

Determination of water activities, osmotic and activity coefficients in aqueous solutions using the hygrometric method

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In the present study we use the hygrometric method for the determination of relative humidities of aqueous electrolyte solutions. The relative humidities of KCl(aq), Na₂SO₄(aq), and NaNO₃(aq) have been measured for different molalities and at temperatures from (278.15 to 323.15) K. The data on the relative humidities allow the deduction of the water activities and the osmotic coefficients at the temperature of 298.15 K. The solute activity coefficients are also determined for the three salts using Pitzer's model. The results obtained by this method are compared with those found in the literature. © 2000 Academic Press

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1. Introduction

The thermodynamic study of aqueous electrolyte solutions is important both for practical and theoretical reasons. Knowledge of the properties of these solutions is required for understanding many important phenomena related to industrial,^(1,2) environmental,⁽³⁾ and geochemical⁽⁴⁾ activities.

For the experimental determination of activity coefficients in aqueous electrolyte solutions, many methods have been widely used. The methods used range from: electromotive force of galvanic cells (e.m.f.),⁽⁵⁾ vapour pressure lowering,^(6–8) isopiestic or vapour pressure equilibration,^(9–12) to freezing temperature depression.^(13,14) Recently, other methods were developed for the study of the properties of electrolyte solutions such as the electro-optic,^(15,16) the piezo-electric,⁽¹⁷⁾ and the electrodynamic balance^(18,19) methods.

In addition to the experimental methods, many theoretical models^(20–23) were formulated in order to explain and predict the experimental behaviour of electrolyte solutions. These models are satisfactory only for dilute or fairly dilute solutions. The acquisition of

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experimental data for concentrated solutions will allow the development of more adequate models.

In this work, we use the hygrometric method⁽²⁴⁾ for determining relative humidities and water activities of non-volatile electrolyte solutions. This method is applied for the middle dilution ($0.1 \text{ mol} \cdot \text{kg}^{-1}$) up to saturation, and at temperatures from about 260 K to 330 K. The relative humidity plays an important role in the study of phase changes and the growth of aerosols. The development of methods based on the relative humidity also facilitates the understanding of atmospheric processes.^(25–28)

The measurements of relative humidities for specified molalities over the temperature range (278.15 to 323.15) K were performed on KCl(aq), Na₂SO₄(aq), and NaNO₃(aq). The osmotic coefficients of the aqueous solutions were evaluated from the relative humidities at the temperature of 298.15 K. The activity coefficients were also determined at this temperature using Pitzer's model.

2. Experimental

The apparatus used is a hygrometer in which a droplet of salt solution⁽²⁴⁾ is maintained on a thin thread. The diameter measurement of previously calibrated droplets permits the knowledge of the relative humidity of aqueous solutions.

In order to avoid distortion of the droplets by the thread, we have used a spider thread of about $0.1 \text{ } \mu\text{m}$ in diameter.^(29–31) The droplets are deposited on the thread by pulverization. The thread is kept tense over a perspex support which is fixed to a cup containing the selected solution (figure 1). The cup is then placed in a wood box whose temperature is regulated by a precision temperature controller. The thermostatted wood box is placed in a regulated chest freezer. The temperature inside the wood box is maintained constant by circulating air with the help of two fans. Two electrical resistances are used for heating the circulated air. The fluctuations of the temperature inside the wood box are kept within $\pm 0.02 \text{ K}$ of the specified temperature. The droplet diameter is measured by a microscope with an ocular equipped with a micrometric screw.

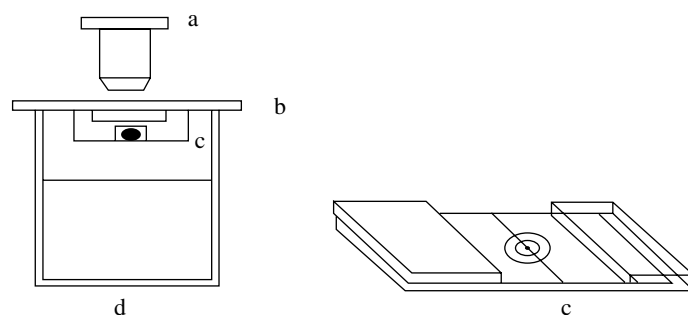


FIGURE 1. Hygrometric apparatus: a, microscope; b, lid; c, thread support; d, cup.

Drops of sodium or lithium chloride solutions were used in the experiments. These chlorides allow a large region of relative humidity to be covered. From the available literature data on the vapour pressures or water activities and the densities of reference solutions,^(9, 24, 32, 33) the dependence of the relative humidity on the molar concentration of the solution is obtained. This dependence allows the variation of the diameter of the drops of the reference solutions to be related to the surrounding relative humidity.

The relative humidity of a salt solution is identified practically with the water activity of the solution. By considering the equality of chemical potential of water in the solution and the surrounding vapour the following relation is obtained:

$$a_w = p_w / p_w^0, \quad (1)$$

where p_w is the partial pressure of the water vapour over the salt solution at temperature T and p_w^0 is the saturation vapour pressure of pure water at the same temperature.

The volume of a droplet of a reference solution with a spherical diameter D is given by

$$V = (4/3)\pi(D/2)^3. \quad (2)$$

The volume of this droplet containing a constant number of moles of solute varies during water condensation or evaporation, causing an increase or decrease in its diameter. By taking the value of relative humidity 0.84 as a reference, we can establish a relation between the ratio of growth K of the droplets and their diameters. This ratio is given by

$$K = D(a_w) / D(a_{\text{ref}} = 0.84), \quad (3)$$

where $D(a_{\text{ref}})$ and $D(a_w)$ are the diameters of the droplets at the reference relative humidity of 0.84 and at the unknown relative humidity a_w , respectively. Equation (3) enables us to relate K to the amount concentration using the relation

$$c = n / V, \quad (4)$$

where c is the amount concentration of the solution constituting the droplet and n is the number of moles of solute which remains constant in this droplet. Thus, we obtain

$$K = \{c(a_{\text{ref}}) / c(a_w)\}^{1/3}, \quad (5)$$

where $c(a_{\text{ref}})$ and $c(a_w)$ are the amount concentrations at the reference humidity of 0.84 and at the amount concentration at the relative humidity a_w , respectively.

The functional relation between the diameter of the droplet and the relative humidity was determined by calibration experiments in which a suspended droplet of NaCl(aq) in the vapour phase was equilibrated with a solution of NaCl(aq) contained in the cup under the same vapour pressure. Similar calibration experiments were performed with LiCl(aq) drops and solutions. In the subsequent experiments, the solution under test was placed in the cup and then equilibrated with a suspended drop of NaCl(aq) or LiCl(aq) which served as a standard. The unknown relative humidity can therefore be determined from measurement of the drop equilibrium diameter $D(a_w)$ at this humidity. Knowing the diameter $D(a_w = 0.84)$ of this droplet at the reference relative humidity of 0.84, we can then calculate K and determine graphically the value of a_w . The values of the ratio of growth K calculated from equation (5) for reference NaCl(aq) and LiCl(aq) are listed in tables 1 and 2.

TABLE 1. Ratio K and corresponding relative humidity a_w at different molalities m of LiCl(aq)

$m/\text{mol} \cdot \text{kg}^{-1}$	K	a_w	$m/\text{mol} \cdot \text{kg}^{-1}$	K	a_w	$m/\text{mol} \cdot \text{kg}^{-1}$	K	a_w
0.10	3.031	0.99 ₆₆	5.14	0.891	0.73	9.95	0.736	0.41
0.20	2.540	0.99 ₃₂	5.41	0.877	0.71	10.27	0.730	0.39
0.36	2.095	0.99	5.70	0.864	0.69	10.60	0.723	0.37
0.95	1.522	0.97	6.00	0.851	0.67	10.94	0.718	0.35
1.40	1.341	0.95	6.31	0.838	0.65	11.32	0.711	0.33
1.80	1.237	0.93	6.61	0.827	0.63	11.70	0.705	0.31
2.19	1.162	0.91	6.90	0.817	0.61	12.14	0.698	0.29
2.59	1.101	0.89	7.16	0.808	0.59	12.65	0.690	0.27
2.99	1.052	0.87	7.41	0.800	0.57	13.20	0.683	0.25
3.35	1.016	0.85	7.67	0.792	0.55	13.79	0.675	0.23
3.52	1.000	0.84	7.97	0.784	0.53	14.41	0.667	0.21
3.68	0.986	0.83	8.31	0.774	0.51	15.10	0.660	0.19
4.03	0.959	0.81	8.64	0.766	0.49	15.95	0.651	0.17
4.37	0.936	0.79	8.97	0.758	0.47	16.95	0.641	0.15
4.63	0.919	0.77	9.31	0.750	0.45	18.12	0.631	0.13
4.87	0.906	0.75	9.62	0.743	0.43	18.86	0.625	0.12

TABLE 2. Ratio K and corresponding relative humidity a_w at different molalities m of NaCl(aq)

$m/\text{mol} \cdot \text{kg}^{-1}$	K	a_w
0.10	3.359	0.99 ₆₆
0.20	2.659	0.99 ₃₄
0.30	2.356	0.99 ₀
0.90	1.639	0.97 ₀
1.49	1.391	0.95
2.05	1.257	0.93
2.58	1.167	0.91
3.09	1.103	0.89
3.55	1.056	0.87
4.01	1.018	0.85
4.24	1.000	0.84
4.46	0.985	0.83
4.90	0.957	0.81
5.33	0.934	0.79
5.74	0.913	0.77
6.14	0.895	0.75

Figure 2 shows the variation of the ratio K as a function of the relative humidity of NaCl(aq) and LiCl(aq). For relative humidities of greater than 0.75 a solution of NaCl or LiCl is used, while for relative humidities of less than 0.75 a solution of LiCl is used. It should be emphasized that the determination of the relative humidity by this method is more precise as the humidity values increase. The relative error incurred in the measurements of the relative humidity is due essentially to the uncertainty of the measured diameters drops ($\approx \pm 0.25$ per cent). The relative error incurred in the relative humidity measurements is therefore $\approx \pm 0.02$ per cent for $a_w > 0.97$, ± 0.05 per cent for $a_w > 0.95$, ± 0.09 per cent for $a_w > 0.90$, ± 0.2 per cent for $a_w > 0.85$, and about ± 0.5 per cent for $a_w > 0.75$. The measurements require precautions such as temperature stability and attainment of hygrometric equilibrium.

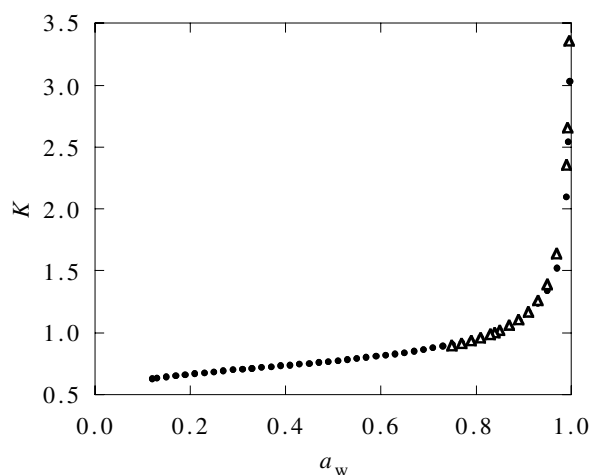


FIGURE 2. Variation of the ratio K of diameters of the droplets as a function of the relative humidity a_w for: ●, LiCl; △, NaCl.

3. Results and discussion

Measurements of droplet diameters as a function of relative humidity were performed for KCl(aq), Na₂SO₄(aq), and NaNO₃(aq) with NaCl(aq) serving as the reference electrolyte. The solutions were prepared from Merck extrapur-grade chemicals and deionized distilled water. In most cases, measurements for a given solution were made on several droplets. The molality of the sample solution held in the cup was determined by measuring its refractive index.

In order to determine the time required to attain hygrometric equilibrium by the droplets under different humidity conditions, we have made measurements of the diameter of droplets at regular time intervals until their stabilization. Curves of droplet growth as a

function of time are drawn for KCl(aq) , $\text{Na}_2\text{SO}_4\text{(aq)}$, and $\text{NaNO}_3\text{(aq)}$. The drop diameter variations as a function of time for different relative humidities ranging from (0.80 to 0.98) and at the temperature of 298.15 K are illustrated in figures 3, 4, and 5. The drop diameters increase rapidly with time until equilibrium is reached and they remain constant. The equilibrium diameters permit the ratio K which corresponds to the relative humidity of the studied solution to be determined.

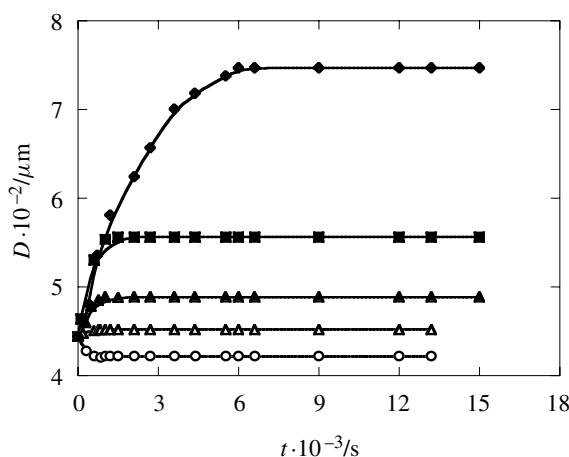


FIGURE 3. Variation of the diameter D of NaCl droplets as a function of time for KCl(aq) at constant relative humidity a_w of: \blacklozenge , $a_w = 0.98$; \blacksquare , $a_w = 0.93$; \blacktriangle , $a_w = 0.89$; \triangle , $a_w = 0.85$; \circ , $a_w = 0.80$.

Attainment of hygrometric equilibrium by a droplet above a solution depends on the relative humidity condition of the solution. This time varies from 10 min for $a_w = 0.85$ to 90 min for $a_w = 0.98$. The growth of the droplet is due to the superposition of two phenomena: the growth of the droplet itself and the establishment of hygrometric equilibrium in the cup containing the solution.

It was noted that for diluted solutions, having important water activities, the equilibrium diameter was high in comparison with that of concentrated solutions. This behaviour can be understood by recognizing that, at low concentration, the amount of water molecules bound to the ions is not big and the number of water molecules that escape to the vapour phase is important. The molecules in the vapour phase condense on the drop which acts as a center of nucleation. The water vapour pressure above the solution increases above that of the drop and hence the diameter increases through condensation. This process occurs for solutions with relative humidities (0.98, 0.95, 0.90, and 0.85) higher than those of the reference drop (0.84). Conversely, evaporation from the droplet takes place if its water vapour pressure is greater than that of the surrounding atmosphere (*i.e.* for relative humidities < 0.84). Such evaporation reduces the diameter of the drop.

Equilibrium times in the hygrometric method are short by comparison with other

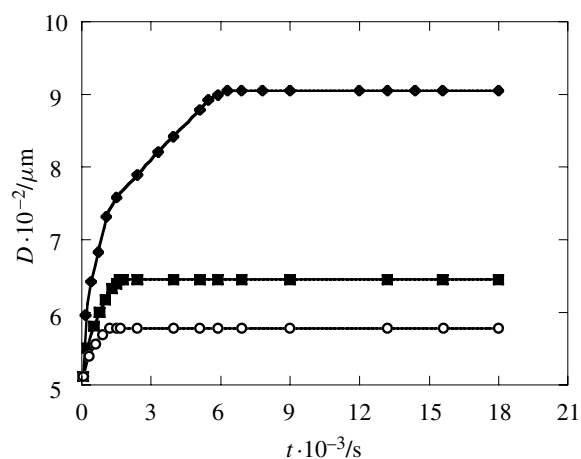


FIGURE 4. Variation of the diameter D of NaCl droplets as a function of time for $\text{Na}_2\text{SO}_4(\text{aq})$ at constant relative humidity a_w of: \blacklozenge , $a_w = 0.98$; \blacksquare , $a_w = 0.93$; \circ , $a_w = 0.90$.

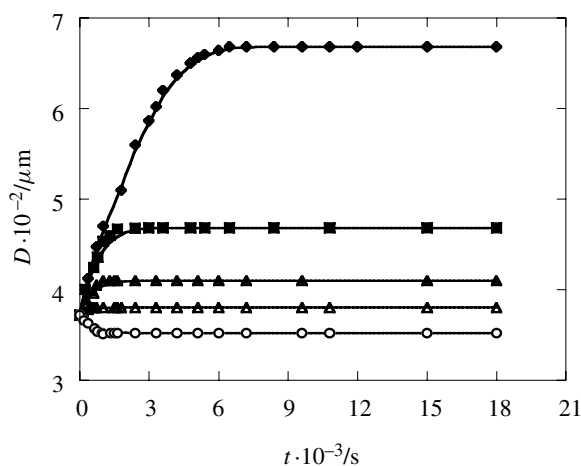


FIGURE 5. Variation of the diameter D of NaCl droplets as a function of time for $\text{NaNO}_3(\text{aq})$ at constant relative humidity a_w of: \blacklozenge , $a_w = 0.98$; \blacksquare , $a_w = 0.93$; \blacktriangle , $a_w = 0.89$; \triangle , $a_w = 0.85$; \circ , $a_w = 0.80$.

techniques. Measurements can therefore be carried out quickly in contrast to the isopiestic method, for example where equilibrium is reached only after several days for a given activity.^(10, 34)

The variation of the relative humidity as a function of temperature was measured at the following molalities: (0.5, 2, and 4) $\text{mol} \cdot \text{kg}^{-1}$ for three different salts over the temperature range (278.15 to 323.15) K. The experimental results are shown in figures 6, 7, and 8. One

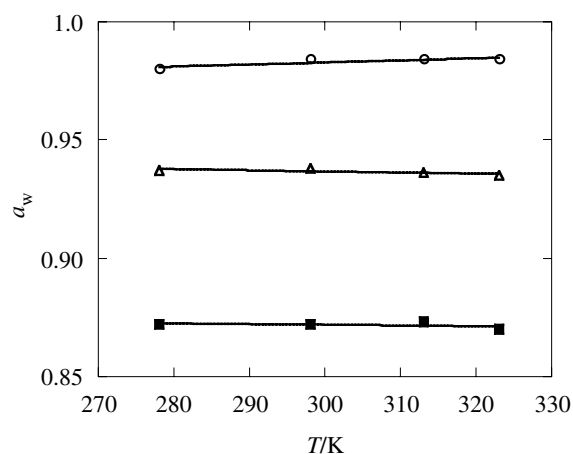


FIGURE 6. Variation of the relative humidity a_w of KCl as a function of temperature at different molalities m : \circ , $m = 0.5 \text{ mol} \cdot \text{kg}^{-1}$; \triangle , $m = 2 \text{ mol} \cdot \text{kg}^{-1}$; \blacksquare , $m = 4 \text{ mol} \cdot \text{kg}^{-1}$.

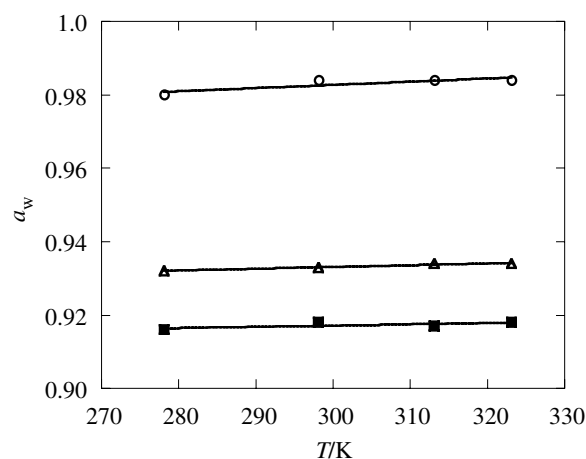


FIGURE 7. Variation of the relative humidity a_w of Na_2SO_4 as a function of temperature at different molalities m . \circ , $m = 0.5 \text{ mol} \cdot \text{kg}^{-1}$; \triangle , $m = 2 \text{ mol} \cdot \text{kg}^{-1}$; \blacksquare , $m = 4 \text{ mol} \cdot \text{kg}^{-1}$.

can conclude that the variation of the relative humidity with the temperature is very small (less than 0.2 per cent) and is within the experimental uncertainty over this temperature range.

We have made measurements of the relative humidity at $T = 298.15 \text{ K}$ for different molalities of the studied solutions. The uncertainty in the relative humidity depends on the measurement accuracy of the diameter of the droplets and is approximately between $(\pm 5 \cdot 10^{-4})$ and $(\pm 2 \cdot 10^{-3})$ over the molality range for the three investigated systems. The increasing error may be due to lower sensitivity of the values of K to changes

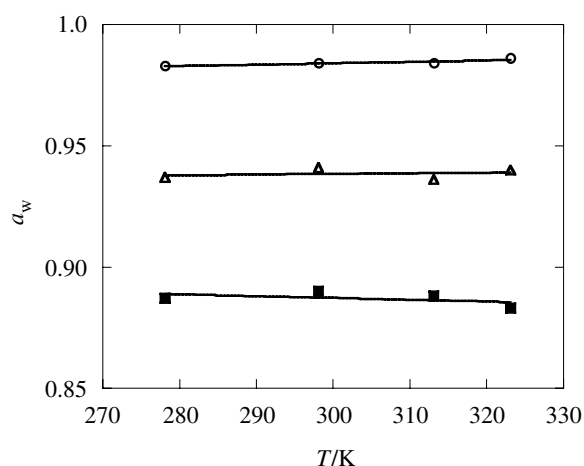


FIGURE 8. Variation of the relative humidity a_w of NaNO_3 as a function of temperature at different molalities m . \circ , $m = 0.5 \text{ mol} \cdot \text{kg}^{-1}$; \triangle , $m = 2 \text{ mol} \cdot \text{kg}^{-1}$; \blacksquare , $m = 4 \text{ mol} \cdot \text{kg}^{-1}$.

in a_w when this ratio decreases. The experimental values of the water activities are represented in figures 9, 10, and 11. Literature data are also shown in the figures. Where the present results can be compared with literature data, the agreement is generally within the experimental uncertainty. For the three salts, we note also an activity lowering when the solution concentration increases. This phenomenon is due to an increase in the number of water molecules associated to the different ions in the solution. Consequently, under thermodynamic equilibrium, the proportion of water molecules passing into the vapour phase decreases.

The ion interaction model developed for electrolytes by Pitzer⁽²¹⁾ has been shown to represent adequately the activity coefficients as functions of molalities. The expressions for the osmotic and activity coefficients ϕ and γ for electrolytes of the 1–1 type are given by

$$\phi = 1 + f^\phi + mB^\phi + m^2C^\phi, \quad (6)$$

$$\ln \gamma = f^\gamma + mB^\gamma + m^2C^\gamma, \quad (7)$$

and for electrolytes of the 1–2 type by

$$\phi = 1 + 2f^\phi + (4/3)mB^\phi + (2^{5/2}/3)m^2C^\phi, \quad (8)$$

$$\ln \gamma = 2f^\gamma + (4/3)mB^\gamma + (2^{5/2}/3)m^2C^\gamma. \quad (9)$$

The quantities f , B , and C were calculated from reference 21.

Using the obtained experimental data for the water activity as a function of molality, we have evaluated the osmotic coefficients for each of the investigated electrolytes. Considering the uncertainty in determining the relative humidity, the overall uncertainty of the osmotic coefficient is estimated to be, at most, $\pm 6 \cdot 10^{-3}$ in the present results. The measured values of the osmotic coefficient of the three systems agree with literature values

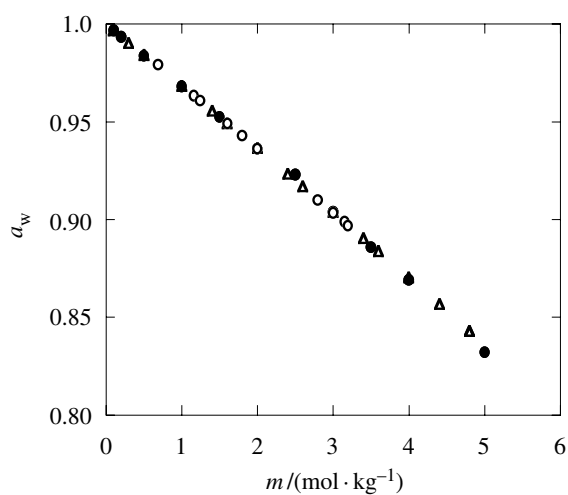


FIGURE 9. Water activity a_w of KCl against molality m at $T = 298.15$ K. ●, Experimental data; △, reference 9; ○, reference 36.

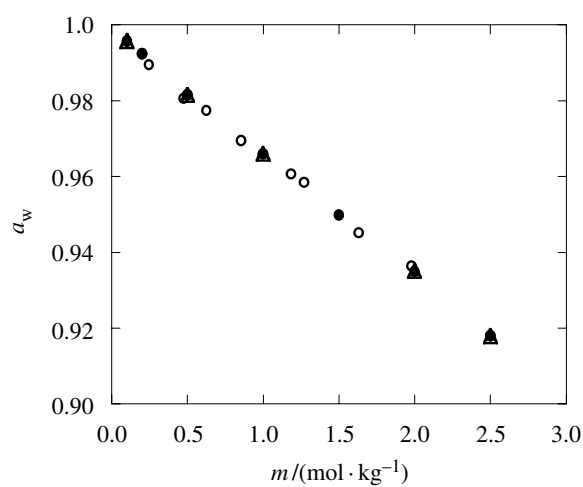


FIGURE 10. Water activity a_w of Na_2SO_4 against molality m at $T = 298.15$ K. ●, Experimental data; ○, reference 6; △, reference 9.

to within $\pm(1 \cdot 10^{-3}$ to $9 \cdot 10^{-3})$, with an average difference of $\pm 6 \cdot 10^{-3}$, and are hence reasonably accurate. The results are listed in tables 3, 4, and 5.

The data on osmotic coefficients have been used to determine the three Pitzer's parameters $\beta^{(0)}$, $\beta^{(1)}$, and C^ϕ in equations (6) and (8) over the molality range studied in this

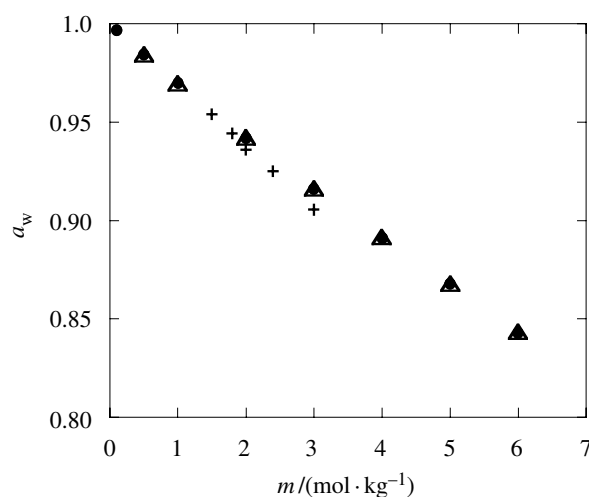


FIGURE 11. Water activity a_w of NaNO_3 against molality m at $T = 298.15$ K. ●, Experimental data; \triangle , reference 9; +, reference 14.

TABLE 3. Osmotic coefficient ϕ , activity coefficient γ , and absolute difference Δ at different molalities m of $\text{KCl}(\text{aq})$ at $T = 298.15$ K

$m / \text{mol} \cdot \text{kg}^{-1}$	K	$\phi_{(\text{expt})}^a$	$\phi_{(\text{calc})}^b$	Δ^c	γ^a	γ^d	Δ^e
0.1	3.405	0.917	0.926	0.009	0.767	0.770	0.003
0.2	2.665	0.905	0.913	0.008	0.716	0.718	0.002
0.5	2.015	0.901	0.899	0.002	0.648	0.649	0.001
1.0	1.607	0.896	0.897	0.001	0.602	0.604	0.002
1.5	1.412	0.900	0.903	0.003	0.581	0.583	0.002
2.0	1.292	0.913	0.913	0.000	0.571	0.573	0.002
2.5	1.207	0.924	0.925	0.001	0.568	0.569	0.001
3.0	1.145	0.934	0.939	0.005	0.569	0.569	0.000
3.5	1.093	0.950	0.954	0.004	0.573	0.572	0.001
4.0	1.054	0.974	0.971	0.003	0.579	0.577	0.002

^aThis work; ^bcalculated from equation (6); ^cabsolute difference between experimental and calculated values of the osmotic coefficient; ^dreference 9; ^eabsolute difference between calculated and literature values of the activity coefficient.

work using a least-squares fit. The calculated values are compared with those reported by Pitzer and Mayorga⁽³⁵⁾ and the results are listed in table 6. The standard deviations for these parameters are less than $5 \cdot 10^{-3}$. The standard deviations for the quantity $\phi_{(\text{calc})} - \phi_{(\text{expt})}$ are $4.6 \cdot 10^{-3}$ for $\text{KCl}(\text{aq})$, $5.8 \cdot 10^{-3}$ for $\text{Na}_2\text{SO}_4(\text{aq})$, and $4.4 \cdot 10^{-3}$ for $\text{NaNO}_3(\text{aq})$, respectively.

TABLE 4. Osmotic coefficient ϕ , activity coefficient γ , and absolute difference Δ at different molalities m of $\text{Na}_2\text{SO}_4(\text{aq})$ at $T = 298.15 \text{ K}$

$m/\text{mol} \cdot \text{kg}^{-1}$	K	$\phi_{(\text{expt})}^a$	$\phi_{(\text{calc})}^b$	Δ^c	γ^a	γ^d	Δ^e
0.1	3.045	0.797	0.790	0.007	0.450	0.452	0.002
0.2	2.505	0.743	0.751	0.008	0.369	0.371	0.002
0.5	1.920	0.691	0.690	0.001	0.269	0.270	0.001
1.0	1.575	0.640	0.643	0.003	0.204	0.204	0.000
1.5	1.391	0.632	0.624	0.008	0.173	0.172	0.001
2.0	1.285	0.621	0.621	0.000	0.155	0.154	0.001
2.5	1.198	0.633	0.626	0.007	0.143	0.144	0.001

^aThis work; ^bcalculated from equation (8); ^cabsolute difference between experimental and calculated values of the osmotic coefficient; ^dreference 9; ^eabsolute difference between calculated and literature values of the activity coefficient.

TABLE 5. Osmotic coefficient ϕ , activity coefficient γ , and absolute difference Δ at different molalities m of $\text{NaNO}_3(\text{aq})$ at $T = 298.15 \text{ K}$

$m/\text{mol} \cdot \text{kg}^{-1}$	K	$\phi_{(\text{expt})}^a$	$\phi_{(\text{calc})}^b$	Δ^c	γ^a	γ^d	Δ^e
0.1	3.405	0.917	0.918	0.001	0.754	0.762	0.008
0.2	2.665	0.905	0.899	0.006	0.695	0.703	0.008
0.5	2.040	0.867	0.871	0.004	0.608	0.617	0.009
1.0	1.639	0.845	0.848	0.003	0.539	0.548	0.009
2.0	1.328	0.829	0.824	0.005	0.470	0.478	0.008
3.0	1.190	0.811	0.811	0.000	0.431	0.437	0.006
4.0	1.106	0.801	0.802	0.001	0.403	0.408	0.005
5.0	1.052	0.786	0.795	0.009	0.383	0.386	0.003
6.0	1.005	0.790	0.788	0.002	0.366	0.371	0.005

^aThis work; ^bcalculated from equation (6); ^cabsolute difference between experimental and calculated values of the osmotic coefficient; ^dreference 9; ^eabsolute difference between calculated and literature values of the activity coefficient.

With the obtained Pitzer's parameters, the solute activity coefficient for each salt can be predicted by using equation (7) for $\text{KCl}(\text{aq})$ and $\text{NaNO}_3(\text{aq})$, and equation (9) for $\text{Na}_2\text{SO}_4(\text{aq})$ (tables 3 to 5). The resulting activity coefficients have been compared with literature values.⁽⁹⁾ Good agreement is obtained with an average difference of $\pm 2 \cdot 10^{-3}$ for $\text{KCl}(\text{aq})$, $\pm 1 \cdot 10^{-3}$ for $\text{Na}_2\text{SO}_4(\text{aq})$, and $\pm 7 \cdot 10^{-3}$ for $\text{NaNO}_3(\text{aq})$.

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TABLE 6. Pitzer's parameters $\beta^{(0)}$, $\beta^{(1)}$, and C^ϕ for KCl(aq), Na₂SO₄(aq), and NaNO₃(aq)

	KCl(aq)	Na ₂ SO ₄ (aq)	NaNO ₃ (aq)
$\beta^{(0)}$	0.04631 (0.04835)	0.02963 (0.01957)	0.00788 (0.00680) ^a
$\beta^{(1)}$	0.21568 (0.21220)	1.01092 (1.11300)	0.13966 (0.17830)
C^ϕ	0.00003 (-0.00084)	0.00171 (0.00497)	-0.00060 (-0.00072)

^aNumbers in bracket are from reference 35.

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