MODIFIED WILSON EQUATION FOR VAPOR-LIQUID AND LIQUID-LIQUID EQUILIBRIA

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A new equation is derived explicitly based on an excess energy equation with Wilson’s local volume fractions and the Gibbs-Helmholtz correlation. The equation is expressed as the combination of the Wilson equation and a volume ratio term which has been introduced as a result of the derivation. The new equation (modified Wilson equation) contains only two parameters for a binary system, and is applicable to both miscible and partially miscible systems. The equation is readily generalized to multicomponent systems without any additional parameters.

The wide applicability of the new equation is shown in representing vapor-liquid and liquid-liquid equilibria for binary and ternary systems.

It is also shown that the original Wilson equation is obtained without obscurity by the same derivation as for the new equation.

Introduction

Phase equilibrium relations are one of the fundamental properties necessary for the calculation of separation processes in chemical industry, and many useful equations have been proposed for expressing the relations.

Recently Wilson38) derived an expression based on the concept of local composition which provides a very good representation of miscible systems including strongly non-ideal mixtures. A particular advantage of the Wilson equation is that it can be generalized to multicomponent mixtures without any additional parameters. However, the Wilson equation having two parameters, which is usually called “Wilson equation”, fails to describe the behavior of immiscible liquid mixtures. To overcome this disadvantage, a third binary constant has been introduced, which permits the Wilson equation to correlate partially miscible systems. Unless the third binary constants are the same for all the constituent binary pairs, however, the three-parameter Wilson equation cannot be generalized for multicomponent systems. In addition, the derivation of both the Wilson and the three-parameter Wilson equations has remained obscure.

On the other hand, based on the concept of local mole fraction and Scott’s two-liquid theory, Renon and Prausnitz28) proposed a new equation (NRTL equation) which describes miscible and immiscible systems with good accuracy. The NRTL equation contains three parameters for a binary system even for partially miscible systems. Renon and Prausnitz28) had some success in trying to surmount this defect by proposing estimation rules for the third parameter (non-randomness factor) according to the constituents of the system. Guffey et al.12) and Marina et al.19), however, pointed out that in some cases these rules are ambiguous and appropriate values must be resorted to a fitting against equilibrium data. Also, there are some limitations in using the equation as suggested by Katayama et al.37).

We have explicitly derived a new equation based on an excess energy equation with Wilson’s local volume fractions and the Gibbs-Helmholtz correlation. The new equation (modified Wilson equation) contains only two parameters for a binary system. Furthermore, the applicability of the new equation to experimental data in the literature has been compared with that of the Wilson and the NRTL equations. The comparison has been made for both vapor-liquid and liquid-liquid equilibria, including ternary systems.

Modified Wilson Equation

In deriving an excess function of a binary solution, we take into account non-randomness in the solution. We assume that the probability of finding a molecule of one type about a central molecule is proportional to the local volume fraction.

By using a procedure similar to that of Scatchard31, Hiranuma40, and Morisue et al.21), the excess enthalpy of the binary solution is written as follows:

\[
\Delta h^E = x_1 \xi_{11}(\lambda_{11} - \lambda_{12}) + x_2 \xi_{22}(\lambda_{12} - \lambda_{22}) \\
\xi_{11} + \xi_{21} = 1, \quad \xi_{12} + \xi_{22} = 1
\]
where $\xi_{ij}$ is the local volume fraction of molecule $i$ in the immediate neighborhood of molecule $j$ and $\lambda_{ij}$ is the interaction energy between $i$-$j$ pair. Furthermore, in the manner of Wilson, we relate the local volume fractions to the over-all volume fractions by

$$\xi_{11} = \Phi_2 \exp\left(-\frac{\lambda_{12}}{RT}\right)$$
$$\xi_{12} = \Phi_2 \exp\left(-\frac{\lambda_{12}}{RT}\right)$$
$$\xi_{21} = \Phi_2 \exp\left(-\frac{\lambda_{21}}{RT}\right)$$
$$\xi_{22} = \Phi_2 \exp\left(-\frac{\lambda_{21}}{RT}\right)$$

(3)

where

$$\Phi_2 = \frac{x_1 v_1}{x_1 v_1 + x_2 v_2}, \quad \Phi_2 = \frac{x_2 v_2}{x_1 v_1 + x_2 v_2}$$

(4)

To obtain an expression for excess Gibbs free energy, the Gibbs-Helmholtz equation is applied

$$\frac{\partial (\Delta g^E / T)}{\partial (1/T)} = \Delta h^E$$

(5)

which was used in explanation of the derivation of the three-parameter Wilson equation by Renon et al. Equation (5) is readily converted into an integration-type equation by selecting the lower limit of integration equal to zero ($1/T=0$).

$$\frac{\Delta g^E}{RT} = 1 \left|_{1/T=0} \right. \Delta h^E \left( \frac{1}{T} \right) + \frac{\Delta g^E}{RT} \left|_{1/T=0} \right.$$

(6)

Now Eq. (1) is substituted into Eq. (6) and the integration is carried out with respect to $1/T$. In the integration of Eq. (6), it is assumed that the quantities ($\lambda_{21} - \lambda_{12}$) and ($\lambda_{12} - \lambda_{22}$) are independent of temperature. Furthermore, when the boundary condition is considered as

$$\frac{\Delta g^E}{RT} \left|_{1/T=0} \right. = 0$$

(7)

the integration results in

$$\frac{\Delta g^E}{RT} = x_1 \ln \frac{\xi_{11} + x_2 \ln \xi_{22}}{x_1 \ln \frac{\Phi_2}{\Phi_1} + x_2 \ln \frac{\Phi_2}{\Phi_1}}$$

(8)

The local volume fractions $\xi_{11}$ and $\xi_{22}$ are derived from Eq. (3) taking account of Eq. (2)

$$\xi_{11} = \frac{x_1}{x_1 + x_2 (v_2/v_1) \exp\left[-\frac{(\lambda_{21} - \lambda_{12})}{RT}\right]} = \frac{x_1}{x_1 + x_2 A_{21}}$$

$$\xi_{22} = \frac{x_2}{x_2 (v_2/v_1) \exp\left[-\frac{(\lambda_{12} - \lambda_{22})}{RT}\right] + x_2} = \frac{x_2}{x_1 A_{12} + x_2}$$

(9)

where

$$A_{12} = \rho_{12} \exp\left[-\frac{(\lambda_{12} - \lambda_{22})}{RT}\right]$$

$$A_{21} = \rho_{21} \exp\left[-\frac{(\lambda_{21} - \lambda_{12})}{RT}\right]$$

$$\rho_{12} = v_1/v_2, \quad \rho_{21} = v_2/v_1$$

(10)

Substitution of Eqs. (4), (9) and (10) into Eq. (8) yields

$$\frac{\Delta g^E}{RT} = -x_1 \ln (x_1 + x_2 A_{21}) - x_2 \ln (x_1 A_{12} + x_2)$$

$$+ x_1 \ln (x_1 + x_2 A_{21}) + x_2 \ln (x_1 A_{12} + x_2)$$

(11)

The activity coefficient for any component $i$ is found by the exact relation

$$RT \ln \gamma_i = \frac{\partial}{\partial n_i} (n_i A^E_{i,j})_{T,P,n_{j,i}}$$

(12)

where $n_i$ is the number of moles of component $i$ and $n_i$ is the total number of moles. By differentiating Eq. (11), namely Eq. (11) being substituted into Eq. (12), the following new equations for activity coefficients are obtained:

$$\ln \gamma_1 = -\ln (x_1 + x_2 A_{21}) + x_1 \left[ \frac{A_{21}}{x_1 A_{12} + x_2 A_{21}} - \frac{A_{12}}{x_1 A_{12} + x_2} \right]$$

$$+ \ln (x_1 + x_2 A_{21}) \cdot x_2 \left[ \frac{\rho_{12}}{x_1 A_{12} + x_2 A_{21}} - \frac{\rho_{21}}{x_1 A_{12} + x_2} \right]$$

(13)

$$\ln \gamma_2 = -\ln (x_2 A_{12} + x_1 A_{21}) + x_2 \left[ \frac{A_{21}}{x_1 A_{12} + x_2 A_{21}} - \frac{A_{12}}{x_1 A_{12} + x_2} \right]$$

$$+ \ln (x_2 A_{12} + x_1 A_{21}) \cdot x_1 \left[ \frac{\rho_{12}}{x_1 A_{12} + x_2 A_{21}} - \frac{\rho_{21}}{x_1 A_{12} + x_2} \right]$$

(14)

where in both equations we call the former two terms the Wilson term and the latter two the volume ratio term.

By the same procedure, the original Wilson equation can also be derived explicitly (see Appendix).

**Generalization to Multicomponent Systems**

The equations for binary solutions presented above are readily generalized to solutions containing any number of components, without any additional ternary or higher order parameters, as in the cases of other local composition equations (Wilson and NRTL equations).

For a multicomponent solution, an excess Gibbs energy is given as

$$\frac{\Delta g^E}{RT} = -\sum_i x_i \ln \frac{\sum_j x_j A_{ij}}{\sum_i x_i A_{ij}} + \sum_i x_i \ln \frac{\sum_j x_j \rho_{ij}}{\sum_i x_i \rho_{ij}}$$

(15)

where

$$A_{ij} = \rho_{ij} \exp\left[-\frac{(\lambda_{ij} - \lambda_{ji})}{RT}\right]$$

$$\rho_{ij} = v_i/v_j$$

(16)

(17)

The activity coefficients can readily be found from Eq. (15) by using the relation of Eq. (12). The result, for any component $i$, is

$$\ln \gamma_i = -\ln \frac{\sum_j x_j A_{ij}}{\sum_i x_i A_{ij}} - \sum_j x_j A_{ij} \frac{\sum_k x_k \rho_{jk}}{\sum_j x_j \rho_{jk}}$$

$$+ \ln \frac{\sum_j x_j \rho_{ij}}{\sum_i x_i \rho_{ij}} + \sum_k x_k \rho_{ki} \frac{\sum_i x_i \rho_{ik}}{\sum_j x_j \rho_{jk}}$$

(18)

**Applicability of Modified Wilson Equation to Phase Equilibrium Data**

1. **Binary vapor-liquid equilibria**

Selected vapor-liquid equilibrium data at low pressures from the literature, shown in Table 1, were...
fitted with the modified Wilson equation, the original Wilson equation and the NRTL equation to compare their relative advantages.

In most cases, when the solution is remote from its critical condition, the following approximate equilibrium equation is acceptable:

$$y_i \phi_i P = y_i \phi_i \exp [v_i (P - \rho)] / RT$$  \hspace{1cm} (19)

The fugacity coefficient $\phi_i$ is given by the virial equation truncated after the second virial coefficient and $\phi_i^2$, the fugacity coefficient at $p_i^*$, also calculated from virial equation, all at the solution temperature. Prausnitz et al.\textsuperscript{27} have discussed this calculation in detail.

To obtain the optimum values of parameters from series of data, the Simplex optimization technique\textsuperscript{27} was adopted. The calculation method used in this work is similar to the one suggested by Prausnitz et al.\textsuperscript{27}, but Ostrowski’s method\textsuperscript{28} was applied to total pressure calculation for isothermal data and bubble point calculation for isobaric data.

Since deviations come from both the scatter of the data and the inadequacy of the equation, they cannot provide directly a measure of the accuracy of equations. Only a comparison of the deviations obtained from different equations with the same set of data gives an indication of relative adequacy of different equations. The systems examined are shown in Table 1. Most of the data are for strongly non-ideal systems under isothermal conditions. Furthermore, Table 1 presents a comparison of experimental vapor-phase mole fractions, total pressures and ratios of activity coefficients with calculated results using two fitting parameters determined for each system from the binary data.

We can draw the following conclusion about representation of binary vapor-liquid equilibria. For both isothermal and isobaric conditions, it is found that the fit through the modified Wilson equation is as good as those obtained using the Wilson and the NRTL equations.

2. Binary liquid-liquid equilibria

While the Wilson equation is not applicable to liquid-liquid systems, the modified Wilson equation can express partial miscibility. The behavior of the new equation was tested by use of experimental data in the literature.

The parameter calculation applied is based on the thermodynamic criterion of equilibrium that the activity of each of two components is the same in both

### Table 1 Comparison of Modified Wilson, Wilson and NRTL equations for representation of binary vapor-liquid equilibria

<table>
<thead>
<tr>
<th>System</th>
<th>Temp. [°C]</th>
<th>No. of Data</th>
<th>Wilson</th>
<th>NRTL</th>
<th>Modified Wilson</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone-acetonitrile</td>
<td>45</td>
<td>10</td>
<td>0.25</td>
<td>1.76</td>
<td>1.40</td>
</tr>
<tr>
<td>Acetone-methanol</td>
<td>760mmHg</td>
<td>12</td>
<td>0.45</td>
<td>2.72</td>
<td>0.47</td>
</tr>
<tr>
<td>Acetone-nitromethane</td>
<td>45</td>
<td>13</td>
<td>0.32</td>
<td>1.45</td>
<td>1.98</td>
</tr>
<tr>
<td>Acetonitrile-benzene</td>
<td>45</td>
<td>12</td>
<td>0.61</td>
<td>2.21</td>
<td>3.02</td>
</tr>
<tr>
<td>Benzene-ethanol</td>
<td>25</td>
<td>9</td>
<td>0.20</td>
<td>2.26</td>
<td></td>
</tr>
<tr>
<td>Benzene-n-heptane</td>
<td>60</td>
<td>14</td>
<td>0.36</td>
<td>4.23</td>
<td>2.05</td>
</tr>
<tr>
<td>CCl4-acetonitrile</td>
<td>45</td>
<td>13</td>
<td>0.43</td>
<td>1.47</td>
<td>1.88</td>
</tr>
<tr>
<td>CCl4-cyclohexane</td>
<td>70</td>
<td>12</td>
<td>0.36</td>
<td>5.02</td>
<td>1.92</td>
</tr>
<tr>
<td>Chloroform-acetone</td>
<td>40</td>
<td>9</td>
<td></td>
<td>1.93</td>
<td></td>
</tr>
<tr>
<td>Cyclohexane-n-heptane</td>
<td>25</td>
<td>11</td>
<td>0.11</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td>Cyclohexane-toluene</td>
<td>25</td>
<td>11</td>
<td>0.48</td>
<td>1.52</td>
<td>2.48</td>
</tr>
<tr>
<td>Diethylamine-CCl4</td>
<td>20</td>
<td>11</td>
<td>0.27</td>
<td>1.14</td>
<td>2.56</td>
</tr>
<tr>
<td>n-Heptane-toluene</td>
<td>25</td>
<td>11</td>
<td>0.35</td>
<td>2.40</td>
<td>2.16</td>
</tr>
<tr>
<td>n-Hexane-ethanol</td>
<td>25</td>
<td>10</td>
<td></td>
<td>4.26</td>
<td></td>
</tr>
<tr>
<td>Methanol-CCl4</td>
<td>35</td>
<td>9</td>
<td>0.40</td>
<td>0.95</td>
<td>1.64</td>
</tr>
<tr>
<td>Nitromethane-benzene</td>
<td>45</td>
<td>12</td>
<td>0.46</td>
<td>2.45</td>
<td>2.65</td>
</tr>
<tr>
<td>Nitromethane-CCl4</td>
<td>45</td>
<td>12</td>
<td>0.50</td>
<td>1.96</td>
<td>2.47</td>
</tr>
<tr>
<td>n-Propanol-benzene</td>
<td>45</td>
<td>11</td>
<td>0.63</td>
<td>2.68</td>
<td>3.34</td>
</tr>
<tr>
<td>Triethylamine-n-butanol</td>
<td>64.5</td>
<td>13</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triethylamine-n-propanol</td>
<td>70.05</td>
<td>20</td>
<td>0.59</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triethylamine-n-propanol</td>
<td>80.10</td>
<td>19</td>
<td>0.49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triethylamine-benzene</td>
<td>90.25</td>
<td>13</td>
<td>0.30</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Arithmetic average: 

$$\Delta y_i = \frac{\sum_{j=1}^N (y_{ij}^\text{exp} - y_{ij}^\text{cal})^2}{M \times 100}, \Delta P = \sqrt{\frac{\sum_{j=1}^N ((P_{ij}^\text{exp} - P_{ij}^\text{cal}))^2}{M \times 100}}, \Delta \ln(y_i/y_2) = \sqrt{\frac{\sum_{j=1}^N [\ln(y_i/y_2)^\text{exp} - \ln(y_i/y_2)^\text{cal}]^2}{M \times 100}}$$

* total pressure data
Table 2  List of parameters of Modified Wilson equation calculated from mutual solubility data

<table>
<thead>
<tr>
<th>System</th>
<th>Temp. °C</th>
<th>Experimental mutual solubilities</th>
<th>Parameters</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)-(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Butanol-water</td>
<td>25</td>
<td>0.4888</td>
<td>0.0189</td>
<td>628.17</td>
</tr>
<tr>
<td>Furural-isooctane</td>
<td>25</td>
<td>0.9569</td>
<td>0.0539</td>
<td>1318.96</td>
</tr>
<tr>
<td>Furural-water</td>
<td>40</td>
<td>0.736</td>
<td>0.016</td>
<td>1139.38</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>0.647</td>
<td>0.022</td>
<td>1067.40</td>
</tr>
<tr>
<td>n-Heptane-furfural</td>
<td>48.8</td>
<td>0.9000</td>
<td>0.0887</td>
<td>2140.51</td>
</tr>
<tr>
<td>1-Hexane-DMSO</td>
<td>25</td>
<td>0.9802</td>
<td>0.0136</td>
<td>2810.14</td>
</tr>
<tr>
<td>Methanol-cyclohexane</td>
<td>25</td>
<td>0.8281</td>
<td>0.1250</td>
<td>123.03</td>
</tr>
<tr>
<td>2-Methylheptane-furfural</td>
<td>25.5</td>
<td>0.9483</td>
<td>0.0448</td>
<td>2260.33</td>
</tr>
<tr>
<td>Triethylamine-water</td>
<td>65</td>
<td>0.8225</td>
<td>0.0036</td>
<td>2227.48</td>
</tr>
</tbody>
</table>

In reference 30), Renon et al. estimated the ternary liquid-liquid equilibrium of the system through the NRTL equation by using selected values of αij to obtain a good representation of the ternary data. We, however, used recommended values of αij for the estimation.

The modified Wilson equation for all systems studied are shown in Table 2. In the lower parts of Fig. 1, ΔG°/RT curve calculated by the new equation presents a convex

part and two concave ones; this indicates that the new equation is able to express the phase splitting. The contributions of the Wilson and volume ratio terms to excess Gibbs free energy are also shown in the figure.

The fact that the Wilson equation cannot represent immiscible behavior follows from its having a limit value in the expression of a positive deviation on excess Gibbs free energy. The three-parameter Wilson equation has surmounted the limitation by multiplying the Wilson equation by a constant larger than 1. On the other hand, the modified Wilson equation has overcome the limitation by the addition of the volume ratio term, which always gives positive values.

Figure 2 shows good agreement between experimental activity coefficients from vapor-liquid equilibria and calculated ones through modified Wilson equation with parameters from the binary liquid-liquid data.

3. Ternary vapor-liquid equilibria

With the modified Wilson equation, using binary data only, six ternary vapor-liquid equilibria were estimated, and the calculated results have been compared with experimental data as shown in Table 3. Calculations were performed with the modified Wilson and the Wilson equations. For all systems, differences between experimental data and calculated values through the new equation are almost the same as those through the Wilson equation.

4. Ternary liquid-liquid equilibria

The NRTL equation can predict ternary liquid-liquid equilibria from binary data, if the best value of non-randomness factor for each constituent binary system is chosen. The modified Wilson equation, on the contrary, is generally applicable and needs no empirical parameters to predict ternary liquid-liquid equilibria.

To show the applicability of the modified Wilson equation to ternary liquid-liquid equilibria, four systems were chosen. The first one has a narrow two-liquid region, the second one has a similarly narrow one and contains water as a constituent, and others have broad ones. Figures 3, 4, 5 and 6 give a
### Table 3 Comparison of Modified Wilson and Wilson equations for prediction of ternary vapor-liquid equilibria

<table>
<thead>
<tr>
<th>System</th>
<th>Temp. [°C]</th>
<th>No. of Data</th>
<th>Wilson</th>
<th>Modified Wilson</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile (1)-benzene (2)-n-heptane (3)</td>
<td>45</td>
<td>33</td>
<td>$d_{y_1}$ 0.88 0.78 0.92 4.74</td>
<td>$d_{y_1}$ 0.65 0.46 0.43 3.80</td>
<td>25</td>
</tr>
<tr>
<td>Acetone (1)-methanol (2)-iso-propanol (3)</td>
<td>55</td>
<td>26</td>
<td>$d_{y_2}$ 0.97 1.02 0.91 0.81</td>
<td>$d_{y_2}$ 1.42 1.24 1.34 1.93</td>
<td>10</td>
</tr>
<tr>
<td>Benzene (1)-n-heptane (2)-n-propanol (3)</td>
<td>75</td>
<td>38</td>
<td>$d_{y_3}$ 2.86 2.81 2.52 2.79</td>
<td>$d_{y_3}$ 2.83 2.76 2.47 2.16</td>
<td>11</td>
</tr>
<tr>
<td>Cyclohexane (1)-n-heptane (2)-toluene (3)</td>
<td>25</td>
<td>16</td>
<td>$d_P$ 0.34 0.19 0.30 1.53</td>
<td>$d_P$ 0.32 0.19 0.29 1.53</td>
<td>16</td>
</tr>
<tr>
<td>n-Hexane (1)-ethanol (2)-benzene (3)</td>
<td>55</td>
<td>43</td>
<td>$d_{y_1}$ 3.06 2.74 2.47 2.91</td>
<td>$d_{y_1}$ 2.91 2.62 2.37 2.46</td>
<td>15</td>
</tr>
<tr>
<td>Methanol (1)-ethanol (2)-acetone (3)</td>
<td>760 mmHg</td>
<td>37</td>
<td>$d_{y_1}$ 1.02 0.49 0.87 0.29*</td>
<td>$d_{y_1}$ 1.12 0.53 0.98 0.29*</td>
<td>1</td>
</tr>
<tr>
<td>Methanol(1)-CCl4(2)-benzene (3)</td>
<td>55</td>
<td>8</td>
<td>$d_{y_1}$ 0.77 0.76 1.65 1.29</td>
<td>$d_{y_1}$ 0.87 0.73 0.76 1.55</td>
<td>33</td>
</tr>
</tbody>
</table>

$\Delta y_i = \sqrt{\frac{\sum (y_{i\text{exp}} - y_{i\text{calc}})^2}{M \times 100}}$, $\Delta P = \sqrt{\frac{\sum (P_{\text{exp}} - P_{\text{cal}})^2}{P_{\text{exp}}^2 / M \times 100}}$, $\Delta T = \sqrt{\frac{\sum (T_{\text{exp}} - T_{\text{cal}})^2}{T_{\text{exp}}^2 / M \times 100}}$

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**Fig. 3** Experimental and calculated liquid-liquid equilibria for the system of acetonitrile (1)-n-heptane (2)-benzene (3) at 45°C

**Fig. 4** Experimental and calculated liquid-liquid equilibria for the system of ethyl acetate (1)-water (2)-ethanol (3) at 40°C

**Fig. 5** Experimental and calculated liquid-liquid equilibria for the system of 1-hexene (1)-dimethyl sulfoxide (2)-5-nonanone (3) at 60°C

**Fig. 6** Experimental and calculated liquid-liquid equilibria for the system of methanol (1)-cyclohexane (2)-carbon tetrachloride (3) at 25°C

Comparison of experimental data with the results calculated from three sets of binary parameters by use of the new equation and the NRTL equation. As shown in these figures, the modified Wilson equation is generally superior to the NRTL equation in representing ternary liquid-liquid equilibrium data.

Estimation of liquid-liquid equilibrium relations is much more sensitive to the parameter values than in the case of vapor-liquid equilibrium relations, especially when the two-liquid phase region is small in the triangular diagram.
Conclusion

Based on an excess energy equation with Wilson's local volume fractions and the Gibbs-Helmholtz correlation, a new equation (modified Wilson equation) has been derived explicitly. The equation which has only two parameters for a binary system can explain the behavior of both miscible and immiscible systems. The wide applicability of the modified Wilson equation has been tested for binary and ternary systems.

For binary mixtures, in representation of binary vapor-liquid equilibria, the modified Wilson equation gives as good fit for all types of mixtures as the Wilson equation. It also, like the NRTL equation, can represent the shape of excess Gibbs energy which gives the existence of a two-liquid phase region, while the Wilson equation cannot.

For multicomponent systems, the modified Wilson equation can be generalized without introducing any additional assumptions and parameters. It predicts ternary vapor-liquid equilibria well and ternary liquid-liquid equilibria fairly well.

A new interpretation of the original Wilson equation is shown in Appendix.

Appendix: New Interpretation of Wilson Equation

An ambiguity is found in the derivation of the original Wilson equation, as Wilson intuitively replaced the over-all volume fractions of the Flory-Huggins equation with his local volume fractions.

In the derivation of the modified Wilson equation, Eq. (11), the boundary condition in Eq. (6) is considered as Eq. (7). On the other hand, there is another way of assumption that at 1/T=0 (infinite temperature) the behavior of the solution is expressed by the Flory-Huggins equation for athermal solutions26 as follows:

\[ \frac{\Delta g^E}{RT} \bigg|_{1/T=0} = x_1 \ln \frac{\phi_1}{x_1} + x_2 \ln \frac{\phi_2}{x_2} \]  

(A-1)

By use of the boundary condition of Eq. (A-1), the integration of Eq. (6) results in

\[ \frac{\Delta g^E}{RT} = x_1 \ln \frac{\xi_{11}}{x_1} + x_2 \ln \frac{\xi_{22}}{x_2} \]

\[ = -x \ln (x_1 + x_2) - x_2 \ln (x_1 x_2 + x_2) \]  

(A-2)

That is, the original Wilson equation has been clearly derived from another boundary condition by the same procedure through which the modified Wilson equation is derived.

If some other equation, e.g. the Flory-Huggins type equation with a parameter, is used for the boundary condition in Eq. (6), the following new equation is derived:

\[ \frac{\Delta g^E}{RT} = -x_1 \ln (x_1 + x_2) - x_2 \ln (x_1 x_2 + x_2) + A \phi_1 \phi_2 \]  

(A-3)

where \( A \) is a parameter which is independent of temperature. If the Scatchard-Hildebrand type equation for regular solutions is adopted for the boundary condition, a corresponding new equation is introduced as follows:

\[ \frac{\Delta g^E}{RT} = -x_1 \ln (x_1 + x_2) - x_2 \ln (x_1 x_2 + x_2) \]

\[ + x_1 \ln (x_1 + x_2) + x_2 \ln (x_1 x_2 + x_2) + A \phi_1 \phi_2 \]  

(A-4)

Addition of a physical term to the original Wilson equation has been suggested recently by Nitta and Katayama28.
VAPOR-LIQUID EQUILIBRIUM RELATIONS FOR THE SYSTEM ACCOMPANIED BY HYPOTHETICAL CHEMICAL REACTION CONTAINING SALT

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In a system accompanied by hypothetical chemical reaction vapor-liquid equilibrium ratio, $K_i$, of component $i$ has been expressed by

$$\log K_i = \frac{-A_i}{T} + B_i$$

where $T$ is the absolute temperature, $A_i$ is a constant determined by reaction system and component $i$, and $B_i$ is a constant determined from vapor-liquid equilibrium data for the liquid composition at conversion 0 and/or 1. The object of this paper is to show that the equation mentioned above can also be applied to the system including salt. Following two systems are herein discussed:

1. propanol-propanol-calcium chloride
2. methanol-ethanol-water-calcium chloride

In these systems $A_i$ implies the salt effect, but its behavior was not definitely observed.

Introduction

Salts may be used as a separating agent for distillation or a catalyst in the operation of distillation accompanied by chemical reaction. It may be therefore useful to investigate the salt effects for vapor-liquid equilibria of systems accompanied by chemical reaction.

The author $^4$ has previously reported that vapor-liquid equilibrium relations for systems accompanied by hypothetical chemical reaction could be expressed in the same way as for a system accompanied by chemical reaction. That is, in a system accompanied by chemical or hypothetical chemical reaction vapor-liquid equilibrium ratio, $K_i$, for component $i$ is correlated by

$$\log K_i = -\frac{A_i}{T} + B_i$$

where $T$ is the absolute temperature, $A_i$ is a constant determined by reaction system and component $i$, and $B_i$ is a constant determined from vapor-liquid equilibrium data for the liquid composition at conversion 0 and/or 1. If vapor-liquid equilibrium relations for their liquid compositions are known, vapor-liquid equilibrium relations for the system accompanied by chemical reaction can be predicted. The object of the present paper is to show that the equation can be applied to systems including salt.