Using the Solvation Model to Predict the Salt Effect on Vapor-Liquid Equilibrium

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ABSTRACT

The vapor-liquid equilibrium (VLE) of a mixture containing dissolved salt behaves quite differently from a mixture composed of volatile components alone. When, to a volatile component system in its equilibrium state, a salt is added, the composition of the vapor phase, as well as the temperature or pressure, will change to another equilibrium state. This change, called the salt effect on VLE, means that prediction requires a different approach than that for the no-salt system.

This is because the structure of the salt-containing system, or electrolyte system, is entirely different from that of the no-salt system, or non-electrolyte system. A typical model of the configuration of a non-electrolyte system is the local composition model. In contrast, a typical model of the configuration of an electrolyte system is the solvation model which we originally presented. The configuration of the non-electrolyte system is entirely different from that of the electrolyte system.

The formation of solvate in electrolyte solutions is well known. The solvation numbers for each ion of the salts have been reported by Marcus, who used Stoke’s radii. We adopted Marcus’s solvation numbers at infinite dilution and confirmed that the numbers determined by our model coincide with Marcus’s ion solvation numbers. We have developed a prediction method that can express such a system thermodynamically based on the solvation model. Our solvation model can express the salt effect fully in terms of change of liquid phase composition and total vapor pressure.

Another approach is a modification of the local composition model, which was originally developed for non-electrolyte systems. Some methods using this approach include the Wilson and NRTL equations. This model extends the local composition model to deal with salt systems by
simply adding electrolyte terms. Such equations have some drawbacks or deficiencies.

1. The modification is incongruous: A non-electrolyte model modified for electrolyte solutions is a misapplication, because of the difference in liquid configuration between non-electrolyte and electrolyte solutions.

2. The extended term is the same as the original term: We examined the extended “electrolyte” NRTL and can present evidence that it is in fact the same equation as in the original “non-electrolyte” NRTL. This means that the modified local composition equation is irrelevant. Furthermore, for most of the observed data we got the same result using the original NRTL as we got using the modified NRTL. Therefore, such equations cannot represent the system satisfactorily. They can only fit the data, by optimizing the error. Consequently, they cannot predict the equilibrium.

In our model, we assume that:

1. The presence of any volatile component in the solution produces solvate with each ion of salt.
2. Salt is perfectly ionized to anion and cation.
3. Solvated molecules cannot contribute to VLE.
4. Free (i.e., not solvated) molecules can contribute to VLE.
5. Solvates do not affect free molecules.

Thus, the number of liquid molecules that determine vapor-liquid equilibria changes from that in the original composition. (We call this resulting changed composition the “effective liquid composition”.)

Using these assumptions, our model affords a more versatile method for predicting and correlating VLE for electrolyte solutions. In our model we have two methods for determining solvation numbers. The first method uses data on the elevation of the boiling point of a pure solvent with a salt. The second works directly from the observed data.

Our model can both predict the salt effect on vapor liquid equilibrium and correlate the observed data. We call the first method the predictive method and the second the correlative method.
Using the predictive method with data on the boiling point elevation of a pure solvent with salt, we can predict and confirm the breaking of the azeotropic point (for example, in an ethanol, water, and NH₄Cl system at 101.3 kPa). At present, no other method can attain this result. We applied the solvation model to predict the methanol, ethanol, water and calcium chloride system, with quite satisfactory results. The solvation numbers used for each volatile component were those determined from the constituent binary volatile components of the salt system.

Our method has the following advantages:

1. The solvation number can be obtained from the vapor pressure lowering data of a pure solvent with salt, or from the salt effect data.
2. The ion solvation number reported independently can also be used.
3. We can predict VLE from the solvation numbers.

Moreover, our model expresses the salt effect more meaningfully. It can explain and demonstrate thermodynamically the mechanism of the salt effect on VLE. A further notable advantage of our model is that the visual interpretation of our parameters reflects more realistically the actual chemical structure of the liquid solution, making it easier to comprehend. We have applied our method for almost all systems reported in the literature with satisfactory results.

INTRODUCTION

It is well known that an azeotropic mixture cannot be separated by means of an ordinary distillation method and that some kinds of salt are significantly effective in reducing the azeotrope. For this reason, investigators in both academia and industry have studied the salt effect on vapor–liquid equilibria. It is quite important to clarify the mechanism of this effect and to advance the method of correlation and prediction.

Though many investigations have been performed in this area, most have been modifications of a conventional thermodynamic model for a non-electrolyte component system, such as the activity
coefficients model. These models combined an extended non-electrolyte activity coefficients model and the Debye–Hückel term. The activity coefficients model term was used for describing short-range interaction by van der Waals force. The Debye–Hückel term was used for describing long-range interaction according to the Coulomb force.

Other examples include Tan’s equation [Tan, 1987], which uses the Wilson equation to describe short-range interaction; the electrolyte NRTL model [Chen, 1982, 1986], which uses the NRTL equation; the extended UNIQUAC model [Sander 1986, Macedo 1990] and the LIQUAC model [Li 1994, Polka 1994] using the UNIQUAC equation; Kikic et al.’s method [Kikic 1991], which uses the UNIFAC equation; Achard et al.’s method [Achard 1994], which uses a modification of the UNIFAC equation; and Yan et al.’s method [Yan et al. 1999], which applies the LIQUAC model to the atomic group contribution method.

However, most of the mixtures in the salt effect system are composed of solvents with salt. Thus, a need exists for a model that is capable of explaining contributions of these two different kinds of components. We originally presented a solvation model in 1975. I theorized that alteration in vapor phase composition might be caused by the formation of solvates by interaction between solvents and salt. I also thought that the solvates might play a part in lowering the vapor pressure of the system. First I proposed, to predict the salt effect on vapor–liquid equilibrium, a model in which a salt forms a preferential solvate with one of the solvents in a binary solvent system [Ohe 1976]. This model was successfully applied to correlate and express the salt effect for 386 binary solvents 47 single-salt systems [Ohe 1991].

This first model, however, has a drawback, in that it cannot sufficiently express the lowering of the vapor pressure, since the lowering is observed over the entire range of the liquid composition of a solvent. Based on the model, the lowering is zero at the end of the composition of the solvent, which does not match the experimental fact.

I then modified the model to overcome this drawback. This subsequent model employed,
instead of a preferential solvation, a solvation between the salt of each of solvent in the mixture. Alteration of vapor phase composition by the salt effect is thought to be caused by the difference, between solvents, in their degree of solvation. This difference of degree corresponds to the preferential solvation [Ohe 1998, 2000]. This latter work examines the relation between solvation number and correlation error. The relation is used to determine the solvation number. And the solvation numbers were used to predict the salt effect on vapor liquid equilibria.

ACM MODEL

To date, extended models for electrolyte solution have been presented for almost all ACMs. Among them, one of the most widely used is that presented by Mock and Chen in 1986. They extended the original NRTL of the Local Composition Model for non-electrolyte solutions, for use with electrolyte solutions. This is the extended model for NRTL. Mock and Chen thought that each species had one of three orientations, with the cation at the center; with the anion; or with a molecule at the center.

This equation is the electrolyte or extended NRTL model. The non-electrolyte term is the original NRTL. The electrolyte term is the extended NRTL. In the original case, three parameters were needed. In contrast, the electrolyte case requires nine parameters. However, I think this extension of the NRTL is not entirely reasonable. The original is based on the local composition model. It does not take into consideration strongly associated species such as are found in electrolyte solutions. In other words, it is not symmetrical.

Notice the following interesting result, in a methanol, water, and calcium chloride system. The fitting was done using only the original NRTL equation – not using the electrolyte NRTL. First, the original NRTL was applied to the mixture, using calcium chloride as the third component. Second, optimization was done by comparing the activity coefficients from the NRTL equation with those gained from observed data.
The fitting is almost perfect. Such a close fit is easy, when using such a large number of parameters – in this case, nine. But the number of parameters is not the point. The basis for accuracy is in the approach used. The point, then, is that the original NRTL can already provide a high degree of capability, even when applied to electrolyte solutions. The essential capabilities of the electrolyte NRTL are also possessed by the original NRTL. Therefore, any data that can be fit using the electrolyte NRTL can just as well be fit using the original NRTL.

The fitting is perfect; however, there are problems with the resulting parameters. For example, the values of the alpha parameters vary greatly from those defined by Renon. Typical values for a volatile system should range from 0.1 to 0.5. But you can see here that alpha 31, alpha 23, and alpha 32 are 6.5624, 9.4757, and 9.5429, which are quite different from the originally defined values. This suggests two things: first, that the original NRTL possesses the capability to express the characteristics of the activity coefficient of an electrolyte system; and second, that the modified NRTL also has this capability.
Table 1  NRTL Parameters

<table>
<thead>
<tr>
<th>τ 1,2</th>
<th>τ 2,1</th>
<th>α 1,2</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.3544</td>
<td>1.286</td>
<td>0.3</td>
</tr>
<tr>
<td>τ 1,3</td>
<td>τ 2,3</td>
<td>α 1,3</td>
</tr>
<tr>
<td>6.6682</td>
<td>1.5556</td>
<td>0.2291</td>
</tr>
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</table>

SOLVATION MODEL

Figure 2 shows two types of models. The first is the local composition model, on which the NRTL model is based. The second is the solvation model that we first presented in 1971. It is clear that in the electrolyte solution, the electrolyte associates strongly with the solvent molecules. Therefore, in the electrolyte solution, it is illogical to apply the local composition model.

We have been studying solvation since 1975. Our first model was the preferential solvation model. In 1996, we developed a solvation model in which each volatile component is solvated with each ion of the salt. We examined preferential solvation in specific cases, using a solvation model in which a non-affinitive component does not make a solvate with salt.

Molecules solvated with salt cannot evaporate, because the salt itself cannot evaporate. Only free molecules – not solvated molecules – can contribute to vapor-liquid equilibria. Thus, the number
of liquid molecules that determine vapor-liquid equilibria changes from that in the original composition. We will call this resulting changed composition the “effective liquid composition”.

We make the following assumptions:

1. Both volatile components make solvates with each ion of a salt.
2. Salt is perfectly ionized to anion and cation.
3. Solvates cannot contribute to vapor liquid equilibria.
4. A free volatile component can contribute to the equilibria.
5. A free volatile component is not affected by the solvate.

1. SOLVATION NUMBER

The solvation number is assumed to be the sum of each ion solvation number. The ion solvation number is determined from Stokes’ radii independently from the salt effect on VLE. The reported ion solvation number by Marcus is at infinite dilution. The ion solvation number can be expressed as

$$ S_{i\text{on (solvent)}} = S_{o\text{ion (solvent)}} - k \cdot x_{i\text{on}} $$

from the examination using salt effect data as shown in Fig. 3. The solvation number $S_{i\text{on salt (solvent)}}$ is given by

$$ S_{i\text{on salt (solvent)}} = \sum S_{i\text{on ion (solvent)}}, $$

considering the ionic valency. For example, $S_{i\text{on CaCl}_2(H_2O)}$ for CaCl$_2$-water is calculated as

$$ S_{i\text{on CaCl}_2(H_2O)} = S_{i\text{on Ca}^{2+}(H_2O)} + 2 \cdot S_{i\text{on Cl}^{-}(H_2O)}. $$

The values at the $x_{i\text{on}} = 0$ are the ion solvation numbers reported by Marcus.

In Fig. 3, each line is determined from the salt effect data. The ion solvation number can be expressed as a straight line. The number is decreased by the increase in ion concentration. The intercept shows the ion solvation number at infinite dilution. The values coincide approximately with the original ion solvation number of Stokes’ radii.
2. LOWERING OF VAPOR PRESSURE

Dissolved salt, which is non-volatile substance, lowers vapor pressure at a given temperature of a solvent. When the behavior of a single solvent and a salt system is assumed to be non-ideal and complete ionization of salt, the pressure of the system is given by Eq. (1):

$$
\pi = P_{\text{solvent}} \times a_{\text{solvent}}
$$  \hspace{1cm} (1)

Since the activity is a product of activity coefficient and mole fraction of solvents: $a_{\text{solvent}} = \gamma_{\text{solvent}} \times x_{\text{solvent}}$ then the activity coefficient for the pressure is determined from Eq. (1) as follows:

$$
\gamma_{\text{solvent}} = \frac{\pi}{P_{\text{solvent}} \times x_{\text{solvent}}}
$$  \hspace{1cm} (2)

The model assumed salt showed complete disassociation. It is assumed that lowering of vapor pressure of pure solvent system is caused by solvated molecule, which does not contribute to vaporization. The activity of the solvent becomes
Then for the solvation number, we can get

\[ S_0 = \frac{1 - x_{\text{salt}}}{x_{\text{salt}}} \cdot \frac{1 - \gamma_{\text{solvent}}}{1 - \gamma_{\text{solvent}} \cdot x_{\text{solvent}}} \] (4)

### 3. EFFECTIVE COMPOSITION OF SOLVENTS SYSTEM CONTAINING SALT

We can assume that the concentration of the solvent is decreased according to the number of solvated molecules. Thus, 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 equilibria, the effective mole fraction \( x'_{ia} \) for the \( i \)-th solvent, on a salt free basis, can be obtained using Eq. (5). Since the sum of solvent mole fraction is equal to 1 \(- x_{\text{salt}} \), and if the solvation number for the \( i \)-th solvent is calculated as \( S_{i0} \cdot x'_i \), then Eq. (5) can be obtained as follows:

\[ x'_{ia} = \frac{x_i - S_{i0} \cdot x'_i \cdot x_{\text{salt}}}{1 - x_{\text{salt}} - \sum_{k=1}^{S_{i0} \cdot x'_k \cdot x_{\text{salt}}} x'_{ia}} \] (5)

We determined experimentally that the solvation number \( S \) is expressed by the relation between a single solvent \( S_0 \) and its composition \( x'_i \). There is a linear relationship between the solvation number \( S \) and the composition of the solvent \( x'_i \).

\[ S_i = S_{i0} \cdot x'_i \]

This relation stems from the molecular numbers of the solvents for each salt molecule changing stoichiometrically as the liquid composition changes. This, then, is one of the strongest pieces of evidence in support of the solvation model. Furthermore, the relation has a physical meaning. It is that the solvation number \( S \) is dependent upon the solvent concentration remaining in a state of being capable of making solvates of salt that are constant at a given mole fraction concentration, since the number of solvent molecules that can be solvated increases according to the amount of solvent.
4. PREDICTION OF SALT EFFECT FROM SOLVATION NUMBER

In the case of a mixed solvents system, lowering of the vapor pressure may be treated in a similar manner. As regards the total pressure of a solvents system, Eq. (6) can be used for a non-ideal solution, corresponding to Eq. (1) for the pure solvent system.

\[ P_{\text{solvent}} = \sum P_i x_i \gamma_i \]  \hspace{1cm} (6)

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

\[ \gamma_{\text{mix,solvent}} = \sum \gamma_i x_i \]  \hspace{1cm} (7)

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

\[ \pi = P_{\text{solvent}} \gamma_{\text{mix, solvent}} (1 - x_{\text{salt}}) \]  \hspace{1cm} (8)

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

\[ \pi = \left( \sum P_i x_i \gamma_i \right) \gamma_{\text{mix,solvent}} (1 - x_{\text{salt}}) \]  \hspace{1cm} (9)

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

\[ \gamma_i = \gamma_i x_i \gamma_{\text{mix,solvent}} (1 - x_{\text{salt}}) / x_i \]  \hspace{1cm} (10)

5. DETERMINATION OF SOLVATION NUMBER

There are two types of methods for determining solvation numbers. One determines directly from observed data of salt effect on VLE. The other uses data on the elevation of the boiling point of a pure solvent with a salt. Hence, our model can both correlate the observed data and predict the salt effect on vapor liquid equilibrium. Figure 4 shows a comparison of the results determined using the two methods. The difference is larger at the lowest salt concentration. Then it decreases as the salt concentration increases.
The formation of solvate in electrolyte solutions is widely well known. The solvation numbers for each ion of the salts have been reported by Marcus, who used Stoke’s radii. We adopted Marcus’s solvation numbers and confirmed that the numbers determined by our model coincide with Marcus’s numbers. Table 2 shows the solvation numbers derived from Marcus, and the results we calculated. The solvation number under the caption “solvation” was determined from observed data on the salt effect on VLE. The solvation number under the caption “Stoke’s radii” was calculated from the solvation number for each ion at infinite dilution of salt, as reported by Marcus. The solvation number under the caption “pure solvent” was determined from observed data on vapor pressure lowering or boiling point raising in a solution of pure solvent with salt.

The solvation numbers for the system of Methanol (1) + Water (2) + NaNO3 (3) (8 mole %) are as follows.

<table>
<thead>
<tr>
<th></th>
<th>S10</th>
<th>S20</th>
<th>S20 - S10</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;Solvation&quot;</td>
<td>6.23</td>
<td>9.24</td>
<td>3.01</td>
</tr>
<tr>
<td>&quot;Stoke’s radii&quot;</td>
<td>8.0</td>
<td>9.8</td>
<td>1.8</td>
</tr>
<tr>
<td>&quot;pure solvent&quot;</td>
<td>6.32</td>
<td>9.34</td>
<td>3.02</td>
</tr>
</tbody>
</table>

It is clear that the solvation number of “pure solvent” coincides with that of “solvation”. This signifies the potential of our method to predict the salt effect on VLE. The difference between S20 and S10 is
a decisive factor in calculating the salt effect, especially in the calculation of effective liquid composition. The value of the Stoke’s difference shows the prediction capability qualitatively. The values shown for Stokes’ radii are the greatest. This is because they are at infinite dilution. The values of definite concentration are less than those of Stokes’ radii because of the activity of each ion.

The solvation number in a pure solvent is a very important factor in this model. The solvation number is used to calculate the liquid effective mole fraction and activity coefficient of vapor pressure depression in a mixed solvent. Thus, the less accurate is the solvation number, the less accurate is the prediction. Therefore, in order to determine the solvation number more accurately, we investigated the relation between the solvation number and correlation error, in a binary solvents + salt system.

RESULTS AND DISCUSSION

Figure 5 shows the results obtained using the solvation numbers based on the Stokes’ radii. Each ion solvation number is shown, which is correlated with the numbers of Stoes’ radii using the salt effect data. The average absolute error of vapor composition and boiling points are also shown.

The γ-x and T–x–y curves obtained using the correlated solvation numbers from observed data are shown in Fig 5. Here it can be seen that the solvation model very effectively shows the salt effect, through the change in activity coefficients, which vary from those of the no-salt system. The activity coefficient of methanol increases, whereas that of water decreases. The raising of the boiling point is also quite well correlated.
Figure 5  The solvation model applied for ethanol-water-NH₄Cl system at 101.3 kPa  
(salt concentration x₃=0.08, Jacques et al., 1974)

Figure 6  The Solvation Model Applied for Methanol+Water+CaCl₂ System at 101.3 kPa

Table 2 compares predictions from the three kinds of solvation numbers. From the table, it can be seen that results from each of the three are satisfactory. The best accuracy is given by the solvation

Ion salvation numbers correlated by salt effect data and reported by Marcus, and accuracy

<table>
<thead>
<tr>
<th></th>
<th>Correlated</th>
<th>Marcus</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂O</td>
<td>EtOH</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>3.3</td>
<td>2.7</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>2.9</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Accuracy

<table>
<thead>
<tr>
<th>AAD T(K)</th>
<th>AAD y₁:mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>0.006</td>
</tr>
</tbody>
</table>
number determined from the observed result. The result from the solvation number determined from the data on vapor pressure lowering of pure solvent + salt has medium accuracy. However, even though the accuracy is not as good, this result is quite significant, since the method can predict the salt effect. The result predicted by the solvation number determined by Stoke’s radii is fairly good. The solvation number is at a fixed concentration of salt of infinite dilution. For this reason, it is difficult to obtain an accurate result; however, the model’s consistency is demonstrated.

For binary solvents + salt systems, we correlated with satisfactory accuracy a total of 81 data sets for isobaric data and 16 data sets for isothermal data. For the isobaric system, the average error calculated for the vapor phase composition was 0.018 mole fraction and the average error calculated for the boiling point was 0.72 K. For the isothermal system, the average error calculated for the vapor phase composition was 0.009 mole fraction and the average error calculated for total pressure was 0.14 kPa.

![Figure 7](image_url)

**Figure 7** Prediction by Solvation Model for Methanol+Ethanol+Water+CaCl₂ System at 101.3 kPa

Next we examined the applicability of the modified model to prediction for a multi-solvents system with a salt. Using the solvation number in a pure solvent + salt system determined from a binary solvent + salt system, we estimated the salt effect of the methanol + ethanol + water + CaCl₂ (16.7
wt.% system at 101.3 kPa for 38 data sets.

The systems used in determining the solvation number of each solvent in a ternary system are for methanol and water, and for ethanol. Fig. 7 shows the result predicted for a bubble point of a system with an average absolute deviation of 0.85 K. This figure also shows the result predicted for the vapor composition of the system in mole fraction, with an average absolute deviation of 0.021 for methanol and 0.020 for ethanol.

CONCLUSION

Our method has the following advantages:

1. Our method can use the solvation number, which is independently obtained from Stokes’ radii.
2. The solvation number can be obtained from the vapor pressure lowering data of a pure solvent with salt, or from the salt effect data.
3. We can predict VLE from the solvation numbers.

Moreover, our model expresses the salt effect more meaningfully. It can explain and demonstrate thermodynamically the mechanism of the salt effect on VLE. A further notable advantage of our model is that the visual interpretation of our parameters reflects more realistically the actual chemical structure of the liquid solution, making it easier to comprehend. We have applied our method for almost all systems reported in the literature with satisfactory results.

Using the Activity Coefficient Model (ACM) for Electrolyte Solutions has a drawback – namely, that it was originally designed for non-electrolytes. Thus, to modify it for electrolyte solutions is a mismatch. Our solvation model has no such problem. Most importantly, the ACM can only correlate or fit data; it cannot predict. Our model can predict the salt effect. And, it can do this using only the solvation numbers from a pure solvent and a salt.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Electrolyte, ca salt conc.</th>
<th>① solvation</th>
<th>② stokes radii</th>
<th>③ pure solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔT</td>
<td>ΔY</td>
<td>ΔT</td>
<td>ΔY</td>
</tr>
<tr>
<td>Methanol(1)–Water(2) at 101.3 kPa</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KCl</td>
<td>m=0.5</td>
<td>0.489</td>
<td>0.026</td>
<td>0.680</td>
</tr>
<tr>
<td></td>
<td>m=1.0</td>
<td>0.895</td>
<td>0.030</td>
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<td></td>
<td>m=2.0</td>
<td>0.715</td>
<td>0.020</td>
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<td></td>
<td>m=4.0</td>
<td>0.673</td>
<td>0.022</td>
<td>6.022</td>
</tr>
<tr>
<td>LiCl</td>
<td>m=1.0</td>
<td>0.945</td>
<td>0.017</td>
<td>1.146</td>
</tr>
<tr>
<td></td>
<td>m=2.0</td>
<td>0.530</td>
<td>0.013</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>m=4.0</td>
<td>0.673</td>
<td>0.022</td>
<td>6.022</td>
</tr>
<tr>
<td>NaF</td>
<td>m=0.25</td>
<td>0.687</td>
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</tr>
<tr>
<td>NaNO₃</td>
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<td>0.012</td>
<td>1.834</td>
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<td>7mol%</td>
<td>0.560</td>
<td>0.018</td>
<td>1.222</td>
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<td></td>
<td>8mol%</td>
<td>0.633</td>
<td>0.014</td>
<td>2.908</td>
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<td>CaCl₂</td>
<td>2mol%</td>
<td>0.739</td>
<td>0.010</td>
<td>0.848</td>
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<tr>
<td></td>
<td>4mol%</td>
<td>0.658</td>
<td>0.006</td>
<td>0.856</td>
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<td></td>
<td>10mol%</td>
<td>1.455</td>
<td>0.010</td>
<td>1.530</td>
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<td>Ethanol(1)–Water(2) at 101.3 kPa</td>
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</tr>
<tr>
<td>NH₄Cl</td>
<td>3mol%</td>
<td>1.294</td>
<td>0.005</td>
<td>0.917</td>
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<tr>
<td></td>
<td>6mol%</td>
<td>0.553</td>
<td>0.008</td>
<td>0.955</td>
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<tr>
<td></td>
<td>8mol%</td>
<td>0.940</td>
<td>0.013</td>
<td>4.226</td>
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<tr>
<td>CaCl₂</td>
<td>16.7wt.%</td>
<td>1.484</td>
<td>0.026</td>
<td>1.427</td>
</tr>
<tr>
<td>Acetone(1)–Methanol(2) at 101.3 kPa</td>
<td></td>
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<tr>
<td>LiCl</td>
<td>0.5mol%</td>
<td>0.264</td>
<td>0.013</td>
<td>0.285</td>
</tr>
<tr>
<td></td>
<td>0.75mol%</td>
<td>0.234</td>
<td>0.011</td>
<td>0.296</td>
</tr>
<tr>
<td></td>
<td>1mol%</td>
<td>0.211</td>
<td>0.012</td>
<td>0.255</td>
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<tr>
<td></td>
<td>3mol%</td>
<td>0.349</td>
<td>0.016</td>
<td>0.446</td>
</tr>
<tr>
<td>NaI</td>
<td>2mol%</td>
<td>0.371</td>
<td>0.011</td>
<td>0.159</td>
</tr>
<tr>
<td></td>
<td>3mol%</td>
<td>0.433</td>
<td>0.014</td>
<td>0.238</td>
</tr>
<tr>
<td></td>
<td>4mol%</td>
<td>0.535</td>
<td>0.017</td>
<td>0.334</td>
</tr>
<tr>
<td></td>
<td>5mol%</td>
<td>0.870</td>
<td>0.027</td>
<td>0.829</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>0.5mol%</td>
<td>0.348</td>
<td>0.011</td>
<td>0.250</td>
</tr>
<tr>
<td></td>
<td>1mol%</td>
<td>0.647</td>
<td>0.039</td>
<td>1.144</td>
</tr>
<tr>
<td></td>
<td>2mol%</td>
<td>0.194</td>
<td>0.030</td>
<td>0.194</td>
</tr>
<tr>
<td>2-Propanol(1)–Water(2) at 101.3 kPa</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>CaCl₂</td>
<td>m=0.4</td>
<td>0.517</td>
<td>0.018</td>
<td>0.593</td>
</tr>
<tr>
<td></td>
<td>m=0.8</td>
<td>0.961</td>
<td>0.017</td>
<td>2.071</td>
</tr>
<tr>
<td></td>
<td>m=1.2</td>
<td>1.807</td>
<td>0.012</td>
<td>3.224</td>
</tr>
<tr>
<td>average</td>
<td>① solvation</td>
<td>② stokes radii</td>
<td>③ pure solvent</td>
<td>ΔT</td>
</tr>
<tr>
<td></td>
<td>0.699</td>
<td>0.017</td>
<td>1.198</td>
<td>0.030</td>
</tr>
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</table>
LIST OF SYMBOLS

\( a_{\text{solvent}} \)  activity for lowering of vapor pressure of pure solvent system
\( n_{\text{salt}} \) mole number of salt
\( n_{\text{solvent}} \) mole number of solvent
\( P \) total pressure of system (kPa)
\( P_{\text{solvent}} \) total pressure of system as solvent system (kPa)
\( P_i \) vapor pressure of pure component \( i \) (kPa)
\( S_{i0} \) solvation number between solvent and salt
\( S_{i0} \) solvation number of salt with pure component of mixed solvent system
\( x \) mole fraction of \( i \)-th solvent existing salt
\( x_i' \) mole fraction of \( i \)-th solvent at salt free basis
\( x_{i_{\text{eff}}} \) effective mole fraction of \( i \)-th solvent at salt free basis
\( x_{\text{salt}} \) mole fraction of salt
\( x_{\text{solvent}} \) mole fraction of solvent

GREEK SYMBOLS

\( \gamma_i \) activity coefficient of conventionally defined
\( \gamma_i' \) activity coefficient for effective mole fraction of \( i \)-th solvent
\( \gamma_i^{\text{solvent}} \) activity coefficient for lowering of vapor pressure of \( i \)-th solvent
\( \gamma_i^{\text{mix,solvent}} \) activity coefficient for lowering of vapor pressure of mixed solvent system

SUBSCRIPT

\( i \) \( i \)-th solvent

REFERENCES
