

# Temperature Dependence of Vapor Pressures over Saturated Aqueous Solutions at Invariant Points of the NaCl + KCl + H<sub>2</sub>O, NaCl + NaNO<sub>3</sub> + H<sub>2</sub>O, KCl + KBr + H<sub>2</sub>O, KCl + KI + H<sub>2</sub>O, KCl + KNO<sub>3</sub> + H<sub>2</sub>O, and KCl + K<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O Systems<sup>†</sup>

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Vapor pressures of water over saturated solutions with regard to two salts, in the NaCl + KCl + H<sub>2</sub>O, NaCl + NaNO<sub>3</sub> + H<sub>2</sub>O, KCl + KBr + H<sub>2</sub>O, KCl + KI + H<sub>2</sub>O, KCl + KNO<sub>3</sub> + H<sub>2</sub>O, and KCl + K<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O systems, are reported in the (278 to 323) K temperature range. The determined vapor pressures served to obtain the water activities, the osmotic coefficients, and the molar enthalpies of vaporization.

## 1. Introduction

The thermodynamic analysis of aqueous solutions of alkali metal halides, nitrates, and sulfates is of significant importance in many natural and industrial processes, and therefore considerable attention in the literature has been directed to binary, ternary, and multicomponent inorganic salt–water systems. The interest in accurate description of thermodynamic properties of aqueous solutions arises from the need to simulate salt precipitation, evaporation of water from salt solutions, concentration, dilution, and mixing under various conditions in geological processes and in industrial procedures. Solubilities, activities, thermal, volumetric, and many other properties have been investigated, mostly in binary systems and evidently much less in systems with more components. From the enormous number of investigations devoted to various aspects and properties of the ternary systems considered here, it is possible to mention only a small part<sup>1–37</sup> (for more comprehensive lists, see various tabulations of data<sup>38–45</sup>). In these systems, only solubilities (phase diagrams) are documented in the literature rather than other physicochemical properties. Usually, desired properties are estimated from developed thermodynamic models by a suitable change in values of parameters taken from binary systems or from model considerations involving activity and osmotic coefficients in ternary systems.<sup>6,9–15,17,18,20–25,36</sup>

Even in the case of the most investigated system, NaCl + KCl + H<sub>2</sub>O, the reported vapor pressure measurements are rather rare. From the direct experimental determinations of vapor pressures, it is worthwhile to mention the measurements of Marcus and Soffer<sup>28</sup> at 298.15 K and at (303.15 to 313.15) K<sup>31</sup> and of Shiah and Tseng<sup>34</sup> at (298.15 to 343.15) K. Hygroscopic determinations of water activities at 298.15 K were performed by Dinane et al.<sup>35</sup>

However, relevant to the subject of this work, for the vapor pressures over aqueous solutions which are saturated with both salts (invariant points), only those determined by Leopold and Johnston<sup>1</sup> for the NaCl + KCl + H<sub>2</sub>O system at (295.34 to 304.23) K, reported by Winston and Bates at (293.15, 298.15, and 303.15) K,<sup>4</sup> and reported by Adams and Merz<sup>2</sup> and Harvie

et al.<sup>21</sup> at 298.15 K exist in the literature. Some information about vapor pressures in binary systems exists, but usually at 298.15 K, in tabulations of saturated solutions which are used to control humidity in biological experiments.<sup>4,5,7,8,43</sup>

In the continuation of studies on the vapor pressure of water saturated with one inorganic salt,<sup>46–57</sup> in this work the saturated solutions in ternary systems in the  $T = 278$  K to  $T = 322$  K temperature range are considered. Determined vapor pressures are also expressed in terms of the water activities  $a_1$  and by combining them with solubilities (taken from the literature) in terms of osmotic coefficients  $\phi$ .

## 2. Experimental

Purum. p.a. reagents (>99 mass percent) sodium chloride, sodium nitrate, potassium chloride, potassium bromide, potassium iodide, potassium nitrate, and potassium sulfate were from Merck or Sigma. All reagents were used in experiments without further purification.

The vapor pressures over saturated solutions were determined using a Rotronic Hygroskop DT1 instrument which was equipped with a measuring station WA-14TH. Since in the investigated systems hydrates are not formed in the solid phase, the saturation was assured by the prolonged mixing of the aqueous phase with excess amounts of both solid salts. The change of temperature was obtained by an external mantle of the measuring station which was heated or cooled by running water from an external thermostat. The thermal stability of the measuring system is estimated to be  $\pm 0.05$  K, and the sensitivity of the used electronic hygrometer is about  $\pm 0.003$  kPa at  $T = 298.15$  K. The employed procedure is similar to that described elsewhere.<sup>46</sup>

## 3. Results and Discussion

The vapor pressures of water over saturated aqueous solutions with regard to two salts, NaCl + KCl, NaCl + NaNO<sub>3</sub>, KCl + KBr, KCl + KI, KCl + KNO<sub>3</sub>, and KCl + K<sub>2</sub>SO<sub>4</sub>, as a function of temperature are presented in Table 1.

If the aqueous solution is saturated with two nonvolatile solutes (i.e., at constant chemical potentials  $\mu_i$ ), the change of vapor pressure  $p$  with temperature  $T$  can be expressed by the Clausius–Clapeyron equation in the form

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<sup>†</sup> Part of the “Gerhard M. Schneider Festschrift”.

$$\left(\frac{dp}{dT}\right)_{\mu_i} = \frac{x_1\Delta\bar{H}_1 + x_2\Delta\bar{H}_2 + x_3\Delta\bar{H}_3}{T[x_1\Delta\bar{V}_1 + x_2\Delta\bar{V}_2 + x_3\Delta\bar{V}_3]}$$

$$\Delta\bar{H}_1 = \bar{H}_1^G - \bar{H}_1^L; \Delta\bar{V}_1 = \bar{V}_1^G - \bar{V}_1^L$$

$$\Delta\bar{H}_2 = \bar{H}_2^S - \bar{H}_2^L; \Delta\bar{V}_2 = \bar{V}_2^S - \bar{V}_2^L$$

$$\Delta\bar{H}_3 = \bar{H}_3^S - \bar{H}_3^L; \Delta\bar{V}_3 = \bar{V}_3^S - \bar{V}_3^L$$

$$x_1 + x_2 + x_3 = 1; i = 1, 2, 3 \quad (1)$$

which generalizes the Modell and Reid<sup>58</sup> result for binary systems. In eq 1,  $x_i$  are mole fractions of components in the solution,  $i = 1, 2, 3$ , where 1 is water, 2 is salt 1, and 3 is salt 2.  $\Delta\bar{V}_i$  and  $\Delta\bar{H}_i$  represent changes in the molar volumes and the molar enthalpies of components, and  $G, L$ , and  $S$  denote gaseous, liquid, and solid phases, respectively. Thus, the pressure–temperature change is related to the change in the volume and the enthalpy associated with evaporating  $x_1$  moles of water while simultaneously crystallizing  $x_2$  moles of salt 2 and  $x_3$  moles of

salt 3. However, taking into account that the mole fractions of salts  $x_2$  and  $x_3$  are small compared with that of water  $x_1$  and that the molar volume of water in the gaseous phase (ideal gas) is considerably larger than the molar volumes of all components in the solid and liquid phases, one has

$$\sum_{i=1}^3 x_i\Delta\bar{H}_i \approx x_1\Delta\bar{H}_1 = x_1\Delta\bar{H}$$

$$\sum_{i=1}^3 x_i\Delta\bar{V}_i \approx x_1\Delta\bar{V}_1 \approx x_1\bar{V}_1^G = x_1RT/p \quad (2)$$

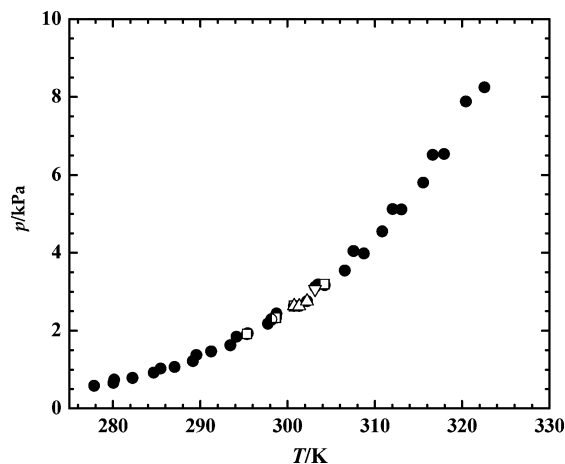
thus, it follows from eq 1 and eq 2 that the Clausius–Clapeyron equation can be approximated by

$$\left(\frac{d \ln p}{dT}\right)_{m_2, m_3} = \frac{\Delta\bar{H}}{RT^2} \quad (3)$$

where the apparent molar enthalpy change is associated with evaporation of water and simultaneous crystallization of salts

**Table 1.** Vapor Pressures  $p$  of Saturated Aqueous Solutions at Temperatures  $T$

$T/K$	$p/kPa$	$T/K$	$p/kPa$	$T/K$	$p/kPa$	$T/K$	$p/kPa$	$T/K$	$p/kPa$	$T/K$	$p/kPa$
NaCl + KCl + H <sub>2</sub> O											
277.85	0.582	295.35	1.909	304.25	3.165	287.05	1.066	300.75	2.635	313.05	5.112
280.05	0.659	295.45	1.932	306.55	3.541	289.15	1.218	300.77	2.641	315.55	5.799
280.15	0.743	297.75	2.177	307.55	4.044	289.55	1.378	301.35	2.633	316.65	6.514
282.25	0.786	298.15	2.276	308.75	3.984	291.25	1.466	302.25	2.756	317.95	6.535
284.65	0.923	298.70	2.336	310.85	4.548	293.45	1.625	303.15	3.120	320.45	7.882
285.45	1.029	298.75	2.437	312.05	5.122	294.15	1.843	303.50	3.182	322.55	8.251
NaCl + NaNO <sub>3</sub> + H <sub>2</sub> O											
279.95	0.675	279.95	0.675	317.45	5.531	289.55	1.205	289.55	1.205		
284.65	0.896	284.65	0.896	322.25	6.952	294.25	1.589	294.25	1.589		
KCl + KBr + H <sub>2</sub> O											
279.55	0.775	298.15	2.579	310.05	4.984	287.85	1.350	303.05	3.410	317.55	7.327
281.45	0.885	298.95	2.662	310.65	5.188	290.15	1.562	303.55	3.510	317.85	7.516
281.95	0.922	299.05	2.691	312.05	5.553	290.35	1.595	304.75	3.711	319.15	7.974
282.05	0.924	299.35	2.763	312.55	5.733	292.95	1.852	304.95	3.777	320.75	8.616
283.65	1.034	300.25	2.892	312.85	5.782	294.65	2.067	306.35	4.077	321.75	9.026
285.05	1.122	300.85	3.032	314.35	6.277	294.65	2.057	308.15	4.524	322.35	9.312
285.15	1.132	302.05	3.235	315.45	6.627	296.65	2.323	308.25	4.515	323.35	9.750
286.05	1.210	303.05	3.377	316.85	7.111	296.95	2.383	308.25	4.532		
KCl + KI + H <sub>2</sub> O											
279.85	0.695	293.35	1.634	303.55	2.975	289.95	1.307	298.95	2.293	311.65	4.631
281.45	0.761	294.75	1.793	303.85	3.036	290.25	1.359	300.05	2.443	312.65	4.837
282.25	0.807	295.05	1.811	305.05	3.231	290.65	1.384	300.05	2.443	313.55	5.082
283.55	0.885	295.05	1.806	305.15	3.259	290.95	1.406	300.25	2.465	314.75	5.423
284.75	0.959	296.05	1.941	306.15	3.433	291.05	1.407	301.05	2.575	316.05	5.789
286.15	1.053	296.25	1.945	306.75	3.560	291.85	1.490	301.35	2.636	317.75	6.294
286.95	1.100	296.45	1.977	307.55	3.690	292.05	1.509	302.05	2.741	318.85	6.660
288.65	1.231	297.25	2.087	308.65	3.945	292.15	1.507	302.15	2.761	320.15	7.116
288.75	1.237	297.85	2.151	308.75	3.955	292.75	1.590	302.35	2.773	321.25	7.556
288.75	1.212	298.65	2.249	310.05	4.253	292.95	1.596	303.25	2.912	322.55	8.064
289.75	1.290	298.75	2.269	310.35	4.298						
KCl + KNO <sub>3</sub> + H <sub>2</sub> O											
279.05	0.738	294.25	2.070	308.85	4.707	288.15	1.410	300.05	2.890	318.95	7.843
280.85	0.846	294.25	2.075	310.95	5.279	289.75	1.566	301.45	3.155	320.95	8.604
281.35	0.905	295.45	2.216	312.55	5.683	289.85	1.578	302.95	3.454	322.15	9.067
283.65	1.036	296.55	2.366	313.35	5.923	291.35	1.766	303.55	3.514	322.75	9.379
284.05	1.082	298.25	2.607	315.45	6.577	292.25	1.811	304.95	3.820	324.75	10.313
285.75	1.209	298.85	2.722	316.45	6.929	292.95	1.940	307.15	4.306		
285.95	1.214	299.65	2.864	316.95	7.103	293.75	2.000	307.85	4.460		
KCl + K <sub>2</sub> SO <sub>4</sub> + H <sub>2</sub> O											
280.15	0.852	298.15	2.697	309.65	5.078	291.15	1.757	303.65	3.652	316.95	7.616
282.95	1.018	298.55	2.739	310.15	5.243	293.85	2.073	304.25	3.815	317.45	7.714
284.15	1.104	298.95	2.844	310.65	5.394	294.45	2.161	305.55	4.063	318.45	8.141
284.85	1.173	298.95	2.818	311.55	5.724	295.15	2.232	306.35	4.291	320.15	8.847
285.35	1.221	299.65	2.937	311.75	5.690	295.85	2.334	307.85	4.715	321.55	9.483
286.25	1.286	300.35	3.082	311.85	5.749	297.05	2.513	308.05	4.694	323.45	10.387
288.25	1.457	301.45	3.225	313.25	6.152	297.15	2.519	308.35	4.756		
289.65	1.597	302.85	3.517	313.95	6.508	297.25	2.537	308.65	4.795		
289.95	1.634	303.45	3.697	316.05	7.191						



**Figure 1.** Vapor pressures  $p$  of saturated aqueous solutions of sodium chloride and potassium chloride as a function of temperature  $T$ .  $\square$ , ref 1;  $\nabla$ , ref 2;  $\triangle$ , ref 4;  $\circ$ , ref 21; and  $\bullet$ , this work.

**Table 2. Coefficients of Equation 4: Vapor Pressures of Saturated Aqueous Solutions**

system	$A$	$B$	$C$	$\sigma(p)/\text{kPa}$
NaCl + KCl + H <sub>2</sub> O	89.254	-8509.7	-10.514	0.120
NaCl + NaNO <sub>3</sub> + H <sub>2</sub> O	19.689	-5100.7	-0.3319	0.015
KCl + KBr + H <sub>2</sub> O	84.584	-8190.8	-9.859	0.018
KCl + KI + H <sub>2</sub> O	59.245	-7030.9	-6.123	0.014
KCl + KNO <sub>3</sub> + H <sub>2</sub> O	146.55	-10915.5	-19.128	0.026
KCl + K <sub>2</sub> SO <sub>4</sub> + H <sub>2</sub> O	66.556	-7386.0	-7.160	0.030

and the molalities are interrelated with the mole fractions by  $m_i = 55.51x_i/(1 - x_i)$ ,  $i = 2, 3$ . The vapor pressure  $p$  is an explicit function of temperature and composition at the invariant point,  $p = f(T, m_2, m_3)$ . If over the considered temperature range the apparent molar enthalpy change depends linearly on  $T$ , then the integral form of eq 3 is

$$\ln[p(T; m_2, m_3)/\text{kPa}] = A + B(T/\text{K})^{-1} + C \ln(T/\text{K}) \quad (4)$$

where

$$\overline{\Delta H}/R = CT - B \quad (5)$$

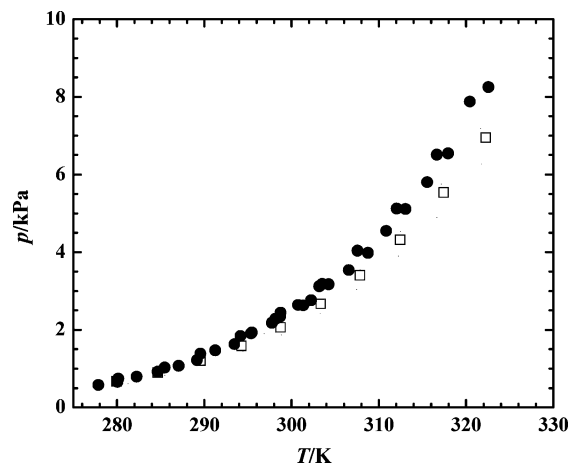
The parameters  $A$ ,  $B$ , and  $C$  for the investigated systems were evaluated by an unweighted multivariate least-squares method using  $p$  values from Table 1, and they are reported in Table 2.

As pointed out above, it is possible to compare our vapor pressures in the sodium chloride–potassium chloride–water system with those in the literature (Figure 1), and as can be observed the agreement is very satisfactory. Figure 2 presents systems with sodium chloride and Figure 3 those with potassium chloride. As can be observed in Figures 2, 3, and 4, irrespective of temperature  $p(\text{NaCl} + \text{KCl} + \text{H}_2\text{O}) > p(\text{NaCl} + \text{NaNO}_3 + \text{H}_2\text{O})$  and  $p(\text{KCl} + \text{K}_2\text{SO}_4 + \text{H}_2\text{O}) > p(\text{KCl} + \text{KBr} + \text{H}_2\text{O}) \approx p(\text{KCl} + \text{KNO}_3 + \text{H}_2\text{O}) > p(\text{KCl} + \text{NaCl} + \text{H}_2\text{O}) > p(\text{KCl} + \text{KI} + \text{H}_2\text{O})$ . The vapor pressure of water is always higher in the systems with potassium salts than with sodium salts; i.e., water passes into the gaseous phase more easily in the case of potassium salts.

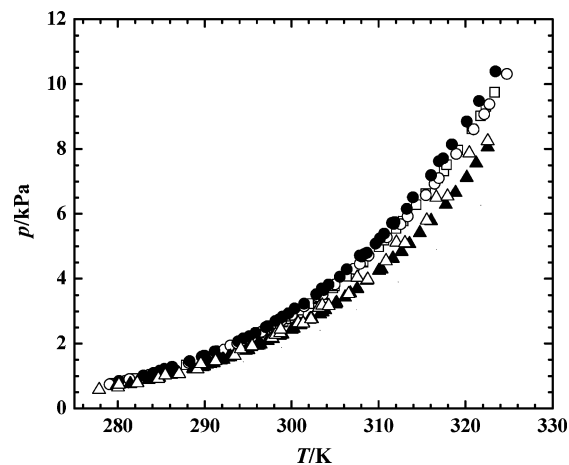
Determined vapor pressures of water  $p$  can be also expressed in terms of the water activity  $a_1(T, m_2, m_3) = p(T, m_2, m_3)/p^*(T)$  and by the value of the osmotic coefficient  $\phi = \phi(T, m_2, m_3)$

$$\phi(T, m_2, m_3) = -\frac{1000}{M_1(\nu_2 m_2 + \nu_3 m_3)} \ln a_1(T, m_2, m_3) \quad (6)$$

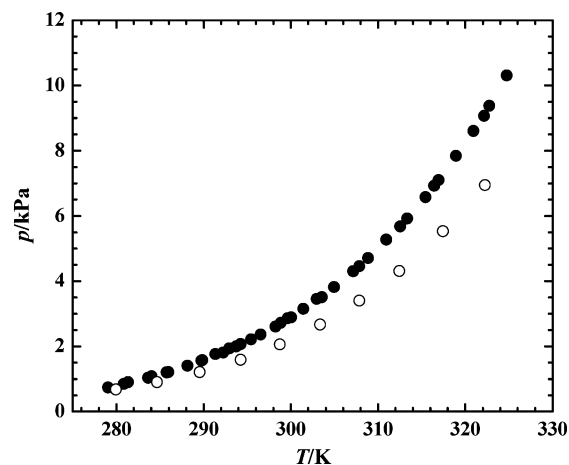
where  $p^*(T)$  are vapor pressures of pure water at given  $T$  and they are available from the Saul and Wagner equation.<sup>59</sup>  $M_1$  is



**Figure 2.** Vapor pressures  $p$  of saturated aqueous solutions as a function of temperature  $T$ .  $\bullet$ , NaCl + KCl + H<sub>2</sub>O;  $\square$ , NaCl + NaNO<sub>3</sub> + H<sub>2</sub>O.

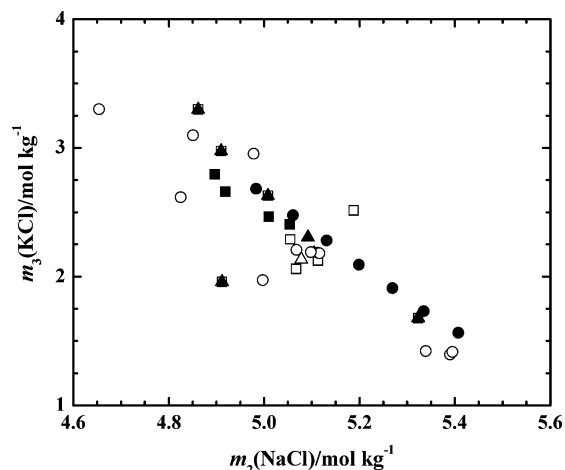


**Figure 3.** Vapor pressures  $p$  of saturated aqueous solutions as a function of temperature  $T$ .  $\bullet$ , KCl + K<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O;  $\square$ , KCl + KBr + H<sub>2</sub>O;  $\circ$ , KCl + KNO<sub>3</sub> + H<sub>2</sub>O;  $\triangle$ , KCl + NaCl + H<sub>2</sub>O;  $\blacktriangle$ , KCl + KI + H<sub>2</sub>O.



**Figure 4.** Vapor pressures  $p$  of saturated aqueous solutions as a function of temperature  $T$ .  $\circ$ , NaCl + NaNO<sub>3</sub> + H<sub>2</sub>O;  $\bullet$ , KCl + KNO<sub>3</sub> + H<sub>2</sub>O.

the molar mass of water;  $\nu_i$ ,  $i = 2, 3$ , denote the sum of stoichiometric coefficients;  $\nu_i = 2$  for 1:1 electrolytes; and  $\nu_i = 3$  for 1:2 electrolytes. Thus, to calculate the osmotic coefficients, knowledge of the composition at the invariant points,  $m_2$  and  $m_3$ , is necessary, and these solubilities were taken from the literature. Phase diagrams, especially in the NaCl + KCl + H<sub>2</sub>O system,<sup>21,22,26,28,31,39,40</sup> were investigated a number of times, and they are relatively well-known and accurate;



**Figure 5.** Compositions of saturated solutions,  $m_2(\text{NaCl})$  and  $m_3(\text{KCl})$ , in the  $\text{NaCl} + \text{KCl} + \text{H}_2\text{O}$  system.  $\Delta$ , ref 21;  $\square$ , ref 22;  $\bullet$ , ref 26;  $\blacksquare$ , refs 28 and 31;  $\blacktriangle$ , ref 39;  $\circ$ , ref 40.

**Table 3.** Coefficients of Equation 7: Molalities of Saturated Solutions  $m_i$ ,  $i = 2, 3$ , and the Mean Standard Deviations

system	A			$\sigma(m_i)$ mol $\cdot\text{kg}^{-1}$
	$a$	$b$	$c$	
$\text{NaCl} + \text{KCl} + \text{H}_2\text{O}$	5.435	-0.0136	$6.127 \cdot 10^{-5}$	0.05
	1.325	0.0329		0.05
$\text{NaCl} + \text{NaNO}_3 + \text{H}_2\text{O}$	4.861	-0.0318	$9.220 \cdot 10^{-5}$	0.02
	4.563	0.0801	$5.721 \cdot 10^{-4}$	0.02
$\text{KCl} + \text{KBr} + \text{H}_2\text{O}$	2.175	0.0100		0.06
	2.704	0.0286		0.14
$\text{KCl} + \text{KI} + \text{H}_2\text{O}$	1.190	0.0100		0.09
	6.890	0.0400		0.22
$\text{KCl} + \text{KNO}_3 + \text{H}_2\text{O}$	3.737	0.0398	$-2.162 \cdot 10^{-4}$	0.06
	0.904	0.0189	$1.404 \cdot 10^{-3}$	0.05
$\text{KCl} + \text{K}_2\text{SO}_4 + \text{H}_2\text{O}$	3.816	0.0355		0.08
	0.0671	$7.787 \cdot 10^{-4}$		0.003

however, the exact location of saturation points is less certain (Figure 5). The reported solubilities of KCl as a function of temperature are not as much scattered as those of NaCl. With regards to solubilities, a similar situation is observed for other pairs of salts.

Removing compositions which are far from average values, the function  $m_i = f(t)$ ,  $i = 2, 3$ , and  $t/^\circ\text{C} = T/\text{K} - 273.15$ , were correlated by two linear or quadratic equations

$$m_2/\text{mol}\cdot\text{kg}^{-1} = A + B(t/^\circ\text{C}) + C(t/^\circ\text{C})^2$$

$$m_3/\text{mol}\cdot\text{kg}^{-1} = a + b(t/^\circ\text{C}) + c(t/^\circ\text{C})^2$$

$$t/^\circ\text{C} = T/\text{K} - 273.15 \quad (7)$$

The coefficients of these equations together with the corresponding mean standard deviations are presented in Table 3.

Compositions of the invariant points, vapor pressures, activities of water, and osmotic coefficients as calculated from eqs 4, 6, and 7 in 5 K intervals are presented in Table 4, and these values can be used to control humidity in experiments.

If vapor pressures of saturated solutions  $p$  are plotted as a function of the total ionic strength  $I$  (Figure 6) where  $I = m_2 + m_3$  for 1:1 electrolytes and  $I = m_2 + 3m_3$  for 1:2 electrolytes, it is observed that alkali metal halides behave differently than nitrates. Changes in vapor pressures over the 45 K temperature interval are similar in all systems, but the corresponding changes in the ionic strength  $I$  are relatively large in the case of nitrates and much smaller in the case of halides. As can be observed in Table 4, the contributions of sodium nitrate, potassium nitrate,

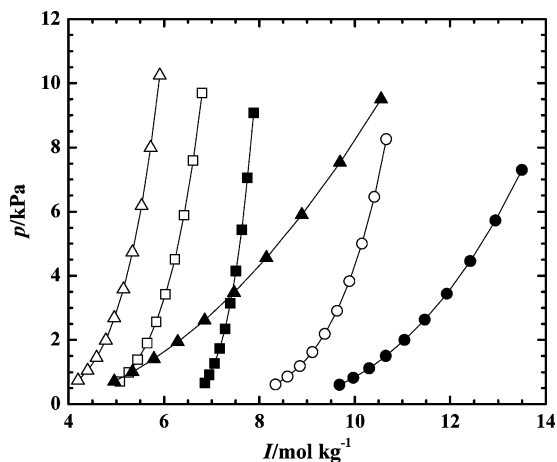
**Table 4.** Calculated Solubilities  $m_2$  and  $m_3$ , Vapor Pressures  $p$ , Water Activities  $a_1$ , and Osmotic Coefficients  $\phi$  at Temperatures  $t/^\circ\text{C} = T/\text{K} - 273.15$

$t/^\circ\text{C}$	$m_2/\text{mol}\cdot\text{kg}^{-1}$	$m_3/\text{mol}\cdot\text{kg}^{-1}$	$p/\text{kPa}$	$a_1$	$\phi$
<b><math>\text{NaCl} + \text{KCl} + \text{H}_2\text{O}</math></b>					
5	5.37	1.49	0.651	0.746	1.184
10	5.30	1.65	0.913	0.744	1.180
15	5.24	1.82	1.265	0.742	1.174
20	5.19	1.98	1.731	0.740	1.165
25	5.13	2.15	2.340	0.739	1.155
30	5.08	2.31	3.130	0.737	1.144
35	5.03	2.48	4.143	0.736	1.131
40	4.99	2.64	5.430	0.736	1.117
45	4.95	2.80	7.049	0.735	1.102
50	4.91	2.97	9.070	0.735	1.086
<b><math>\text{NaCl} + \text{NaNO}_3 + \text{H}_2\text{O}</math></b>					
5	4.70	4.98	0.597	0.684	1.090
10	4.55	5.42	0.820	0.668	1.124
15	4.41	5.89	1.114	0.653	1.147
20	4.26	6.39	1.498	0.641	1.159
25	4.12	6.92	1.995	0.630	1.163
30	3.99	7.48	2.631	0.620	1.158
35	3.86	8.07	3.438	0.611	1.146
40	3.74	8.68	4.454	0.603	1.129
45	3.62	9.33	5.723	0.597	1.107
50	3.50	10.0	7.296	0.591	1.081
<b><math>\text{KCl} + \text{KBr} + \text{H}_2\text{O}</math></b>					
5	2.22	2.85	0.704	0.807	1.176
10	2.27	2.99	0.993	0.809	1.119
15	2.32	3.13	1.381	0.810	1.075
20	2.37	3.28	1.892	0.809	1.041
25	2.42	3.42	2.559	0.807	1.016
30	2.47	3.56	3.417	0.805	0.998
35	2.52	3.71	4.508	0.801	0.988
40	2.57	3.85	5.880	0.797	0.983
45	2.62	3.99	7.587	0.791	0.983
50	2.67	4.13	9.689	0.785	0.988
<b><math>\text{KCl} + \text{KI} + \text{H}_2\text{O}</math></b>					
5	1.25	7.09	0.612	0.702	1.180
10	1.30	7.29	0.858	0.699	1.159
15	1.36	7.49	1.186	0.695	1.140
20	1.42	7.69	1.618	0.692	1.122
25	1.48	7.89	2.181	0.688	1.107
30	1.54	8.09	2.906	0.685	1.092
35	1.60	8.29	3.830	0.681	1.079
40	1.66	8.49	4.997	0.677	1.067
45	1.72	8.69	6.453	0.673	1.057
50	1.77	8.89	8.257	0.669	1.047
<b><math>\text{KCl} + \text{KNO}_3 + \text{H}_2\text{O}</math></b>					
5	3.93	1.03	0.708	0.812	1.166
10	4.11	1.23	1.007	0.820	1.029
15	4.29	1.50	1.407	0.825	0.923
20	4.45	1.84	1.932	0.826	0.844
25	4.60	2.25	2.610	0.824	0.786
30	4.74	2.73	3.473	0.818	0.746
35	4.87	3.28	4.555	0.810	0.719
40	4.98	3.91	5.895	0.799	0.702
45	5.09	4.60	7.529	0.785	0.693
50	5.19	5.36	9.501	0.770	0.689
<b><math>\text{KCl} + \text{K}_2\text{SO}_4 + \text{H}_2\text{O}</math></b>					
5	3.99	0.071	0.742	0.851	1.093
10	4.17	0.075	1.044	0.851	1.049
15	4.35	0.079	1.449	0.850	1.013
20	4.53	0.083	1.983	0.848	0.983
25	4.70	0.087	2.681	0.846	0.960
30	4.88	0.090	3.581	0.844	0.941
35	5.06	0.094	4.730	0.841	0.927
40	5.24	0.098	6.180	0.837	0.916
45	5.41	0.102	7.993	0.834	0.908
50	5.59	0.106	10.24	0.829	0.903

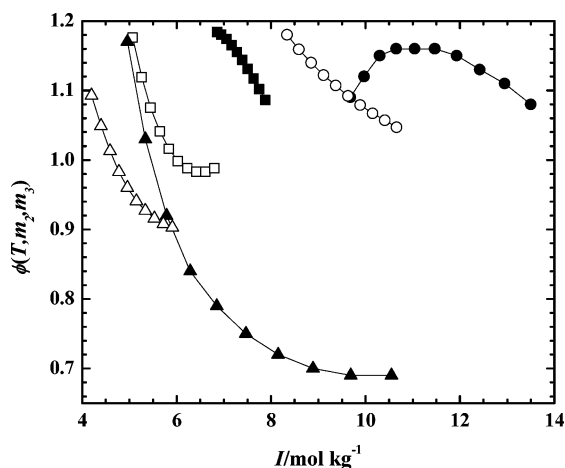
and potassium iodide to the ionic strength of solution are predominant when that of potassium sulfate is negligible.

In the  $\text{NaCl} + \text{KCl} + \text{H}_2\text{O}$  system, the relative humidities (water activities multiplied by 100) as determined in the (293.15





**Figure 6.** Vapor pressures of water over saturated solutions  $p$  as a function of the total ionic strength  $I$ . ■, NaCl + KCl + H<sub>2</sub>O; ●, NaCl + NaNO<sub>3</sub> + H<sub>2</sub>O; □, KCl + KBr + H<sub>2</sub>O; ○, KCl + KI + H<sub>2</sub>O; ▲, KCl + KNO<sub>3</sub> + H<sub>2</sub>O; △, KCl + K<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O.



**Figure 7.** Osmotic coefficients  $\phi(T, m_2, m_3)$  of saturated solutions as a function of the total ionic strength  $I$ . ■, NaCl + KCl + H<sub>2</sub>O; ●, NaCl + NaNO<sub>3</sub> + H<sub>2</sub>O; □, KCl + KBr + H<sub>2</sub>O; ○, KCl + KI + H<sub>2</sub>O; ▲, KCl + KNO<sub>3</sub> + H<sub>2</sub>O; △, KCl + K<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O.

to 303.15) K interval are about 74 % (Table 4), and they are slightly higher than the corresponding values of (70 to 74) % from the literature.<sup>1,2,4,21</sup> At 303.15 K, Adams and Merz<sup>2</sup> measured relative humidities of 68 % in the NaCl + NaNO<sub>3</sub> + H<sub>2</sub>O system, of 79 % in the KCl + KNO<sub>3</sub> + H<sub>2</sub>O system, and of 86 % in the KCl + K<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O system when our values are 62 %, 82 %, and 84 %, respectively.

With an exception of the KCl + KNO<sub>3</sub> + H<sub>2</sub>O and KCl + K<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O systems, the change of osmotic coefficients  $\phi(T, m_2, m_3)$  with  $I$  is relatively small (Figure 7), which means also that their temperature dependence is weak because the ionic strength of the solutions always increases with temperature.

## Conclusions

Vapor pressures of water over saturated solutions with regard to two salts, in the NaCl + KCl + H<sub>2</sub>O, NaCl + NaNO<sub>3</sub> + H<sub>2</sub>O, KCl + KBr + H<sub>2</sub>O, KCl + KBr + H<sub>2</sub>O, KCl + KI + H<sub>2</sub>O, KCl + KNO<sub>3</sub> + H<sub>2</sub>O, and KCl + K<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O systems, were determined in the (278 to 323) K temperature range. It was observed that the vapor pressure of water is always higher in the systems with potassium salts than with sodium salts. Changes in vapor pressures with temperature are similar in all systems, but the corresponding changes in the ionic strength of

saturated solutions are more important in the case of nitrates than halides. In particular, the contributions of sodium nitrate, potassium nitrate, and potassium iodide to  $I$  are larger than those of the second salt when that of potassium sulfate is negligible.

## Acknowledgment

The authors appreciate the technical assistance of Mrs. Mary Mamana.

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Received for review December 14, 2008. Accepted March 28, 2009.

JE800963G