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Development of a solution model to correlate solublilties of inorganic compounds in water vapor under high temperatures and pressures

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Figure 1-7

Abstract

A solution model, based on the regular solution theory coupled with Flory-Huggins entropy term, was developed for the calculation of solubilities of inorganic compounds in water vapor under high temperatures and pressures. The solubilities of sodium chloride (NaCl), potassium hydroxide (KOH), sodium sulfate (Na_2SO_4), lead oxide (PbO), silicon oxide (SiO_2), lithium nitrate ($LiNO_3$), sodium nitrate ($NaNO_3$) and potassium nitrate (KNO_3) were correlated by optimizing internal energies and molar volumes of inorganic compounds which give their solubility parameters.

Keywords : solubility, water, salt, inorganic compound, regular solution theory

1. Introduction

The solubilities of inorganic salts at high temperature and pressure in water vapor are important in the field such as SCWO (supercritical water oxidation) technology. SCWO is an emerging technology for the treatment of the organic wastes. The properties of water above its critical point(647K, 22.1MPa)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 the reactor. In order to prevent the corrosion, alkalis are added as a neutralization reagent. As a result, inorganic salts such as NaCl and Na_2SO_4 precipitate and cause plugging of the reactor. For effective discharge of these inorganic salts from the reactor, their solubility data in water are very important to design the

SCWO process [1]. In this study, therefore, a solution model was proposed to estimate the solubilities of inorganic salts and other inorganic compounds.

2. Solutions model

2.1 Approximation of solubility

The phase equilibria between solid and dense fluid phases can be approximated as the solid-liquid equilibria. Therefore, the solubility of a solid solute in a compressed fluid can be expressed by the following model which is derived from the regular solution theory and the athermal solution theory [2-3].

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

where subscripts 1 and 2 respectively denote water and solute and Δh^m and T^m indicate the heat of fusion and the melting point. They are listed in Table 1. Further, v and δ represent the molar volume and the solubility parameter.

2.2 Solublility parameter of water

The solubility parameter of liquid water was evaluated by the following expression according to Sagara et al. [4].

$$\delta_1 = \frac{\sqrt{6 v_1^s \varepsilon_{11} N_A}}{v_1} \qquad (2)$$

where v_1^s is the solid molar volume of water (v_1^s=1.963 × 10^{-5} m^3/mol), ε_{11} is the pair potential energy, and N_A is the Avogadro's number. The value of ε_{11} was determined by using the approach proposed by Sagara et al. [4]. Namely, the solubility parameter given by

Eq. (2) was fitted to the experimental solubility parameter:

$$\delta_1 = \sqrt{\left(\frac{\Delta h_1^{vap} / RT}{Z_1^V - Z_1^V} - 1 \right) \left(Z_1^V / Z_1^L \right) P_1^s} \tag{3}$$

where Δh_1^{vap} and P_1^s 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 fitted to the experimental value given by Eq. (3) at T_r = 0.7 to evaluate the value of ε_{11}. T_r = 0.7 was selected by Sagara et al. [4] 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} which is divided by the Boltzmann's constant *k* are shown in Fig. 1. This figure shows the comparison of the calculated solubility parameters of water by Eq. (2) with the experimental data by Eq. (3). In the present solution model, the solubility parameters of water were obtained by Eq. (2) and the unknown variable, the pair potential energy, was determined using the experimental data by Eq. (2). Eq. (2) can give the solubility parameters of water as a function of molar volume at given temperature and pressure. In this work, therefore, Eq. (2) was extended to the vapor region. The molar volume of water vapor, v_1, was calculated by IAPWS-IF97 [5].

2.3 Solubility parameters of inorganic compounds

On the other hand, the solubility parameter of solute is given by the following equation [6]:

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

where is Δu_2 the cohesive energy due to intermolecular potential energy.

2.4 Molar volume of solid solute in dense fluid

Iwai et al. [7] have empirically presented the following relation between the molar volume of solute v_2 and the density of supercritical fluid ρ_1 as

$$\ln v_2 = \alpha_2 \ln \rho_1 + \beta_2 \quad (5)$$

where Δu_2 in Eq.(4) and α_2, β_2 in Eq.(5) are considered as adjustable parameters. As fewer number of parameters will be convenient for the industrial application, so α_2 is set to a constant value.

3. Results and Discussion

The values of parameters fitted for inorganic salts and other inorganic compounds are listed in Table 2. The correlated results for the solubilities of NaCl, KOH, SiO_2 and $NaNO_3$ are shown in Figs. 2 - 5. The solubilities of $LiNO_3$, $NaNO_3$ and KNO_3, which have the same anion, are compared at 748 K in Fig. 6. $LiNO_3$ shows the highest solubility in water vapor among the inorganic compounds containing NO_3^-. Furthermore, the comparison of the solubility parameters was examined by the deviations of the solubility parameters of the inorganic compounds from that of water in Fig. 7. The difference between the solubility parameters of salts and that of water is related to the miscibility of salts in water. When the difference is smaller, the salts become more miscible in water. Fig 7 explains which salt is most miscible in water. These results are consistent with those in Fig.6. It will show the soundness of the present model. The smallest deviation of $LiNO_3$ proves the highest solubility compared with the inorganic compounds containing NO_3^- such as $NaNO_3$ and KNO_3.

Among the present systems, α_2 can be treated as a constant (α_2 = -1.0) while α_2 = -1.34 for the solubility correlation of several hydrocarbons in supercritical carbon dioxide [7]. The values of α_2 are the same order of magnitude. Further, β_2 is found to be a constant for the given inorganic salts and other compounds. On the other hand, the cohesive energy Δu_2 in Eq.4 slightly depends on the temperature as shown in Table 2.

Acknowledgements

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Table 1.
Physical properties of inorganic compounds

Inorganic compound	T^m (K)	Δh^m (J/mol)	Reference
NaCl	1074	28158	8
KOH	679	8619	8
Na_2SO_4	1157	23849	8
PbO	1159	25522	8
SiO_2	1696	7699	8
$LiNO_3$	527	25500	9
$NaNO_3$	583	16000	9
KNO_3	610	12000	9

Table 2.
Parameters and AAD (Absolute Average error Deviation) of water(1) + inorganic compound(2) systems (α_2 = -1.0).

Inorganic compound	β_2	T(K)	$\Delta u_2 \times 10^{-4}$ (J/mol)	AAD (%)	Reference
NaCl	-2.62	673	12.62	6.9	10
		723	13.98	56.4	10, 11
		773	14.06	22.2	10, 11
		823	14.74	19.4	10, 11
KOH	-3.55	723	10.53	6.5	12
		748	10.91	5.5	12
		773	11.13	6.5	12
Na_2SO_4	-5.74	773	9.26	20.8	13
PbO	-5.99	673	6.64	9.6	14
		723	6.97	3.1	14
		773	7.41	7.2	14
SiO_2	-5.74	673	7.60	6.9	14
		773	7.75	6.7	14
$LiNO_3$	-2.69	748	15.32	3.7	15
$NaNO_3$	-3.35	723	11.14	0.8	15
		748	11.49	2.5	15
		773	11.70	9.6	15
		798	12.09	6.4	15
KNO_3	-3.49	748	11.12	4.8	15

$\mathrm{AAD}(\%) = 1/N\left(\sum\left|C^{\exp} - C^{\mathrm{cal}}\right| / C^{\exp}\right)\times 100$,

C: Concentration of salt[ppm], N: Number of experimental data

Figure Captions

Fig. 1. Solubility parameter of water.

Fig. 2. Solubilities of NaCl in water vapor.

Fig. 3. Solubilities of KOH in water vapor.

Fig. 4. Solubilities of SiO_2 in water vapor.

Fig. 5. Solubilities of $NaNO_3$ in water vapor.

Fig. 6. Comparison of solubilites of KNO_3, $NaNO_3$ and $LiNO_3$ in water vapor at 748 K.

Fig. 7. Comparison of solubility parameters of water, KNO_3, $NaNO_3$ and $LiNO_3$ at 748 K.

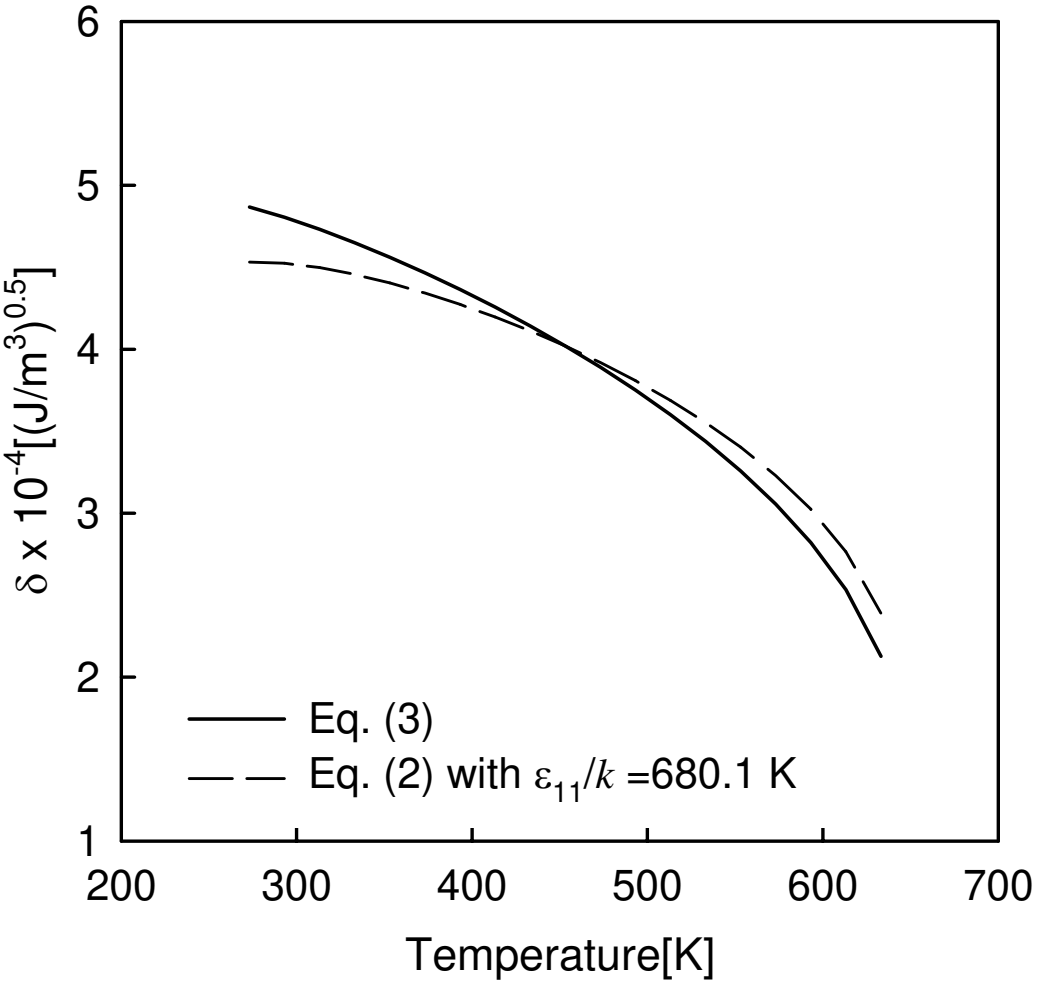
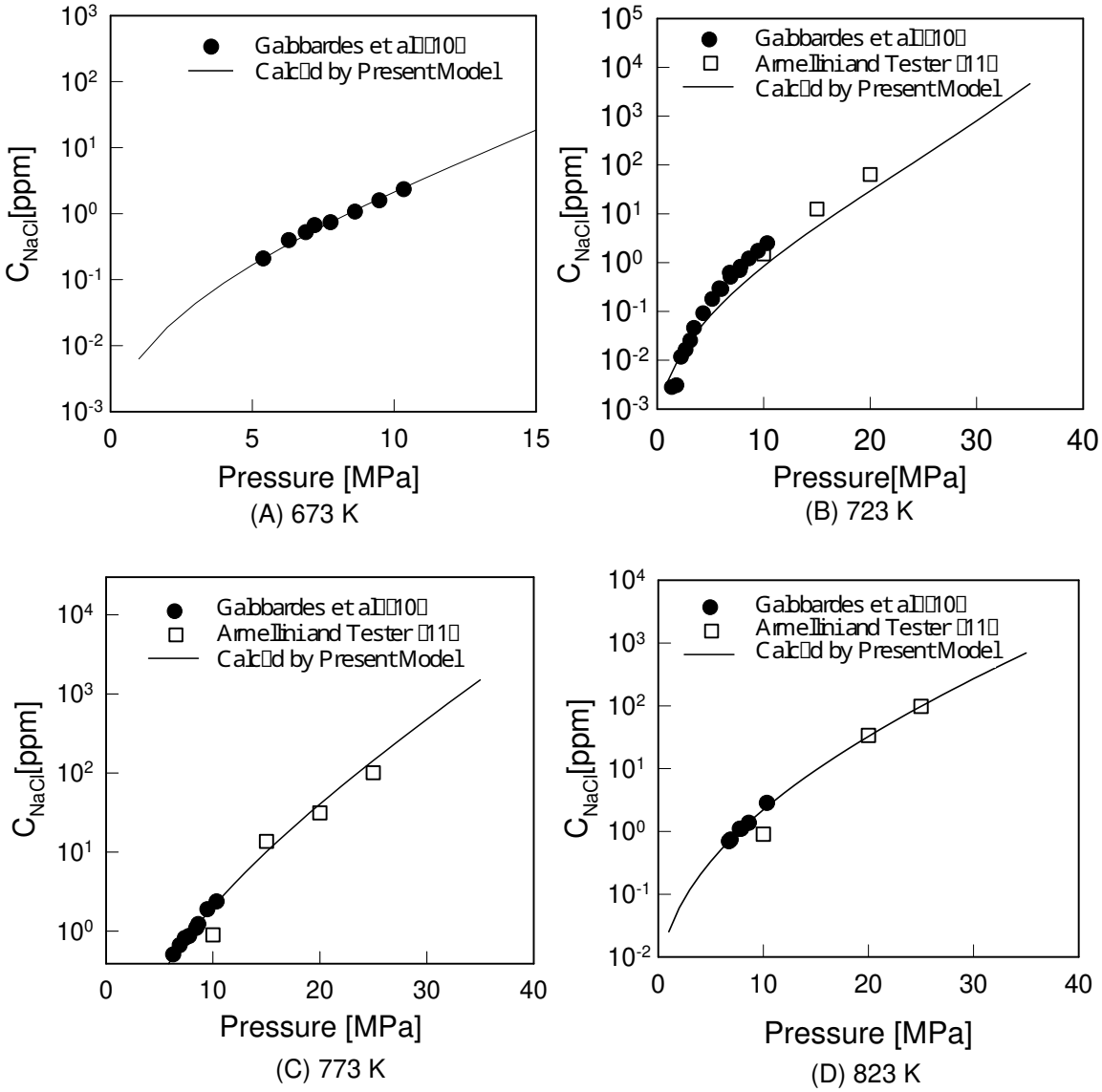

6
5
4
3
2
1
200
300
400
500
600
700
δ x 10^-4 r[(J/m^3)^0.5]
Temperature[K]
Eq. (3)
Eq. (2) with ε11/k =680.1 K

Fig. 1


Gabbardes et al. [10]
Calcd by Present Model
C_NaCl [ppm]
Pressure [MPa]
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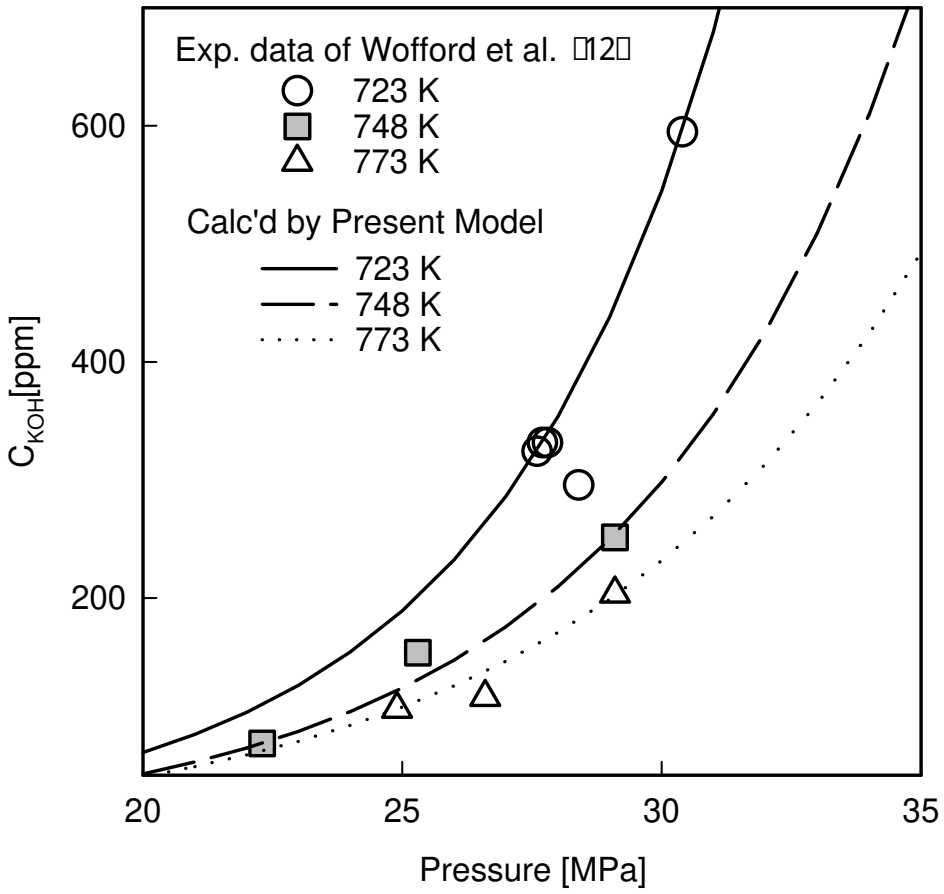
Armellini and Tester [11]
Pressure[MPa]
(B) 723 K
(C) 773 K
(D) 823 K

Fig. 2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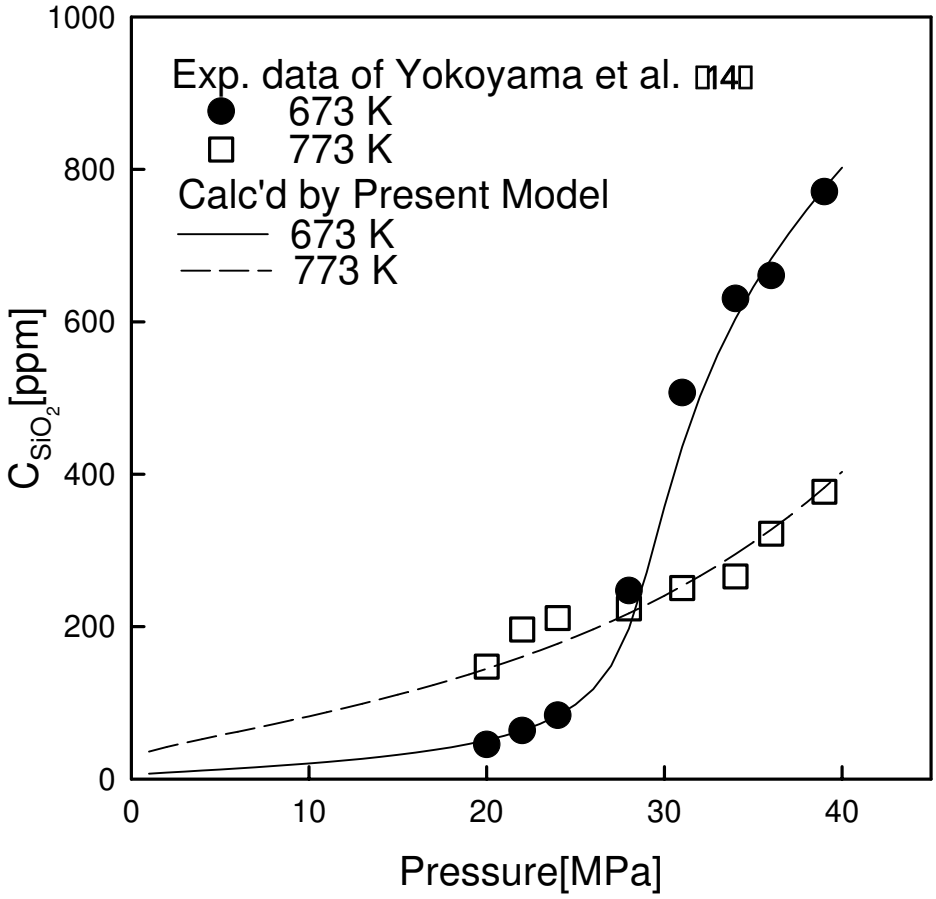
723 K
748 K
773 K
Calc'd by Present Model
723 K
748 K
773 K
600
400
200
C_{KOH}[ppm]
20
25
30
35
Pressure [MPa]

Fig. 3.


Exp. data of Yokoyama et al. [14]
673 K
773 K
Calc'd by Present Model
673 K
773 K
C_{SiO_2}[ppm]
Pressure[MPa]
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200
400
600
800
1000
0
10
20
30
40

Fig . 4.

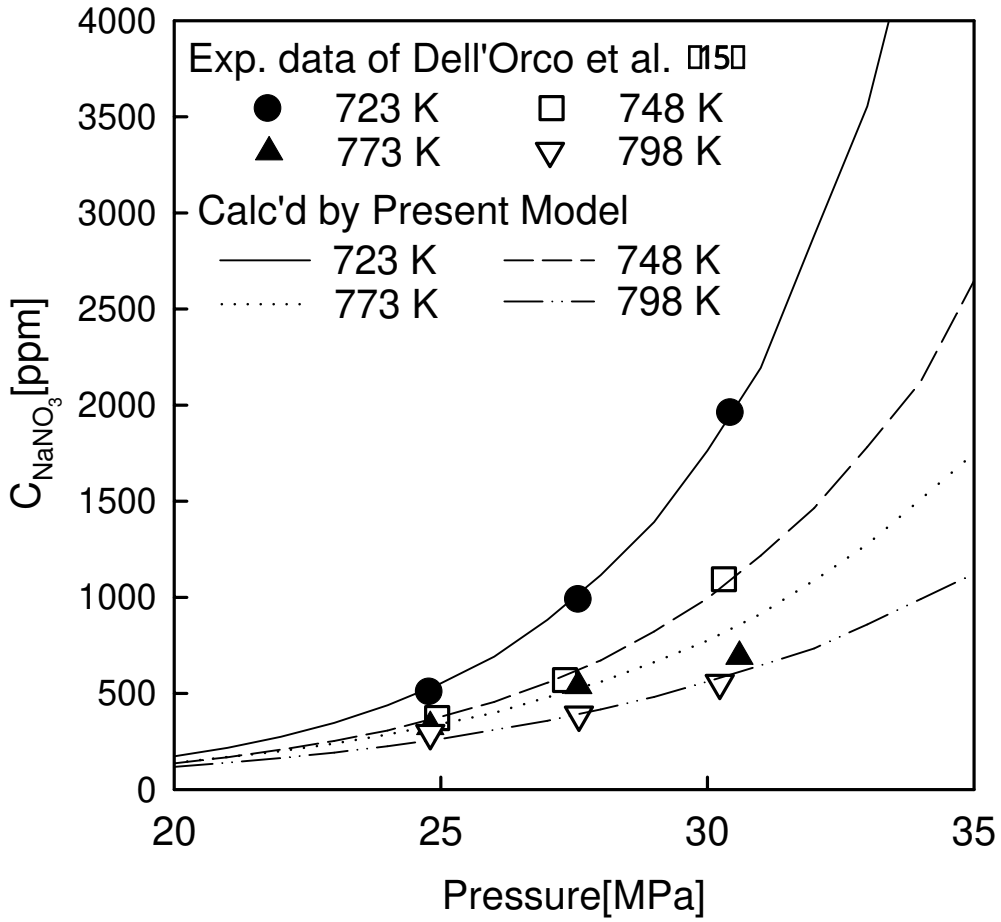

Exp. data of Dell'Orco et al. [15]
723 K
748 K
773 K
798 K
Calc'd by Present Model
723 K
748 K
773 K
798 K
C_{NaNO_3}[ppm]
Pressure[MPa]
0
500
1000
1500
2000
2500
3000
3500
4000
20
25
30
35

Fig . 5.

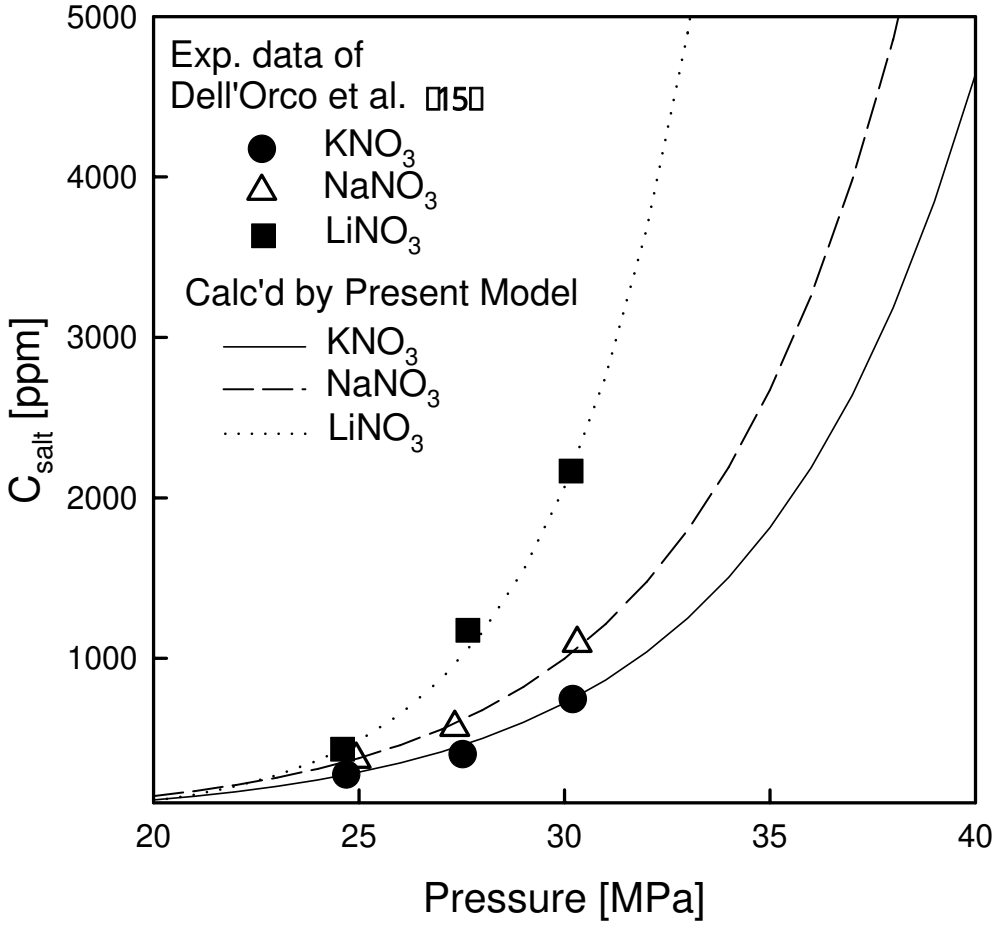
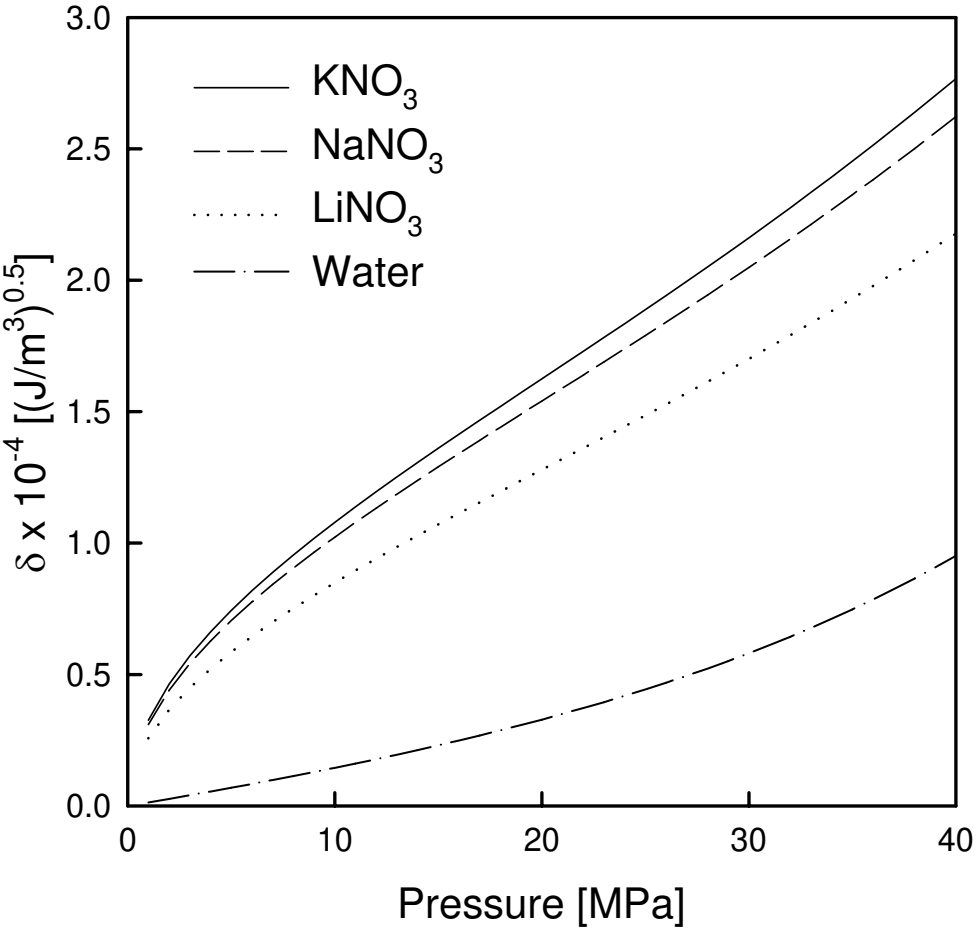

5000
4000
3000
2000
1000
20
25
30
35
40
C_{salt} [ppm]
Pressure [MPa]
Exp. data of
Dell'Orco et al. [15]
KNO_3
$NaNO_3$
$LiNO_3$
Calc'd by Present Model
KNO_3
$NaNO_3$
$LiNO_3$

Fig . 6.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2.0
1.5
1.0
0.5
0.0
0
10
20
30
40
KNO3
NaNO3
LiNO3
Water
δ x 10-4 [(J/m3)0.5]
Pressure [MPa]

Fig . 7