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A Modified Rackett Equation Applied to Water and Aqueous NaCl and KCl Solutions

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The Rackett equation is modified for the calculations of the liquid volumes of H_2O, H_2O + NaCl (up to 25.0 NaCl mass %), and H_2O + KCl (up to 4.0 KCl mass %) solutions under vapor-saturated conditions. Two terms are added to the index part of the Rackett equation for describing the volumetric property of liquid water. The average of the absolute deviations from the *NBS/NRC Steam Tables* at 293.15 K to 643.15 K in steps of 10 K becomes 0.39%. The effect of the dissolved salt on the volumetric property is included in the index part. The equations for molar volumes of aqueous NaCl solutions at 373.15 K to 773.15 K and aqueous KCl solutions at 373.15 K to 643.15 K are obtained on the basis of the previous experimental results. The average of the absolute deviations for aqueous NaCl solutions is 0.77%, and that for the aqueous KCl solutions is 0.63%.

Introduction

Saturated liquid volumes have been correlated with various types of equations (e.g., summary by Reid et al.[1]). The Rackett equation[2] is one such equation and is expressed as follows.

$$V = V_c Z_c^{(1-T_r)^{2/7}} \tag{1}$$

where V, V_c, Z_c, and T_r stand for the molar volume of saturated liquid, the critical molar volume, the critical compressibility factor, and the reduced temperature, respectively. Rackett[2] reported that eq 1 works well for water at $T_r > 0.82$. The correlation becomes worse with a decrease in temperature. Spencer and Danner[3] replaced Z_c by a substance-specific constant (Z_{RA}) for improving the accuracy of the equation. When Z_{RA} is different from the critical compressibility factor, the accuracy of the modified equation becomes worse on approaching the critical temperature.

The Rackett equation or its modification by Spencer and Danner has been applied to the nonelectrolyte solutions and their mixtures (see Reid et al.[1]). However, applications of this equation to aqueous electrolyte solutions have not been carried out. Among the electrolyte solutions, aqueous NaCl and KCl solutions are considered here for such an application. The volumetric properties of these solutions have been studied by many workers (e.g., summary by Anderko and Pitzer[4,5]). Various equations of state have been proposed for these aqueous electrolyte solutions above 573.15 K (e.g., Anderko and Pitzer,[4,5] Tanger and Pitzer,[6] and Hovey et al.[7]). At the lower temperatures, Pitzer equations have been obtained for these solutions.[8,9] The simplicity of the Rackett equation for describing the liquid volumes might be useful for geochemical or engineering applications when the volumetric properties are concerned.

This paper consists of two parts. First, this study modifies the Rackett equation by adding two correction terms for describing the molar volumes of liquid water at 293.15 K to 643.15 K ($0.453 < T_r < 0.994$). The second part is to describe the molar volumes of aqueous NaCl and KCl solutions up to 773.15 K and 643.15 K, respectively.

Modification of the Rackett Equation

This study modifies the index part of the Rackett equation. The proposed equation is as follows.

$$V = V_c Z_c^{\{(1-T_r)^{2/7}+f(T_r)\}} Z_c^{g(T,x)} \tag{2}$$

The function *f(T*$_r$*)* corrects the deviations of the Rackett equation from the molar volumes of pure water at low temperatures and is dependent on the reduced temperature. The effect of the dissolved salt is expressed as *g(T,x)*, which depends on the absolute temperature (T) and the mole fraction of the salt. Dissociation of the salt species is not considered here.

The present study obtains the volumetric data from the literature values at the critical conditions and the vapor-saturated conditions to three significant digits. Then an equal weight is placed on each datum. The accuracy of the literature data is shown in later sections. This study computes the critical compressibility factors to three significant digits from the pressure−volume−temperature relations in the referenced works. Then, the critical molar volume and the critical compressibility factor are expressed as functions of the salt concentration.

Critical Properties of Water and Aqueous NaCl and KCl Solutions. The critical properties of pure water have been studied extensively and are taken from the *NBS/NRC Steam Tables*[10] in this study. The *Steam Tables* list the critical density to three significant digits.

Although the critical temperatures of aqueous NaCl solutions have been reported by many works,[11−25] the other critical properties have not been studied extensively. Knight and Bodnar[21] gave the temperature−pressure−volume−composition (up to 30 mass % NaCl) relation at the critical conditions. They obtained the relation with the synthetic fluid inclusion technique.[26] Khaibullin and

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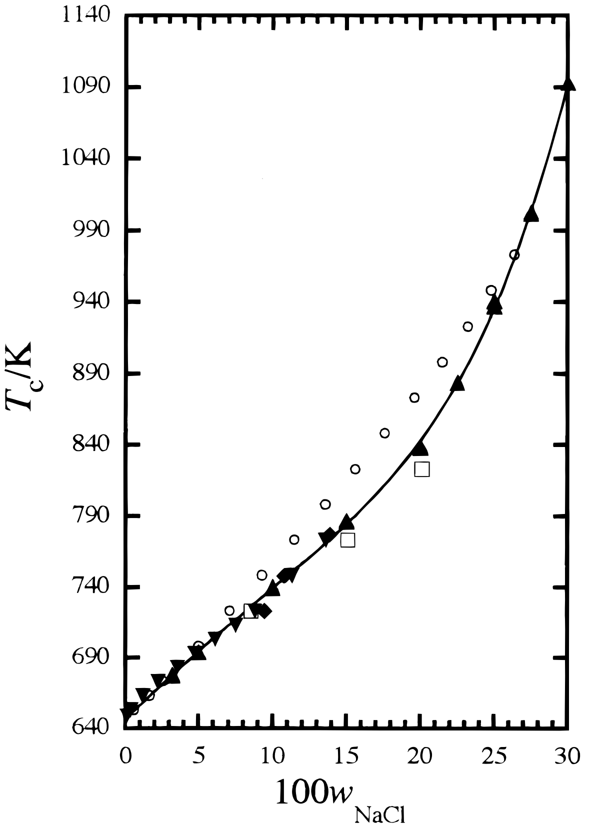

Figure 1. Critical temperatures (T_c) of aqueous NaCl solutions against the mass % value of NaCl (100w_{NaCl}). The solid line shows the present result. Symbols represent the following works: ○, Sourirajan and Kennedy;[13] □, Urusova;[16] ◆, Rosenbauer and Bischoff;[19] ▲, Knight and Bodnar;[21] ▼, Bischoff and Pitzer.[22] For the sake of clarity, some works treating with aqueous solutions of <10 mass % NaCl are not shown. See text for the explanation of the regression line.

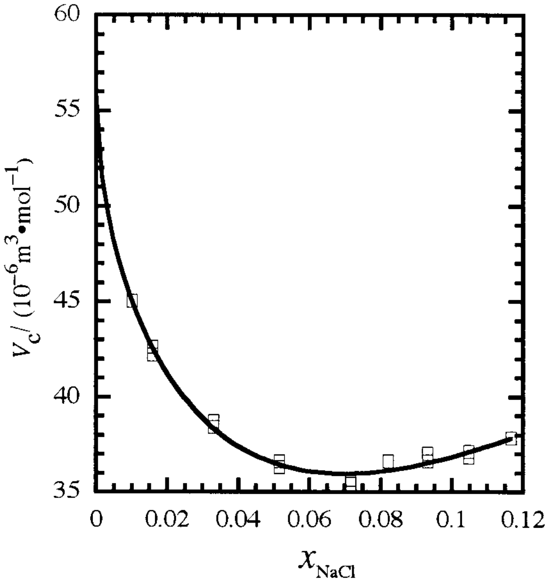

Figure 2. Critical molar volumes (V_c) of aqueous NaCl solutions against the mole fraction of NaCl (x_{NaCl}). The solid line shows the present result. Squares show the computed molar volumes from the experimental results of Knight and Bodnar.[21] Experimental results on 3 mass % or less concentrated solutions are not included here. See text for the explanation of the regression line.

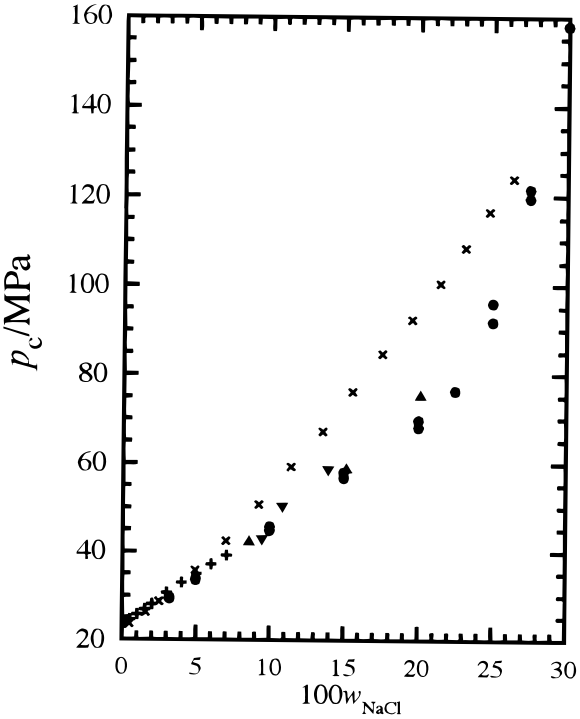

Figure 3. Critical pressures (p_c) of aqueous NaCl solutions against the mass % value of NaCl (100w_{NaCl}). Symbols represent the results of the following works: ●, this study; +, Ölander and Liander;[12] ×, Sourirajan and Kennedy;[13] ▲, Urusova;[16] ▼, Rosenbauer and Bischoff.[19] For the sake of clarity, some works treating with aqueous solutions of <10 mass % NaCl are not shown.

Borisov[14] and Abdulagatov et al.[25] also reported the experimental results on critical volumes. The NaCl concentrations at the critical points were <3.0 mass % in those studies. Thus, this study relies on the experimental results of Knight and Bodnar.[21]

Knight and Bodnar[21] claimed that the critical temperatures have the accuracies ±0.2 K at 647.15 K, ±2.0 K at 846.15 K, and ±5.0 K at 933.15 K. Their critical temperatures agree well with those of previous works at low concentrations (Figure 1). In this study, w denotes the mass fraction of the subscript salt. When the NaCl concentrations are from 10 to 25 mass %, their temperatures are systematically lower than those reported by Sourirajan and Kennedy[13] but are close to those of Urusova,[16] Rosenbauer and Bischoff,[19] and Bischoff and Pitzer.[22] From the formation conditions of the synthetic fluid inclusions, the critical molar volumes are computed by the equation of Anderko and Pitzer[4] and are shown in Figure 2. The critical volumes calculated in this study are thought to have the accuracy $\pm 1 \times 10^{-7}$ m^3·mol^{-1}, which corresponds to ±0.2% to ±0.3% accuracy. The accuracy is based on that property of the equation of Anderko and Pitzer.[4] The critical temperature and the computed molar volume are substituted into the equation of Anderko and Pitzer[4] for obtaining the corresponding critical pressure. The errors of the temperature and volume data at the critical condition are propagated to the error of the computed critical pressure. The computed results are compared with those of other works (Figure 3). They are systematically lower than those of Sourirajan and Kennedy[13] at 5 to 25 mass % but are almost consistent with the results of Urusova[16] and Rosenbauer and Bischoff.[19] The accuracy in critical pressure is assumed to be 1% at 0 mass % and becomes worse at the higher concentrations. It is considered to be 10% at 30 mass %. Because the critical compressibility factors are calculated from the pressure−volume−temperature relation, the ac-

Table 1. Critical Properties of Water and Aqueous NaCl and KCl Solutions[a]

H_2O

$T_c/\mathrm{K} = 647.126$, $V_c/(\mathrm{m^3 \cdot mol^{-1}}) = 55.9 \times 10^{-6}$, $Z_c = 0.229$

$H_2O + \mathrm{NaCl}$: $0 \leq \mathrm{NaCl\ mass\ \%} \leq 30.0$

$T_c/\mathrm{K} = 647.126 + 9.65552c + 0.0230725c^2 - 0.0125208c^3 + 0.000584799c^4$

$V_c/(\mathrm{m^3 \cdot mol^{-1}}) = (55.9 - 105.865y - 154.137y^2 + 1475.17y^3 - 1722.92y^4) \times 10^{-6}$

$Z_c = 0.229 - 0.00217332\mathrm{c} + 0.00155298c^2 - 0.000103687c^3 + 0.00000234374c^4$

$H_2O + \mathrm{KCl}$: $0 \leq \mathrm{KCl\ mass\ \%} \leq 4.06$

$T_c/\mathrm{K} = 647.126 + 12.2868c - 0.785253c^2$

$V_c/(\mathrm{m^3 \cdot mol^{-1}}) = (55.9 - 127.671y + 242.344y^2) \times 10^{-6}$

$Z_c = 0.229 - 0.0132774c + 0.00450036c^2$

[a] The c stands for the mass % value of the salt. The unit y denotes $\{x/(1 - x)\}^{0.5}$, where x stands for the mole fraction of the salt.

curacy in that property is considered to be from around 1% to 10%. With the increase in the salt concentration, the uncertainty in the critical compressibility factor becomes large.

Critical properties of KCl solutions are taken from the tabulated values of Potter et al.[27] because only their work showed the pressure−volume−temperature−concentration relation at the critical conditions. The maximum concentration of KCl was 0.568 molal (or 4.062 mass %). The available data sets on the critical properties are, thus, very limited. Potter et al.[27] claimed that the temperatures, pressures, and densities at the critical conditions have the accuracies ±1.0 K, ±0.1 MPa, and ±5 kg·m^{-3}. Then critical compressibility factors are considered to have the accuracy ±0.5%. This study does not include their results at 0.006 molal concentration to avoid overweighing the properties at the dilute region.

The critical properties of NaCl and KCl solutions are expressed by the fourth-degree polynomial function and the quadratic function of the concentration, respectively. Critical temperatures and critical compressibility factors are expressed as functions of mass percent. Critical molar volumes are expressed by the polynomial functions of $\{x/(1 - x)\}^{0.5}$, where x stands for the mole fraction of the salt. Best-fit equations were obtained by linear least-squares regression analyses. Results of the computations and the critical properties of pure water are listed in Table 1. Regression lines for temperatures and molar volumes are shown in Figures 1, 2, 4, and 5.

The use of $\{x/(1 - x)\}^{0.5}$ for the regressions of the volumetric data makes the sums of the squared residuals (in terms of 10^{-12} m^{-6}·mol^{-2}) for aqueous NaCl and KCl solutions 1.26 and 0.49, respectively. If we express the critical volume as the function of the mole fraction of the salt, the sums of the squared residuals for aqueous NaCl and KCl solutions become 10.02 and 1.27, respectively. When the critical volume is expressed as a function of the mass percent of the salt, the sums are 5.76 for aqueous NaCl solution and 1.18 for aqueous KCl solution. Therefore, the functions of $\{x/(1 - x)\}^{0.5}$ fit the volumetric data well. The variable $\{x/(1 - x)\}^{0.5}$ is introduced on the basis of simple assumptions. First, the present study considers the following relation along the critical line.

$$V^{\mathrm{tot}} = n_{\mathrm{water}} V° + n_s \Phi_s$$
$$= (n_{\mathrm{water}} + n_s)\left(\frac{n_{\mathrm{water}}}{n_{\mathrm{water}} + n_s} V° + \frac{n_s}{n_{\mathrm{water}} + n_s} \Phi_s\right) \quad (3)$$

where V^{tot}, $V°$, and Φ_s stand for the volume of the aqueous solution containing n_{water} moles of water and n_s moles of salt, the molar volume of pure water, and the apparent molar volume of the salt, respectively, at a critical point. Therefore, $V°$ is constant. Then, the following approximation of the molar volume of the aqueous solution (V) is assumed.

$$V = V° + \frac{n_s}{n_{\mathrm{water}}} \Phi_s$$
$$= V° + \frac{x}{1 - x} \Phi_s \quad (4)$$

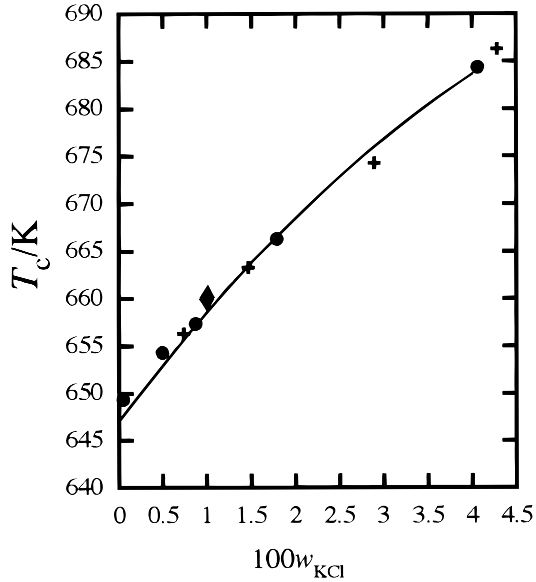

Figure 4. Critical temperatures (T_c) of aqueous KCl solutions against the mass % value of KCl (100w_{KCl}). The solid line shows the present result. Symbols represent the following works: ▼, Khaibullin and Borisov;[14] +, Marshall and Jones;[15] ●, Potter et al.;[27] ▲, Abdulagatov et al.[25] See text for the explanation of the regression line.

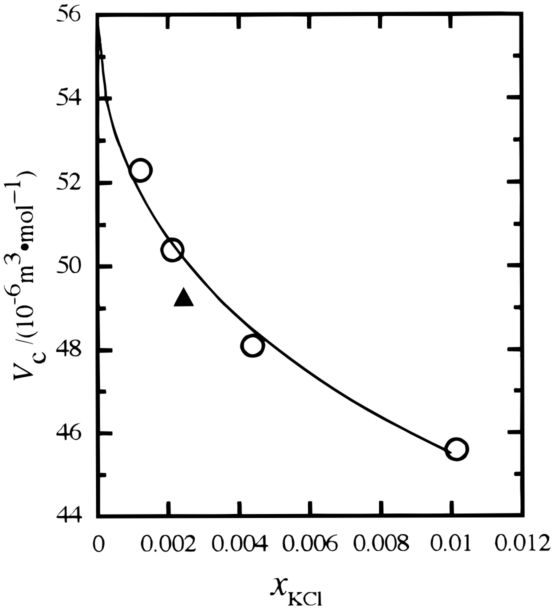

Figure 5. Critical molar volumes (V_c) of aqueous KCl solutions against the mole fraction of KCl (x_{KCl}). The solid line shows the present result. Symbols represent the following works: ○, Potter et al.;[27] ▲, Abdulagatov et al.[25] See text for the explanation of the regression line.

Table 2. Volumetric Properties of H_2O + NaCl Referenced in This Study

	temp	mass %	data points
Rogers and Pitzer[8]	373.15 K to 453.15 K	0.581−22.613	45
Abdulagatov et al.[25]	473 K to 713 K	1.000−25.01	60
Crovetto et al.[29]	623.15 K	1.440−14.917	4
Urusova[16]	723.15 K to 773.15 K	10.0−20.1	4

The volume of the aqueous solution can also be written as follows.

$$V^{\mathrm{tot}} = n_{\mathrm{water}}\bar{V}_{\mathrm{water}} + n_{\mathrm{s}}\bar{V}_{\mathrm{s}} \tag{5}$$

where bars indicate the partial molar volumes of the subscript components. Then the partial molar volume of the salt can be expressed as follows.

$$\bar{V}_{\mathrm{s}} = \left(\frac{\partial V^{\mathrm{tot}}}{\partial n_{\mathrm{s}}}\right)_{n_{\mathrm{water}}} = \Phi_{\mathrm{s}} + n_{\mathrm{s}}\left(\frac{\partial \Phi_{\mathrm{s}}}{\partial n_{\mathrm{s}}}\right)_{n_{\mathrm{water}}} = \Phi_{\mathrm{s}} + \left(\frac{\partial \Phi_{\mathrm{s}}}{\partial \ln n_{\mathrm{s}}}\right)_{n_{\mathrm{water}}} = \Phi_{\mathrm{s}} + \left(\frac{\partial \Phi_{\mathrm{s}}}{\partial \ln(n_{\mathrm{s}}/n_{\mathrm{water}})}\right)_{n_{\mathrm{water}}} = \Phi_{\mathrm{s}} + \left(\frac{\partial \Phi_{\mathrm{s}}}{\partial \ln(x/(1-x))}\right)_{n_{\mathrm{water}}} \tag{6}$$

From eq 6, the apparent molar volume of the salt is considered to be a function of $x/(1-x)$. Accordingly, the partial molar volumes of the salt and water can be expressed as functions of $x/(1-x)$. On the basis of these relations (eqs 4 and 6), the critical molar volumes are regressed with the function $\{x/(1-x)\}^{0.5}$.

Modified Rackett Equation for Water. The volumetric property of pure water is taken from the *Steam Tables*[10] at temperatures from 293.15 K to 643.15 K in steps of 10 K. These temperatures correspond to the T_{r} values of 0.4530 to 0.9939. This study obtains $f(T_{\mathrm{r}})$ as the following form.

$$f(T_{\mathrm{r}}) = 0.0397358(1 - T_{\mathrm{r}}^{-1}) - 0.0208359(1 - T_{\mathrm{r}}^{-1})^2 \tag{7}$$

The coefficients are obtained by the nonlinear least-squares regression technique[28] with the following objective function (F).

$$F = \sum[1 - V_{\mathrm{calc}}/V_{\mathrm{ref}}]^2 \tag{8}$$

By the inclusion of $f(T_{\mathrm{r}})$, eq 2 without the $g(T,x)$ term gives the relative deviations, $1 - V_{\mathrm{calc}}/V_{\mathrm{ref}}$, from −0.86% (at 593.15 K) to 0.39% (at 393.15 K). The average of the absolute deviations (AAD) is 0.39%, where the AAD value of N data points is obtained from the following equation.

$$\mathrm{AAD}(\%) = \frac{100}{N}\sum_{i=1}^{N}|1 - V_{\mathrm{calc}}/V_{\mathrm{ref}}| \tag{9}$$

Modified Rackett Equation for NaCl Solution. The volumetric properties of NaCl solutions at vapor-saturated pressures have been studied extensively (e.g., summary of Bischoff[24]). This study takes the data array in the compilation of Rogers and Pitzer[8] and the experimental results of Abdulagatov et al.,[25] Crovetto et al.,[29] and Urusova.[16] The referenced temperature−concentration regions are listed in Table 2. The reduced temperatures of the referenced data points range from 0.421 (22.613 mass % at 373.15 K) to 0.994 (1.0 mass % at 653.15 K) on the basis of the equation in Table 1. Khaibullin and Borisov,[14] Copeland et al.,[30] and Gehrig et al.[31] obtained the volumetric properties covering almost the same temperature−concentration regions as those of Abdulagatov et al.[25] or Urusova.[16] This study considers that the last two data sets gave the precise data.

Rogers and Pitzer[8] compiled the densities up to 6.0 molal and 573.15 K under the vapor-saturated conditions. The tabulated densities at the highest concentration were extrapolated values. This study takes their tabulated densities of up to 5 molal solutions and picks up the density data from 373.15 K to 453.15 K in steps of 20 K. In that temperature−concentration region, they claimed 0.07% accuracy in density. Above 473.15 K, their equation is based only on the experimental results of Hilbert,[32] according to Majer et al.[33] Since then, some experimental results have been reported. This study refers to the recent experimental results of Abdulagatov et al.[25] above 453.15 K. Abdulagatov et al.[25] claimed that the accuracy in the saturation temperature at a specific density is about 0.4 K. Then the claimed accuracy is converted into the accuracy of the saturated liquid volume. The accuracy of the liquid volume is estimated to be better than ±1% for all the data and much better than ±0.5% for the results at low temperatures. Abdulagatov et al.[25] obtained the density at 693 K and 5 mass % at the vapor−liquid equilibrium condition while Khaibullin and Borisov[14] and Knight and Bodnar[21] indicated the one-phase field at that condition. This study does not incorporate this data point. The experimental results of Crovetto et al.[29] were claimed to have an accuracy of about ±0.1% at 623.15 K. Urusova[16] showed that the experimental results have an accuracy of ±0.4% to ±1.0% at 723.15 K and 773.15 K at concentrations < 30 mass %.

From eqs 2 and 7, we obtain the following equation.

$$g(T,x) = \frac{\log\left(\frac{V}{V_{\mathrm{c}}}\right)}{\log Z_{\mathrm{c}}} - (1 - T_{\mathrm{r}})^{2/7} - 0.0397358(1 - T_{\mathrm{r}}^{-1}) + 0.0208359(1 - T_{\mathrm{r}}^{-1})^2 \tag{10}$$

The g values are plotted against the mole fraction of NaCl at 373.15 K, 473 K, 573 K, 673 K, and 773.15 K (Figure 6). The dissolution of the salt significantly affects the index part of eq 2. The obtained g values from 113 data points (Table 2) are regressed by the following equation.

$$g = (x - x_{\mathrm{c}})^{b_1}\{(\sum_{i=0}^{j} b_{i+2}x^{i/N}) + T(b_{j+3}x^{m/N} + b_{j+4}x^{n/N})\} = (x - x_{\mathrm{c}})^{b_1}\{(b_2 + \cdots + b_{j+2}x^{j/N}) + T(b_{j+3}x^{m/N} + b_{j+4}x^{n/N})\} \tag{11}$$

The integer N is varied from 1 to 4. This study considers $j = 1, 2, 3,$ or 4 and the integers m and n from 0 to j and 0 to $m - 1$. The x_{c} stands for the mole fraction of NaCl at the critical conditions and is computed from the experimental mass percent data with the equation in Table 1. When the temperature is below the critical temperature of water, the x_{c} value is set to be 0. Therefore, the g values become 0 at any critical points, which results in the calculated molar volumes being equal to the critical volumes at any critical points. By the nonlinear least-squares regression with the objective function F (eq 8), the regression coefficients are obtained for all of the considered equations. When the regression analyses yield negative b_1 values, those equations are considered as inappropriate.

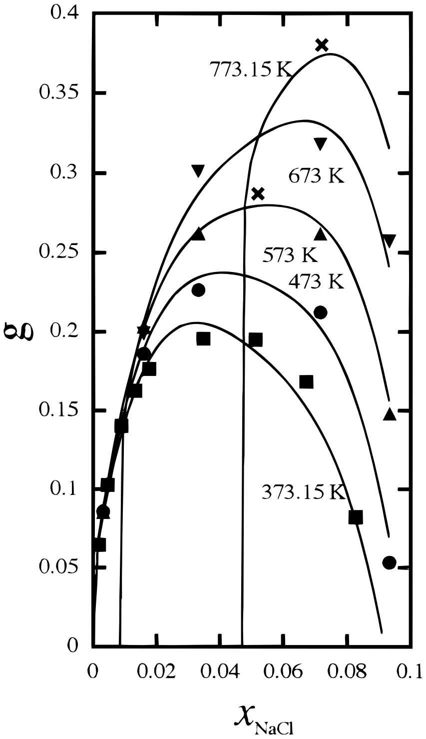

Figure 6. Relation between g (eq 10) and the mole fraction of NaCl (x_{NaCl}). Symbols designate the following temperatures: ■, 373.15 K; ●, 473 K; ▲, 573 K; ▼, 673 K; ×, 773.15 K. Regression lines at the labeled temperatures are obtained with eq 12. See text for the explanation of the regression lines.

Then, this study compares the AAD values (eq 9) from the rest of the results and obtains the following equation.

$$g = (x - x_c)^{0.0620291}[(2.93787 \times 10^4)x^4 - (5.91853 \times 10^3)x^3 + (4.76777 \times 10^2)x^2 - (1.17842 \times 10)x - (7.39632 \times 10^{-2}) - (1.07776 \times 10^{-2})Tx] \quad (12)$$

It should be noted that the b_1 value (0.0620291 in eq 12) is very sensitive to the referenced data sets. When the high-temperature data are overweighed, the value becomes close to 0.

After substitutions of eqs 7 and 12 into eq 2, saturated liquid volumes are computed. The AAD value becomes 0.77%. Relative deviations from the referenced data range from −4.13% (15.1 mass % at 773.15 K) to 3.04% (10 mass % at 723.15 K). Those are shown in temperature−concentration−relative deviation space (Figure 7). Among 113 data points, five data points lying at and above 693 K show absolute deviations larger than 2%. In general, the present equation shows large deviations (both positive and negative ones) at the high and low temperatures. The sign of the deviations depends not only on the temperature but also on the salt concentration.

Modified Rackett Equation for KCl Solution. There are many studies on the densities of aqueous KCl solutions above 100 °C.[11,17,25,27,29,34−36] When two or more works reported the volumetric data in the same temperature−concentration region, this study considers only the most or more comprehensive data set. Considerations of Pabalan and Pitzer[9] are also taken into account. The present study considers the data sets listed in Table 3. The referenced data sets correspond to the reduced temperatures of 0.548 (3.594 mass % at 373.15 K) to 0.979 (0.497 mass % at 639.15 K) on the basis of the equation in Table 1. Because of the scarcity of the data above 647 K, this study considers only the data below the critical temperature of pure water.

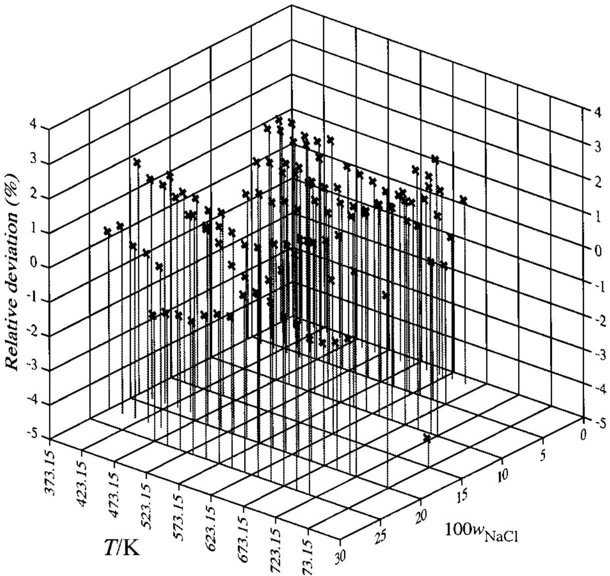

Figure 7. Temperature−concentration−relative deviation relations for the molar volumes of aqueous NaCl solutions.

Table 3. Volumetric Properties of H_2O + KCl Referenced in This Study

	temp	mass %	data points
Rodnyanskii et al.[34]	373.15 K to 573.15 K	1.830−3.594	10
Khaibullin and Borisov[14]	373.15 K to 643.15 K	1	28
Potter et al.[27]	460.15 K to 640.15 K	0.497−4.062	48
Crovetto et al.[29]	623.10 K to 623.11 K	1.830−3.594	2
Abdulagatov et al.[25]	626.43 K	1.002	1

Rodnyanskii et al.[34] and Khaibullin and Borisov[14] did not show the accuracy of the measurements. Therefore, the accuracy of the data sets is partly uncertain. Potter et al.[27] claimed that their measurements have an accuracy of ±3 kg·m^{-3}. The accuracies of the experimental data in Crovetto et al.[29] and Abdulagatov et al.[25] are the same as those for the measurements on aqueous NaCl solutions.

The g values for KCl solutions at 373.15 K and around 573.15 K are plotted against the mole fraction of KCl (Figure 8). By the same procedure with NaCl solution, this study obtains the following equation for representing the g values from 89 data points listed in Table 3.

$$g = (x - x_c)^{0.674500}[(6.86497 \times 10^2)x - 8.12764 - (7.32316 \times 10^{-1})Tx + (4.01875 \times 10^{-3})T] \quad (13)$$

After substitution of eqs 7 and 13 into eq 2, saturated liquid volumes are computed. The average of the absolute deviations for 89 data points is calculated to be 0.63%. Relative deviations from the referenced data range from −1.31% (1.787 mass % at 562.15 K) to 2.58% (3.594 mass % at 623.15 K) and are shown in temperature−concentration−relative deviation space (Figure 9). Among 89 data points, two at 623.15 K show deviations larger than 2%. The absolute deviations generally become large above 573.15 K.

Conclusions

This study modifies the Rackett equation for describing the saturated liquid volumes of H_2O, H_2O + NaCl, and H_2O

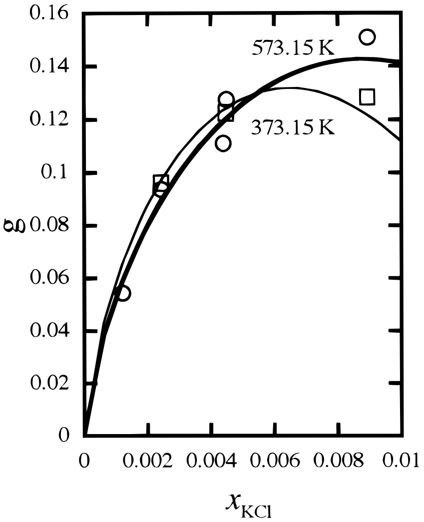

Figure 8. Relation between g (eq 10) and the mole fraction of KCl (x_{KCl}). Symbols designate the following temperatures: □, 373.15 K; ○, 573.15 K. Two data points at 570.15 K and 574.15 K are included. Regression lines at the labeled temperatures are obtained with eq 13. See text for the explanation of the regression lines.

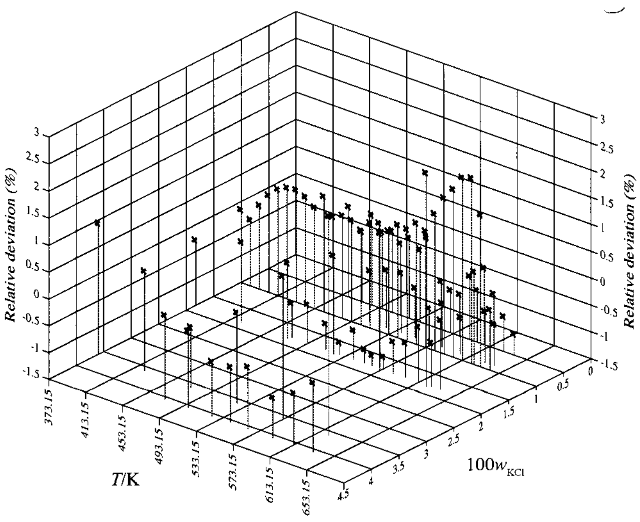

Figure 9. Temperature−concentration−relative deviation relations for the molar volumes of aqueous KCl solutions.

+ KCl solutions up to 643.15 K, 773.15 K, and 643.15 K, respectively. The concentrations of NaCl in the solutions are up to 25 mass %, and those of KCl are up to 4.0 mass %. The obtained equations are as follows.

H_2O:

$$V = V_c Z_c^{(1-T_r)^{2/7}+0.0397358(1-T_r^{-1})-0.0208359(1-T_r^{-1})^2} \tag{14}$$

H_2O + NaCl:

$$V = V_c Z_c^{(1-T_r)^{2/7}+0.0397358(1-T_r^{-1})-0.0208359(1-T_r^{-1})^2} \times Z_c^{(x-x_c)^{0.0620291}(29378.7x^4-5918.53x^3+476.777x^2-11.7842x-0.0739632-0.0107776Tx)} \tag{15}$$

H_2O + KCl:

$$V = V_c Z_c^{(1-T_r)^{2/7}+0.0397358(1-T_r^{-1})-0.0208359(1-T_r^{-1})^2} \times Z_c^{(x-x_c)^{0.674500}(686.497x-8.12764-0.732316Tx+0.00401875T)} \tag{16}$$

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