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Higashi, Hidenori
Division of Material Engineering, Graduate School of Natural Science and Technology, Kanazawa University

Iwai, Yoshio
Department of Chemical Engineering, Faculty of Engineering, Kyushu University

Kitani, Yoshiaki
Department of Chemical Engineering, Faculty of Engineering, Kyushu University

Matsumoto, Kota
Department of Chemical Engineering, Faculty of Engineering, Kyushu University

他

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Application of Association Model for Solubilities of Alkali Metal Chloride in Water Vapor at High Temperatures and Pressures

Hidenori HIGASHI[1], Yoshio IWAI[2], Yoshiaki KITANI[2],
Kota MATSUMOTO[2], Yusuke SHIMOYAMA[2]
and Yasuhiko ARAI[2]
[1]*Division of Material Engineering, Graduate School of Natural Science and Technology, Kanazawa University,*
Kakuma-machi, Kanazawa-shi, Ishikawa 920-1192, Japan
[2]*Department of Chemical Engineering, Faculty of Engineering,*
Kyushu University, 744, Motooka, Nishi-ku, Fukuoka-shi,
Fukuoka 819-0395, Japan

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An association model with a cubic equation of state was adopted to calculate the solubilities of alkali metal chlorides in water vapor under high temperatures and pressures. The solubilities of sodium chloride (NaCl) and potassium chloride (KCl) were correlated by optimized association numbers and equilibrium constants. The correlated results represented well the experimental results. The logarithm of equilibrium constants show linear functions of reciprocal of the absolute temperature.

Introduction

Solubility of inorganic salts at high temperatures and pressures in water vapor is important in the field such as supercritical water oxidation (SCWO) technology. The properties of water above its critical point (647 K, 22.1 MPa) bring about rapid and complete decomposition of such wastes. In the SCWO process, when organic compounds including halogen are decomposed, hydrogen halides cause remarkable corrosion of a reactor. In order to prevent the corrosion, alkalis are added as a neutralization reagent. As a result, inorganic salts such as sodium chloride (NaCl) and potassium chloride (KCl) precipitate and cause plugging of the reactor. For effective discharge of these inorganic salts from the reactor, their solubility data in water at high temperatures and pressures are very important to design the SCWO process (DiPippo *et al.*, 1999).

Sourirajan and Kennedy (1962) reported the solubilities of sodium chloride in water vapor at high temperatures and pressures. Bischoff *et al.* (1986) measured the vapor–liquid equilibria for water + sodium chloride system by a static method. Galobardes *et al.* (1981), Alekhin and Vakulenko (1987), and Armellini and Tester (1993) also reported the solubilities of sodium chloride in water vapor by a dynamic method. Their solubility data are markedly different from each other. Pitzer and co workers (Pitzer and Pabalan, 1986; Pitzer and Tanger, 1988; Bischoff and Pitzer, 1989; Tanger and Pitzer, 1989; Pitzer, 1998; Hovey *et al.*, 1990) proposed an empirical equation of state for water + sodium chloride system and water + potassium chloride system. Anderko and Pitzer (1993) calculated the vapor–liquid equilibria for water + sodium chloride and showed good representation to the experimental data. Belhachemi and Gotouk (1999) studied the phase diagrams of the water–phenol–salt systems (KCl, NaCl, LiCl, $CaCl_2$, and $MgCl_2$). The influence of the cation concentration and ionic radius on the binodal curves and the maxima critical point coordinates has been shown. Sedlbauer and Wood (2004) examined the thermodynamic properties of dilute NaCl aqueous solutions near the critical point of water. Shin *et al.* (2001) applied a solution model to estimate the solubilities of inorganic salts and some other inorganic compounds. The authors (Higashi *et al.*, 2005) measured the solubilities of sodium chloride and potassium chloride in water vapor at high temperatures and pressures. The solution model was adopted to correlate with the experimental data. However, the solubility data of alkali metal chlorides in water vapor at high temperature and high pressure, especially in vapor–solid equilibrium regions, are limited and no correlation method has been established yet.

In this study, therefore, an association model with a cubic equation of state was proposed to correlate the solubilities of sodium chloride and potassium chloride. The equilibrium constant and the association number were treated as adjustable parameters. The association number was constant for each salt and the logarithm

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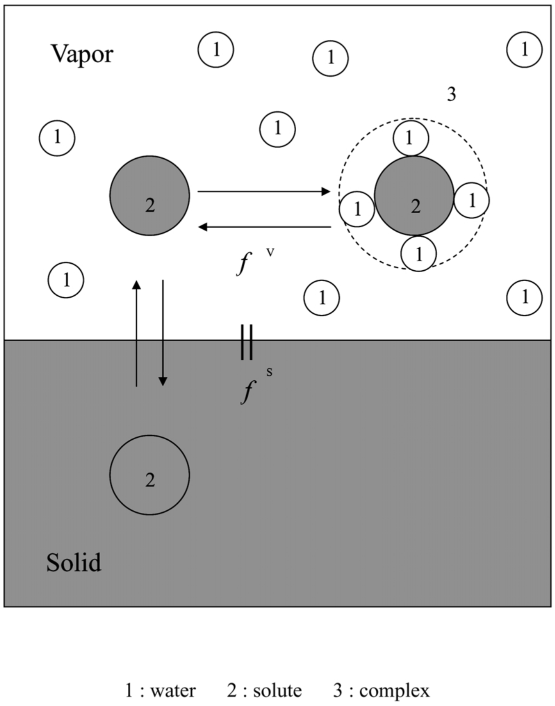

Fig. 1 Schematic image of an association model

of equilibrium constants was plotted as functions of the reciprocal of the absolute temperature.

1. Association Model

The dielectric constant of water is very small at high temperature. So it is considered that inorganic salts such as alkali metal chlorides are unionized and water molecules associated with the unionized salts. The imagination of association model is shown in **Figure 1**. In this case, the system is considered a pseudo ternary system consisted of water (1), solute (2), and hydration complex (3). The equilibrium of the association is expressed by Eq. (1).

$$\text{Solute} + \nu\text{H}_2\text{O} \overset{K}{\rightleftarrows} \text{Solute}(\text{H}_2\text{O})_\nu \tag{1}$$

where ν is the association number and K is an equilibrium constant. The equilibrium constant is represented by the ratio of fugacities, f.

$$K = \frac{\left(f_3^{\text{V}}/f_3^{\text{o}}\right)}{\left(f_2^{\text{V}}/f_2^{\text{o}}\right)\left(f_1^{\text{V}}/f_1^{\text{o}}\right)^\nu} = \frac{f_3^{\text{V}}}{f_2^{\text{V}}\left(f_1^{\text{V}}\right)^\nu}\,\frac{f_2^{\text{o}}\left(f_1^{\text{o}}\right)^\nu}{f_3^{\text{o}}} \tag{2}$$

where f_i^{o} is the fugacity of component i at a reference condition. Furthermore, the constant K' is defined by the following equation.

$$K\,\frac{f_3^{\text{o}}}{f_2^{\text{o}}\left(f_1^{\text{o}}\right)^\nu} = \frac{f_3^{\text{V}}}{f_2^{\text{V}}\left(f_1^{\text{V}}\right)^\nu} = K' \tag{3}$$

While the sum of the mole fractions in the vapor phase equals to unity.

$$x_1 + x_2 + x_3 = 1 \tag{4}$$

The amounts of substances in the vapor phase are represented by the following equations for each component, respectively.

$$n_{2\text{T}} = n_{2\text{S}} + n_{2\text{C}} \qquad \text{(solute)} \tag{5}$$

$$n_{1\text{T}} = n_{1\text{S}} + n_{1\text{C}} = n_{1\text{S}} + \nu\, n_{2\text{C}} \qquad \text{(water)} \tag{6}$$

where, $n_{1\text{S}}$ and $n_{2\text{S}}$ are the amounts of water and solute which exist solely in the vapor phase. $n_{1\text{C}}$ and $n_{2\text{C}}$ are the amounts of water and solute in complexes. Further, the mole fractions of each component in the vapor phase are represented as

$$x_1 = \frac{n_{1\text{S}}}{n_{1\text{S}} + n_{2\text{S}} + n_{2\text{C}}} \tag{7}$$

$$x_2 = \frac{n_{2\text{S}}}{n_{1\text{S}} + n_{2\text{S}} + n_{2\text{C}}} \tag{8}$$

$$x_3 = \frac{n_{2\text{C}}}{n_{1\text{S}} + n_{2\text{S}} + n_{2\text{C}}} \tag{9}$$

Thus, the solubility of a mass fraction, w_2, is expressed by the following equation.

$$\begin{aligned} w_2 &= \frac{n_{2\text{T}} \cdot M_2}{n_{1\text{T}} \cdot M_1 + n_{2\text{T}} \cdot M_2} \\ &= \frac{\left(n_{2\text{S}} + n_{2\text{C}}\right) \cdot M_2}{n_{1\text{S}} \cdot M_1 + \left[n_{2\text{S}} + (\nu+1)n_{2\text{C}}\right] \cdot M_2} \end{aligned} \tag{10}$$

where, M is the molar mass. Equation (10) is replaced by the following expression by using mole fractions.

$$w_2 = \frac{\left(x_2 + x_3\right) \cdot M_2}{x_1 \cdot M_1 + \left[x_2 + (\nu+1)x_3\right] \cdot M_2} \tag{11}$$

The mole fraction of solute, x_2, was given as the following equations by the solid–vapor equilibria (Prausnitz *et al*., 1999).

Table 1 Antoine constants (Stull, 1947)

	A	B	C	Temperature range [K]
NaCl	10.07184	8388.497	–82.638	1138–1738
KCl	9.78236	7440.691	–122.709	1094–1680

Table 2 Properties of pure substances

	M [g mol^{-1}]	T_C [K]	P_C [MPa]	ω [—]	$v_2^S \times 10^5$ [m^3 mol^{-1}]
Water	18.015	647.14[a]	22.064[a]	0.3440[a]	—
NaCl	58.44	3400[b]	35.46[b]	0.1293[c]	2.696[d]
KCl	74.55	3200[b]	22.29[b]	0.0800[c]	3.742[d]

[a] Poling *et al.* (2001)
[b] Kirshenbaum *et al.* (1962)
[c] $\omega = -\log(P^{\circ}/P_C)_{T/T_C=0.7} - 1.000$ (Pitzer, 1955)
[d] Hearn *et al.* (1969)

$$x_2 = \frac{P_2^{\text{sat}}}{P}\frac{1}{\varphi_2^{\text{V}}}\exp\left[\frac{v_2^{\text{S}}\left(P - P_2^{\text{sat}}\right)}{RT}\right] \tag{12}$$

where P_2^{sat} is the saturated vapor pressure, v_2^{S} is the solid molar volume and φ_2^{V} is the fugacity coefficient of solute in the vapor phase. The saturated vapor pressure was calculated by the Antoine equation.

$$\log P_2^{\text{sat}} = A - \frac{B}{T + C} \tag{13}$$

where A, B and C are the constants given by Stull (1947) and listed in **Table 1**. The vapor pressures were extrapolated by the Antoine equation.

The fugacity of the complex was expressed as

$$f_3^{\text{V}} = \varphi_3^{\text{V}} P x_3 \tag{14}$$

Then the mole fraction of the complex, x_3, was given by the following equation derived from Eqs. (3) and (14).

$$x_3 = \frac{K'}{P\varphi_3^{\text{V}}} f_2^{\text{V}} \left(f_1^{\text{V}}\right)^{\nu} \tag{15}$$

The mole fraction of water, x_1, was calculated by Eq. (4) with x_2 and x_3 obtained by Eqs. (12) and (15), respectively.

2. Equation of State

The fugacity coefficients of each component were calculated by the Soave–Redlich–Kwong equation of state (SRK-EOS; Soave, 1972). The SRK-EOS is shown as follows,

$$P = \frac{RT}{v - b} - \frac{a}{v(v - b)} \tag{16}$$

The conventional mixing rules and combining rules as follows were used for the mixture in the present study.

$$a = \sum_i \sum_j x_i x_j \left(a_i a_j\right)^{0.5} \tag{17}$$

$$b = \sum_i x_i b_i \tag{18}$$

where a and b are the energy and size parameters calculated by critical properties and the acentric factor. The properties used in this work are listed in **Table 2**. However, the critical properties of complex are unknown. The energy and size parameters of alkanes (C_1–C_6), of which critical properties were listed by Poling *et al.* (2001), were plotted as a function of the carbon number. The energy parameters showed a quadratic function of the carbon number and the size parameters showed a linear function of the carbon number. The following approximation formula was adopted empirically.

$$a_3 = \nu^2 a_1 + a_2 \tag{19}$$

$$b_3 = \nu b_1 + b_2 \tag{20}$$

3. Results and Discussion

The constant K' and the association number ν were treated as adjustable parameters and determined by the experimental values of solubility. The values of the

Table 3 Parameters for correlation and deviations

T [K]	$\log(K')[K';\ \mathrm{Pa}^{-\nu}]$				Reference
	Adjusted	Deviation [%]	Eqs. (21), (22)	Deviation [%]	
Water + NaCl, $\nu = 4$					
623	−22.28	4.9	−22.46	35.9	Higashi *et al.* (2005)
643	−22.98	7.8	−22.96	9.9	Higashi *et al.* (2005)
653	−23.30	12.4	−23.20	30.6	Higashi *et al.* (2005)
673	−23.74	14.6	−23.65	23.3	Galobardes *et al.* (1981), Higashi *et al.* (2005)
723	−24.74	21.4	−24.67	26.5	Galobardes *et al.* (1981), Armellini and Tester (1993)
773	−25.56	27.1	−25.56	27.1	Galobardes *et al.* (1981), Armellini and Tester (1993)
823	−26.26	18.9	−26.34	22.9	Galobardes *et al.* (1981), Armellini and Tester (1993)
Water + KCl, $\nu = 6$					
643	−37.57	16.9	−37.57	16.9	Higashi *et al.* (2005)
653	−37.89	8.3	−37.87	8.5	Higashi *et al.* (2005)
673	−38.44	8.2	−38.44	8.2	Higashi *et al.* (2005)

$$\text{Deviation [\%]} = \frac{1}{N}\sum^{N}\left|w_2^{\mathrm{cal}} - w_2^{\mathrm{exp}}\right| \Big/ w_2^{\mathrm{exp}} \times 100, \quad N = \text{Number of experimental data}$$

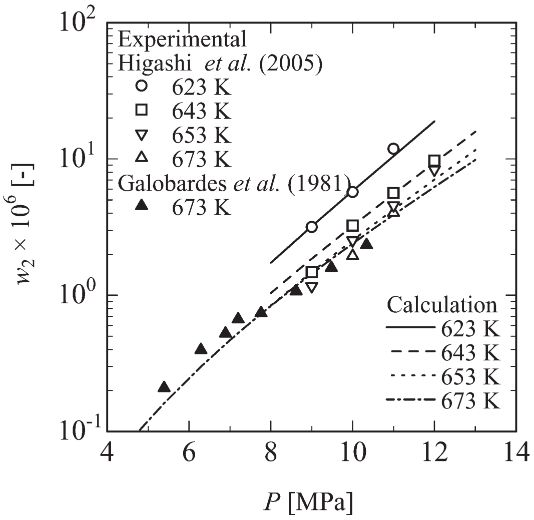

Fig. 2 Correlated results by the association model for solubilities of sodium chloride in water vapor at 623–673 K

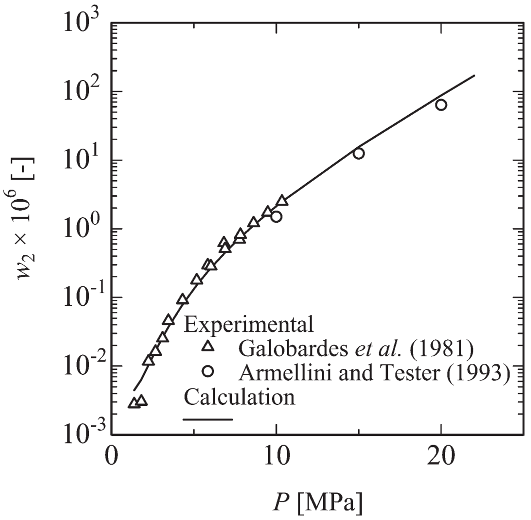

Fig. 3 Correlated results by the association model for solubilities of sodium chloride in water vapor at 723 K

parameters were listed in **Table 3**. The correlated results for water + sodium chloride and water + potassium chloride are shown in Table 3 and **Figures 2–6**. The association numbers for sodium chloride and potassium chloride are 4 and 6, respectively. The correlated results by the solution model show good agreement with the experimental data.

Further, the relationships between the optimized equilibrium constants of sodium chloride and potassium chloride and the reciprocal of the absolute temperature were shown in **Figure 7**. The logarithm of equilibrium constants shows a linear function of the reciprocal of the absolute temperature.

$$\log K' = \frac{9941}{T} - 38.42 \qquad : \mathrm{NaCl} \tag{21}$$

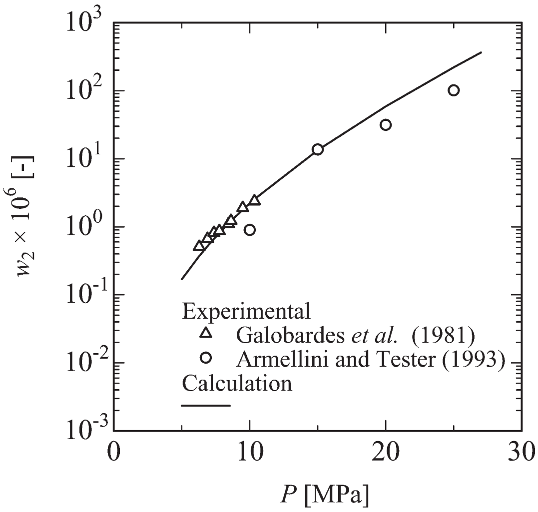

Fig. 4 Correlated results by the association model for solubilities of sodium chloride in water vapor at 773 K

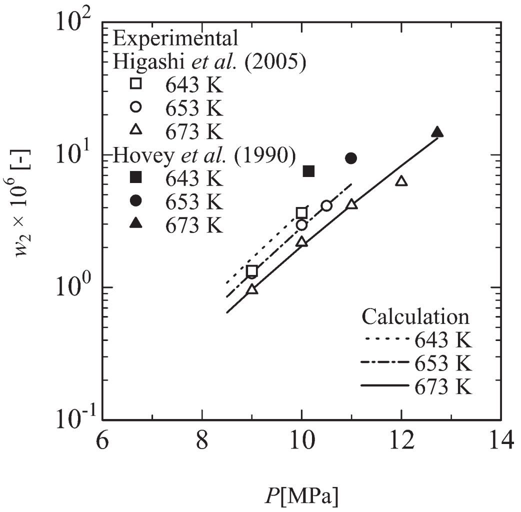

Fig. 6 Correlated results by the association model for solubilities of potassium chloride in water vapor at 643–673 K

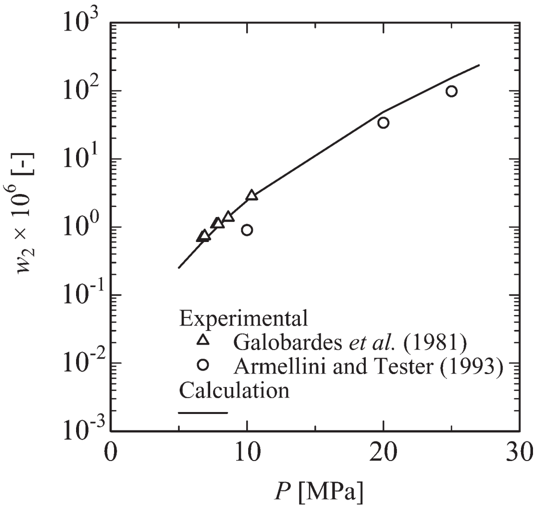

Fig. 5 Correlated results by the association model for solubilities of sodium chloride in water vapor at 823 K

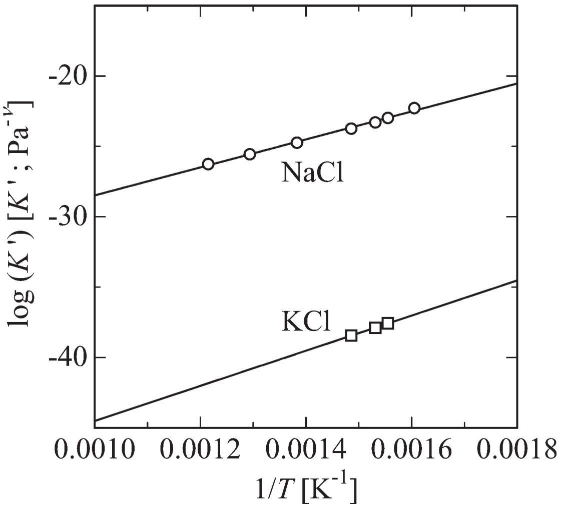

Fig. 7 Relationships between the logarithm of equilibrium constants and the reciprocal of the absolute temperature

$$\log K' = \frac{12489}{T} - 57.00 \quad : \mathrm{KCl} \tag{22}$$

The correlation performance with the relationship is shown in Table 3. The calculated results of the solubility for sodium chloride and potassium chloride in water vapor by this approximation qualitatively represent the tendency in which the solubility decreases with increasing temperature in the high pressure region.

Conclusions

The solubilities of sodium chloride and potassium chloride in water vapor were correlated by the association model coupled with the equation of state. The correlated results are in good agreement with the experimental results. The association numbers for sodium chloride and potassium chloride are 4 and 6, respectively. The optimized equilibrium constants of sodium chloride and potassium chloride show a linear function of reciprocal of the absolute temperature.

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Nomenclature

a = energy parameter in the equation of state [J m^3 mol^{-2}]
b = size parameter in the equation of state [m^3 mol^{-1}]
f = fugacity [Pa]
K = equilibrium constants [—]
K' = equilibrium constants [Pa$^{-\nu}$]
M = molar mass [g mol^{-1}]
n = amount of component [mol]
P = pressure [Pa]
R = gas constant [J mol^{-1} K^{-1}]
T = absolute temperature [K]
w = mass fraction [—]
x = mole fraction [—]

φ = fugacity coefficient [—]
ν = association number [—]

<Subscript>
C = complex in the vapor phase
S = solo in the vapor phase
T = total
1 = solvent (water)
2 = solute (salt)
3 = complex (hydrate)

<Superscript>
S = solid
sat = saturated
V = vapor
o = reference condition

Literature Cited

Alekhin, Yu. V. and A. G. Vakulenko; "Solubility and Thermodynamic Properties of Sodium Chloride in Water Vapor at 300–500°C and ≤300 bar," *Geokhimiya*, **10**, 1468–1481 (1987)

Anderko, A. and K. S. Pitzer; "Equation-of-State Representation of Phase Equilibria and Volumetric Properties of the System Sodium Chloride–Water above 573 K," *Geochim. Cosmochim. Acta*, **57**, 1657–1680 (1993)

Armellini, F. J. and J. W. Tester; "Solubility of Sodium Chloride and Sulfate in Sub- and Supercritical Water Vapor from 450–550°C and 100–250 bar," *Fluid Phase Equilib.*, **84**, 123–142 (1993)

Belhachemi, B. and A. A. Gotouk; "Salt Effect on Liquid–Liquid Equilibrium of the Water–Phenol–Salt System (KCl, NaCl, LiCl, $CaCl_2$ and $MgCl_2$)," *J. de Chem. Phys. et de Physico-Chimie Biologique*, **96**, 1186–1197 (1999)

Bischoff, J. L. and K. S. Pitzer; "Liquid–Vapor Relations for the System Sodium Chloride–Water: Summary of the P–T–x Surface from 300 to 500°C," *Am. J. Sci.*, **289**, 217–248 (1989)

Bischoff, J. L., R. J. Rosenbauer and K. S. Pitzer; "The System Sodium Chloride–Water: Relations of Vapor–Liquid Near the Critical Temperature of Water and Vapor–Liquid–Halite from 300 to 500°C," *Geochim. Cosmochim. Acta*, **50**, 1437–1444 (1986)

DiPippo, M. M., K. Sako and J. W. Tester; "Ternary Phase Equilibria for the Sodium Chloride–Sodium Sulfate–Water System at 200 and 250 bar up to 400°C," *Fluid Phase Equilib.*, **157**, 229–255 (1999)

Galobardes, J. F., D. R. Vanhare and L. B. Rogers; "Solubility of Sodium Chloride in Dry Steam," *J. Chem. Eng. Data*, **26**, 363–366 (1981)

Hearn, B., M. R. Hunt and A. Hayward; "Solubility of Cupric Oxide in Pure Subcritical and Supercritical Water," *J. Chem. Eng. Data*, **14**, 442–447 (1969)

Higashi, H., Y. Iwai, K. Matsumoto, Y. Kitani, F. Okazaki, Y. Shimoyama and Y. Arai; "Measurement and Correlation for Solubilities of Alkali Metal Chlorides in Water Vapor at High Temperature and Pressure," *Fluid Phase Equilib.*, **228/229**, 547–551 (2005)

Hovey, J. K., K. S. Pitzer, J. C. Tanger, J. L. Bischoff and R. J. Rosenbauer; "Vapor–Liquid Phase Equilibria of Potassium Chloride–Water Mixtures: Equation-of-State Representation for KCl–H_2O and $NaCl$–H_2O," *J. Phys. Chem.*, **94**, 1175–1179 (1990)

Kirshenbaum, A. D., J. A. Cahill, P. J. McGonigal and A. V. Grosse; "The Density of Liquid NaCl and KCl and an Estimate of Their Critical Constants together with Those of the Other Alkali Halides," *J. Inorg. Nucl. Chem.*, **24**, 1287–1296 (1962)

Pitzer, K. S.; "Volumetric and Thermodynamic Properties of Fluids. I. Theoretical Basis and Virial Coefficients," *J. Amer. Chem. Sci.*, **77**, 3427–3433 (1955)

Pitzer, K. S.; "Aqueous Electrolytes at Near-Critical and Supercritical Temperatures," *Int. J. Thermophys.*, **19**, 355–366 (1998)

Pitzer, K. S. and R. T. Pabalan; "Thermodynamics of Sodium Chloride in Steam," *Geochim. Cosmochim. Acta*, **50**, 1445–1454 (1986)

Pitzer, K. S. and J. C. Tanger; "Near-Critical Sodium Chloride–Water System: An Equation of State and Discussion of Anomalous Properties," *Int. J. Thermophys.*, **9**, 635–648 (1988)

Poling, B. E., J. M. Prausnitz and J. P. O'Connel; The Properties of Gases and Liquids, 5th ed., McGraw-Hill, New York, U.S.A. (2001)

Prausnitz, J. M., R. N. Lichtenthaler and E. G. de Azevedo; Molecular Thermodynamics of Fluid–Phase Equilibria, 3rd ed., Prentice Hall PTR, New Jersey, U.S.A. (1999)

Sedlbauer, J. and R. H. Wood; "Thermodynamic Properties of Dilute NaCl(aq) Solutions near the Critical Point of Water," *J. Phys. Chem. B*, **108**, 11838–11849 (2004)

Shin, H. Y., K. Matsumoto, H. Higashi, Y. Iwai and Y. Arai; "Development of a Solution Model to Correlate Solubilities of Inorganic Compounds in Water Vapor under High Temperatures and Pressures," *J. Supercritical Fluids*, **21**, 105–110 (2001)

Soave, G.; "Equilibrium Constants from a Modified Redlich–Kwong Equation of State," *Chem. Eng. Sci.*, **27**, 1197–1203 (1972)

Sourirajan, S. and G. C. Kennedy; "The System H_2O–NaCl at Elevated Temperatures and Pressures," *Am. J. Sci.*, **260**, 115–141 (1962)

Stull, D. R.; "Vapor Pressure of Pure Substances Organic Compounds," *Ind. Eng. Chem.*, **39**, 517–540 (1947)

Tanger, J. C. and K. S. Pitzer; "Thermodynamics of Sodium Chloride–Water: A New Equation of State for the Near-Critical Region and Comparisons with Other Equations for Adjoining Regions," *Geochim. Cosmochim. Acta*, **53**, 973–987 (1989)