Use of the SSF equations in the Kojima-Moon-Ochi thermodynamic consistency test of isothermal vapour-liquid equilibrium data

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The Kojima-Moon-Ochi (KMO) thermodynamic consistency test of vapour–liquid equilibrium (VLE) measurements for 32 isothermal data sets of binary systems of various complexity was applied using two fitting equations: the Redlich-Kister equation and the Sum of Symmetrical Functions. It was shown that the enhanced reliability of the fitting of the experimental data can change the conclusions drawn on their thermodynamic consistency in those cases of VLE data sets that are estimated to be near the border of consistency.

Keywords: thermodynamic consistency test, vapour–liquid equilibria, binary system.

INTRODUCTION

The design of processes in the chemical industry requires accurate vapour-liquid equilibrium data (VLE) and other thermodynamic data sets under the process conditions. However, measurements of phase equilibrium variables: composition of the vapour and liquid phases, temperature and pressure, are subject to systematic and random errors, due to complicated physical and chemical interactions between the constituents of the mixture. Therefore the character of the thermodynamic behaviour of some systems might be very complex. The consequence might be an inadequacy of the thermodynamic functions $g^E/(RT)$ and $\ln(\gamma_1/\gamma_2)$ which are related to the consistency test of the VLE data. Hence, it is necessary, prior using these data to check their mutual agreement in the thermodynamic sense, i.e., to perform the thermodynamic consistency test. Respecting these facts an analytical form representing the solution of the Gibbs-Duhem equation should be selected, which should include an adequate number of parameters in order to ensure a reliable representation of the experimental data. The number of these parameters has to be adjusted to a degree which should correspond to the accuracy and precision of the experimental measurements.

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One of the early procedures for testing the thermodynamic consistency of VLE data was the area test. This procedure represents a consistency criterion for assessing experimental data from the entire composition range. The area test is based on the integral Gibbs-Duhem equation. It is often used in the form which was introduced by Redlich and Kister, although some other authors have performed its supplements and changes.

For testing the consistency of individual points, the point test was developed. A few different procedures have been proposed; all of them are based on the differential Gibbs-Duhem equation.

It is of particular importance to check the consistency of the VLE data in the dilute composition region. Kojima, Moon and Ochi developed a thermodynamic consistency test (designated as the KMO test) of VLE data in this domain, incorporating also the area and the point tests in their procedure.

The purpose of the present work was to examine the influence of the form of the relationships for the molar excess Gibbs free energy $g^E/(RT)$ and for the thermodynamic function $\ln(\gamma_1/\gamma_2)$ which are used during the testing of the thermodynamic consistency of isothermal VLE data. In this respect, the applicability of the four parameter Redlich-Kister equation (RK) and the six-parameter Sum of Symmetrical Functions (SSF) was examined for a large number of data sets of non-electrolyte binary systems with different degrees of complexity.

A BRIEF SURVEY OF CONSISTENCY TESTS

The procedures for testing the thermodynamic consistency of VLE data are systematized in Table I. They can be classified into two categories: 1) the area tests and 2) the point tests. The tests are given chronologically and the footnote of this Table points out the statistical character in the corresponding cases.

TABLE I. Procedures for testing the thermodynamic consistency of VLE data

<table>
<thead>
<tr>
<th>Testing procedure</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>The area tests</strong></td>
<td></td>
</tr>
<tr>
<td>Redlich-Kister (1948)</td>
<td>1</td>
</tr>
<tr>
<td>Herington (1951)</td>
<td>2</td>
</tr>
<tr>
<td>Samuels-Urichson-Stievenson (1972)*</td>
<td>3</td>
</tr>
<tr>
<td>Kojima-Moon-Ochi (1990)</td>
<td>8</td>
</tr>
<tr>
<td><strong>The point tests</strong></td>
<td></td>
</tr>
<tr>
<td>Liebermann-Fried (1972)</td>
<td>4</td>
</tr>
<tr>
<td>Van Ness-Byer-Gibbs (1973)*</td>
<td>5</td>
</tr>
<tr>
<td>Fredenslund-Gmehling-Rasmussen (1977)</td>
<td>6</td>
</tr>
<tr>
<td>Dohnal-Fenclova (1985)*</td>
<td>7</td>
</tr>
<tr>
<td>Kojima-Moon-Ochi (1990)</td>
<td>8</td>
</tr>
</tbody>
</table>

*Tests which include a statistical procedure

The area test was established by Redlich and Kister. It is based on the integral form of the Gibbs-Duhem equation:
Under isothermal conditions and at low pressures, the Gibbs-Duhem equation reduces to the form

$$\int_0^1 \sum_{i=1}^c (x_i \, d \ln \gamma_i) = 0$$

It follows from this equation that if the experimental data satisfy the Gibbs-Duhem equation, the total area under the curve $\ln(\gamma_1/\gamma_2)$ over the entire composition range should vanish. VLE measurements are always liable to smaller or larger errors, depending on the instrumentation used and on the accuracy of the experimental manipulation, so that the area defect represents a measure of data inconsistency. For non-electrolyte systems, the composition dependence of $\ln(\gamma_1/\gamma_2)$ can be approximated by the Redlich-Kister equation. The same authors developed a procedure for testing the thermodynamic consistency of ternary systems. Herington extended the procedure of Redlich and Kister by introducing the concept of the fractional area defect (the area defect divided by the total area), and in this way tested the experimental data in two manners. Samuels, Ulrichson and Stevenson introduced the concept of the local area defect into their testing procedure. The expected standard deviation in the local area defect is given in terms of the standard deviations in the measured quantities $x, y, P$, and $T$. Once the local area defects and their predicted standard deviations are known, the total area defect and its predicted standard deviation are obtained. This method was developed for determining the amount of nonsatisfaction of the overall test for VLE data that is to be expected on the basis of random experimental uncertainties. Data which satisfy the overall test within these limits, as well as the local area test, are said to be consistent within the bounds established by their experimental uncertainties, while data which do not, are said to show significant systematic error and hence are termed inconsistent. Since area tests do not enable the inconsistency of individual points to be ascertained, some additional approaches were established which are based on the differential Gibbs-Duhem equation, representing procedures of the points test. Liebermann and Fried derived two consistency tests for excess molal properties $z^E$ of binary mixtures. They employed the functions $z_1^E/x_2^2$ and $z_2^E/x_1^2$ to check the reliability of thermodynamic data, because they are more sensitive to errors than the functions $z_1^E$ and $z_2^E$. Another approach was given by van Ness, Byer and Gibbs; their procedure is based on reduced data sets, i.e., sets which are made up of three instead of four measurable variables, necessary to completely define the equilibrium state. Since the experimental uncertainty is likely to be the greatest for the vapour composition, the authors suggested a procedure for data reduction that is based on just $P - x$ isothermal binary data sets. Values for $y$, calculated by the iterative procedure, can finally be compared to the measured values as a check of the thermodynamic consistency of the VLE data. These authors also considered the effect of random error in the measured variables on the error in the calculated thermodynamic functions. Estimates of the standard deviations in the functions...
$g^E/(RT)$ and $\ln(\gamma_1/\gamma_2)$, when these quantities are calculated for a finite data set, are given by equations derived in the manner of Ulrichson and Stevenson.\textsuperscript{10} Fredenslund, Gmehling and Rasmussen\textsuperscript{6} developed their procedure on the same basis, but instead of cubic parabola, utilized by the authors,\textsuperscript{5} they resorted to represent the composition dependence of $g^E/(RT)$ by Legendre polynomials. In order to determine the type of systematic error, Dohnal and Fenclova\textsuperscript{7} used a complex statistical procedure for testing the consistency of VLE data. Kojima, Moon and Ochi\textsuperscript{8} developed a new procedure, the infinite dilution test, completing in this way the methodology of checking the thermodynamic consistency of VLE data, consisting now of the area test, the point test and the infinite dilution test.

A SHORT PRESENTATION OF THE KMO CONSISTENCY TEST

Bearing in mind the purpose of the present work, outline in the introduction: examination of the effect of the analytical form of the solution of the Gibbs-Duhem equation under isothermal conditions, the thermodynamic consistency test of Kojima, Moon and Ochi\textsuperscript{8} was chosen since, in addition to the area and the point test, it enables the VLE data to be tested in the very sensitive infinite dilution region. In this procedure, the thermodynamic functions $g^E/(RT)$ and $\ln(\gamma_1/\gamma_2)$ were approximated by the Redlich-Kister expansion with two to four parameters, depending on the character of the investigated systems.

Kojima, Moon and Ochi\textsuperscript{8} proposed the following relationships:

For the area test:

$$A = 100|A^*|$$

$$A^* = \int_0^1 \ln \left( \frac{\gamma_1}{\gamma_2} \right) dx_1 + \int_0^1 \varepsilon dx_1$$

where $\varepsilon$ should be used for isothermal data

$$\varepsilon = \left( \frac{v^M \rho}{RT} \right) \left( \frac{dP}{dx_1} \right)$$

For the point test:

$$\delta = 100 \sum_{j=1}^{n} |\delta_j| / n$$

where $n$ stands for the number of data points and

$$\delta^* = \frac{d(g^E/RT)}{dx_1} - \ln(\gamma_1/\gamma_2) - \varepsilon$$

For the infinite dilution test:
\[ I_1 = 100|I_1^*| \]  
\[ I_2 = 100|I_2^*| \]  
\[ I_1^* = \left[ \frac{g^E / RT}{x_1 x_2} \right]_{x_i=0} - \ln(\gamma_1 / \gamma_2)_{x_i=0} / \ln(\gamma_1 / \gamma_2)_{x_i=0} \]  
\[ I_2^* = \left[ \frac{g^E / RT}{x_1 x_2} \right]_{x_i=0} - \ln(\gamma_1 / \gamma_2)_{x_i=0} / \ln(\gamma_1 / \gamma_2)_{x_i=0} \]  

In all of the tests mentioned, the extended Redlich-Kister equations
\[ g^{E/(RT)} = x_1 x_2 [B + C(x_1 - x_2) + D(x_1 - x_2)^2 + E(x_1 - x_2)^3 + F(x_1 - x_2)^4 + ...] \]  
and
\[ \ln(\gamma_1 / \gamma_2) = a + b(x_2 - x_1) + c(6x_1x_2 - 1) + d(x_2 - x_1)(1 - 8x_1x_2) + e(x_2 - x_1)^2(10x_1x_2 - 1) + ... \]
were used. The number of parameters in Eq. (10) were two to four, whereas Eq. (11) is a four parameter expression.

THE SSF EQUATION

When mixtures of complex behaviour are examined, for which the VLE data were determined using precise measuring methods, it can appear justified to use relationships containing a larger number of parameters than those used in the work of Kojima et al.\(^8\) In the present work, the six parameter expressions, also known as the SSF equations, which were proposed by Hogalski and Malanowski,\(^9\) have been employed to fit the experimental VLE data:
\[ \frac{g^E}{RT} = A_1 x_1 x_2 \left( \frac{x_1}{a_1 + a_1 x_2} \right) + A_2 x_1 x_2 \left( \frac{x_1}{a_2 + a_2 x_2} \right) + A_3 x_1 x_2 \left( \frac{x_1}{a_3 + a_3 x_2} \right) \]  
\[ \ln \left( \frac{\gamma_1}{\gamma_2} \right) = B_1 \left( \frac{b_1 x_2 - x_1 b_1}{b_1} \right)^3 + B_2 \left( \frac{b_2 x_2 - x_1 b_2}{b_2} \right)^3 + B_3 \left( \frac{b_3 x_2 - x_1 b_3}{b_3} \right)^3 \]  
where
\[ a_i = (q_{1,i}/q_{2,i})^{0.5} \quad q_{2,i} = 1 - q_{1,i} \]  
\[ b_i = (r_{1,i}/r_{2,i})^{0.5} \quad r_{2,i} = 1 - r_{1,i} \]
RESULTS AND DISCUSSION

Two ways for testing the thermodynamic consistency of isothermal binary VLE data were applied to a large number of data sets. One of them was presented in the work of Kojima, Moon and Ochi\(^8\) and the other one was obtained by substituting the working RK Eqs. (10) and (11) by the SSF Eqs. (12) and (13). Absolute values of function \(e\) defined by Eq. (3) were neglected as was previously proposed.\(^8\)

The criteria for the area test, the point test and the infinite dilution test were taken from the work of Kojima \textit{et al.}\(^8\) and are given in Table II. The results of the tests are characterized by the sign “+” (consistent) and “−” (non consistent).

<table>
<thead>
<tr>
<th>Testing procedure</th>
<th>Criterion</th>
<th>Character</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area test</td>
<td>(A &lt; 3)</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>(A \geq 3)</td>
<td>−</td>
</tr>
<tr>
<td>Point test</td>
<td>(δ &lt; 5)</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>(δ \geq 5)</td>
<td>−</td>
</tr>
<tr>
<td>Infinite dilution test</td>
<td>(I_1) and (I_2 &lt; 30)</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>(I_1) and (I_2 \geq 30)</td>
<td>−</td>
</tr>
</tbody>
</table>

The computational procedures performed by the RK and SSF equations were tested using 32 binary data sets of various systems, which include physical and chemical interactions of different degrees of complexity. The following classes of systems were tested: alcohols+water, alcohols+aromatics, ketones+aromatics and ketones+cycloalkanes. Table III presents the selected binary systems, the corresponding working conditions (temperature), the standard deviation and percentage average absolute deviation for the functions \(g_E/(RT)\) and \(\ln(g_1/g_2)\), the results of the consistency testing, as well as the sources of the experimental data.

According to the results of the thermodynamic consistency testing (see Table III), all the examined data sets can be classified into two categories. The first of them is made up of the sets (No. 1–27), for which identical conclusions about the thermodynamic consistency of the VLE data can be drawn, applying the criteria from Table II, irrespectively of which of the calculational procedures were used (those based on the RK or SSF equations). The second category is formed by the sets (No. 28–32) for which differing results of testing are obtained, depending on the chosen way of computation.

A comparison of the corresponding standard deviations \(σ\) and percentage average absolute deviations PAAD for all the systems tested, given in Table III, shows that the approximation of the function \(g_E/(RT)\) is better using the SSF equation than using RK equation. For the set (No. 29) of the system ethanol+water at \(t = 55.0\) °C, these approximations are shown in Fig. 1. It can be seen from this Figure that the experimental \(g_E/(RT)\) values are better approximated by the SSF equation (dotted line) than the RK equation (solid line). Also, it can be noticed from the values of \(σ\) and PAAD given in Table III, that the experimental \(\ln(g_1/g_2)\) values are approximated equally well by both the RK or the SSF equation.
TABLE III. Results of thermodynamic consistency tests of VLE data

<table>
<thead>
<tr>
<th>No.</th>
<th>System</th>
<th>$\delta$ (°C)</th>
<th>$\Delta g^e / (RT)$</th>
<th>$\ln (\gamma_1/\gamma_2)$</th>
<th>$\delta$</th>
<th>$A$</th>
<th>$I_{1,2}$</th>
<th>$\Delta g^e / (RT)$</th>
<th>$\ln (\gamma_1/\gamma_2)$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ethanol-benzene</td>
<td>50.0</td>
<td>0.095</td>
<td>3.251</td>
<td>0.017</td>
<td>2.404</td>
<td>14.40</td>
<td>(-)</td>
<td>5.24</td>
<td>(+)</td>
</tr>
<tr>
<td>2</td>
<td>ethanol-benzene</td>
<td>40.0</td>
<td>0.090</td>
<td>3.607</td>
<td>0.071</td>
<td>9.060</td>
<td>11.01</td>
<td>(+)</td>
<td>0.94</td>
<td>(+)</td>
</tr>
<tr>
<td>3</td>
<td>ethanol-benzene</td>
<td>50.0</td>
<td>0.080</td>
<td>3.330</td>
<td>0.038</td>
<td>6.005</td>
<td>10.70</td>
<td>(-)</td>
<td>0.23</td>
<td>(+)</td>
</tr>
<tr>
<td>4</td>
<td>ethanol-benzene</td>
<td>60.0</td>
<td>0.089</td>
<td>3.146</td>
<td>0.024</td>
<td>4.54</td>
<td>47.98</td>
<td>(-)</td>
<td>4.96</td>
<td>(+)</td>
</tr>
<tr>
<td>5</td>
<td>ethanol-toluene</td>
<td>65.0</td>
<td>0.354</td>
<td>12.83</td>
<td>0.017</td>
<td>3.197</td>
<td>44.32</td>
<td>(-)</td>
<td>5.74</td>
<td>(+)</td>
</tr>
<tr>
<td>6</td>
<td>ethanol-toluene</td>
<td>70.0</td>
<td>0.353</td>
<td>12.84</td>
<td>0.010</td>
<td>1.568</td>
<td>42.51</td>
<td>(-)</td>
<td>6.57</td>
<td>(+)</td>
</tr>
<tr>
<td>7</td>
<td>ethanol-toluene</td>
<td>75.0</td>
<td>0.350</td>
<td>13.31</td>
<td>0.007</td>
<td>1.91</td>
<td>39.65</td>
<td>(-)</td>
<td>7.68</td>
<td>(+)</td>
</tr>
<tr>
<td>8</td>
<td>ethanol-toluene</td>
<td>80.0</td>
<td>0.346</td>
<td>13.75</td>
<td>0.018</td>
<td>2.977</td>
<td>36.48</td>
<td>(-)</td>
<td>9.26</td>
<td>(+)</td>
</tr>
<tr>
<td>9</td>
<td>ethanol-toluene</td>
<td>85.0</td>
<td>0.334</td>
<td>13.63</td>
<td>0.024</td>
<td>4.095</td>
<td>35.65</td>
<td>(-)</td>
<td>10.49</td>
<td>(-)</td>
</tr>
<tr>
<td>10</td>
<td>ethanol-water</td>
<td>40.0</td>
<td>0.552</td>
<td>55.15</td>
<td>0.021</td>
<td>4.035</td>
<td>6.44</td>
<td>(-)</td>
<td>2.04</td>
<td>(+)</td>
</tr>
<tr>
<td>11</td>
<td>ethanol-water</td>
<td>50.0</td>
<td>0.233</td>
<td>8.124</td>
<td>0.044</td>
<td>5.314</td>
<td>13.63</td>
<td>(-)</td>
<td>5.34</td>
<td>(+)</td>
</tr>
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<td>12</td>
<td>ethanol-water</td>
<td>54.0</td>
<td>0.216</td>
<td>9.521</td>
<td>0.024</td>
<td>9.582</td>
<td>36.76</td>
<td>(-)</td>
<td>7.95</td>
<td>(+)</td>
</tr>
<tr>
<td>13</td>
<td>ethanol-water</td>
<td>39.0</td>
<td>0.249</td>
<td>72.33</td>
<td>0.024</td>
<td>9.572</td>
<td>36.76</td>
<td>(-)</td>
<td>7.95</td>
<td>(+)</td>
</tr>
<tr>
<td>14</td>
<td>ethanol-water</td>
<td>50.0</td>
<td>0.220</td>
<td>2.253</td>
<td>0.014</td>
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<td>23.98</td>
<td>(-)</td>
<td>2.63</td>
<td>(+)</td>
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<tr>
<td>15</td>
<td>ethanol-water</td>
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<td>0.492</td>
<td>0.010</td>
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<td>(+)</td>
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<td>4.975</td>
<td>0.031</td>
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<td>(+)</td>
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<td>19</td>
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<td>0.118</td>
<td>4.085</td>
<td>0.076</td>
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<td>(+)</td>
<td>2.52</td>
<td>(+)</td>
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<tr>
<td>20</td>
<td>ethanol-water</td>
<td>90.0</td>
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<td>47.43</td>
<td>0.084</td>
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<td>82.72</td>
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<td>27.64</td>
<td>(+)</td>
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<tr>
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<td>0.210</td>
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<td>(+)</td>
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<td>(+)</td>
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</tr>
<tr>
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<td>4.717</td>
<td>0.034</td>
<td>13.04</td>
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<td>(+)</td>
<td>0.75</td>
<td>(+)</td>
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<tr>
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<td>0.023</td>
<td>5.999</td>
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<td>(+)</td>
<td>12.11</td>
<td>(+)</td>
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<td>1.467</td>
<td>5.45</td>
<td>(+)</td>
<td>2.64</td>
<td>(+)</td>
</tr>
<tr>
<td>27</td>
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<td>25.0</td>
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<td>0.011</td>
<td>5.651</td>
<td>0.82</td>
<td>(+)</td>
<td>0.58</td>
<td>(+)</td>
</tr>
<tr>
<td>28</td>
<td>acetone-benzene</td>
<td>60.0</td>
<td>0.050</td>
<td>4.717</td>
<td>0.034</td>
<td>13.04</td>
<td>6.44</td>
<td>(+)</td>
<td>0.75</td>
<td>(+)</td>
</tr>
<tr>
<td>29</td>
<td>acetone-benzene</td>
<td>43.0</td>
<td>0.119</td>
<td>2.996</td>
<td>0.052</td>
<td>19.28</td>
<td>20.91</td>
<td>(-)</td>
<td>5.27</td>
<td>(+)</td>
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<tr>
<td>30</td>
<td>acetone-benzene</td>
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<td>0.020</td>
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<td>2.510</td>
<td>5.28</td>
<td>(+)</td>
<td>2.10</td>
<td>(+)</td>
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<td>31</td>
<td>acetone-benzene</td>
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<td>1.225</td>
<td>0.044</td>
<td>6.815</td>
<td>4.72</td>
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<td>(+)</td>
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<tr>
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<td>methanol-toluene</td>
<td>35.0</td>
<td>0.052</td>
<td>1.364</td>
<td>0.035</td>
<td>6.769</td>
<td>6.08</td>
<td>(-)</td>
<td>0.92</td>
<td>(+)</td>
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<tr>
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<td>methanol-toluene</td>
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<td>0.148</td>
<td>20.49</td>
<td>2.93</td>
<td>(+)</td>
<td>0.28</td>
<td>(+)</td>
</tr>
</tbody>
</table>

$\delta$ = the point test; $A$ = the area test; $I_{1,2}$ = the infinite dilution test; $\sigma = \left( \frac{\sum (f_{exp} - f_{cal})^2}{n - m} \right)^{0.5}$; PAAD = 100 $\left| \frac{f_{exp} - f_{cal}}{f_{exp}} \right|$ where $f_{exp} = \frac{\gamma_1}{\gamma_2}$ or $\ln(\gamma_1/\gamma_2)$, $n$ is the number of experimental points and $m$ is the number of parameters in the fitting equations.
For the mentioned set, these approximations are given in Fig. 2 from which it can be seen that the curves corresponding to the RK and the SSF equation are coincident.

As can be seen from Eq. (5), the point test requires the derivatives of the function \( \frac{g^E}{RT} \) and the function \( \ln\left(\frac{g_1}{g_2}\right) \). Differences in the quality of fitting the \( \frac{g^E}{RT} \) data by the SSF equation, compared to the fitting by the RK equation, proved certain conclusions on the consistency of the data, drawn by applying the point test. It can be noticed that for the first category of sets (No. 1–27), regardless of the differing numerical values of \( \delta \), the sign of the point test, specified in Table II, remained unchanged. Hence, it might be expected that the use of fitting functions having a larger number of parameters would not influence the final results of the testing of the thermodynamic consistency for data sets acquired with insufficient precision of the VLE measurements.

According to Table III, the conclusions about the thermodynamic consistency were changed for the second category of data sets (No. 28–32). For the data set (No. 28) of the 1-propanol-water system, a better fit of the \( \ln(\gamma_1/\gamma_2) \) data was obtained using the SSF equation than with the RK equation, and the sign of the area test was changed. For the sets of this category (No. 29–31), better approximations of both the \( g^E/(RT) \) and \( \ln(\gamma_1/\gamma_2) \) data were obtained using the SSF equation and changes in the numerical values of the point test (\( \delta \)) resulted; in other words, the final conclusions about the consistency were changed for the data sets of the corresponding systems. An attempt was
Fig. 3. \( \frac{dg^{E}/RT}{dx} \) and \( \ln(\gamma_1/\gamma_2) \) versus \( x_1 \) for the system ethanol(1)–water(2) at \( t = 55.0^\circ \text{C} \). ■ - experimental points.\(^{14}\) Lines indicate the four parameter RK equation.

Fig. 4. \( \frac{dg^{E}/RT}{dx} \) and \( \ln(\gamma_1/\gamma_2) \) versus \( x_1 \) for the system ethanol(1)–water(2) at \( t = 55.0^\circ \text{C} \). ■ - experimental points.\(^{14}\) Lines indicate the six parameter SSF equation.

Fig. 5. \( (g^{E}/RT)/x_1x_2 \), \( \ln \gamma_1 \), and \( \ln \gamma_2 \) versus \( x_1 \) for the system ethanol(1)–water(2) at \( t = 55.0^\circ \text{C} \). ■, ◆, ○ - experimental points.\(^{14}\) Lines indicate the four parameter RK equation.

Fig. 6. \( (g^{E}/RT)/x_1x_2 \), \( \ln \gamma_1 \), and \( \ln \gamma_2 \) versus \( x_1 \) for the system ethanol(1)–water(2) at \( t = 55.0^\circ \text{C} \). ■, ◆, ○ - experimental points.\(^{14}\) Lines indicate the six parameter SSF equation.
made to fit the above mentioned thermodynamic functions for the sets (No.28–31) using a six parameter RK equation, however, no changes in the conclusions on the consistency were obtained. Also, it can be noticed that in addition to the number of parameters present in the fitting function, its form should also be taken into account.

The terms $d\left(\frac{g^E}{RT}\right)/dx$ and $\ln\left(\frac{g_1}{g_2}\right)$, which constitute the point test, along with their approximation by the RK and the SSF equations are shown in Figs. 3 and 4, respectively, for the system ethanol–water (No. 29). It can be seen from these Figures that a better agreement between the curves was achieved when the SSF equation was employed.

The results obtained by applying the KMO infinite dilution test, which was briefly described above, are given in Table III. It can be noticed that these results are coincident regardless of whether they were calculated by incorporating the RK or SSF equation. Figs. 5. and 6. show the corresponding experimental values of the data set (No. 29) for the thermodynamic functions $\left(\frac{g^E}{RT}\right)(x_1,x_2)$ and $\ln\gamma_1$, which form the infinite dilution test, along with their approximation by the RK and SSF equations. These Figures also illustrate the previously outlined observation.

The data set (No. 32) of Table III should be considered separately, since the standard deviation $\sigma$ for $\ln(\gamma_1/\gamma_2)$ fitted by means of the RK equation is somewhat lower than when the SSF equation was used. On the contrary, the percentage average absolute deviation PAAD is considerably lower when the SSF equation was employed. The use of the six parameter RK equation gave no improvement in $\sigma$ (0.157), but the PAAD results (12.21) approached very closely those obtained from the SSF equation.
Figs. 7 and 8 show the quality of the fits for \( g^E/(RT) \) and \( \ln(\gamma_1/\gamma_2) \) of the data set (No. 32) obtained by both the RK and the SSF equations.

The results of this work indicate that the use of fitting equations with a larger number of parameter (here the SSF equation) is justified only if the isothermal experimental VLE data sets were determined with a considerable accuracy. Testing of the consistency of VLE data in this way, would lead to more realistic assessments, particularly for data sets lying in the vicinity of the border of consistency. When such data are tested by procedures unable to produce reliable fits, the final conclusion of the consistency testing may not be quite reliable.

CONCLUSIONS

The thermodynamic consistency test of VLE data proposed by Kojima-Moon-Ochi (KMO) was used in the present work, in view of its applicability to the data sets having different degrees of precision. For this purpose, in addition to the four-parameter RK equation, that was incorporated in the original KMO testing procedure, the six-parameter SSF equation was used. Both of these equations were applied to 32 isothermal binary data sets, with interactions between the molecules of different degrees of complexity (alcohols+water, alcohols+aromates, ketones+aromates and ketones+cycloalkanes).

The results of the present work show that for 27 data sets, the same conclusions about the thermodynamic consistency of their VLE data were reached by applying any of the equations mentioned above. On the contrary, for the remaining 5 data sets, mutually different results on their consistency were obtained, depending on the form of the fitting equation incorporated into the testing procedure.

Analysis of the above results indicate that these observations are a consequence of the reliability of fitting the thermodynamic functions, which constitute the consistency testing procedure, by means of equations with an adequate number of parameters (here the SSF equation).

In this respect, it is necessary to bring into accord the number of parameters as well as the form of the fitting equation, used in the testing procedure, with the degree of the reliability of the VLE measurements. Namely, for high-quality measurements, the use of an adequate fitting equation with a larger number of parameters can be required. Testing less reliable data in the same way would, in most cases, not be justified.

LIST OF SYMBOLS

- \( a, b, c, d \) – parameters of Eq. (11)
- \( a_1, a_2, a_3 \) – parameters of Eq. (12)
- \( A_1, A_2, A_3 \) – parameters of Eq. (12)
- \( B, C, D \) – parameters of Eq. (10)
- \( b_1, b_2, b_3 \) – parameters of Eq. (13)
- \( B_1, B_2, B_3 \) – parameters of Eq. (13)
- \( g^E \) – molar excess Gibbs energy
- \( h^M \) – enthalpy of mixing
- \( P \) – pressure
PAAD – percentage average absolute deviation
R – gas constant
T – absolute temperature
t – temperature
υ^M – volume of mixing
x_i – mole fraction of component i in the liquid
y_i – mole fraction of component i in the vapour
\gamma – activity coefficient of component i
σ – standard deviation

И В О Д

КОРИШЋЕЊЕ SSF ЈЕДНАЧИНЕ У КОЈИМА-МООН-ОСЋИТЕ ТЕРМОДИНАМИЧКОМ ТЕСТУ КОНЗИСТЕНЦИЈЕ ИЗОТЕРМСКЕ РАВНОТЕЖЕ ПАРА–ТЁННОСТ

ЈЕЛЕНА М. ЈЕЛИЋ, АЛЕКСАНДАР Ж. ТАСИЋ, БОЈАН Д. БОРЂЕВИЋ
и СЛОБОДАН П. ШЕРЂАНОВИЋ
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Којима-Мун-Осчи термодинамички тест конзистенције равнотеже пара–тённост је примењен на 32 скупа изотермских података бинарних система различите сложености користећи две једначине за апроксимацију: Ридлих-Кистер и Суме Симетричних Функција. Показано је да побољшање квалитета апроксимације експерименталних података може променити закључке у односу на њихов термодинамички тест конзистенције код оних скупова података равнотеже пара–тённост, за које се процени да су близу граници конзистентности.

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