JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

Temperature Dependence of Vapor Pressures over Saturated Aqueous Solutions at Invariant Points of the NaCl + KNO_3 + H_2O, NaCl + Na_2CO_3 + H_2O, and NaCl + Na_2SO_4 + H_2O Systems

Alexander Apelblat* and Eli Korin

Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer Sheva, 84105 Israel

ABSTRACT: Vapor pressures of water over saturated solutions with regard to two salts, in the NaCl + KNO_3 + H_2O, NaCl + Na_2CO_3 + H_2O, and NaCl + Na_2SO_4 + H_2O systems are reported in the (278 to 323) K temperature range. The determined vapor pressures were used to obtain the water activities, the molar enthalpies of vaporization and the osmotic coefficients. Compositions of invariant points from the literature were correlated as a function of temperature with the aid of quadratic equations. These equations served to determine the molar enthalpies of solution.

1. INTRODUCTION

The thermodynamic analysis of aqueous solutions of inorganic salts is of vital importance in geological and in many industrial processes such as salt precipitation, evaporation of water from brines, concentration, dilution, and mixing. There is no surprise that considerable attention was directed in the literature to the binary, ternary, and multicomponent inorganic salt—water systems. Thermal, volumetric, activities, solubilities, and many other physical properties have been experimentally determined, mostly in binary systems and evidently much less in the systems with three or more components. Solubilities (phase diagrams) are better documented in the literature than other physicochemical properties.[1−8] (see for example the remarkable investigation of Freeth[9]). In the absence of reliable data, the desired properties are estimated from various thermodynamic models (only a short list is mentioned here).[10−23] Values of parameters used in these models are taken from isopiestic or other measurements performed in binary and ternary systems to give activity and osmotic coefficients.[12,24−38] From the ternary systems investigated here, the most complete thermodynamic analysis was performed by Rard et al.[39] for the NaCl + Na_2SO_4 + H_2O system. The above-mentioned investigations are concerned with different ranges of temperature and salts concentration, but evidently their attention was rarely directed to the eutonic solutions where solutions are saturated with both salts (invariant points of the system).

This investigation is a continuation of our previous work[40] which dealt with aqueous ternary systems of NaCl with KCl, KBr, and $NaNO_3$ and KCl with NaBr, KBr, KI, KNO_3, and K_2SO_4 at invariant points. These systems as well as those considered here have a considerable technological and geochemical interest taking into account that in many natural brines the predominant ions are sodium, potassium, chloride, nitrate, and sulfate.

The vapor pressures over saturated solutions in the NaCl + KNO_3 + H_2O, NaCl + Na_2CO_3 + H_2O, and NaCl + Na_2SO_4 + H_2O systems in the T = 278 K to T = 322 K temperature range are considered here. To the best of the author's knowledge, the vapor pressures over the eutonic solutions in these systems are unknown in the literature. Determined vapor pressures are expressed also in terms of the water activities a_1 and by combining them with solubilities (taken from the literature) in terms of the osmotic coefficients ϕ. From the temperature dependence of vapor pressures $p(T)$ and solubilities $m_i(T)$ the molar enthalpies of vaporization and the molar enthalpies of solution at invariant points are evaluated. The results from this and from a previous investigation[40] are compared for the following systems NaCl + $NaNO_3$ + H_2O and NaCl + KNO_3 + H_2O and NaCl + Na_2SO_4 + H_2O and KCl + K_2SO_4 + H_2O.

2. EXPERIMENTAL SECTION

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

The vapor pressures over saturated solutions were determined using the Rotronic Hygroskop DT1 instrument which was equipped with a measuring station WA-14TH. The saturation of solutions was assured by the prolonged mixing of the aqueous phase with excess amounts of both solid salts. The compositions of the solid phases were not determined. The thermal stability of the measuring system is estimated to be ± 0.05 K and the sensitivity of the used electronic hygrometer is about ± 0.003 kPa at T = 298.15 K. The employed procedure is similar to that described in ref 41.

3. RESULTS AND DISCUSSION

If the aqueous solution is saturated with two nonvolatile solutes (i.e., at constant chemical potentials μ_i) then the change of vapor pressure $p(T)$ with temperature T can be expressed by

Special Issue: John M. Prausnitz Festschrift

Received: September 26, 2010
Accepted: March 1, 2011
Published: March 15, 2011

the Clausius−Clapeyron equation in the form

$$\left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)_{\mu_i} = \frac{x_1\Delta\overline{H_1}+x_2\Delta\overline{H_2}+x_3\Delta\overline{H_3}}{T[x_1\Delta\overline{V_1}+x_2\Delta\overline{V_2}+x_3\Delta\overline{V_3}]}$$

$$\begin{aligned}\Delta\overline{H_1} &= \overline{H_1^{\mathrm{G}}}-\overline{H_1^{\mathrm{L}}}; &\quad \Delta\overline{V_1} &= \overline{V_1^{\mathrm{G}}}-\overline{V_1^{\mathrm{L}}}\\ \Delta\overline{H_2} &= \overline{H_2^{\mathrm{S}}}-\overline{H_2^{\mathrm{L}}}; &\quad \Delta\overline{V_2} &= \overline{V_2^{\mathrm{S}}}-\overline{V_2^{\mathrm{L}}}\\ \Delta\overline{H_3} &= \overline{H_3^{\mathrm{S}}}-\overline{H_3^{\mathrm{L}}}; &\quad \Delta\overline{V_3} &= \overline{V_3^{\mathrm{S}}}-\overline{V_3^{\mathrm{L}}}\end{aligned}$$

$$x_1+x_2+x_3 = 1; \quad i = 1, 2, 3 \tag{1}$$

which generalizes the Model and Reid[42] expression for binary systems. $\Delta\overline{V_i}$ and $\Delta\overline{H_i}$ represent changes in the molar volume and the molar enthalpy of vaporization. G, L, and S denote the gaseous, liquid and solid phases respectively and x_i are mole fractions of components in the solution, $i = 1, 2, 3$, where 1-water, 2-salt 1, and 3-salt 2. 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 1 and x_3 moles of salt 2. However, taking into account that the mole fractions of salts, even at saturation, are small as compared with that of water 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, we have

$$\sum_{i=1}^{3} x_i\Delta\overline{H_i} \approx x_1\Delta\overline{H_1} = x_1\Delta\overline{H}$$

$$\sum_{i=1}^{3} x_i\Delta\overline{V_i} \approx x_1\Delta\overline{V_1} \approx x_1\overline{V_1^{\mathrm{G}}} = x_1RT/p \tag{2}$$

It follows from eqs 1 and 2 that the Clausius−Clapeyron can be approximated by

$$\left(\frac{\mathrm{d}\ln p}{\mathrm{d}T}\right)_{m_2, m_3} = \frac{\overline{\Delta H}}{RT^2} \tag{3}$$

where the apparent molar enthalpy change is associated with the evaporation of water and simultaneous crystallization of salts. The mole fractions x_i are interrelated with molalities by $m_i = 1000x_i/(1 - x_i)/M_1$, $i = 2$ and 3 and M_1 is the molar mass of water. Thus, the vapor pressure $p(T)$ 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

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

where

$$\frac{\overline{\Delta H}}{R} = [C(T/K) - B] \tag{5}$$

The parameters A, B, and C for the investigated systems were evaluated by an unweighted multivariate least-squares method using the vapor pressure values from Table 1.

The composition of the invariant points as a function of temperature, taken from the literature, was approximated by the quadratic equation

$$\{m_i/\mathrm{mol\cdot kg^{-1}}\}_{m_{j\neq i}} = a_i + b_i(T/\mathrm{K}) + c_i(T/\mathrm{K})^2 \tag{6}$$

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

T/K	p/kPa	T/K	p/kPa	T/K	p/kPa
		$NaCl + KNO_3 + H_2O$			
280.45	0.720	294.25	1.704	308.65	3.869
281.85	0.790	296.15	1.905	309.55	4.041
284.55	0.940	298.85	2.250	312.25	4.650
286.35	1.058	299.75	2.362	314.95	5.318
289.55	1.283	301.65	2.620	316.55	5.756
290.75	1.385	303.25	2.886	321.45	7.212
293.45	1.639	305.15	3.187		
		$NaCl + Na_2CO_3 + H_2O$			
280.25	0.706	294.45	1.779	312.25	5.086
280.45	0.716	298.65	2.334	312.55	5.161
284.95	0.988	298.75	2.322	316.85	6.384
285.45	1.008	302.95	2.996	317.05	6.533
289.65	1.320	303.25	3.023	321.45	8.199
289.85	1.340	307.55	3.929	321.85	8.273
294.25	1.794	308.05	4.023		
		$NaCl + Na_2SO_4 + H_2O$			
280.15	0.708	298.45	2.477	312.25	5.578
284.55	0.981	298.65	2.504	312.55	5.669
284.95	1.003	302.95	3.273	316.65	7.188
289.35	1.379	303.15	3.303	317.15	7.322
289.35	1.366	307.55	4.289		
293.95	1.867	307.85	4.344		
293.95	1.853	312.05	5.574		

where the coefficients a_i, b_i, and c_i were also determined by an unweighted multivariate least-squares method.

Thermodynamically, the solubility-against temperature relation is of the form[43]

$$\frac{\partial\ln\{m_i\}_{m_{j\neq i}}}{\partial(1/T)} = -\frac{\Delta H_i}{R\left(1+\dfrac{\partial\ln\gamma_i}{\partial\ln m_i}\right)_{m_{j\neq i}}} \tag{7}$$

where ΔH_i is the molar enthalpy of solution of component i and γ_i is its activity coefficient (the hydration of the salt in the solid phase and the type of electrolyte are ignored in eq 7). If the change of activity coefficients with concentration near the invariant points is also neglected then using eqs 6 and 7, the apparent molar enthalpy of solution can be expressed in terms of a_i, b_i, and c_i coefficients as

$$\overline{\Delta H}_i = RT^2\left\{\frac{b_i + 2c_i(T/K)}{a_i + b_i(T/K) + c_i(T/K)^2}\right\} \tag{8}$$

and its value has only an indicative character.

$NaCl + KNO_3 + H_2O$ System. Vapor pressures of water over solutions with the invariant points composition of all investigated systems are presented in Table 1 and the coefficients A, B, and C with corresponding mean standard deviations in Table 2. In Figure 1 are compared vapor pressures of $NaCl + KNO_3 + H_2O$ with those of $NaCl + NaNO_3 + H_2O$ and $KCl + KNO_3 + H_2O$ reported in our previous investigation.[40] As can be observed, that irrespective of temperature, $p(KCl + KNO_3 + H_2O) > p(NaCl$

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

system	A	B	C	$\sigma(p)$/kPa
$NaCl + KNO_3 + H_2O$	80.699	−7908.0	−9.374	0.020
$NaCl + Na_2CO_3 + H_2O$	59.159	−7156.5	−6.028	0.028
$NaCl + Na_2SO_4 + H_2O$	100.53	−9199.1	−12.073	0.019

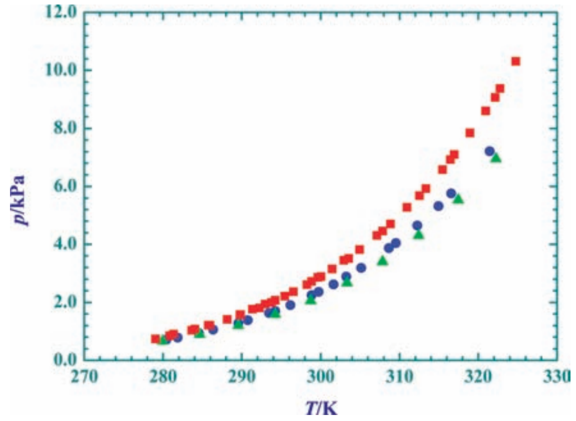

Figure 1. Vapor pressures p of saturated aqueous solutions as a function of temperature T. Sodium chloride + sodium nitrate, green triangles; potassium chloride + potassium nitrate, red squares, ref 40; sodium chloride + potassium nitrate, blue circles, this work.

$+ KNO_3 + H_2O) > p(NaCl + NaNO_3 + H_2O)$. Thus, the vapor pressure of water is always higher in the systems with potassium salts than with sodium salts which means that water passes into the gaseous phase more easily in the case of potassium than sodium salts.

The 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 a value of the osmotic coefficient $\phi = \phi(T, m_2, m_3)$

$$\phi(T, m_2, m_3) = -\frac{1000}{M_1(\nu_2 m_2 + \nu_3 m_3)} \ln a_1(T, m_2, m_3) \qquad (9)$$

where $p^*(T)$ are vapor pressures of pure water at a given T and they are available from the Saul and Wagner equation.[44] M_1 is the molar mass of water and ν_i, i = 2 and 3, denotes the stoichiometric coefficients, $\nu_i = 2$ for 1:1 electrolytes and $\nu_i = 3$ for 1:2 electrolytes. It follows from eq 9 that the accuracy of the determined osmotic coefficients depends on how accurately the composition of solutions at invariant points is known.

The phase diagram of the $NaCl + KNO_3 + H_2O$ system is relatively simple[1−3] but the scattering of experimental solubilities of NaCl prevents to fitting them using eq 6. However, the overall change of m_{NaCl} with T is rather small so the average value: $m_{NaCl} = (6.50 \pm 0.21)\ \mathrm{mol \cdot kg^{-1}}$ was used in the calculations. On the contrary, potassium nitrate solubility increases significantly with an increase of temperature and its solubility can be represented up to 373 K by

$$\{m_{KNO_3}/\mathrm{mol \cdot kg^{-1}}\}_{m_{NaCl}} = 170.495 - 1.2283(T/\mathrm{K}) + 0.002246(T/\mathrm{K})^2$$
$$\sigma(\{m_{KNO_3}/\mathrm{mol \cdot kg^{-1}}\}_{m_{NaCl}}) = 0.36 \qquad (10)$$

Table 3. Solubilities m_2 and m_3, Vapor Pressures p, Water Activities a_1, and Osmotic Coefficients ϕ at Temperatures T

T/K	m_2/mol·kg^{-1}	m_3/mol·kg^{-1}	p/kPa	a_1	ϕ
		$NaCl + KNO_3 + H_2O$			
278.15	6.50[a]	2.57	0.613	0.703	0.94
283.15	6.50	2.73	0.857	0.699	0.94
288.15	6.50	3.00	1.181	0.693	0.93
293.15	6.50	3.39	1.605	0.687	0.90
298.15	6.50	3.89	2.154	0.680	0.87
303.15	6.50	4.50	2.857	0.673	0.83
308.15	6.50	5.22	3.745	0.665	0.79
313.15	6.50	6.05	4.855	0.657	0.75
318.15	6.50	7.00	6.231	0.648	0.71
323.15	6.50	8.06	7.917	0.639	0.67
		$NaCl + Na_2CO_3 + H_2O$			
278.15	5.58	0.59	0.616	0.701	1.53
283.15	5.27	0.91	0.889	0.704	1.47
288.15	4.88	1.33	1.262	0.707	1.40
293.15	4.40	1.85	1.764	0.710	1.32
298.15	3.69	2.59	2.432	0.712	1.24
303.15	3.88	2.46	3.305	0.714	1.24
308.15	4.07	2.33	4.435	0.716	1.22
313.15	4.26	2.21	5.879	0.718	1.21
318.15	4.43	2.10	7.702	0.719	1.21
323.15	4.60	1.99	9.978	0.720	1.20
		$NaCl + Na_2SO_4 + H_2O$			
278.15	5.93	0.18	0.612	0.701	1.59
283.15	5.81	0.33	0.885	0.720	1.45
288.15	5.63	0.56	1.258	0.738	1.30
293.15	5.50	0.73	1.762	0.754	1.19
298.15	5.56	0.69	2.432	0.767	1.12
303.15	5.63	0.66	3.309	0.780	1.04
308.15	5.69	0.62	4.444	0.790	0.99
313.15	5.75	0.60	5.894	0.799	0.94
318.15	5.81	0.57	7.725	0.806	0.90
323.15	5.88	0.55	10.009	0.811	0.87

[a] See text.

Using eqs 4, 6, and 10, the compositions of the invariant points, vapor pressures, activities of water, and osmotic coefficients in 5 K intervals are calculated and they are presented in Table 3. As can be observed, with increasing T, the content of sodium chloride is constant, that of potassium nitrate strongly increases and water activities and osmotic coefficients decrease. The apparent molar enthalpy of solution of potassium nitrate as a function of temperature is positive ($\overline{\Delta H} = 21.1\ \mathrm{kJ \cdot mol^{-1}}$ at 298.15 K) and has a maximum at about 313.15 K. The apparent molar enthalpy of vaporization in the $NaCl + KNO_3 + H_2O$ system at 298.15 K is $\overline{\Delta H} = 42.5\ \mathrm{kJ \cdot mol^{-1}}$.

$NaCl + Na_2CO_3 + H_2O$ System. The vapor pressures of water over invariant points in the $NaCl + Na_2CO_3 + H_2O$ system are plotted in Figure 2 together with those of the $NaCl + Na_2SO_4 + H_2O$ and $KCl + K_2SO_4 + H_2O$ (taken from our previous work[40]). In systems as shown previously, potassium salts have higher vapor pressures than sodium salts $p(KCl + K_2SO_4 + H_2O) > p(NaCl + Na_2SO_4 + H_2O) > p(NaCl + Na_2CO_3 + H_2O)$.

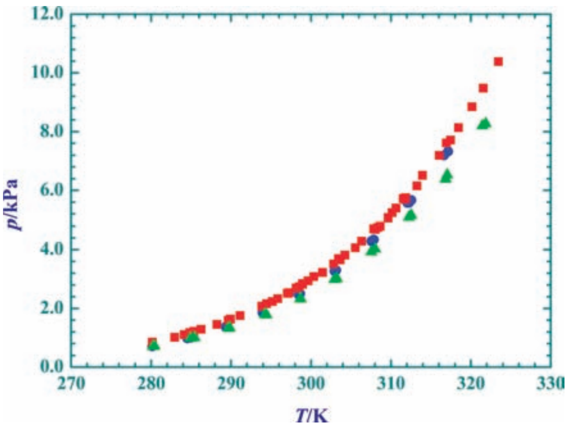

Figure 2. Vapor pressures p of saturated aqueous solutions as a function of temperature T. Potassium chloride + potassium sulfate, red squares, ref 40; sodium chloride + sodium carbonate, green triangles; sodium chloride + sodium sulfate, blue circles, this work.

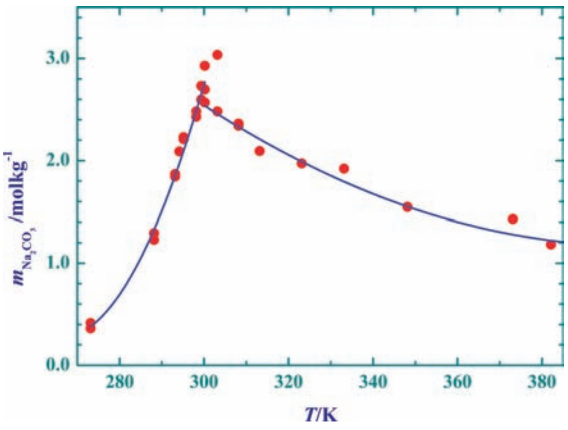

Figure 4. Sodium carbonate content in solutions with the invariant point composition in the sodium chloride + sodium carbonate + water system as a function of temperature T. Red circles, refs 1−3 and 9; continuous lines are calculated in this work.

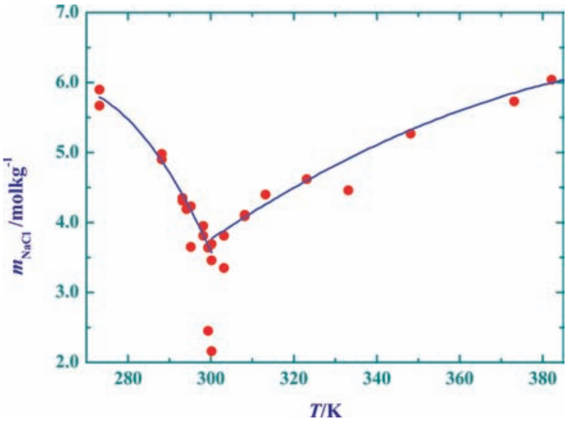

Figure 3. Sodium chloride content in solutions with the invariant point composition in the sodium chloride + sodium carbonate + water system as a function of temperature T. Red circles, refs 1−3 and 9; continuous lines are calculated in this work.

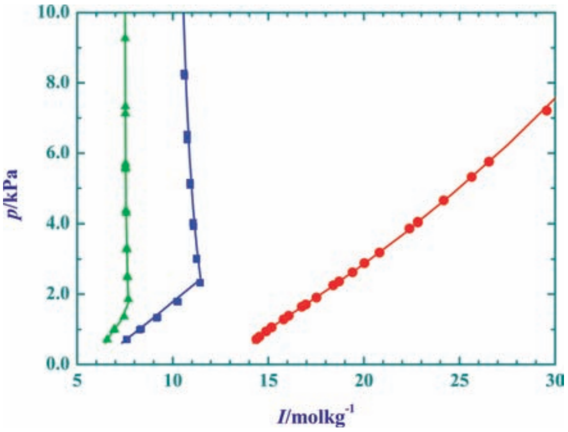

Figure 5. Vapor pressure of water over saturated solutions p as a function of the total ionic strength I. Red circles, NaCl + KNO_3 + H_2O; blue squares, NaCl + Na_2CO_3 + H_2O; green triangles, NaCl + Na_2SO_4 + H_2O.

The phase diagram of this system is more complicated because in the NaCl + Na_2CO_3 + H_2O system, $Na_2CO_3\cdot 10H_2O$ is stable to about 298 K and at higher temperatures above 303 K $Na_2CO_3\cdot H_2O$ is stable. In between, over a small temperature range, from about (298 to 303) K $Na_2CO_3\cdot 7H_2O$ exists.[1−3,9] In the Na_2CO_3 + H_2O system, the transformation in the solid phase from $Na_2CO_3\cdot 10H_2O$ to $Na_2CO_3\cdot 7H_2O$ occurs at 305.15 K and from $Na_2CO_3\cdot 7H_2O$ to $Na_2CO_3\cdot H_2O$ at 308.55 K.[8] Since near 300 K the exact location of the saturated solutions is uncertain (Figures 3 and 4), it is assumed that only two branches of the solubility curve exist, which means that the existence of sodium carbonate heptahydrate is completely neglected.

In the region of sodium carbonate decahydrate existence, the contents of sodium chloride and sodium carbonate in saturated solutions can be expressed by

$$\{m_{NaCl}/\text{mol}\cdot\text{kg}^{-1}\}_{m_{Na_2CO_3}} = -117.584 + 0.9376(T/K) - 0.001779(T/K)^2$$
$$\sigma(\{m_{NaCl}/\text{mol}\cdot\text{kg}^{-1}\}_{m_{Na_2CO_3}}) = 0.09 \qquad (11)$$

$$\{m_{Na_2CO_3}/\text{mol}\cdot\text{kg}^{-1}\}_{m_{NaCl}} = 150.04 - 1.1270(T/K) + 0.002120(T/K)^2$$
$$\sigma(\{m_{Na_2CO_3}/\text{mol}\cdot\text{kg}^{-1}\}_{m_{NaCl}}) = 0.07 \qquad (12)$$

and when the solid phase exists with sodium carbonate monohydrate we have

$$\{m_{NaCl}/\text{mol}\cdot\text{kg}^{-1}\}_{m_{Na_2CO_3}} = -21.930 + 0.1315(T/K) - 0.00153(T/K)^2$$
$$\sigma(\{m_{NaCl}/\text{mol}\cdot\text{kg}^{-1}\}_{m_{Na_2CO_3}}) = 0.07 \qquad (13)$$

$$\{m_{Na_2CO_3}/\text{mol}\cdot\text{kg}^{-1}\}_{m_{NaCl}} = 22.488 - 0.1061(T/K) + 0.00132(T/K)^2$$
$$\sigma(\{m_{Na_2CO_3}/\text{mol}\cdot\text{kg}^{-1}\}_{m_{NaCl}}) = 0.07 \qquad (14)$$

In all systems, as is observed in Figures 1 and 2, the vapor pressure of water over invariant points $p(T, m_2, m_3)$ is a

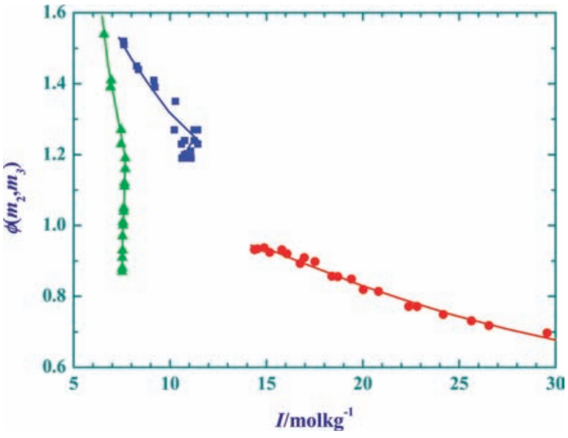

Figure 6. Osmotic coefficient of saturated solutions $\phi(m_2,m_3)$ as a function of the total ionic strength I. Red circles, NaCl + KNO_3 + H_2O; blue squares, NaCl + Na_2CO_3 + H_2O; green triangles, NaCl + Na_2SO_4 + H_2O.

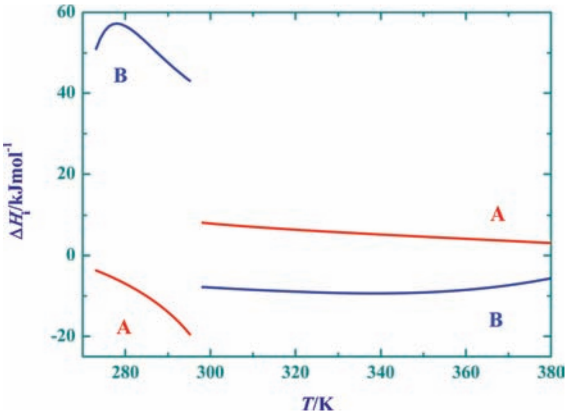

Figure 7. Apparent molar enthalpies of solution of components in the NaCl + Na_2CO_3 + H_2O system as a function of temperature T (eq 8). A, sodium chloride; B, sodium carbonate.

monotonic increasing function with concave upward curvature ($\partial p(T, m_2, m_3)/\partial T > 0$ and $\partial^2 p(T, m_2, m_3)/\partial T^2 > 0$). The existence of different hydrates of salts in the solid phase on the pressure $p(T, m_2, m_3)$ curve is unseen. However, the situation is completely different if $p(T, m_2, m_3)$ is plotted as a function of the total ionic strength I where $I = m_2 + m_3$ for 1:1 electrolytes and $I = m_2 + 3m_3$ for 1:2 electrolytes (Figure 5). As is evident, in systems with two hydrates in the solid phase, the curve of $p(T, m_2, m_3)$ has two branches with different curvatures. The same is true when the osmotic coefficients $\phi(T, m_2, m_3)$ are considered as a function of the ionic strength I (Figure 6).

Since solubilities are known from eqs 11−14, it is possible to determine the apparent molar enthalpy of solution of sodium chloride and sodium carbonate using eq 8. The results of calculations are plotted in Figure 7. When sodium carbonate decahydrate exists in the solid phase $\overline{\Delta H}_{\mathrm{NaCl}} < 0$ and $\partial\overline{\Delta H}_{\mathrm{NaCl}}/\partial T < 0$; the apparent molar enthalpy of solution of sodium carbonate is large and positive, $\overline{\Delta H}_{\mathrm{Na_2Co_3}} > 0$, and has a maximum near 278 K. In the sodium carbonate monohydrate region, $\overline{\Delta H}_{\mathrm{NaCl}} > 0$ and $\partial\overline{\Delta H}_{\mathrm{NaCl}}/\partial T < 0$ and $\overline{\Delta H}_{\mathrm{Na_2Co_3}} < 0$ when its change with T is small (at 298.15 K $\overline{\Delta H}_{\mathrm{NaCl}} = 8.1\ \mathrm{kJ\cdot mol^{-1}}$ and $\overline{\Delta H}_{\mathrm{Na_2Co_3}} = -7.8\ \mathrm{kJ\cdot mol^{-1}}$). $\phi(T, m_2, m_3)$ decreases with temperature, $\partial\phi(T, m_2, m_3)/\partial T < 0$ (Table 3) and the apparent molar enthalpy of vaporization in the NaCl + Na_2CO_3 + H_2O system at 298.15 K is $\overline{\Delta H} = 44.5\ \mathrm{kJ\cdot mol^{-1}}$.

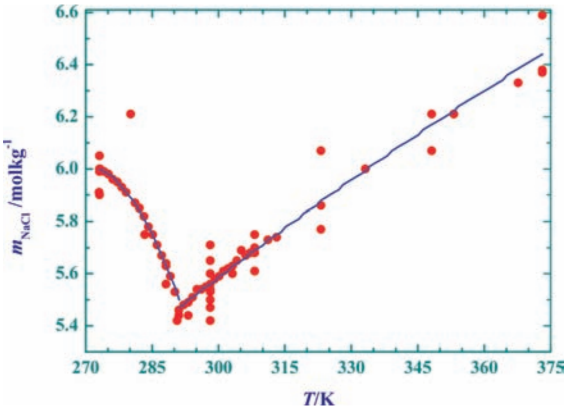

Figure 8. Sodium chloride content in solutions with the invariant point composition in the sodium chloride + sodium sulfate + water system as a function of temperature T. Red circles, refs 1−3; continuous lines are calculated in this work.

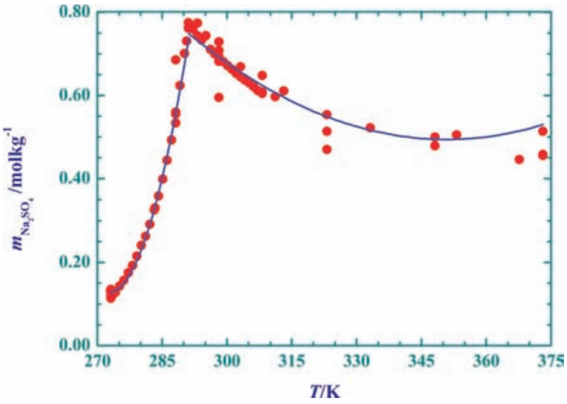

Figure 9. Sodium carbonate content in solutions with the invariant point composition in the sodium chloride + sodium sulfate + water system as a function of temperature T. Red circles, refs 1−3; continuous lines are calculated in this work.

NaCl + Na_2SO_4 + H_2O System. As expected, the vapor pressures of water over invariant points in the NaCl + Na_2SO_4 + H_2O system are lower than the corresponding KCl + K_2SO_4 + H_2O system[40] (Figure 2).

Results of many determinations of solubility in the NaCl + Na_2SO_4 + H_2O system are compiled in refs 1−3. There is general agreement that $Na_2SO_4\cdot 10H_2O$ exists up to about 291 K wheras anhydrous sodium sulfate exists above this temperature (Figures 8 and 9). However, the accuracy of these determinations is probably not specially high. Even at 298.15 K, the scattering of solubilities of NaCl is unacceptable large (Figure 8). Nevertheless, the transformation of the decahydrate to the anhydrous salt is clearly manifested if the vapor pressure of water over saturated solutions $p(T, m_2, m_3)$ is related to the total ionic strength of solutions I (Figure 5). The same is observed in Figure 6 in the case of the osmotic coefficients $\phi(T, m_2, m_3)$.

In the region of sodium sulfate decahydrate existence, the contents of sodium chloride and sodium sulfate in the saturated

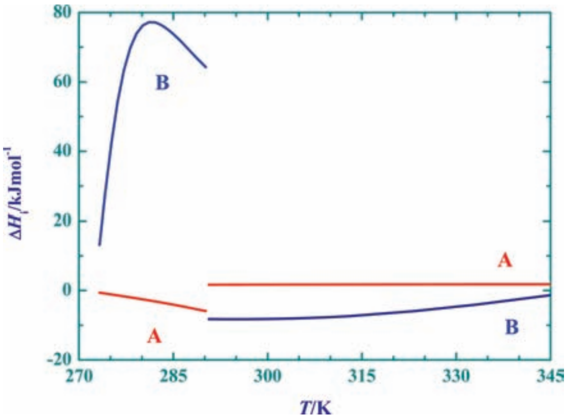

Figure 10. Apparent molar enthalpies of solution of components in the NaCl + Na_2SO_4 + H_2O system as a function of temperature T (eq 8). A, sodium chloride; B, sodium sulfate.

solutions are given by

$$\{m_{\mathrm{NaCl}}/\mathrm{mol\cdot kg^{-1}}\}_{m_{\mathrm{Na_2SO_4}}} = -82.789 + 0.6558(T/\mathrm{K}) - 0.001211(T/\mathrm{K})^2$$
$$\sigma(\{m_{\mathrm{NaCl}}/\mathrm{mol\cdot kg^{-1}}\}_{m_{\mathrm{Na_2SO_4}}}) = 0.01 \qquad (15)$$

$$\{m_{\mathrm{Na_2SO_4}}/\mathrm{mol\cdot kg^{-1}}\}_{m_{\mathrm{NaCl}}} = 130.130 - 0.9542(T/\mathrm{K}) + 0.001751(T/\mathrm{K})^2$$
$$\sigma(\{m_{\mathrm{Na_2SO_4}}/\mathrm{mol\cdot kg^{-1}}\}_{m_{\mathrm{NaCl}}}) = 0.01 \qquad (16)$$

In this region, the molality of NaCl in the saturated solution decreases when the temperature increases and that of Na_2SO_4 increases, but sodium chloride continues to be the predominant component in the mixture (Figures 8 and 9).

Above 291 K, anhydrous sodium sulfate exists in the solid phase and the solubilities of components can be expressed by

$$\{m_{\mathrm{NaCl}}/\mathrm{mol\cdot kg^{-1}}\}_{m_{\mathrm{Na_2SO_4}}} = 0.1708 + 0.02216(T/\mathrm{K}) - 0.000017(T/\mathrm{K})^2$$
$$\sigma(\{m_{\mathrm{NaCl}}/\mathrm{mol\cdot kg^{-1}}\}_{m_{\mathrm{Na_2SO_4}}}) = 0.06 \qquad (17)$$

$$\{m_{\mathrm{Na_2SO_4}}/\mathrm{mol\cdot kg^{-1}}\}_{m_{\mathrm{NaCl}}} = 9.2848 - 0.05012(T/\mathrm{K}) + 0.00007143(T/\mathrm{K})^2$$
$$\sigma(\{m_{\mathrm{Na_2SO_4}}/\mathrm{mol\cdot kg^{-1}}\}_{m_{\mathrm{NaCl}}}) = 0.02 \qquad (18)$$

In this region, the reverse situation is observed, the content of NaCl increases, and that of Na_2SO_4 decreases (Figures 8 and 9).

The behavior of the apparent molar enthalpy of solution of sodium chloride and sodium sulfate in the NaCl + Na_2SO_4 + H_2O system is similar to that in the NaCl + Na_2CO_3 + H_2O system (Figures 7 and 10). When sodium carbonate decahydrate exists in the solid phase $\overline{\Delta H}_{\mathrm{NaCl}} < 0$ and $\partial\overline{\Delta H}_{\mathrm{NaCl}}/\partial T < 0$; in the case of sodium sulfate the apparent molar enthalpy of solution is large and positive, $\overline{\Delta H}_{\mathrm{Na_2CO_3}} > 0$, and has a maximum near 281 K. Changes with T in the sodium sulfate region are rather small. $\overline{\Delta H}_{\mathrm{NaCl}} > 0$ but $\partial\overline{\Delta H}_{\mathrm{NaCl}}/\partial T > 0$ and $\overline{\Delta H}_{\mathrm{Na_2CO_3}} < 0$ and also $\overline{\Delta H}_{\mathrm{Na_2CO_3}} > 0$. At 298.15 K we have: $\overline{\Delta H}_{\mathrm{NaCl}} = 1.7\ \mathrm{kJ\cdot mol^{-1}}$ and $\overline{\Delta H}_{\mathrm{Na_2CO_3}} = -8.2\ \mathrm{kJ\cdot mol^{-1}}$. Osmotic coefficients $\phi(T, m_2, m_3)$, as in other systems, decrease with temperature, $\partial\phi(T, m_2, m_3)/\partial T < 0$ (Table 3) and the apparent molar enthalpy of vaporization in the NaCl + Na_2SO_4 + H_2O system at 298.15 K is $\overline{\Delta H} = 46.6\ \mathrm{kJ\cdot mol^{-1}}$.

Determined here, the relative humidities $(100\cdot a_1(T, m_2, m_3))$ are rather close, the highest, 77 % at 298.15 K, is in the aqueous saturated solution with NaCl + Na_2SO_4. In other systems we have 71 % saturated with NaCl + Na_2CO_3 and 68 % with NaCl + KNO_3. In the systems with sodium sulfate and sodium carbonate, the water activities increase with T, $\partial a_1(T, m_2, m_3)/\partial T > 0$, but with potassium nitrate the opposite situation is observed $\partial a_1(T, m_2, m_3)/\partial T < 0$ (Table 3).

■ CONCLUSIONS

Vapor pressures of water over saturated solutions with regards to two salts in the NaCl + KNO_3 + H_2O, NaCl + Na_2CO_3 + H_2O, and NaCl + Na_2SO_4 + H_2O systems were determined in the $T = 278$ K to $T = 322$ K temperature range. As was observed previously,[40] the vapor pressure of water is always higher in the systems with potassium salts than with sodium salts.

In all systems, changes in vapor pressure with temperature are monotonic functions of T. The same took place with other derived from $p(T, m_2, m_3)$ quantities, the water activities, the osmotic coefficients and the apparent molar enthalpies of vaporization (Tables 1 and 3, Figures 1 and 2). However, if they are considered as a function of the total ionic strength I, their curves acquire a quite different character which expresses indirectly the change in composition of the solid phase with T (Figures 5 and 6). The apparent molar enthalpies of solution originate from temperature dependence of the solubilities in invariant points, $m_i(T)$, and therefore represents directly the changes in the solid phase (Figures 7 and 10).

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: apelblat@bgu.ac.il.

■ ACKNOWLEDGMENT

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

■ DEDICATION

This work is dedicated to Professor John M. Prausnitz for his invaluable contributions to the thermodynamics of solutions.

■ REFERENCES

(1) Seidell, A.; Linke, W. F. *Solubilities of Inorganic and Organic Compounds*. Supplement to the 3rd ed.; Van Nostrand: New York, 1952.

(2) Stephen, H., Stephen, T., Eds.; *Solubilities of Inorganic and Organic Compounds*; Pergamon Press: Oxford, 1963.

(3) Linke, W. F., Ed.; *Solubilities of Inorganic and Metal-Organic Compounds*; American Chemical Society: Washington, DC, 1965.

(4) Parker, V. B. *Thermal Properties of Aqueous Uni-univalent Electrolytes*; U.S. Nat. Bureau of Standards: Washington, DC, 1965.

(5) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed. (revised); Butterworths: London, 1968.

(6) Smith-Magowan, D.; Goldberg, R. N. A Bibliography of Sources of Experimental Data Leading to Thermal Properties of Binary Aqueous Electrolyte Solutions, Special Publ. 537; U.S. Nat. Bureau of Standards: Washington, DC, 1979.

(7) Silcock, H. L., Ed.; *Solubilities of Inorganic and Organic Compounds*; Pergamon Press: Oxford, U.K., 1979.

(8) Broul, M.; Nyvlt, T. J.; Söhnel, O. *Solubility in Inorganic Two-components Systems*; Elsevier Sci. Publ. Co.: Amsterdam, 1981.

(9) Freeth, F. A. The system Na$_2$O-CO$_2$-NaCl-H$_2$O considered as two-four component systems. *Phil. Trans. R. Soc. (London)* **1923**, *223*, 35–87.

(10) Lerman, A. Model of chemical evolution of a chloride lake-the Dead Sea. *Geochim. Cosmochim. Acta* **1967**, *31*, 2309–2330.

(11) Covington, A. K.; Lilley, T. H.; Robinson, R. A. Excess free energies of aqueous mixtures of some alkali halide salt pairs. *J. Phys. Chem.* **1968**, *72*, 2759–2763.

(12) Robinson, R. A.; Platford, R. F.; Childs, C. W. Thermodynamics of aqueous mixtures of sodium chloride, potassium chloride, sodium sulfate and potassium sulfate at 25° C. *J. Solution Chem.* **1972**, *1*, 167–172.

(13) Meissner, H. P.; Kusik, C. L. Aqueous solutions of two or more strong electrolytes. Vapor pressures and solubilities. Ind. Eng. Process. *Des. Develop.* **1973**, *12*, 205–208.

(14) Sangster, J.; Teng, T. T.; Lenzi, F. A General method of calculating the water activity of supersaturated aqueous solutions from ternary data. *Can. J. Chem.* **1973**, *51*, 2626–2631.

(15) Pitzer, K. S.; Kim, J. J. Thermodynamics of electrolytes. IV. Activity and osmotic coefficients for mixed electrolytes. *J. Am. Chem. Soc.* **1974**, *78*, 5701–5707.

(16) Wood, J. R. Thermodynamics of brine-salt equilibria - I The systems NaCl-KCl-MgCl$_2$-CaCl$_2$-H$_2$O and NaCl-MgSO$_4$-H$_2$O at 25 °C. *Geochim. Cosmochim. Acta* **1975**, *39*, 1147–1163.

(17) Harvie, C. E.; Weare, J. H. The prediction of mineral solubilities to high concentration at 25 °C. *Geochim. Cosmochim. Acta* **1980**, *44*, 981–997.

(18) Harvie, C. E.; Eugster, H. P.; Weare, J. H. Mineral equilibria in the six-componenent seawater system Na-K-Ca-SO4-Cl-H$_2$O. II: Compositions of the saturated solutions. *Geochim. Cosmochim. Acta* **1982**, *46*, 1603–1618.

(19) Conceição, M.; de Lima, P.; Pitzer, K. S. Thermodynamics of electrolyte mixtures of NaCl with Na$_2$SO$_4$ and with MgCl$_2$. *J. Solution Chem.* **1983**, *12*, 187–199.

(20) Harvie, C. E.; Møller, N.; Weare, J. H. The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO$_4$-OH-HCO$_3$-CO$_2$-H$_2$O system to high ionic strengths at 25 °C. *Geochim. Cosmochim. Acta* **1984**, *48*, 723–751.

(21) Kumar, A.; Patwardhan, V. S. Prediction of vapor pressure of aqueous solutions of single and mixed electrolytes. *Can. J. Chem. Eng.* **1986**, *64*, 831–837.

(22) Møller, N. The prediction of mineral solubilities in natural waters. A chemical equilibrium model for the Na-Ca-Cl-SO$_4$ + H$_2$O system, to high temperature 25° - 250° C and concentration. *Geochim. Cosmochim. Acta* **1988**, *52*, 821–837.

(23) Marliacy, P.; Hubert, N.; Schuffenecker, L.; Solimando, R. Use of Pitzer's model to calculate thermodynamic properties of aqueous solutions of Na$_2$SO$_4$ + NaCl between 273.15 and 373.15 K. *Fluid Phase Equilib.* **1998**, *148*, 95–106.

(24) Lanier, R. D. Activity coefficients of sodium chloride in aqueous three-component solutions by cation-sensitive glass electrodes. *J. Phys. Chem.* **1965**, *69*, 3992–3998.

(25) Butler, J. N.; Hsu, P. T.; Synnott, J. C. Activity coefficient measurements in aqueous sodium chloride — sodium sulfate electrolytes using sodium amalgam electrodes. *J. Phys. Chem.* **1967**, *71*, 910–914.

(26) Wu, Y. C.; Rush, R. M.; Scatchard, G. Osmotic and activity coefficients for binary mixtures of sodium chloride, sodium sulfate, magnesium sulfate, and magnesium chloride in water at 25°. I. Isopiestic measurements on the four systems with common ions. *J. Phys. Chem.* **1968**, *72*, 4048–4053.

(27) Platford, R. F. Isopiestic measurements on the system H$_2$O - NaCl - Na$_2$SO$_4$ at 25° C. *J. Chem. Eng. Data* **1968**, *13*, 46–48.

(28) Synott, J. C.; Butler, J. N. The mean activity coefficient of sodium sulfate in aqueous sodium sulfate - sodium chloride electrolytes. *J. Phys. Chem.* **1968**, *72*, 2474–2477.

(29) Bezboruah, C. P.; Covington, A. K.; Robinson, R. A. Excess Gibbs energies of aqueous mixtures of alkali metal chlorides and nitrates. *J. Chem. Thermodyn.* **1970**, *2*, 431–437.

(30) Childs, C. W.; Platford, R. F. Excess free energies of mixing at temperatures below 25°. Isopiestic measurements on the systems H$_2$O - NaCl - Na$_2$SO$_4$ and H$_2$O - NaCl - MgSO$_4$. *Aust. J. Chem.* **1971**, *24*, 2487–2491.

(31) Platford, R. F. Isopiestic determination of solubilities in mixed salt solutions. Two salt systems. *Am. J. Sci.* **1972**, *272*, 959–1968.

(32) Kirgintsev, A. N.; Luk'yanov, A. V. Thermodynamic characteristics of saturated aqueous solutions of salts. *Russ. J. Inorg. Chem.* **1967**, *12*, 1070–1072.

(33) White, D. R., Jr.; Bates, R. G. Osmotic coefficients and activity coefficients of aqueous mixtures of sodium chloride and sodium carbonate at 25 °C. *Aust. J. Chem.* **1980**, *33*, 1903–1908.

(34) Sarada, S.; Anathaswany, J. Thermodynamic properties of electrolyte solutions: emf study of the system sodium chloride - sodium sulfate - water at 25, 35 and 45° C. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 81–84.

(35) Tishchenko, P. Ya.; Bychkov, A. S.; Hrabéczy-Páll, A.; Tóth, K. Activity coefficients for the system NaCl + Na$_2$SO4 + H$_2$O. Application of Pitzer's equations. *J. Solution Chem.* **1992**, *21*, 261–274.

(36) Galleguillos-Castro, H. R.; Hernández-Luis, F.; Fernández-Merida, L.; Esteso, M. A. Thermodynamic study of the NaCl + Na$_2$SO$_4$ + H$_2$O system by emf measurements at four temperatures. *J. Solution Chem.* **1999**, *28*, 791–807.

(37) Marliacy, P.; Solimando, R.; Bouroukba, M.; Schuffenecker, L. Thermodynamics of crystallization of sodium sulfate decahydrate in H$_2$O + NaCl + Na$_2$SO$_4$; application to Na$_2$SO$_4\cdot$10H$_2$O based latent heat storage materials. *Thermochim. Acta* **2000**, *344*, 85–94.

(38) Marliacy, P.; Schuffenecker, L.; Solimando, R. Vapor pressure and dissolution enthalpy measurements in ternary [H$_2$O + NaCl + Na$_2$SO$_4$] between 298 and 363 K. *J. Chem. Eng. Data* **2003**, *48*, 241–248.

(39) Rard, J. A.; Clegg, S. L.; Platford, R. F. Thermodynamics of {zNaCl + (1-z)Na$_2$SO$_4$} (aq.) from T = 278.15 K to T = 318.15 K and representation with an extented ion-interaction (Pitzer) model. *J. Chem. Thermodyn.* **2003**, *35*, 967–1008.

(40) Apelblat, A.; Korin, E. Temperature dependence of vapor pressures over saturated aqueous solutions at invariant points of the NaCl + KCl + H$_2$O, NaCl + NaNO3 + H$_2$O, KCl + KBr + H$_2$O, KCl + KI + H$_2$O, KCl + KNO$_3$ + H$_2$O, and KCl + K$_2$SO$_4$ + H$_2$O systems. *J. Chem. Eng. Data* **2009**, *54*, 1619–1624.

(41) Apelblat, A.; Korin, E. The vapor pressures of saturated aqueous solutions of sodium chloride, sodium bromide, sodium nitrite, potassium iodate, and rubidium chloride at temperatures from 277 to 323 K. *J. Chem. Thermodyn.* **1998**, *30*, 59–71.

(42) Modell, M.; Reid, R. C. *Thermodynamics and Its Applications*; Prentice-Hall: Englewood Cliffs, NJ, 1974; pp 338−339.

(43) Williamson, A. T. The exact calculation of heats of solution from solubility data. *Trans. Faraday Soc.* **1944**, *40*, 421–436.

(44) Saul, S.; Wagner, W. International equations for the saturation properties of ordinary water substance. *J. Phys. Chem. Ref. Data* **1987**, *16*, 893–901.