A CORRELATION OF EXCESS THERMODYNAMIC PROPERTIES FOR ALCOHOL—NONPOLAR SOLVENT SYSTEMS BY A CONTINUOUS LINEAR ASSOCIATION MODEL

Tomoshige NITTA and Takashi KATAYAMA
Department of Chemical Engineering, Osaka University, Toyonaka, Osaka, Japan

The vapor-liquid equilibrium and heat of mixing data for binary mixtures of alcohols-nonpolar substances are analyzed by using a continuous linear association model. New sets of values for association constant and enthalpy of hydrogen bond formation for aliphatic alcohols are presented which represent vapor-liquid equilibria better than the sets by Renon and Prausnitz. The physical interaction parameter, which has been treated so far as an adjustable parameter, is correlated satisfactorily with solubility parameter and branching parameter. The estimation of vapor-liquid equilibria for alcohol-hydrocarbon systems is possible by use of the correlation.

Introduction

In a solution which contains one or some kinds of polar components, association between molecules often plays an important role in nonideality of thermodynamic properties of the solutions. We have a research program for study of associated solutions which have chemical interactions between like and/or unlike molecules. In a previous paper we discussed the excess thermodynamic properties of some associated solutions by using continuous linear association models (I) and (II), and also discussed the applicability of the model (II) to the vapor-liquid equilibrium relations of binary mixtures of alcohols and interacting solvents.

In this paper aliphatic alcohol and nonpolar systems are investigated to gain a general idea of the applicability of a continuous linear association model for alcohols and to obtain the necessary parameters for self-association of each alcohol. We have collected and reduced a large body of reliable isothermal thermodynamic data for binary mixtures of alcohols and nonpolar substances.

The associated solution theory of Flory-Huggins type combined with a linear association model was first presented by Kretschmer and Wiebe, and recently rederived by Renon and Prausnitz (Kretschmer-Wiebe type). A different type of equations and correlation for alcoholic solutions were presented by Wiehe and Bagley (Wiehe-Bagley type). Renon and Prausnitz gave the values of association constant and enthalpy of hydrogen bond formation for methanol, ethanol, n-propanol, and iso-propanol by using the association model of Kretschmer-Wiebe type. Their values are, however, suspected to be high when vapor-liquid equilibrium data for alcoholic solutions are correlated.

In this work the Kretschmer-Wiebe type equations are used, and new sets of association parameters for alcohols are obtained which represent vapor-liquid equilibria better than do the sets by Renon and Prausnitz. Physical interaction constants are also correlated satisfactorily by use of the concepts of apparent solubility parameter for alcohols and branching parameter defined by Funk and Prausnitz for saturated hydrocarbons. As a result, estimation of vapor-liquid equilibria for alcohol—hydrocarbon systems has become possible from the properties of each pure substance. Correlations of heat of mixing data with the association constants in this work are, however, worse than those by Renon and Prausnitz.

1. Association Model and Fundamental Equations

An alcohol molecule (A) has one oxygen atom and one active hydrogen atom. Many association models...
used for alcohols are such as linear or cyclic dimer, cyclic tetramer, continuous linear polymers, etc. The continuous linear association model, as shown in Fig. 1, is assumed in this paper for the interpretation of thermodynamic properties of alcoholic solutions. Nonpolar substance (B), such as saturated hydrocarbon, is assumed to be inert and to exist only as monomer.

The basic assumptions of the associated solution theory have been presented in a previous paper, in which the activity coefficients of A and B components are derived as follows.

\[
\ln \gamma_A = \ln(C_{A,0} x_{A,0}^{C_A}) - \nu_A (\sum_{i} C_{A,i} + C_B - \sum_{i} C_{A,i}^2) \\
+ (b \nu_A (RT) \Phi_A) \\
\ln \gamma_B = \ln(C_{B,0} x_{B,0}^{C_B}) + 1 - \nu_B (\sum_{i} C_{A,i} + C_B) \\
+ (b \nu_B (RT) \Phi_B) \\
\]

where \( b \) is a physical interaction parameter. The distribution of associated complexes is determined by the association constants of complex formation. The association constants defined by molar density are assumed to be independent of the number of associated molecules as

\[
K_A^{(c)} = \frac{C_{A,0}}{C_{A,0} x_{A,0}^{C_A}} \\
\]

Monomer concentration is given by

\[
C_{A,i} = \frac{2C_{A,0}}{1 + 2K_A^{(c)} C_A + (1 + 4K_A^{(c)} C_A)^{1/2}} \\
\]

Total concentration of monomer and associated complexes of alcohol is

\[
\sum_i C_{A,i} = \frac{2C_{A,0}}{1 + (1 + 4K_A^{(c)} C_A)^{1/2}} \\
\]

Heat of mixing for this system is given by

\[
h^E = (- \Delta h_A^m) x_A \left( \frac{\sum C_{A,i}}{C_A} - \frac{\sum C_{A,i}^2}{C_A^2} \right) \\
+ b' \sum \Phi_A \Phi_B (x_A \nu_A x_B \nu_B) \\
\]

where \( \Delta h_A^m \) is the association energy of complex formation and \( b' \) is a physical interaction parameter for heat of mixing, which is given by Eq. (7).

\[
b' = b - T \frac{db}{dT} \\
\]

The dimensionless association constant \( K_A \) is defined as

\[
K_A = K_A^{(c)} \nu_A \\
\]

The enthalpy of association \( \Delta h_A^m \) is interrelated with temperature dependence of \( K_A \) as

\[
\Delta h_A^m = -R \frac{\partial \ln K_A}{\partial (1/T)} \\
\]

The extension of this theory to multicomponent systems containing one alcohol and inert solvents is performed without difficulty. The equations for a mixture of \( m \) components are as follows.

\[
\ln \gamma_A = \ln(C_{A,0} x_{A,0}^{C_A}) - \nu_A (\sum_{i} C_{A,i} + \sum_{i} C_{A,i}^2) \\
+ (b \nu_A (RT) \sum \sum \Phi_A \Phi_B (b_{a,b} - \frac{1}{2} b_{a,b})) \\
\ln \gamma_B = \ln(C_{B,0} x_{B,0}^{C_B}) + 1 - \nu_B (\sum_{i} C_{A,i} + \sum_{i} C_{B,i}) \\
+ (b \nu_B (RT) \sum \sum \Phi_A \Phi_B (b_{a,b} - \frac{1}{2} b_{a,b})) \\
\]

\[
h^E = (- \Delta h_A^m) x_A \left( \frac{\sum C_{A,i}}{C_A} - \frac{\sum C_{A,i}^2}{C_A^2} \right) \\
+ \frac{\sum x_A \nu_A}{(1/2 \sum \sum \Phi_A \Phi_B b_{a,b}} \\
\]

where \( \sum' \) means summation for \( a \neq A, \) and \( C_{A,i}, \sum C_{A,i} \) are given by the same Eqs. (4) and (5), respectively.

2. Determination of Association Constants and Enthalpy of Association for Alcohols

The binary systems investigated in this work are listed in Table 1 with literature cited. From the above equations the activity coefficients are calculated with two parameters \( K_A \) and \( b \), while the heat of mixing is with three parameters \( K_A, \Delta h_A^m, \) and \( b' \).

The values for two parameters \( (K_A, b) \) are determined from each set of isothermal vapor-liquid equilibrium data by using the least-square fitting techniques given by Marquardt. In these calculations vapor-phase nonidealities were taken into account using the empirical method of O'Connell and Prausnitz for second virial coefficients. Six types of objective functions were examined and are summarized in Table 2. The average differences of the values for \( K_A \) determined from these objective functions for each set of data are given in Table 3, which shows that the values for \( K_A \) are almost the same in each class \( (\gamma \text{ and } P \text{ in Table 2) } \), but are different by about 25–55% in average deviation between classes \( (\gamma \text{ and } P \text{ in Table 2) }. \) As shown in the parentheses in Table 3, isothermal total pressure data \( (P \times T) \) were most available so that the correlation for \( K_A \) was based upon the values obtained from the type number 5 in class \( P \).

Fig. 2 shows the association constant \( K_A \) obtained for ethanol. All points are under the broken line which represents the association constant given by Renon and Prausnitz for ethanol. The slope of the solid line gives -4.5 kcal/mole for enthalpy of hydrogen bond
### Table 1  List of data used in this work for vapor-liquid equilibrium (V-L) and heat of mixing (H-M)

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>$\delta_n$ (25°C)</th>
<th>MeOH V-L</th>
<th>EtOH V-L</th>
<th>n-ProOH V-L</th>
<th>iso-ProOH V-L</th>
<th>n-BuOH V-L</th>
<th>MeOH H-M</th>
<th>EtOH H-M</th>
<th>n-ProOH H-M</th>
<th>iso-ProOH H-M</th>
<th>n-BuOH H-M</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-Octane</td>
<td>6.86</td>
<td>17</td>
<td>4</td>
<td>18</td>
<td>17</td>
<td>51</td>
<td>17</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta$-Octane</td>
<td>7.28</td>
<td>8</td>
<td>6</td>
<td>13</td>
<td>6</td>
<td>25</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Heptane</td>
<td>7.44</td>
<td>52</td>
<td>9</td>
<td>46</td>
<td>10</td>
<td>37</td>
<td>47</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Octane</td>
<td>7.52</td>
<td>3</td>
<td>15</td>
<td>5</td>
<td>42</td>
<td>33</td>
<td>16</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methylcyclohexane</td>
<td>8.13</td>
<td>4</td>
<td>19</td>
<td>14</td>
<td></td>
<td></td>
<td>42</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>8.20</td>
<td>22</td>
<td>12</td>
<td>7</td>
<td></td>
<td></td>
<td>33</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>8.6</td>
<td>40</td>
<td>2</td>
<td>30</td>
<td></td>
<td></td>
<td>31</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 2  Summary of objective functions used for the least-square method

<table>
<thead>
<tr>
<th>Class</th>
<th>Type number</th>
<th>Objective function</th>
</tr>
</thead>
<tbody>
<tr>
<td>( g^E )</td>
<td>1</td>
<td>( \sum (\frac{g_{cal} - g_{obs}}{g_{obs}})^2 )</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>2</td>
<td>( \sum \left( \frac{(\ln g_1)<em>{cal} - (\ln g_1)</em>{obs}}{(\ln g_2)_{obs}} \right)^2 )</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>( \sum \left( \frac{(\ln g_2)<em>{cal} - (\ln g_2)</em>{obs}}{(\ln g_2)_{obs}} \right)^2 )</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>( \sum \left( \frac{(\ln P_{cal} - P_{obs})^2}{(\ln P_{obs})^2} \right)^2 )</td>
</tr>
</tbody>
</table>

### Table 3  Average deviations in the values of \( K_a \) obtained from different objective functions

<table>
<thead>
<tr>
<th>Alcohol as one component</th>
<th>Average deviation [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>i/j*</td>
<td>( \gamma/P )</td>
</tr>
<tr>
<td>i/j*</td>
<td>2/3</td>
</tr>
<tr>
<td>Methanol</td>
<td>3.3</td>
</tr>
<tr>
<td>Ethanol</td>
<td>2.6</td>
</tr>
<tr>
<td>n-Propanol</td>
<td>3.3</td>
</tr>
<tr>
<td>iso-Propanol</td>
<td>4.2</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>1.4</td>
</tr>
<tr>
<td>Total</td>
<td>3.0</td>
</tr>
</tbody>
</table>

* The symbol i/j denotes the averaging method

\[
\bar{K}_a = \frac{1}{n} \sum_{j=1}^{n} K_a(\text{from type } j \text{ obj. fn.})
\]

** The figure in parentheses is the number of isothermal vapor-liquid equilibrium data used for the calculation.

### Table 4  Values of constants and molar volumes for aliphatic alcohols at 25°C

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>( K_a^{(0)} [-] )</th>
<th>( \Delta H_a^{(0)} \text{ [kcal/mole]} )</th>
<th>( \delta_a^{(0)} \text{ [cal/cc]^{1/2}} )</th>
<th>( \gamma \text{ [cc/mole]} )</th>
<th>( K_a^{(o)} \text{ [l/mole]} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>510</td>
<td>-4.5</td>
<td>8.3</td>
<td>40.16</td>
<td>20.5</td>
</tr>
<tr>
<td>Ethanol</td>
<td>200</td>
<td>-4.5</td>
<td>8.3</td>
<td>58.65</td>
<td>11.7</td>
</tr>
<tr>
<td>n-Propanol</td>
<td>110</td>
<td>-4.5</td>
<td>8.3</td>
<td>75.14</td>
<td>8.27</td>
</tr>
<tr>
<td>iso-Propanol</td>
<td>85</td>
<td>-4.5</td>
<td>8.2</td>
<td>76.95</td>
<td>6.54</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>80</td>
<td>-4.5</td>
<td>8.3</td>
<td>92.00</td>
<td>7.36</td>
</tr>
</tbody>
</table>
formation. The solvent effects were not recognized clearly for the values of $K_A$ obtained from the binary mixtures of different solvents in Table 1. By use of the average value of $K_A$ at 25°C ($K_A^{(25)}=200$) a set of two parameters ($\Delta h_A$, $b'$) was calculated from heat of mixing data at 25°C for binary mixtures containing ethanol by the least-square method. This gives the value for $\Delta h_A$ viz. $-4.5$ kcal/mole in agreement with the above value. The absolute values of $\Delta h_A$ calculated in such a manner at other temperatures increase with rising temperature. However, the form of temperature dependence for $\Delta h_A$ was not adopted from the viewpoint of simplicity of correlation for vapor-liquid equilibria.

For methanol, $n$-propanol, iso-propanol, and $n$-butanol the values of $K_A$ at 25°C were determined from vapor-liquid equilibrium data by fixing the values of $\Delta h_A$ as $-4.5$ kcal/mole, because there are fewer reliable isothermal data for these alcohols than for ethanol. New sets of $K_A$ and $\Delta h_A$ obtained for alcohols are summarized in Table 4.

3. Correlation of Physical Interaction Parameter $b$ with Solubility Parameters

By using the association constants given in Table 4, the values of $b$ and $b'$ have been calculated by the least-square method. As temperature rises, the values of $b$ decrease slightly, while those of $b'$ increase strongly. The parameter $b$ has been correlated with solubility parameter and estimated easily as follows, because the temperature dependence is relatively small. The parameter $b$ is expressed as

$$b=(\delta_A-\delta_B)^2+2\delta_A\delta_B l_{AB}$$

(13)

where $\delta_A$ is an apparent solubility parameter of alcohol and $l_{AB}$ is a binary constant which represents the deviation from geometric mean assumption for cross cohesive energy density.

The determination of the value of $\delta_A$ for each alcohol is somewhat arbitrary, and two methods were tried for correlation. One of them is the use of the value of solubility parameter of homomorph for alcohol. The other is the value of root of internal pressure reported by Wiehe and Bagley. We have selected the latter method mainly from the success of correlation for $l_{AB}$. The values of $\delta_A$ are listed in Table 4. All values for solubility parameters $\delta_A$ and $\delta_B$ used for the correlation are those at 25°C.

The calculated binary constant $l_{AB}$ is correlated with the branching parameter $r$ defined by Funk and Prausnitz as

$$r=\frac{\text{number of methyl groups}}{\text{total number of carbons}}$$

The scattered points on the same $r$ correspond to the isothermal data at different temperatures. The success of the correlation for binary constant $l_{AB}$ with the branching parameter may suggest the necessity to distinguish force constants between methyl and methylene groups, as Funk and Prausnitz had already shown. If no experimental data are available, the results in Fig. 3 are applicable for estimation of $b$. Although a similar correlation for $b'$ is possible, we do not adopt it because the values of $b'$ depend on temperature considerably.

4. Comparison of the Correlation with Experimental Data

The comparison of the correlation with experimental data is made in two ways. One is to fix the association parameters and to treat the physical interaction parameters as adjustable ones. Comparisons between calculated and experimental values are made for each alcoholic solution, and standard deviations in this work are compared with those by Renon and Prausnitz. The other is to estimate all parameters from the correlation and to compare the calculated vapor-phase
compositions or relative volatilities with isobaric vapor-liquid equilibrium data.

Table 5 shows the standard deviations in total pressure and heat of mixing when the physical interaction parameters are treated as adjustable ones. The selected values in this work give a better correlation for vapor-liquid equilibria but a poorer one for heats of mixing than those by Renon and Prausnitz. Some examples for comparison with experimental data of the correlation in this work are shown in Figs. 4, 5 and 6. They show that this model with proposed association parameters gives a good representation of the properties of alcohol— inert solvent systems. Fig. 7 shows the activity coefficients against composition for n-propanol—n-heptane system corresponding to Fig. 5. The relative contributions of chemical and physical interaction terms are also shown in Fig. 7.

The contribution of a physical interaction term for excess free energy is less than 20% for many systems except for methanol—hydrocarbon systems, showing
Table 6 Comparison of $b$-values from the correlation with those for best fitting for the isobaric vapor-liquid equilibrium data

<table>
<thead>
<tr>
<th>System</th>
<th>Pressure [mmHg]</th>
<th>Literature cited</th>
<th>$b$-value from Eq. (13)</th>
<th>Av. dev. [%] in $b_f^*$</th>
<th>Av. dev. [%] in $b_a^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol-α-Hexane</td>
<td>760</td>
<td>43)</td>
<td>3.01</td>
<td>0.9</td>
<td>7.6</td>
</tr>
<tr>
<td>Ethanol-Methylcyclopentane</td>
<td>760</td>
<td>43)</td>
<td>3.04</td>
<td>1.3</td>
<td>7.8</td>
</tr>
<tr>
<td>iso-Propanol-Methylcyclohexane</td>
<td>500</td>
<td>27)</td>
<td>2.93</td>
<td>2.0</td>
<td>9.2</td>
</tr>
</tbody>
</table>

* Average deviation in vapor-phase mole fraction; $\sum \left| \frac{y_{cal} - y_{obs}}{y_{obs}} \right| \times 100/n$

** Average deviation in relative volatility; $\sum \left| \frac{a_{cal} - a_{obs}}{a_{obs}} \right| \times 100/n$

*** Experimental boiling temperatures at each composition are used.

**** Systems not included in the correlation of $l_{AB}$ with $r$ as in Fig. 3.

phase separation at room temperature. Almost the same results are obtained for heats of mixing, except that at lower temperatures the chemical contribution decreases rapidly, as Hwa and Ziegler\(^{14}\) had already shown. It should be noted that for alcoholic solutions the chemical contribution decreases for excess free energy but increases for heat of mixing with rising temperature.

For alcohol–carbon tetrachloride systems, this model is applied successfully for vapor-liquid equilibria but not for heats of mixing, which suggests some interactions between unlike molecules.

Several isobaric vapor-liquid equilibrium data were compared with the proposed correlation for $K_A$ and $b$. The calculation technique presented by Prausnitz, \textit{et al.}\(^{32}\) was used after making a necessary change for SUBROUTINE ACTCO. The results are summarized in Table 6. Two of the three systems in Table 6 are not included in the correlation of $l_{AB}$ with $r$ as in Fig. 3. The average deviations in vapor-phase mole fraction, relative volatility, and temperature are 1–2\(^{\circ}\), 7–10\(^{\circ}\), and 0.3–0.5\(^{\circ}\)C, respectively. Although the calculations are performed by use of the best-fitting values for parameter $b$, the average deviations are not so improved as shown in Table 6. These results show that the correlations obtained for association and physical interaction parameters are sufficient for practical use.

5. Discussion

The values of association parameters obtained in this work are different from those by Renon and Prausnitz.\(^{35}\) They chose the value for $\Delta H_A^0$ viz. $-6.0$ kcal/mole for all alcohols and fixed $K_A$ value at 50\(^{\circ}\)C for each alcohol, which are larger values than those in this work. The reason for this difference is the fact that more weight is given in the calculation to the data for vapor-liquid equilibria in this work, but to excess enthalpy in their work. This suggests that the values for association parameter obtained from liquid-liquid equilibrium data such as methanol-cyclohexane system may differ with those values, when Kretschmer-Wiebe type equations are used to represent phase separation. This situation may be caused by the inadequacy of the associated solution theory and/or a continuous linear association model for alcoholic solutions. In spite of this inadequacy, the correlations of the thermodynamic properties may be sufficient for practical use, when remembering the character of approximation of this theory and/or model.

Wiebe and Bagley\(^{48}\) presented a similar correlation for binary alcohol-aliphatic hydrocarbon solutions, based on a single experimental point for each system. Their theory differs from Kretschmer-Wiebe type theory mainly in two points; one is the definition of an association constant, and the other is the neglect of the physical effects and their introduction of an additional adjustable parameter which originally relates to the ratio of molecular sizes. Recent investigation of thermodynamic properties of alcoholic solutions by infrared spectroscopic study in our laboratory\(^{36}\) shows that the Wiebe-Bagley type equations are more suitable than the Kretschmer-Wiebe type to interpret both vapor-liquid equilibrium and infrared spectroscopic data by one parameter for self-association constant for alcohol. The reason for selection of Kretschmer-Wiebe type equation in this work is mainly from the viewpoint of facility in extending this continuous linear association model to alcoholic solutions containing the interacting solvents ($A_1B_1$ Model\(^{38}\)). That is, while an analytical solution\(^{28}\) is easily obtained in Kretschmer-Wiebe’s theory in the case of solving the simultaneous equations for the molecular balance, an approximate or numerical method\(^{30}\) must be used in Wiebe-Bagley’s theory.

Acknowledgement

The authors are grateful to Messrs. Tamon Nagano and Hiastoshi Fukui for their assistance in data collection and numerical calculations in this work.

Nomenclature

\[ b, b' = \text{physical interaction parameter} \]
\[ C = \text{molar density} \]