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Abstract

A flow type apparatus was designed and constructed to measure the solubilities of salts in water vapor at high temperature and pressure. The apparatus was equipped with an additional pure water line to prevent the clogging by precipitated solid salts at the outlet of an equilibrium cell. The solubilities of sodium chloride and potassium chloride in water vapor were measured at 623 to 673 K and 9.0 to 12.0 MPa. In order to verify the soundness of this method and the performance of the apparatus, the experimental results for the solubilities of sodium chloride at 673 K were compared with the literature data. The present data are in good agreement with the literature data. The solubilities of sodium chloride are similar to those of potassium chloride at the same temperatures and pressures. The isobaric solubilities decrease with increasing temperature at the experimental pressure range. The experimental results of solubilities were correlated by a solution model. The molar volumes and the energy parameters of salts were treated as adjustable parameters and were optimized with the present and literature data. The adjusted energy parameters for salts can be related to a linear function of the temperature. The correlated results show good agreement with the experimental data.

1. Introduction

Recently, the oxidative decomposition technology of the toxic substances such as dioxin and poly chloro biphenyl (PCB) by using supercritical water (SCW) has been paid much attention and in the stage of practical use at present. In such a process, when organic compounds including halogen are decomposed, hydrogen halides such as hydrochloric acid produce and cause remarkable corrosion of the reactor. In order to prevent the corrosion, alkalis are added as the neutralization reagent, which result in generation and precipitation of alkali metal salts. The effective discharge of these alkali metal salts from the reactor is an important problem for the practical use of the apparatus. Therefore, the solubility data of these alkali metal salts in water vapor at high temperatures and pressures are very important as a fundamental knowledge to design the supercritical water decomposition processes.

Sourirajan and Kennedy [1] reported the solubilities of sodium chloride in water vapor at high temperature and pressure. Bischoff et al. [2] measured the vapor-liquid equilibria for water + sodium chloride system by a static method. Galobardes et al. [3], Alekhin and Vakulenko [4], and Armellini and Tester [5] also reported the solubilities of sodium chloride in water vapor by dynamic method. Their solubility data are different markedly each other, but the recent data by Armellini and Tester are almost the same to the data by Galobardes et al. Pitzer and co workers proposed an empirical equation of state for water + sodium chloride system and water + potassium chloride system [6-11]. Anderko and Pitzer [12] calculated the vapor-liquid equilibria for water + sodium chloride and show good representation to the experimental data. Shin et al. [13] applied a solution model to estimate the solubilities of inorganic salts and some other inorganic compounds. However, the solubility data of alkali metal chlorides in water vapor at high temperature and high pressure, espetially vapor-solid equilibrium regions, are limited and correlation method is not established.

In this work, the solubilities of sodium chloride and potassium chloride in water vapor were measured at the temperature from 623 to 673 K and at the pressure from 9.0 to 12.0 MPa. The experimental data were correlated by a solution model. The interaction parameters were adjusted by the solubility data. The molar volumes and the energy parameters of salts were treated as adjustable parameters and were optimized with the present and literature data.

2. Experiment

2.1 Materials

Extra pure grade of sodium chloride and potassium chloride, which were supplied by Wako Pure Chemical Industries, Ltd, were used without further purification. The purities of alkali metal chlorides are more than 99.5 % and ultra pure water purified by MILLI-QLABO (Millipore Corporation) was used.

2.2 Apparatus and procedure

A schematic diagram of the apparatus is shown in Figure 1. An equilibrium cell (12) was made of Hastelloy C. The inside diameter and height of the cell were 12 mm and 100 mm, respectively. About 1.0 g of salts was packed into the cell with small pieces of Hastelloy to prevent channeling. The cell was set in an air bath (11) which was remodeled from a gas chromatography oven. The temperature in the air bath was controlled within ± 0.5 K. After the cell was heated up to required temperature, pure water was supplied by a feed pump of water (3). The flow rate of water was measured by a digital balance (17). A back pressure regulator (V1) was used to maintain a constant pressure within the system and the pressure was controlled within ± 0.1 MPa. Pressurized water was heated by a preheating coil (10) and supplied to bottom of the cell. Pure water was also supplied by an additional water feed pump (4) to the top of the

cell to avoid the pipe above the cell was filled up with solid salts. Water vapor passed through the cell was cooled in a water bath (14) and decompressed through an expansion valve (V8). Five samples of 50ml were collected at intervals of 30 min and analyzed for cation with an ion chromatography (JASCO Co., Ltd.). The concentration of anion was also measured by some samples to confirm the accuracy of the solubilities. The solubilities of salts in water vapor were determined from the concentrations of cation in the samples and the flow rates of water. The solubilities were independent of the flow rate of water from 2.0 to 4.0 ml min^{-1}.

2.3 Results and Discussion

   The experimental results obtained in this work are shown in Table 1 and Figures 2 and 3. The each sample was analyzed three times and the reproducibilities were within $\pm\ 0.5 \times 10^{-6}$ in mass fraction. The experiments were carried out more than three times and averaged. The present data for sodium chloride are in good agreement with the data of Galobardes et al. [3] at 673K. The solubilities of potassium chloride are smoothly close to the three phase equilibrium points [11] of the system. The soundness of this method and the performance of the apparatus were verified. The solubilities of each salt increase with increasing pressure, and decrease with increasing temperature, because the density of water vapor strongly influences on the solubility, and the density of water vapor increases with increasing pressure and decreases with increasing temperature. It is noted that the solubilities of each salt are almost the same at the same conditions.

3. Correlation

3.1 Approximation of solubility

The phase equilibria between solid and dense fluid phases can be approximated as the solid-liquid equilibria. Treating high temperature and pressure fluid as an expanded liquid and assuming that solvent does not dissolve into solid phase, the solubility (mole flaction) of the solute, y_2, in high temperature and pressure fluid can be expressed by the following model [14] which combined a regular solution theory [15] and an athermal solution theory [16].

$$\ln y_2 = \frac{\Delta h_2^m}{RT}\left(\frac{T}{T_2^m}-1\right)-\frac{v_2}{RT}\left(\delta_1-\delta_2\right)^2-1+\frac{v_2}{v_1}-\ln\frac{v_2}{v_1}$$

(1)

where Δh_2^m and T_2^m indicate the heat of fusion and the melting point of the solute, respectively. R and T are the gas constant and absolute temperature. The heat of fusion and the melting point of the solute were listed in Table 2. v and δ represent the molar volume and the solubility parameter. Subscripts 1 and 2 denote water and solute, respectively. The calculated mole fraction of the salt can be easily converted to the mass fraction, w_2.

3.2 Solublility parameter of water

The solubility parameter of liquid water can be calculated by the following expression proposed by Sagara et al.[18].

$$\delta_1 = \frac{\sqrt{6v_1^S\varepsilon_{11}N_0}}{v_1}$$

(2)

where v_1^S is the solid molar volume ($v_1^S = 1.963\times 10^{-5}$ m^3 mol^{-1} [19]), N_0 is the Avogadro number, v_1 is the molar volume, and ε_{11} is the pair potential energy parameter. The value of ε_{11} was determined by using the approach proposed by Sagara et al. [18]. Namely, the solubility parameter given by Eq. (2) was fitted to the experimental solubility parameter:

$$\delta_1 = \sqrt{\left(\frac{\Delta h_1^{vap}/RT}{Z_1^V-Z_1^L}-1\right)\left(\frac{Z_1^V}{Z_1^L}\right)P_1^{vap}}$$

(3)

where $\Delta h_1{}^{vap}$ and $P_1{}^{vap}$ denote the heat of vaporization and the saturated vapor pressure of water, respectively. Further, $Z_1{}^{V}$ and $Z_1{}^{L}$ are the compressibility factors of water in vapor and liquid phases, respectively.

The calculated result by Eq. (2) was adjusted to the experimental value given by Eq. (3) at reduced temperature $T_r = 0.7$ to evaluate the value of ε_{11}. The reduced temperature was selected by Sagara et al. [18] as a standard temperature to obtain a reliable parameter for wide range of temperature including near critical temperature. The calculated results of solubility parameters as a function of temperature and the value of ε_{11} divided by the Boltzmann constant k are shown by Shin et al. [13]. In the present solution model, the solubility parameters of water were obtained by Eq. (2) and the pair potential energy was determined using the experimental data and the optimum value of ε_{11}/k is 680.1 K. The solubility parameters of water were given as a function of molar volume at given temperatures and pressures. In this work, therefore, Eq. (2) was extended to the vapor region. The molar volumes of water vapor, v_1, were calculated by IAPWS-IF97 [20].

3.3 Solublility parameters of solutes

The solubility parameter of the solute, δ_2 , in Eq.(1) is given by the following equation [21]:

$$\delta_2 = \sqrt{\Delta u_2 / v_2} \tag{4}$$

where Δu_2 is the cohesive energy due to intermolecular potential energy. Iwai et al. [14] have presented the following relation between the molar volume of solute, v_2 (m^3 mol^{-1}) , and the density of solvent, ρ_1 (kg m^{-3}).

$$\ln v_2 = \alpha_2 \ln \rho_1 + \beta_2 \tag{5}$$

The values of α_2 and β_2 were proposed by Shin et al. [13] for sodium chloride. β_2 for potassium chloride and Δu_2 for each salts were treated as adjustable parameters and optimized with the present data and literature data [3, 5].

3.4 Results and Discussion

The values of parameters adjusted for sodium chloride and potassium chloride are listed in Table 3. The parameters determined by Shin et al. [13] also listed in Table 3. The correlated results for the solubilities of sodium chloride and potassium chloride with the optimized parameters are shown in Figures 2 and 3. The correlated results by the solution model show good agreement with the experimental data.

Further, the optimized energy parameters of sodium chloride and potassium chloride show a linear relationship with temperature as shown in Figure 4.

$$\Delta u_2 = 0.16491\ T + 14.23 : \text{NaCl} \tag{6}$$

$$\Delta u_2 = 0.22428\ T + 30.13 : \text{KCl} \tag{7}$$

The correlation performance with the relationship are shown in Table 3. The deviations become larger. However, the calculated results with this approximation qualitatively represent the tendency in which the solubilities decrease with increasing temperature at high pressure region.

4. Conclusions

The solubilities of sodium chloride and potassium chloride in water vapor were measured at temperatures from 623 to 673 K and pressures from 9.0 to 12.0 MPa. The soundness of this method was verified due to the good agreement with the literature data for sodium chloride at 673 K. The correlated results by using a solution model satisfactorily represent the experimental data and the interaction parameters were related to a liner function of temperature.

Acknowledgment

List of symbols

Δh^{m} heat of fusion [J mol^{-1}]

Δh^{vap} heat of vaporization [J mol^{-1}]

k Boltzmann constant [J K^{-1}]

N_0 Avogadro number [mol^{-1}]

P^{vap} saturated vapor pressure [Pa]

R *g*as constant [J mol^{-1} K^{-1}]

T absolute temperature [K]

T^{m} melting point [K]

Δu cohesive energy [J mol^{-1}]

v molar volume [m^3 mol^{-1}]

y mole fraction in water vapor (solubility) [-]

Z compressibility factor [-]

Greek letters

α parameter [-]

β parameter [-]

ε pair potential energy parameter [J]

δ solubility parameter [$(J\,m^{-3})^{1/2}$]

ρ density [$kg\,m^{-3}$]

Subscripts

r   reduced value

1   water

2   solute (sodium chloride or potassium chloride)

Superscripts

L   liquid phase

S   solid phase

V   vapor phase

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Table 1 Experimental results for solubilities (mass fraction) of sodium chloride and potassium chloride in water vapour.

NaCl	623 K		643 K	
	P [MPa]	$w_2 \times 10^6$[-]	P [MPa]	$w_2 \times 10^6$[-]
	9.0	3.17	9.0	1.48
	10.0	5.73	10.0	3.24
	11.0	11.88	11.0	5.63
			12.0	9.72
	653 K		673 K	
	P [MPa]	$w_2 \times 10^6$[-]	P [MPa]	$w_2 \times 10^6$[-]
	9.0	1.16	10.0	1.95
	10.0	2.53	11.0	4.04
	11.0	4.56	12.0	6.32
	12.0	8.34		
KCl	643 K		653 K	
	P [MPa]	$w_2 \times 10^6$[-]	P [MPa]	$w_2 \times 10^6$[-]
	9.0	1.33	9.0	1.28
	10.0	3.64	10.0	2.96
			10.5	4.13
	673 K			
	P [MPa]	$w_2 \times 10^6$[-]		
	9.0	0.951		
	10.0	2.178		
	11.0	4.166		
	12.0	6.225		

Table 2 Physical properties of salts

Salt	T^m [K]	Δh^m [kJ mol^{-1}]	Ref.
NaCl	1074	28.20	17
KCl	1044	26.28	17

Table 3 Parameters for correlation ($\alpha_2 = -1.0$ *).

Salt	T [K]	Δu_2 [kJ mol^{-1}] Adjusted	Dev. [%]	Δu_2 [kJ mol^{-1}] Eqs. (6), (7)	Dev. [%]	Ref. of data
NaCl	623	113.7	6.8	117.0	41.1	This work
$\beta_2 = -2.62$ *	643	119.5	11.8	120.3	15.4	This work
	653	122.4	16.2	121.9	17.6	This work
	673	126.1	9.2	125.2	12.5	This work, 3
	723	139.8 *	56.4	133.5	97.7	3, 5
	773	140.6 *	22.2	141.7	25.8	3, 5
	823	147.4 *	19.3	150.0	34.8	3, 5
KCl	643	174.6	7.9	174.3	8.2	This work
$\beta_2 = -1.90$	653	176.2	2.0	176.6	5.8	This work
	673	181.2	11.0	181.1	11.0	This work

*) Determined by Shin et al. [13]

$$\text{Dev.}[\%] = \frac{1}{N}\left(\sum_{}^{N} \left| w_2^{\text{calc}} - w_2^{\text{exp}} \right| \Big/ w_2^{\text{exp}} \right) \times 100, \ N = \text{Number of experimental data points.}$$

Figure Captions

Figure 1   Schematic diagram of flow type experimental apparatus.

(1), (2) feed reservoir ; (3), (4) water feed pump ; (5), (6) pressure gauge ;
(7), (8) one way valve ; (9) precision pressure gauge ; (10) preheating coil ; (11) air bath ;
(12) equilibrium cell ; (13) flexible heater ; (14) water bath ; (15) filter ; (16) flask ;
(17) digital balance ; (18) safety valve ; (V1) back pressure regulator ; (V2 -V7) stop valve ;
(V8) expansion valve

Figure 2   Solubilities of sodium chloride in water vapor.

Experimental: This work, ($\triangledown$) 623 K, ($\square$) 643 K, ($\bigcirc$) 653 K, ($\triangle$) 673 K;

Galobardes et al.[3], ($\blacktriangle$) 673 K.

Calculated results by the solution model (parameters were optimized):

(——) 623 K, (− −) 643 K, (······) 653 K, (− · −) 673 K

Figure 3   Solubilities of potassium chloride in water vapor.

Experimental: This work, ($\square$) 643 K, ($\bigcirc$) 653 K, ($\triangle$) 673 K;

Hovey et al.[11], ($\blacksquare$) 643 K, ($\bullet$) 653 K, ($\blacktriangle$) 673 K, Three phase

 equilibria.

Calculated results by the solution model (parameters were optimized):

(− −) 643 K, (······) 653 K, (− · −) 673 K

Figure 4   Temperature dipendence of energy parameters.
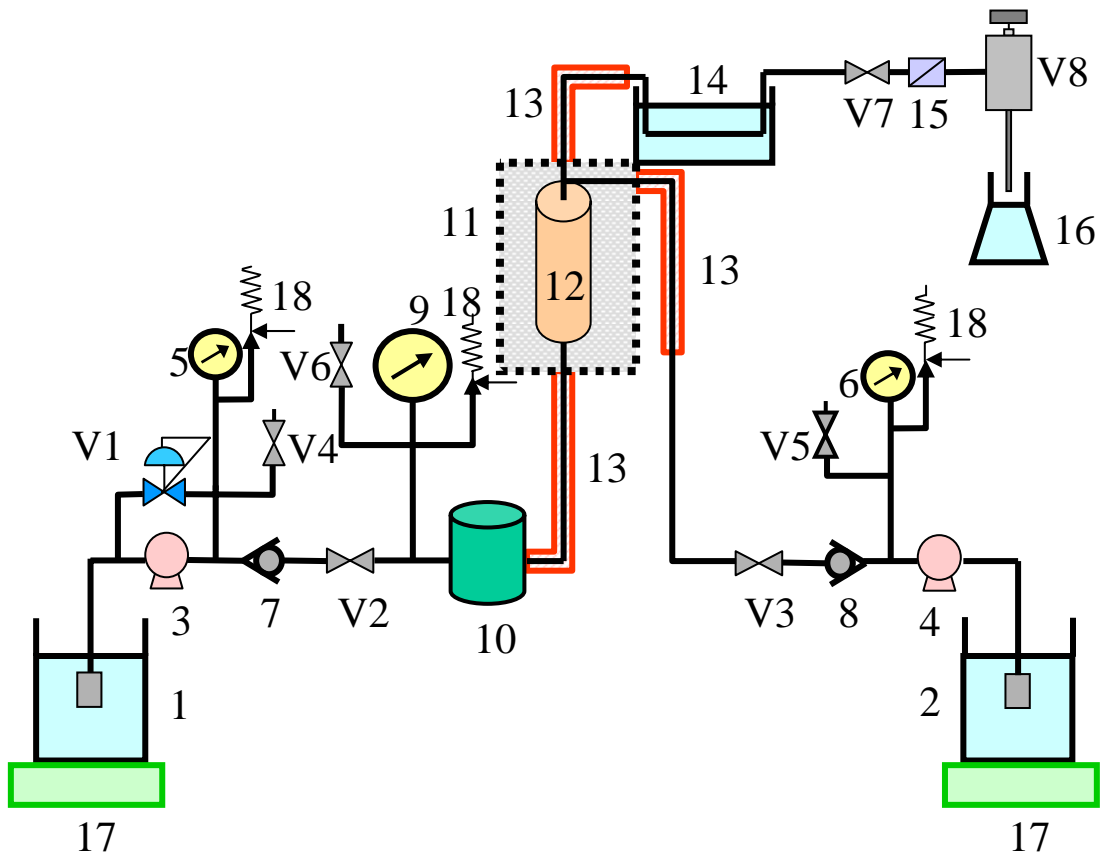
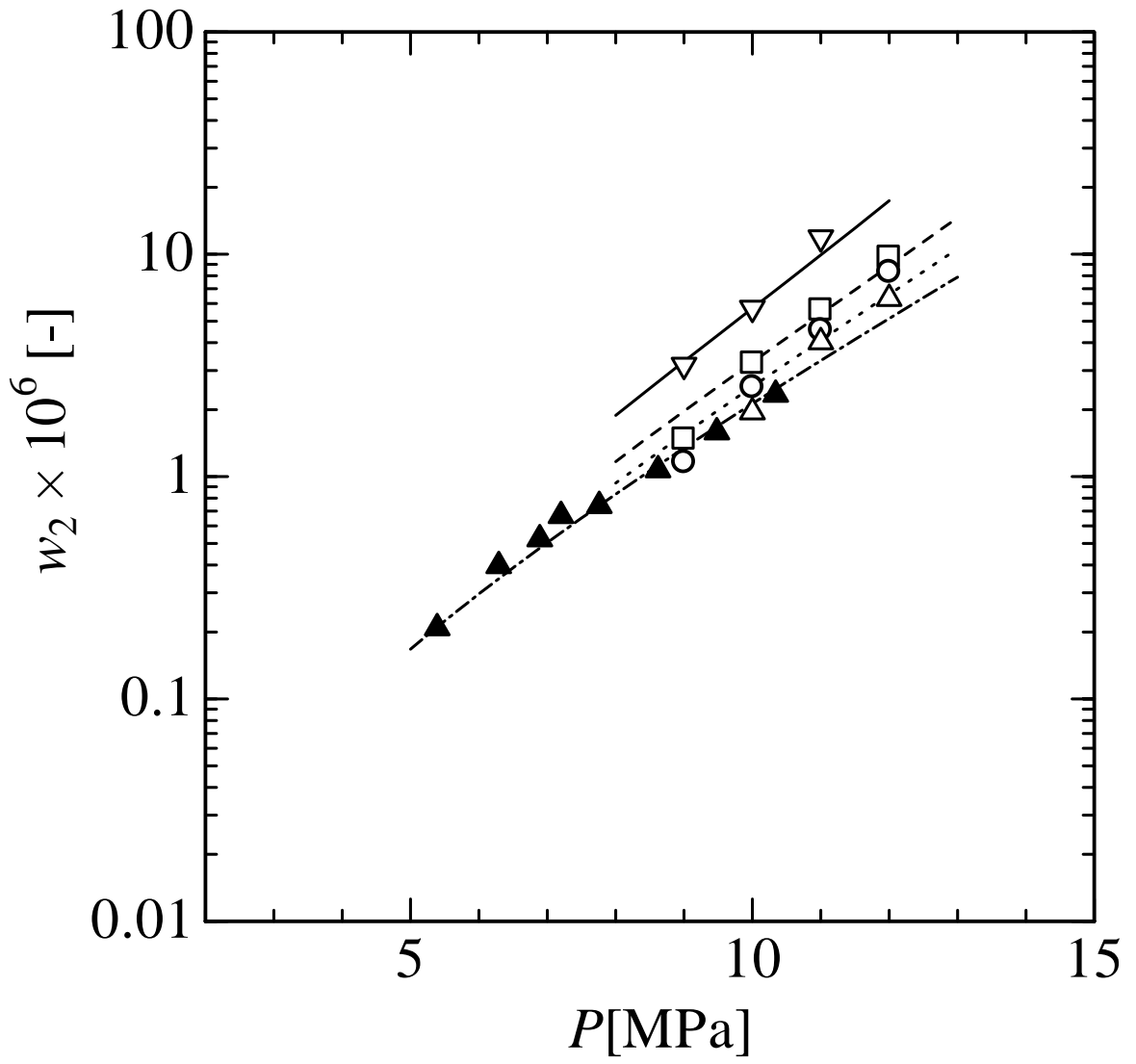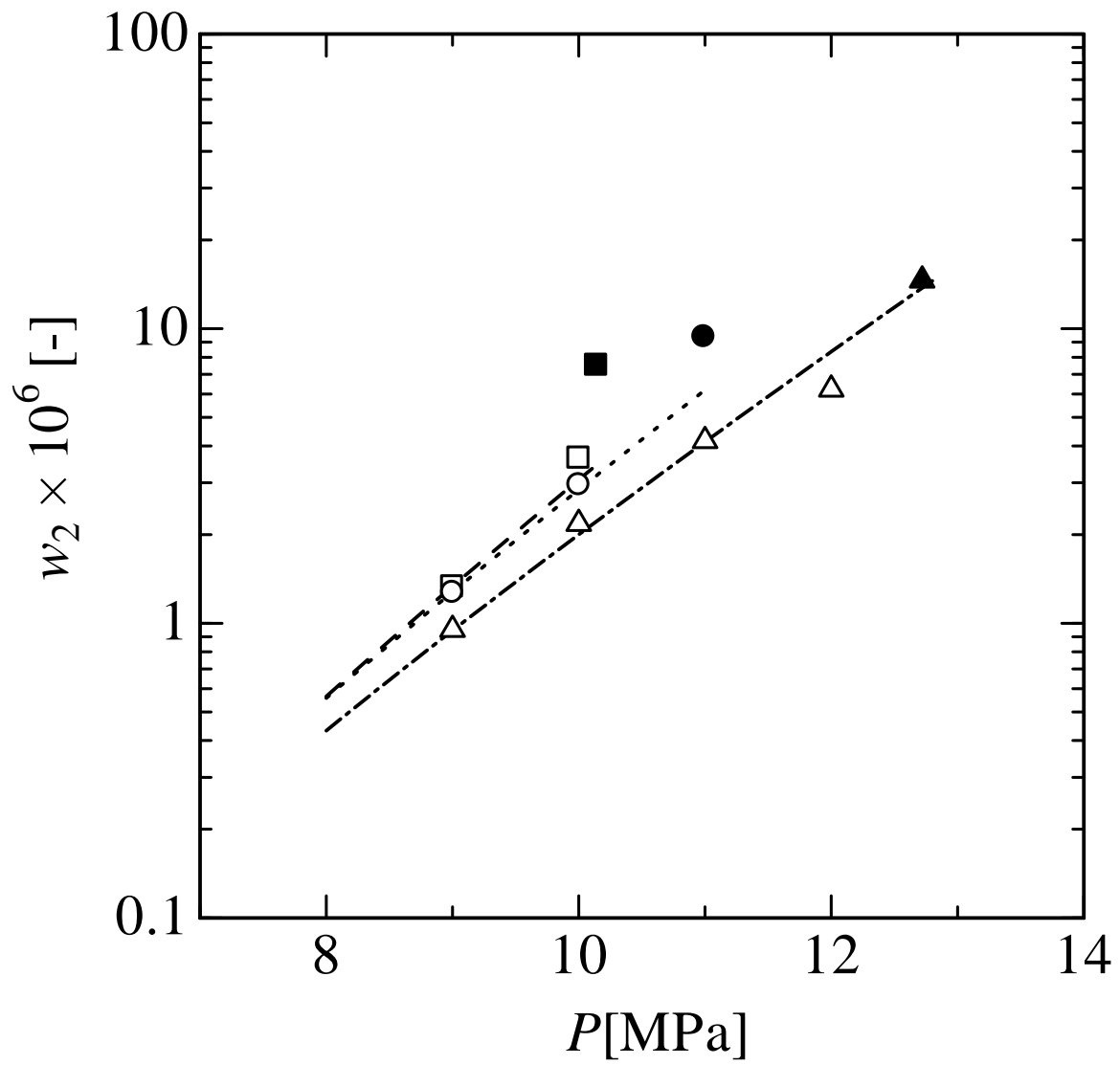Experimental: This work, ($\bigcirc$) NaCl, ($\square$) KCl
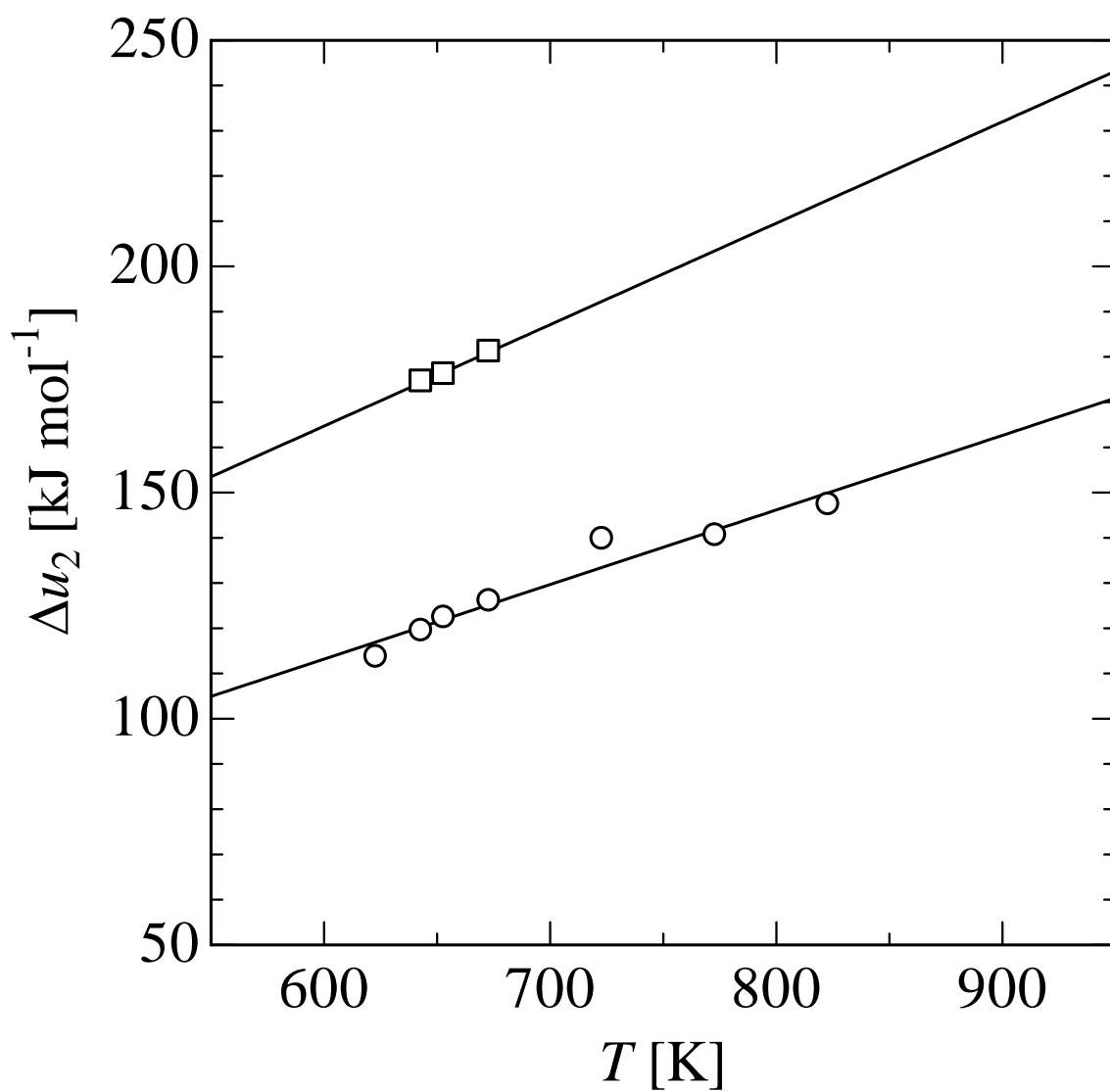
Fig.1 Higashi et al

Fig.2 Higashi et al.

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Fig.4 Higashi et al.