

Prediction of salt effect on vapor–liquid equilibria

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Abstract

In this paper, a newly proposed model based on solvation between pure solvent and salt for prediction of salt effect on vapor–liquid equilibria is presented by using only the vapor pressure depression data of pure solvent + salt systems that compose the mixed solvent with salt system. The proposed model predicts thermodynamically the salt effect by solvation number between each pure solvent and salt determined from the vapor pressure depression data with an assumption of the vapor pressure depression caused by the solvation. Three points differ from the originally proposed model by the author [S. Ohe, 1976. *Advances in Chemistry Series*, No. 155, American Chemical Society.]. First, it is assumed that each solvent component solvates with salt instead of the preferential solvation of the original model. It, however, is superficial phenomenon, since the difference between the solvation numbers is thought to be equivalent to it. Second, it is also assumed that the vapor pressure depression is caused by the solvation. Third, the method predicts the effect from VLE with no salt and vapor pressure depression data of pure solvent with salt. The salt effect on vapor–liquid equilibria was satisfactorily predicted for a methanol + ethanol + water + CaCl_2 (16.7 wt.%) system from the solvation numbers determined from vapor pressure depression data of methanol + CaCl_2 , ethanol + CaCl_2 , and water + CaCl_2 system. © 1998 Elsevier Science B.V.

Keywords: Vapor–liquid equilibria; Salt effect; Preferential solvation; Depression of vapor pressure

1. Introduction

A model in which a salt forms preferential solvate with one of the solvents in a binary solvent system was already proposed to predict salt effect on vapor–liquid equilibrium [1]. For 386 two-solvent + 47 single-salt systems, the model was successfully examined [2]. The following two

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relations were found: (1) preferential solvation number at constant salt molar concentration shows linear relation with solvated solvent molar concentration; (2) the solvation number extrapolated to the concentration at 100% of solvated solvent decreases linearly, as the salt concentration increases. The relations by the model were satisfactory observed over the entire range of solvent concentrations, giving a total mean of the absolute deviation in the vapor phase mole fraction of 0.012.

However, the model should be modified as described below. It is assumed that the salt dissolved in the solvent mixture solvates with each solvent component. As a result of it, 'a preferential solvate' is observed. The numbers of preferential solvate corresponds to the difference of solvation numbers of the salt for each solvent molecule.

2. Depression of vapor pressure

Vapor pressure at a given temperature of a solvent is depressed by adding non-volatile substances that is salt with the degree of its amount. When the behavior of a single solvent and a salt system is assumed to be non-ideal and complete dissociation of salt, the pressure of the system is given by the Eq. (1):

$$\pi = P_{\text{solvent}} \cdot a_{\text{solvent}} \quad (1)$$

Since the activity is a product of mean activity coefficient and mole fraction of solvent: $a_{\text{solvent}} = \gamma_{\text{solvent}}^{\pm} \cdot X_{\text{solvent}}$, then the activity coefficient for the pressure is determined from Eq. (1):

$$\gamma_{\text{solvent}}^{\pm} = \pi / (P_{\text{solvent}} \cdot X_{\text{solvent}}) \quad (2)$$

It is assumed that depression of vapor pressure of pure solvent system is caused by solvated molecule which does not contribute to vaporization. The activity of the solvent becomes:

$$a_{\text{solvent}} = (n_{\text{solvent}} - n_{\text{salt}} \cdot S_o) / \{(n_{\text{solvent}} - n_{\text{salt}} \cdot S_o) + n_{\text{salt}}\}$$

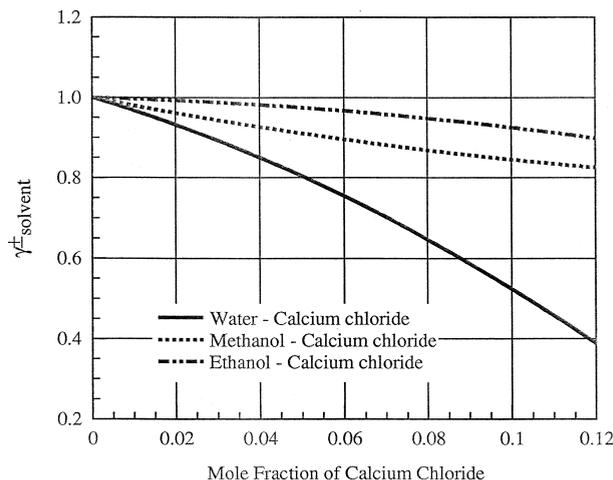


Fig. 1. Mean activity coefficients for vapor pressure depression.

Table 1

Correlation equation parameters for mean activity coefficient of solvent in vapor pressure depression at 101.3 kPa

No.	Solvents	Salts	Parameters of correlation equation ^a			Author(s)
			<i>a</i>	<i>b</i>	<i>c</i>	
1	Ethanol	CaCl ₂	-5.011	-0.240	1.000	Nishi [4] Ohe et al. [5]
2	Methanol	CaCl ₂	4.627	-2.005	1.000	Ohe et al. [5]
3	Methanol	NaSCN	-14.677	-0.298	1.000	Illiuta et al. [6]
4	Methyl acetate	NaSCN	-0.174	0.544	1.000	Illiuta et al. [6]
5	Propanol	CaCl ₂	4.888	-1.030	1.000	Illiuta et al. [6]
6	Water	CaCl ₂	-16.801	-3.081	1.000	Patill et al. [3]

^a $\gamma_{\text{solvent}}^{\pm} = ax^2 + bx + c$, where x is mole fraction of salt.

Dividing both of the denominator and numerator by $n_{\text{solvent}} + n_{\text{salt}}$ will give:

$$a_{\text{solvent}} = (X_{\text{solvent}} - X_{\text{salt}} \cdot S_0) / (1 - X_{\text{salt}} \cdot S_0) \quad (3)$$

where $X_{\text{solvent}} = 1 - X_{\text{salt}}$. Therefore solvation number S_0 is given as:

$$S_0 = (X_{\text{solvent}} - a_{\text{solvent}}) / \{(-a_{\text{solvent}}) \cdot X_{\text{salt}}\} \quad (4)$$

Mean activity coefficient may be thought to be the function of salt concentration. From observed data of depression of vapor pressure [3–5], the relations between mean activity coefficient and salt concentration at atmospheric pressure are determined by Eq. (2) for two alcohols and water with calcium chloride as shown in Fig. 1. Table 1 shows correlation equation parameters for pure solvent + salt system with the other solvents and salt, over the range from 0 to 0.12 mole fraction of salt at isobaric 101.3 kPa, accompanied by the boiling point raising. The solvation numbers between pure solvent and salt are calculated by Eq. (4) for above mentioned system as shown in Fig. 2.

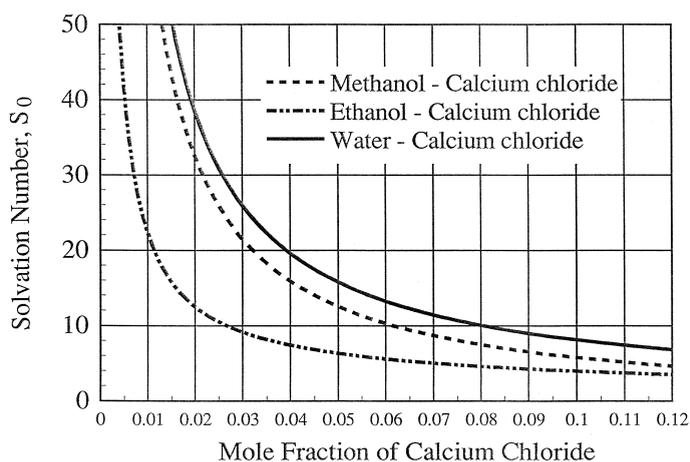


Fig. 2. Solvation number between pure solvent and salt.

3. Effective composition of solvent system containing salt

As the concentration of solvent is assumed to be decreased by the number of solvated molecules, the actual solvent composition participating in the vapor–liquid equilibrium is changed. Assuming that a salt forms the solvates with each component and that the solvated molecules do not contribute to vapor–liquid equilibrium, since the sum of solvent mole fraction is equal to $1 - X_{\text{salt}}$, and the solvation number for i th solvent is calculated as $S_{i_o} \cdot X_i$, the effective mole fraction X_{i_a} for the solvent component is given by:

$$X_{i_a} = (X_i - S_{i_o} \cdot X_i \cdot X_{\text{salt}}) / (1 - X_{\text{salt}} - \sum S_{i_o} \cdot X_i \cdot X_{\text{salt}}) \quad (5)$$

4. Prediction of salt effect from solvation number

In the case of mixed solvent system, depression of vapor pressure may be treated in a similar manner. As total pressure of solvent system, Eq. (6) is given for non-ideal solution which corresponds to the Eq. (1) given for the pure solvent system.

$$P_{\text{solvent}} = \sum P_i \cdot \gamma_i \cdot X_{i_a} \quad (6)$$

The mean activity coefficient for vapor pressure depression is assumed to be average of mean activity coefficient of each solvent with its mole fraction. Eq. (7) may be derived from the above assumption.

$$\gamma_{\text{mix, solvent}}^{\pm} = \sum \gamma_{i, \text{solvent}}^{\pm} \cdot X_i \quad (7)$$

Therefore, the basic equation to calculate salt effect on vapor–liquid equilibrium corresponds to Eq. (1) is Eq. (8).

$$\pi = P_{\text{solvent}} \cdot \gamma_{\text{mix, solvent}}^{\pm} \cdot (1 - X_{\text{salt}}) \quad (8)$$

Since π_{solvent} is determined from Eq. (6), substitution of Eq. (6) into Eq. (8) gives the relation:

$$\pi = (\sum P_i \cdot \gamma_i \cdot X_{i_a}) \cdot \gamma_{\text{mix, solvent}}^{\pm} \cdot (1 - X_{\text{salt}}) \quad (9)$$

The relation between activity coefficient of conventionally defined and that given by Eq. (9) is:

$$\gamma_i = \gamma_i \cdot \gamma_{\text{mix, solvent}}^{\pm} \cdot (1 - X_{\text{salt}}) \quad (10)$$

The assumption of Eq. (7) was examined with the experimental values for three binary solvent systems: methanol + ethanol + CaCl_2 , methanol + water + CaCl_2 , and ethanol + water + CaCl_2 system, calculating by Eq. (9). The comparisons of calculated with observed values [5,2,4] for mean activity coefficients are shown in Fig. 3.

The activity coefficients predicted for the three binary solvent system containing CaCl_2 are shown

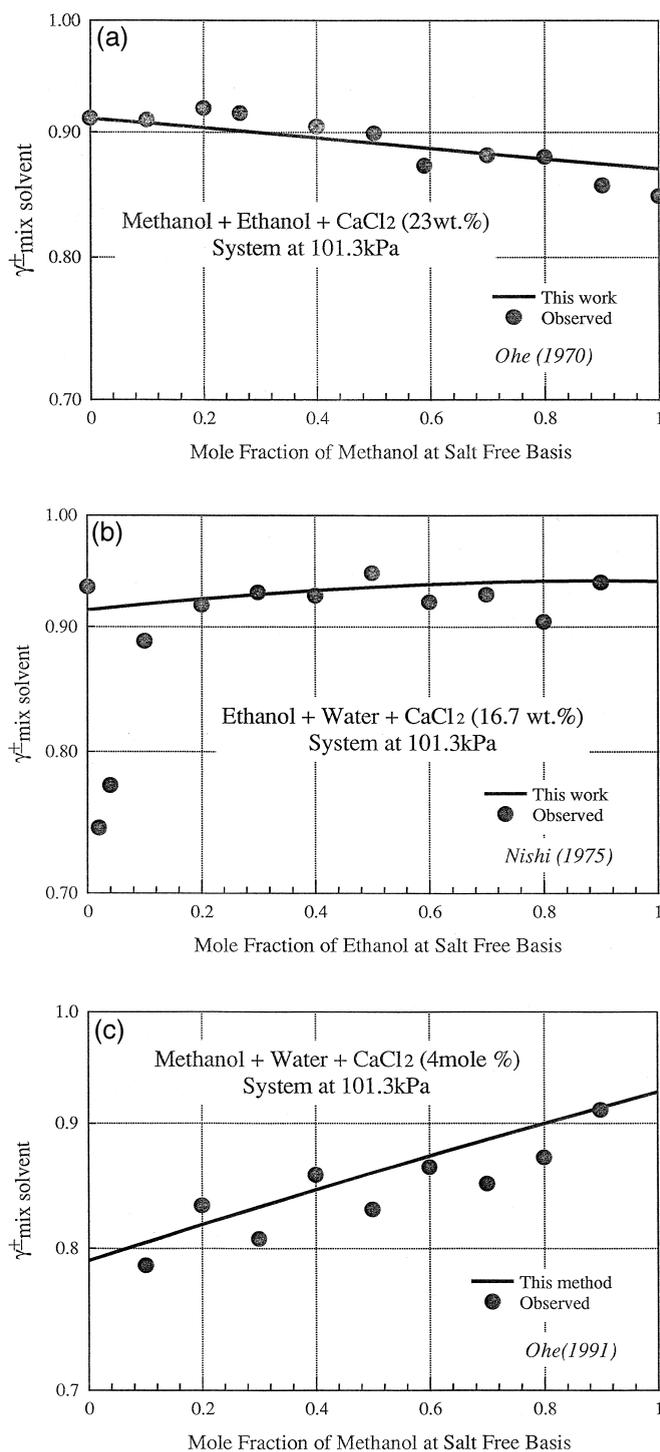


Fig. 3. (a) Mean activity coefficients for vapor pressure depression. (b) Mean activity coefficients for vapor pressure depression. (c) Mean activity coefficients for vapor pressure depression.

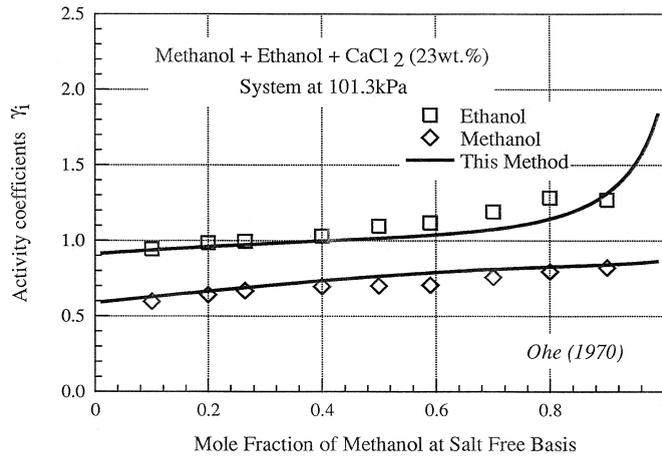


Fig. 4. Activity coefficients for binary solvent and salt system.

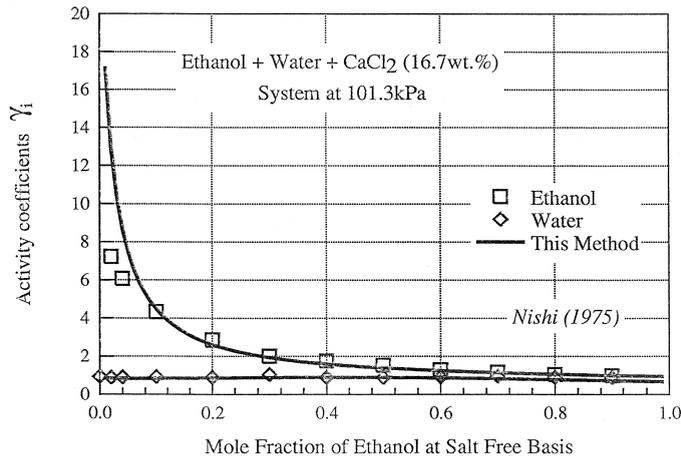


Fig. 5. Activity coefficients for binary solvent and salt system.

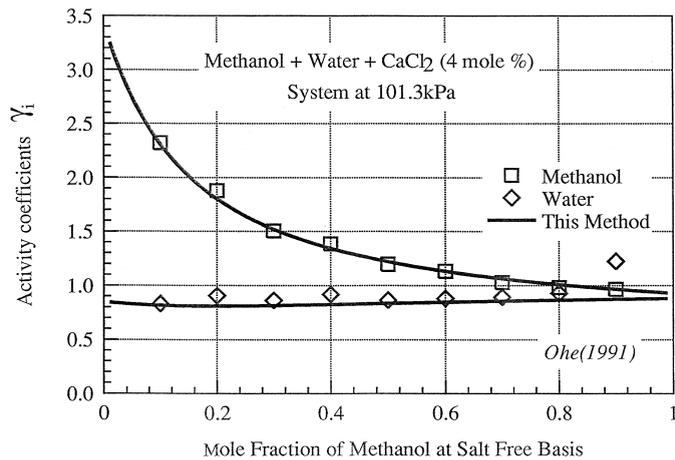


Fig. 6. Activity coefficients for binary solvent and salt system.

Table 2

Wilson parameters for solvent binary system used for prediction of salt effect at 101.3 kPa

No.	Solvent binary system	Wilson parameters		System numbers for parameters from Ohe [7]
		Λ_{12}	Λ_{21}	
1	Acetonitrile(1) + water(2)	0.31151	0.19027	220
2	Ethanol(1) + water(2)	0.18165	0.78386	431
3	Ethyl acetate(1) + ethanol(2)	0.62367	0.66736	713
4	Methanol(1) + ethanol(2)	2.30756	0.20397	120
5	Methanol(1) + water(2)	0.55148	0.89781	189
6	Methyl acetate(1) + methanol(2)	0.32735	0.71155	550

as the conventional coefficient in Figs. 4–6. The activity coefficient of each solvent component at its own zero mole fraction does not approach to unity because of depression of its vapor pressure.

5. Procedure of prediction

The procedure for predicting the salt effect from the solvation number S_o pure solvent is described below.

(a) Obtain the solvation number S_o to be formed by pure solvent. S_o is obtained on Eq. (4), by estimating $\gamma_{\text{solvent}}^{\pm}$ using correlation equation and its parameters in Table 1.

(b) Calculate effective compositions: X_{ia} of solvent system by solvation number and salt concentration using corresponding Eq. (5).

(c) Calculate activity coefficients: γ_i for each component of solvent system by activity coefficient equation for example, Wilson Equation using effective composition X_{ia} .

(d) Estimate mean activity coefficients: $\gamma_{\text{mix,solvent}}^{\pm}$ in Eq. (7), from $\gamma_{i,\text{solvent}}^{\pm}$ of each pure solvent component for depression of vapor pressure of solvent system according to salt concentration.

(e) Predict vapor phase composition and boiling point or total pressure by Eq. (9). Wilson

Table 3

Predicted result for salt effect on vapor–liquid equilibria

No.	System	Salt	Salt concentration	Data points	$\Delta y_i _{\text{av.}}^a$ [–]	$\Delta T _{\text{av.}}^b$ [K]	Author(s)
1	Acetone + methanol	CaCl ₂	10 wt.%	7	0.112	1.02	Ohe [8]
2	Acetonitrile + water	CaCl ₂	10 wt.%	5	0.039	0.49	Sada et al. [9]
3	Ethyl acetate + ethanol	CaCl ₂	10 wt.%	9	0.024	0.87	Hashitani and Hirata [10]
4	Methanol + water	CaCl ₂	16.7 wt.%	9	0.019	0.62	Nishi [4]
5	Methyl acetate + methanol	CaCl ₂	15 wt.%	4	0.032	0.92	Hashitani and Hirata [10]
6	Methyl acetate + methanol	NaSCN	2 mole%	12	0.036	1.01	Illiuta et al. [6]
7	Methyl acetate + methanol	NaSCN	4 mole%	12	0.038	1.13	Illiuta et al. [6]
8	Propanol + water	CaCl ₂	2 mole%	13	0.019	0.95	Illiuta et al. [6]
9	Propanol + water	CaCl ₂	4 mole%	13	0.031	1.62	Illiuta et al. [6]
10	Methanol + ethanol + water	CaCl ₂	16.7 wt.%	38	0.023	0.44	Ohe [11]

$$^a \Delta|y_i|_{\text{av.}} = \sum |y_{i,\text{calcd}} - y_{i,\text{exptl}}| / \text{no. of data point } s.$$

$$^b \Delta|T|_{\text{av.}} = \sum |T_{\text{calcd}} - T_{\text{exptl}}| / \text{no. of data point } s.$$

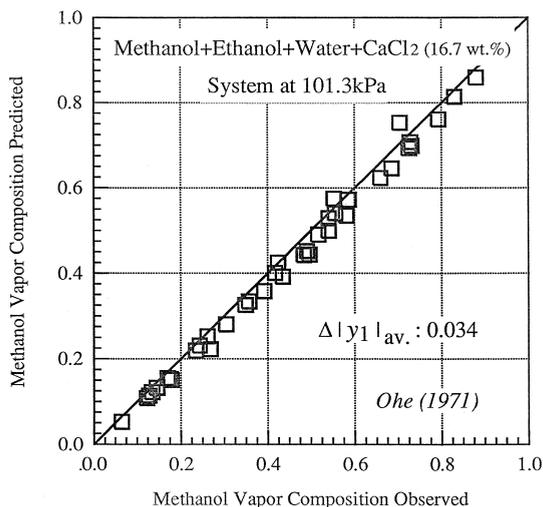


Fig. 7. Comparison between methanol vapor composition observed and predicted by the presented method.

parameters for solvent binary system used to predict salt effect at 101.3 kPa are shown in Table 2. The parameters at 101.3 kPa were taken from Ohe [7], shown with system numbers in the reference.

6. Results and discussions

The predicted results are shown in Table 3. Nine binary solvent + salt and one ternary + salt systems were predicted by the proposed method. Systems of number 1, 2, 3, and 5 were calculated by assuming that each component of methanol, water, ethanol was solvated with salt. Three-solvent–one-salt system was examined in order to confirm the applicability of newly proposed model for prediction of a multi-component solvent–one-salt system, using only the solvation numbers of the

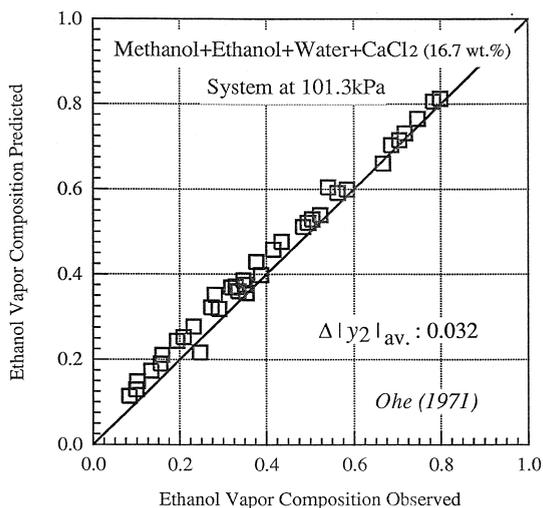


Fig. 8. Comparison between ethanol vapor composition observed and predicted by the presented method.

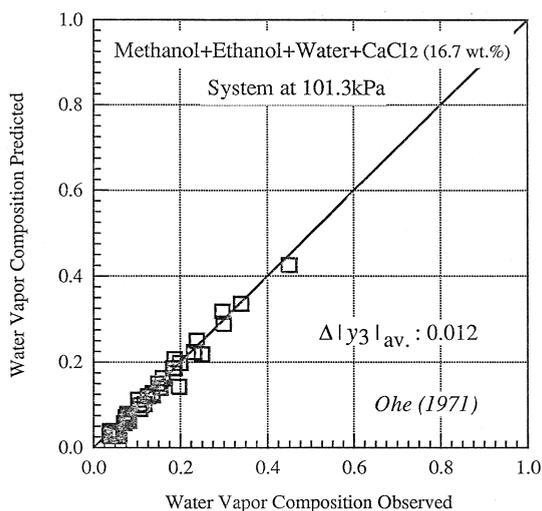


Fig. 9. Comparison between water vapor composition observed and predicted by the presented method.

pure solvent–salt systems that compose the multi-component system. The salt effect on isobaric vapor–liquid equilibrium was satisfactorily predicted for a methanol–ethanol–water–calcium chloride (16.7 wt.%) system.

The comparisons between observed [11] and predicted vapor compositions and boiling point are shown in Figs. 7–10. The average of the absolute deviations in the vapor phase mole fractions with 38 data sets for each component were 0.025 for methanol, 0.031 for ethanol and 0.012 for water, respectively. The mean of the absolute deviations in the boiling point was 0.44 K. The agreement of the mentioned ternary solvent system with one salt with observed values was as good as in the binaries: methanol + water + CaCl_2 , methanol + ethanol + CaCl_2 and ethanol + water + CaCl_2 system. The accuracy of boiling point predicted by this work were slightly better than those of the originally proposed method (mean deviation 0.95 K) by author.

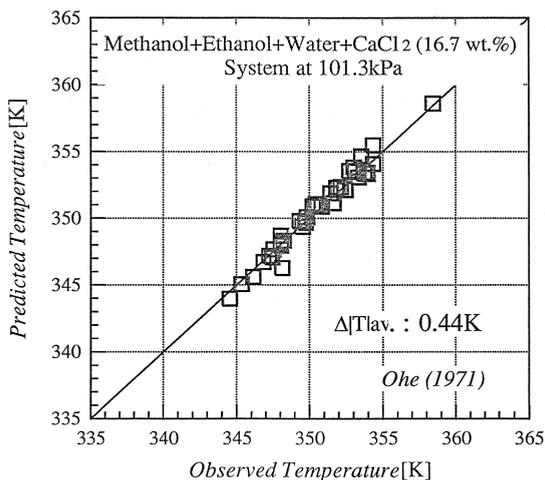


Fig. 10. Comparison between observed and predicted temperatures by the presented method.

7. Conclusions

A newly developed model based on solvation between each solvent and salt to predict and to analyze salt effect on vapor–liquid equilibria was proposed and successfully applied to binary and ternary solvent systems with salt.

(1) It is found that the prediction method of salt effect based on solvation is applicable to multi-component solvent–salt system as well as binary solvent–salt system.

(2) The required data for the prediction is only the solvation number S_o which is determined from the data of depression of vapor pressure in pure solvent–salt system. Another data required is the vapor–liquid equilibrium data of the corresponding solvent system without salt. The applicability of the proposed model is thought almost all of the system including salt. However, lacking of the vapor pressure depression data for organic solvent and salt systems, the systems to be able to be predicted limited. Therefore, the data of depression vapor pressure pure organic solvent with salt are expected to be observed in the near future.

8. List of symbol

a_{solvent}	Activity for depression of vapor pressure of pure solvent system [–]
n_{salt}	Mole number of salt [–]
n_{solvent}	Mole number of solvent [–]
P	Vapor pressure [kPa]
P_{solvent}	Vapor pressure of solvent [kPa]
S_o	Solvation number between solvent and salt [–]
S_{io}	Solvation number of salt with pure component of mixed solvent system [–]
X_i	Mole fraction of i th solvent component existing salt [–]
X_{ia}	Effective mole fraction of i th solvent component existing salt [–]
X_{salt}	Mole fraction of salt [–]
X_{solvent}	Mole fraction of solvent [–]
γ_i	Activity coefficient of conventionally defined [–]
$\gamma_{i,\text{solvent}}^{\pm}$	Mean activity coefficient for depression of vapor pressure of i th solvent [–]
γ_i	Activity coefficient of solvent with no salt [–]
$\gamma_{\text{mix},\text{solvent}}^{\pm}$	Mean activity coefficient for depression of vapor pressure of mixed solvent system [–]
π	Total pressure of the system [kPa]
i	i th solvent [–]

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