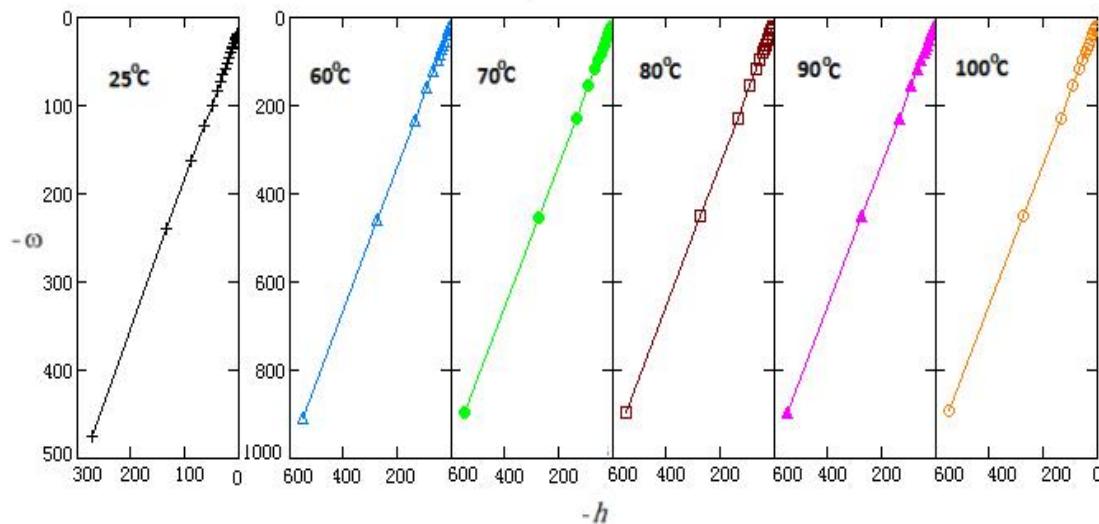


Fig.1 Plot of ω against h for NaCl solution at different temperature; cross, triangle, circle and square: experimental data; straight lines: fitted by Eq. 6

Inserting concentrations into the linear equations of ω vs. h at different temperatures and combining Eq.(4), we obtain a set of osmotic coefficients which are called as corrected ones. The results are listed in Table2, where the digit in parenthesis is a value in third decimal place, for example, (+1) represents +0.001, (-2), -0.002, etc., showing the deviation between the corrected and the original one obtained by experiment. The algebraic sum of the corrected result and the digit in parenthesis is just the original osmotic coefficient obtained by experiments.

Table 2. The corrected and original molal osmotic coefficients of NaCl solution at 25, 60, 70, 80, 90 and 100°C

m	25	60	70	80	90	100 °C
0.05	0.941**	0.940 (0)	0.939 (0)	0.938 (0)	0.936 (0)	0.935 (0)
0.1	0.932 (0)	0.929 (0)	0.927 (0)	0.926 (0)	0.924 (0)	0.923 (0)
0.2	0.924(+1)	0.921 (0)	0.919 (0)	0.918 (0)	0.916 (0)	0.914 (0)
0.3	0.922 (0)	0.920 (-1)	0.917 (0)	0.916 (0)	0.914 (0)	0.912 (-1)
0.4	0.921 (-1)	0.921 (0)	0.918 (+1)	0.917 (0)	0.915 (0)	0.913 (-1)
0.5	0.922 (-1)	0.923 (0)	0.921 (0)	0.919 (+1)	0.917 (0)	0.915 (0)
0.6	0.923 (0)	0.926 (+1)	0.924 (+1)	0.923 (0)	0.920 (+1)	0.917 (+1)

0.7	0.925 (+1)	0.930 (+1)	0.928 (0)	0.926(+1)	0.924 (0)	0.921 (0)
0.8	0.928 (+1)	0.934 (+1)	0.933 (+1)	0.931 (0)	0.928 (+1)	0.925 (+1)
1.0	0.935 (+1)	0.944 (0)	0.942 (0)	0.940 (0)	0.938 (-1)	0.934 (+1)
1.5	0.957**	0.971 (-3)	0.970 (-2)	0.967 (-1)	0.964 (-1)	0.960 (0)
2.0	0.984 (-1)	1.000 (-1)	1.000 (-2)	0.997 (-2)	0.993 (-2)	0.988 (-2)
2.5	1.014 (-1)	1.031 (0)	1.030 (-1)	1.027 (-1)	1.022 (0)	1.017 (-1)
3.0	1.047 (-2)	1.063(-2)	1.061 (-2)	1.057 (0)	1.052 (+1)	1.047 (+1)
3.5	1.081(-1)	1.094(-2)	1.091 (-1)	1.087 (-1)	1.081 (+1)	1.076 (+1)
4.0*	1.115(+1)	1.125(+5)	1.121 (+6)	1.117 (+3)	1.110 (+3)	1.105 (0)

*By thermodynamic assessment (see 4.1 of Discussions in text), the corrected values should be 1.128~1.130, 1.125~1.127, 1.118~1.120 and 1.111~1.113 for $m = 4$ at 60, 70, 80 and 90°C, respectively.

**There are not the original data corresponding to $m = 0.05$ and 1.5 at 25 °C, they are added by the linear relation presented.

It is known from Table 2 that the difference between the corrected and the original data is not large in most cases ($m < 0.4$), being within the experimental and calculative uncertainty ($0 \sim \pm 0.002$) except the datum for $m = 1.5$ at 60°C, and the data for $m = 4.0$ at 60, 70, 80 and 90°C should be considered because they exceed the experimental uncertainty. The later (4 points) has been corrected according to a thermodynamic assessment (see 4.1 of Discussions). These corrected data are annotated below Table 2.

3.2 The Osmotic Coefficient of NaCl Solution as a Function of Temperature

Plot of the original osmotic coefficients Φ of NaCl solution against $m^{0.5}$ at different temperature, is shown in Fig.2. It can be seen that these curves are quite close at all temperature researched, showing that the difference of the osmotic coefficients of NaCl solution is not large within the temperature range researched. Due to lack of the data between 25° and 60°C, only the changes of the osmotic coefficients for NaCl solution between 60°C to boiling temperature of water are considered.

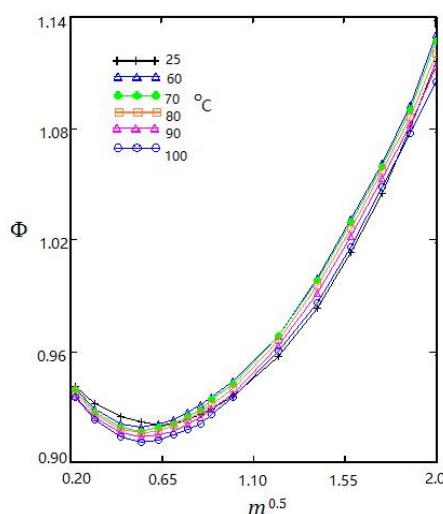


Fig. 2 The curves of Φ vs. $m^{0.5}$ for NaCl solution at different temperature; cross, triangle, circle and square: experimental data; solid line: corrected values

Two ways could be applied to express the osmotic coefficients as a function of temperature. One is on spline estimation which could be called as a graphic method. Another is on the fitting equations for parameters k_1 , k_2 , α_1 and α_2 .

3.2.1 Spline Estimation

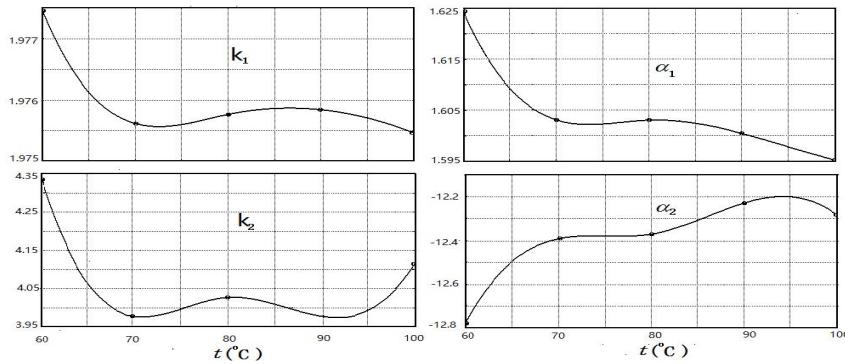


Fig. 3 The spline curves of parameters k_1 , k_2 , α_1 and α_2 .

As a preliminary estimate, the spline approximation could be used. Based on Table 1, it can draw up four spline curves for k_1 , k_2 , α_1 and α_2 with temperature change, respectively, as shown in Fig. 3. Thus these parameters within 60~100°C can be given briefly.

3.2.2 Fitting equations for k_1 , k_2 , α_1 and α_2

The parameters k_1 and k_2 and the slope α_1 and the intercept α_2 for six straight lines have been obtained at different temperatures (see Table 1). By the curve fitting, the changes of them with temperature are shown as follows,

$$P_1 = a_1 + b_1 t + c_1 t^{0.5} + d_1/t^{0.5} + e_1 \ln(t)/t \quad (7-1)$$

$$P_2 = a_2 + b_2 t + c_2 t^{0.5} \ln(t) + d_2/t^{0.5} + e_2 \ln(t)/t \quad (7-2)$$

where P_1 represents k_1 or α_1 and P_2 , k_2 or α_2 . t is temperature in Celsius. The coefficients a , b , c , d and e are listed in Table 3 and the goodness of fit for P_1 and P_2 is all over 0.9999. From these equations, it can be seen that the k_1 and α_1 vary with temperature t on the same rule, so are k_2 and α_2 . Such phenomenon may not be general, although the same situation occurs also in KBr solution (see Appendix).

Table 3 Coefficients a , b , c , d and e of Eqs. 7-1 and 7-2 for k_1 , α_1 , k_2 and α_2

Parameter	a_1	b_1	c_1	d_1	e_1
k_1	83.066817	0.093189521	-4.2644939	-897.82064	912.3809
α_1	813.21317	0.93275669	-42.686046	-8985.2216	9130.8015
k_2	a_2 38870.318	b_2 93.375744	c_2 -475.71993	d_2 -502315.57	e_2 519752.62
α_2	-36295.356	-87.162836	444.11453	468890.9	-485149.45

The change of k_1 , k_2 , α_1 and α_2 with temperature as shown in Fig. 4, from which it can be seen that the trends of these curves are basically same as the spline curves in Fig. 3.

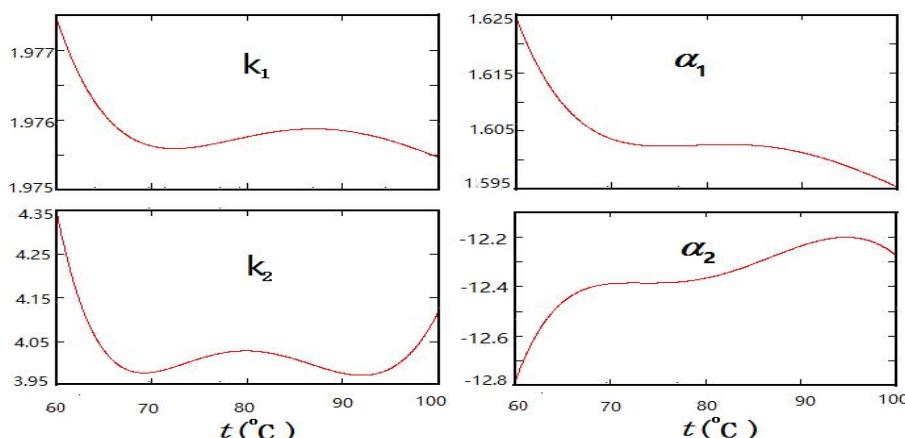


Fig.4 Change of parameters k_1 , k_2 , α_1 and α_2 with temperature

Substituting Eqs. (7-1) and (7-2) into Eqs. (4) and (6), we obtain a set of curves of the osmotic coefficients with the change of temperature at a given concentration. It is only given the curves of the osmotic coefficients against temperature for NaCl solution of $m = 0.5, 1.0, 2.0, 3.0$ and 4.0 in Fig.5. For $m = 4$, an apparent association degree of electrolyte molecules, ε (see Discussions 4.1) should be taken into account. The ε is a function of temperature as ε (mean) = $a + bt^2 + c/\ln(t) + d/t^{0.5}$ with $a = 103.05071$, $b = -5.5981429 \times 10^{-5}$, $c = -816.36304$ and $d = 747.80093$. From Fig. 5, It can be seen that the Φ decrease gradually as temperature increases at a given concentration.

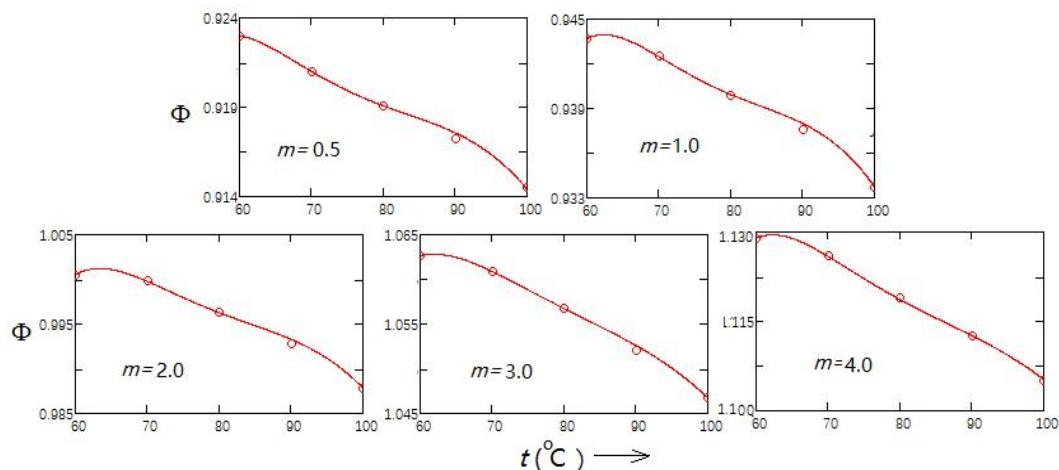


Fig.5 The curves of the osmotic coefficients against temperature for NaCl solution of $m = 0.5, 1.0, 2.0, 3.0$ and 4.0

The osmotic coefficients calculated by Eqs. (7-1) and (7-2) are called as the predicted value, which is expressed by the solid lines in Fig.6. The dotted lines are the values corrected according to data in Table 1 and the black points the experimental value. The three values, predicted, corrected and original, agree quite well. The difference between them all within the experimental uncertainty regardless of the absolute or relative errors. In particular, the curves of the predicted and the corrected almost coincide.

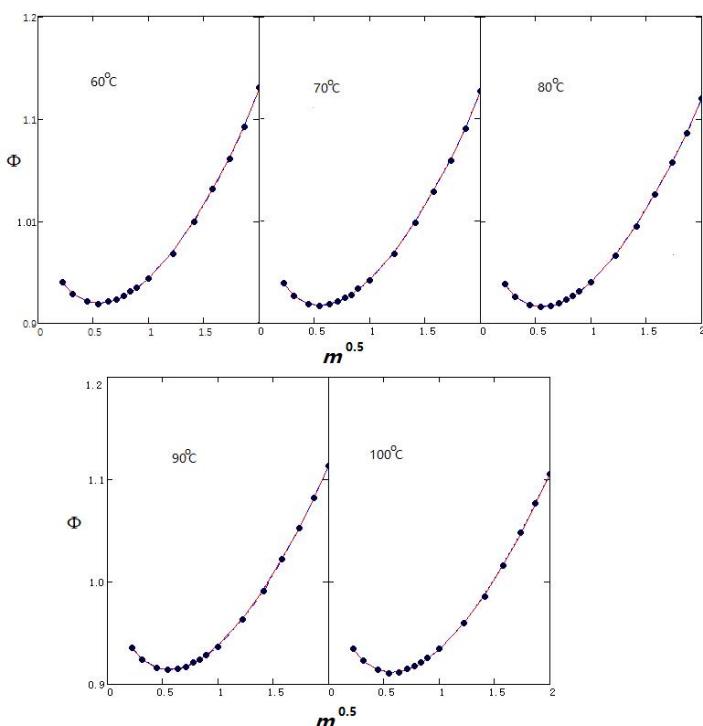


Fig. 6 Plots of Φ vs. $m^{0.5}$ for NaCl solution within 60 to 100°C; black point, original data; dotted line, predicted and solid line, corrected.

IV. Discussions

4.1 Assessment to the osmotic coefficients of NaCl solution

It is known from Table 2 that the difference between the corrected and the original data is not large in most cases ($m < 0.4$), being within the experimental and calculative uncertainty ($0 \sim \pm 0.002$) of the original data except the datum for $m = 1.5$ at 60°C . This error might be an accidental one introduced in the original record or calculation or something else.

However, the difference between the original and the corrected data for $m = 4.0$ at $60, 70, 80$ and 90°C should be considered because they exceed the experimental uncertainty. There are two cases: this may be resulted by measurement errors, or it may be caused by association of electrolyte ions [26, 27], i.e. a locally pseudo-lattice arrangement of solute ions and solvent molecules at high concentrations [1] either. The authors tend to the second case, because the original values are all higher than the corrected, rather than some higher or others lower. In addition, this phenomenon does not appear in KBr solution of $m = 4$ at all (see Appendix). Usually, at the same concentration, the lower the solubility, the more likely it is to form the association of ions. Compared the solubility of both NaCl and KBr in pure water, the latter is significantly greater than the former [29]. Obviously, the ion association would cause abnormal change in the activity. In this case, the osmotic coefficients "corrected" in $m = 4$ for NaCl solution are only an extension of those under complete dissociation in the range of $m = 0.05\text{--}3.5$, not the truly needed data at this concentration. For obtaining truly values, the pseudo-lattice formed must be considered.

Here an apparent association degree of electrolyte molecules, ε [26] is introduced to obtain four data corrected for NaCl solution of $m = 4.0$ at $60, 70, 80$ and 90°C . Let the number of ions be $v(1-\varepsilon)$ in Eq. (5). The osmotic coefficients corrected for these points are $1.128\text{--}1.130, 1.125\text{--}1.127, 1.118\text{--}1.120$ and $1.111\text{--}1.113$ when $\varepsilon = 0.0015\text{--}0.0023, 0.0018\text{--}0.0027, 0.0006\text{--}0.0015$ and $0.00028\text{--}0.0012$ corresponding to $60, 70, 80$ and 90°C , respectively. It can be seen that the ε value increases first, to a maximum, and then decreases within the temperature studied. This reflects a change of the internal structure of the solution with temperature.

4.2 The osmotic coefficients of NaCl solution with temperature

There are two ways to obtain the osmotic coefficients of NaCl solution. One is that the parameters (k_1, k_2, α_1 and α_2) obtained by the linear fitting to the original activities at a given temperature, then these thermodynamic amounts of different concentrations at this temperature can be got by Eqs. (4) and (6). As stated before, these data are called as the corrected ones. Another is these parameters (k_1, k_2, α_1 and α_2) are fitted, respectively, as the temperature functions (Eqs. 7-1 and 7-2), then according to them, the thermodynamic amounts of different temperature at a given concentration can be acquired. These data are called as the predicted ones.

However, the corrected and the predicted values could not be agreed very well sometimes. This may be due to overfitting to the original data in obtaining the corrected values. For example, the thermodynamic parameter k_1 obtained under the condition of statistics $Q^2 = 0.99999996$, could not be sure that Eq. (7-1) has the better results than those at $Q^2 = 0.99999994$. The overfitting to k_1 could make the loss of fitting accuracy of k_1 to temperature t . The other parameters (k_2, α_1 and α_2) have the same situation. In order to acquire the high precision of the activities or the osmotic coefficients and approximately consistent data from two sets of ways, an objective function R is constructed as follow as

$$R = |\Phi_2 - \Phi_1| \quad (8)$$

where Φ_1 and Φ_2 are the corrected and the predicted data, respectively. Both processes (i.e. good linear relation of ω vs. h and good fitting of k_1, k_2, α_1 and α_2 against temperature) run simultaneously by means of a computer under the condition that the difference between Φ_1 and the the original data is less than the experimental uncertainty. When the objective function R is also smaller than the uncertainty of the measured data, for example, $R < 10^{-3}$ in the present research, the optimization ends.

V. Conclusion

Based on the linear relationship between a dimensionless-thermodynamic potential of solvent and the probability-distribution of water in single electrolyte solution, using an optimized method, the corrected osmotic coefficients of NaCl electrolyte solutions at $25, 60, 70, 80, 90$ and 100°C (in Table 2), and the relationships between the osmotic coefficients from 0.05 to 4.0 molalities and temperature within 60 to 100°C (Eqs. 7-1 and 7-2) are obtained. It is shown that all of the experimentally measured data are in the experimental uncertainty except that the error of individual point ($m=1.5$ at 60°C) was caused accidentally. For the NaCl solution of $m=4$ within 60 to 90°C , exists the locally pseudo-lattice arrangement of solute ions and solvent molecules more or less. The present method can be applied for reproduction and prediction well for the osmotic coefficients of the studied system. The recommended method in the present paper would be general to a certain extent.

APPENDIX

The osmotic coefficients for KBr solution

The original data for KBr solution are taken from literature[14]. As the same as NaCl solution, the dimensionless-thermodynamic potential of solvent and the probability-distribution of water in KBr solution are also remarkably correlated linearly, the linear relevance coefficients being over 0.9999999 at all temperature researched. The relative data are given in Table A1 from where it can be acquired that the parameter k_1 and the slope α_1 varies with temperature as

$$P_{A1} = a_{A1} + b_{A1}t + c_{A1}t^{0.5}\ln(t) + d_{A1}t^{-0.5} + e_{A1}\ln(t)/t \quad (\text{A-1})$$

and the parameter k_2 and the intercept α_2 varies with temperature as,

$$P_{A2} = a_{A2} + b_{A2}t + c_{A2}t^2\ln(t) + d_{A2}t^e + e_{A2}t^{0.5}\ln(t) \quad (\text{A-2})$$

where P_{A1} and P_{A2} represent, respectively, k_1 or α_1 and k_2 or α_2 ; t , temperature in Celsius. It can be seen that k_1 and α_1 vary similarly with temperature, so do k_2 and α_2 . The coefficients for Eqs. (A-1) and (A-2) are listed in Table A2. The corrected and original molal osmotic coefficients of KBr solution at different temperature are listed in Table A3. The meaning of the digit in parenthesis of Table A3 is same as Table 2 of text part. The algebra sum of the corrected and the digit in parenthesis is just the original osmotic coefficients given by literature. The curves of the corrected (based on Table A3) and predicted (based on Table A2) Φ for KBr at 60, 70, 80, 90 and 100°C are drawn in Fig. A1 where it can be seen that the corrected, predicted and the original data agree well. The curves of the predicted and the corrected are almost coincide. Both absolute or relative errors are all less than 10^{-4} .

Table A1 The parameters k_1 , k_2 , slope α_1 and intercept α_2 of straight lines of ω against h for KBr solution at 25, 60, 70, 80, 90 and 100°C

	25	60	70	80	90	100°C
k_1	1.975580323	1.972621390	1.975304392	1.975706422	1.976316555	1.975492791
k_2	3.510179734	1.882988101	2.344423191	2.684519231	2.741698789	2.673811699
α_1	1.61238311	1.572798599	1.594079132	1.598135245	1.60040134	1.592532701
α_2	-9.528897378	-8.443789107	-9.040819299	-9.475307827	-9.579353767	-9.474187378

Table A2 Coefficients a , b , c , d and e of Eqs. A-1 and A-2 for k_1 , α_1 , k_2 and α_2 of KBr solution

Parameters	a_{A1}	b_{A1}	c_{A1}	d_{A1}	e_{A1}
k_1	-202.25695	-0.49307712	2.5070876	2636.8078	-2727.2885
α_1	-1379.5932	-3.3447727	16.984495	17822.761	-18430.987
	a_{A2}	b_{A2}	c_{A2}	d_{A2}	e_{A2}
k_2	22.3616	2.4276901	-8.7197978.10 ⁻⁴	1.0504393.10 ⁻⁴⁴	-4.8333287
α_2	-28.745372	-2.5872916	9.4779759.10 ⁻⁴	-9.5006862.10 ⁻⁴⁵	5.094449

Table A3 The corrected and original molal osmotic coefficients for KBr solution at different temperature (digit in parenthesis is that at third decimal place, which plus the corrected value is the original ones)

m	25	60	70	80	90	100°C
0.1	0.928 (0)	0.924 (0)	0.922 (0)	0.922 (0)	0.920 (0)	0.920 (0)
0.2	0.916 (0)	0.913 (0)	0.912 (0)	0.912 (0)	0.911 (0)	0.910 (0)
0.3	0.910 (0)	0.909 (0)	0.909 (0)	0.909 (0)	0.908 (0)	0.907 (0)
0.4	0.907 (-1)	0.908 (0)	0.908 (0)	0.908 (0)	0.907 (0)	0.906 (0)
0.5	0.905 (-1)	0.909 (0)	0.909 (0)	0.909 (0)	0.908 (0)	0.907 (-1)
0.6	0.904 (0)	0.910 (+1)	0.910 (+1)	0.910 (0)	0.909 (0)	0.908 (0)
0.8	0.905 (0)	0.915 (0)	0.915 (0)	0.915 (-1)	0.914 (0)	0.913 (-1)
1.0	0.907 (0)	0.920 (0)	0.921 (-1)	0.920 (0)	0.920 (0)	0.919 (0)

1.5	0.915 (0)	0.937 (-1)	0.937 (0)	0.937 (0)	0.937 (0)	0.935 (+1)
2.0	0.927 (0)	0.954 (-1)	0.955 (0)	0.955 (+1)	0.955 (0)	0.954 (+1)
2.5	0.940 (+1)	0.972 (-1)	0.973(0)	0.973 (+1)	0.974 (0)	0.972 (+1)
3.0	0.954(+1)	0.989 (-1)	0.991 (0)	0.992 (0)	0.993 (-1)	0.991 (+1)
3.5	0.969 (0)	1.005 (0)	1.008 (0)	1.010 (0)	1.011 (-1)	1.009 (+1)
4.0	0.984 (0)	1.020 (+2)	1.024 (+2)	1.027 (+1)	1.029 (-1)	1.027 (+1)

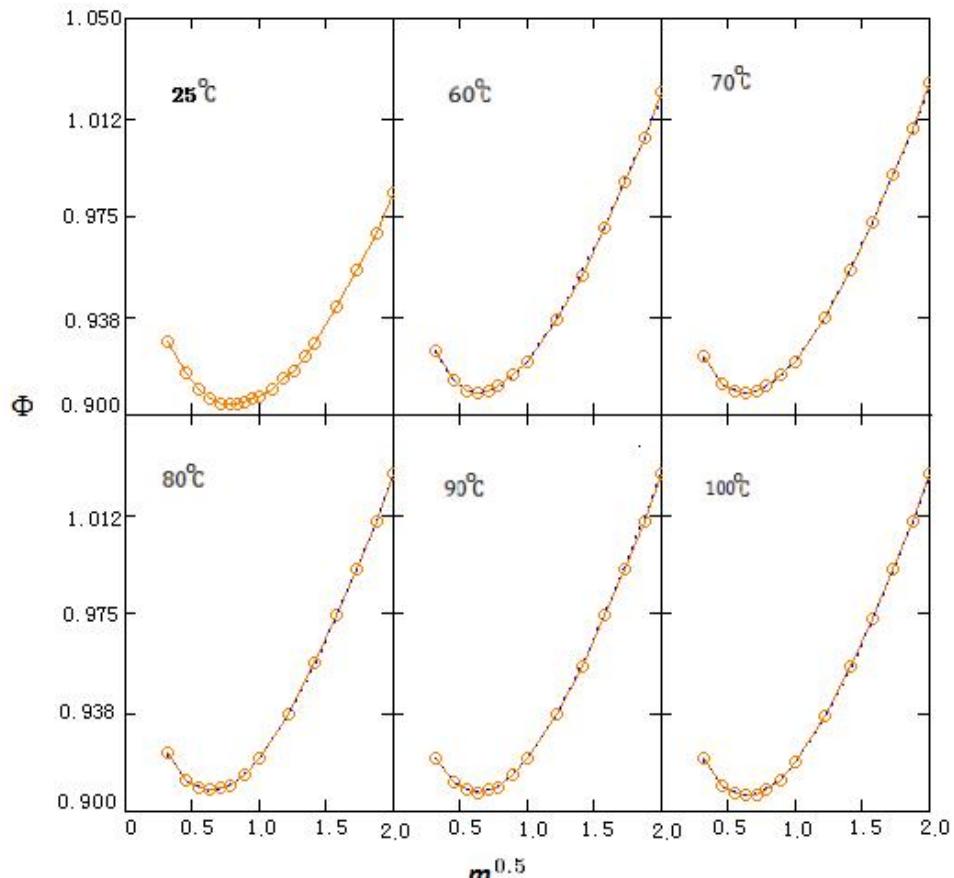


Fig.A1 Plots of Φ vs. $m^{0.5}$ for KBr at 25, 60, 70, 80, 90 and 100°C; circle, original data; solid line, corrected; dotted line, predicted, (there are not the predictive values at 25 °C)

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