A Study of Liquid Systems with Miscibility Gaps: Water-Ethylene Glycol Monobutyl Ether Mixtures

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In this paper we show that in binary liquid systems with miscibility gaps, the forces related to the formation of spatially ordered regions near the critical solution temperature, \( T_c \), prevalently involve interactions of type AA and BB rather than interactions of type AB, A and B being the components of the mixture. For this purpose we have measured the viscosity and proton spin-lattice relaxation as a function of temperature and concentration in water-ethylene glycol monobutyl ether systems. With a method previously described, which allows to determine the contributions to the relaxation that arise from the coupling of protons belonging to molecules of different types, the mixed translational contributions near \( T_c \) due to interactions of type AB and the mixed translational contributions one would obtain if the same region were not critical, have been calculated. The knowledge of these quantities allowed us to evaluate the viscosity per cent deviation due to the critical phenomenon, considering this to be essentially related to interactions of type AB. Comparison with the per cent deviation of the measured viscosity shows that the two sets of values are quite different. The difference must be due to interactions of type AA and BB.

1. Introduction

In binary liquid systems with miscibility gaps the anomalous behaviour of certain physical parameters near the critical solution temperature, \( T_c \), has not yet been clearly interpreted. Light-scattering measurements indicate that a formation of spatially ordered regions whose dimensions increase as the temperature approaches \( T_c \), precedes the separation, at \( T_c \), of a binary mixture into two phases. It is a question of interest whether these regions are prevalently formed by molecular arrangements of type AA and BB rather than arrangements involving AB neighbours, A and B being the components of the mixture.

The present work concerns proton spin-lattice relaxation and viscosity measurements in water-ethylene glycol monobutyl ether systems. The two components are completely miscible below 47.3°C at a glycol mole fraction, \( f_B \), equal to 0.050. Higher critical solution temperatures correspond to different concentration values; they were determined for the range 0.043 \( \leq f_B \leq 0.074 \) from the position of the discontinuity point on the viscosity-temperature curve. The two components are completely miscible at all temperatures for \( f_B < 0.02 \) and \( f_B > 0.2 \). The systems tested by us are certainly not free of AB interaction; the existence of molecular AB association is proved by the presence of a maximum in the curves presenting the viscosity and the reciprocal of the proton spin-lattice relaxation time, \( T_1 \), as a function of concentration. Concentration at these maxima is far from the concentration range corresponding to the critical region so that the two effects do not interfere.

2. Molecular Interactions and Spin-Lattice Relaxation

Useful information about the kind and strength of molecular interactions in liquid binary mixtures may be obtained from proton spin-lattice relaxation measurements. \( T_1 \) determinations allow us to evaluate in many cases the translational contributions to the relaxation that arise from the coupling of protons belonging to different molecular species. This is described in detail elsewhere where it is shown that the reciprocal of the proton spin-lattice relaxation time, \( T_1 \), observed in an ideal mixture of two components both containing protons, and resulting from all the relaxation mechanisms present in solution, may be expressed as

\[
\frac{1}{T_{1,a}} = f_A \left( \frac{1}{T_{1,A}} + f_B \left( \frac{1}{T_{1,B}} \right) \right) + f_B \left( \frac{1}{T_{1,B}} \right) \left( \frac{1}{T_{1,B}} \right) \left( \frac{1}{T_{1,B}} \right) - \left( \frac{1}{T_{1,B}} \right) \left( \frac{1}{T_{1,B}} \right) \left( \frac{1}{T_{1,B}} \right) \right)
\]

where \( f_A \) and \( f_B \) being the mole fractions of the components in the mixture, \( T_{1,A} \) and \( T_{1,B} \) the relaxa-
tion times of the pure liquids, \((1/T_1)_{\text{trans}, A}\) and \((1/T_1)_{\text{trans}, B}\) the “mixed” translational contributions, that is the contributions to the relaxation of the mixture that arise from the coupling of spins attached to molecules of different type. \(T_{1, A}\) and \(T_{1, B}\) may be considered to be given by

\[
1/T_{1, A} = (1/T_1)_{\text{rot}, A} + (1/T_1)_{\text{trans}, A}
\]
\[
1/T_{1, B} = (1/T_1)_{\text{rot}, B} + (1/T_1)_{\text{trans}, B}
\]

where \((1/T_1)_{\text{rot}, A}\), \((1/T_1)_{\text{rot}, B}\) and \((1/T_1)_{\text{trans}, A}\), \((1/T_1)_{\text{trans}, B}\) respectively, are the rotational and translational contributions to the relaxation of the pure liquids.

Equation (1) was deduced starting from results obtained by Mitchell and Einsner in several liquid mixtures \(^3\); it can be applied to systems with a molecular AB interaction that is not very strong, in the assumption that this interaction affects the rotational and translational contributions of A and B much less than the mixed translational contributions. Therefore, in Equation (1), \((1/T_1)_{\text{rot}, A}\), \((1/T_1)_{\text{rot}, B}\) and \((1/T_1)_{\text{trans}, A}\), \((1/T_1)_{\text{trans}, B}\) for these systems are still assumed to be equal to the rotational and translational contributions of the pure components. The application to systems such as benzene-acetic acid mixtures gives quite satisfactory results in spite of the approximations leading to Equation (1) \(^2\).

According to Moniz, Steele and Dixon \(^5\), we assume that the spin-lattice relaxation model of Bloembergen, Purcell and Pound \(^6\) is adequate in giving the translational contributions of the pure components, which, therefore, may be calculated by the equation

\[
(1/T_1)_{\text{trans}} = \frac{3}{2} \pi^2 \gamma^4 \hbar^2 (\eta /k T),
\]

\((\eta /k T)\) being, respectively, the density of protons and the viscosity of the pure liquid. The more accurate treatment of translational diffusion made by Torrey \(^7\), \(^8\) leads to evaluating translational contributions that are substantially the same. The result for a system of protons in the case of diffusion where the mean squared flight distance, \(\langle r^2 \rangle\), is small as compared with the molecular diameter, \(a\), and \(c \tau \ll 1\), is

\[
(1/T_1)_{\text{trans}} = \frac{4}{5} \pi^3 \gamma^4 \hbar^2 (\eta /k T)
\]

where \(D = k T / 6 \pi \eta a \) is the diffusion coefficient. If the elementary step is large as compared with \(a\), one must multiply the above result by \(5 \langle r^2 \rangle / 12 a^2\).

Since under actual circumstances one has both processes occurring in a liquid, the correct expression will be somewhere in between. This leads to the result

\[
(1/T_1)_{\text{trans}} = \frac{3}{5} \pi^2 \gamma^4 \hbar^2 \frac{Q \eta}{k T} \left(1 + \frac{5}{12} \left(\frac{r^2}{a^2}\right)\right),
\]

In order to evaluate the \(\langle r^2 \rangle / a^2\) ratio, one must take some assumptions regarding the microscopic diffusion process. We may refer to the model of Cohen and Turnbull \(^9\) based on the concept that statistical redistribution of the “free volume” occasionally opens up voids large enough for diffusive displacement. In this theory, which is in agreement with experiment \(^10\), \(^11\) and consistent with the Stokes-Einstein model, the mean jump distance is near the molecular diameter. Consequently, we may assume that \(\langle r^2 \rangle / a^2\) is not very different from unity and the numerical factor

\[
\frac{6}{5} \left(1 + \frac{5}{12} \left(\frac{\langle r^2 \rangle}{a^2}\right)\right) \approx 17/10.
\]

This value is close to \(3/2\). On the other hand, Eq. (2) has successfully been used by Moniz, Steele and Dixon \(^5\).

When the AB interaction is rather strong, the application of Eq. (1) is restricted to regions near \(f_B = 0\) and \(f_B = 1\), in the assumption that there the structures of the components are not yet deeply modified. In the remaining concentration range, the \(T_{1, A}\) determinations in these cases can give only qualitative information. Since the variation law expressed by Eq. (1) is nearly linear for ideal systems \(^2\), we can say that the greater the deviation of the \(1/T_{1, A}\) experimental curve from the straight line, the greater is the strength of the molecular interaction; moreover, an experimental curve that rises above the straight line joining \(1/T_{1, A}\) to \(1/T_{1, B}\) indicates essentially a decrease in the molecular mobility, while a curve that sags below corresponds to the opposite case. The first case is certainly related to molecular association processes.

The critical region for water-ethylene glycol monobutyl ether systems is near \(f_B = 0\). The application of Eq. (1) to this region requires a suitable separation of the effects due to possible overlapping of different molecular interactions. Actually, Eq. (1) allows us to calculate in the critical region the mixed translational contributions that one would expect if substantial interactions of type AA and BB did not occur. Since we want to estimate the molecular in-
Interactions in the critical region that are essentially of type AB, the adoption of the usual diffusive models appears to be quite correct for the calculation of the translational contributions of the pure components in this region. Moreover, Anderson and Gerritz have shown that the spatially ordered regions related to the critical phenomenon are formed by uncomplexed molecules whose self-diffusion coefficients and rotational correlation times are unmistakably those of individual molecules.

3. Experimental Procedures and Results

The relaxation time \( T_{1.a} \) was measured, as a function of concentration, in the water-ethylene glycol monobutyl ether systems with a method described in detail elsewhere. The measurements, at 13.0 MHz and 30.6 °C, 36.2 °C, 38.9 °C, 43.4 °C, 45.8, 47.8 °C, were condensed in the critical region. A stream of carbon tetrachloride, heated in a thermostatic bath, was used in order to regulate the temperature of the cell containing the sample; the temperature was controlled up to 0.05 °C. The accuracy in the \( T_{1.a} \) measurements was estimated to be about 5%. The return of the proton signal to the equilibrium value in the relaxation process was always found to be exponential within the limits of resolution of the apparatus. The samples were deoxygenated and the actual concentrations of the tested mixtures determined with methods previously described.

Viscosity determinations were performed, as a function of temperature, for mixtures with glycol mole fraction varying from 0.043 to 0.074; each set of measurements was carried up to temperatures some degrees above the critical temperature, in order to determine the discontinuity point corresponding to \( T_c \). The viscosity was also measured, as a function of concentration, at 36 °C. The viscosity values were obtained with a rotative Couette viscosimeter; the bath temperature was controlled up to 0.02 °C. The accuracy in the measurements was estimated to be better than 0.5%. The physical parameters of the pure components used for the viscosity determinations were the same as those of the components used for the \( T_{1.a} \) measurements.

The \( 1/T_{1.a} \) values obtained at various temperatures for the water-ethylene glycol monobutyl ether mixtures are plotted in Fig. 1 versus glycol mole fraction. Figure 2 shows the experimental viscosity as a function of concentration, at 36 °C. The diagrams of Fig. 1 and 2 show a maximum at about the same concentration \( (f_b \approx 0.45) \); the strength of the interaction between the components is greatest in this region. Notice that the maximum becomes less marked as the temperature increases; this is what one would expect since the molecular interactions of type AB are certainly hindered by a temperature increase.

Another maximum occurs in the \( 1/T_{1.a} \)-curve at 47.8 °C in the critical region and renders evident the existence of association processes in this region.

The anomalous behaviour of the viscosity \( \eta \) as the temperature approaches \( T_c \), is emphasized by the diagrams of Fig. 3, from which it results that...
by the equation

\[ \eta = B T^{\gamma} \exp\left(\frac{K}{(T - T_0)}\right) \]  

(4)

deduced from the COHEN-TURNBULL\(^\text{9}\) theory, \(T_0\) being the glass-transition temperature and \(B\) and \(K\) other quantities depending on the liquid considered. Nevertheless, if the thermal range explored is rather limited, as in the case of Fig. 3, in a region sufficiently far from \(T_c\) the non-Arrhenius behaviour is not evident.

Each curve of Fig. 3 was drawn up to the corresponding critical temperature. The values of \(T_c\) obtained for the tested mixtures with the method indicated in Section 1 are reported in Table 1 together with the corresponding values of the maximum viscosity per cent deviation. It results that the anomalous behaviour of \(\eta\) near \(T_c\) becomes more marked as the value of \(f_B\) approaches 0.050.

Table 1. Critical solution temperature, \(T_c\), and maximum viscosity per cent deviation \((\Delta \eta/\eta)_{\text{max}}\) , for different values of the glycol mole fraction, \(f_B\).

<table>
<thead>
<tr>
<th>(f_B)</th>
<th>(T_c) (°C)</th>
<th>((\Delta \eta/\eta)_{\text{max}}) max</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.043</td>
<td>47.9</td>
<td>6.7</td>
</tr>
<tr>
<td>0.045</td>
<td>47.8</td>
<td>7.1</td>
</tr>
<tr>
<td>0.050</td>
<td>47.3</td>
<td>13.4</td>
</tr>
<tr>
<td>0.055</td>
<td>47.4</td>
<td>12.9</td>
</tr>
<tr>
<td>0.063</td>
<td>47.3</td>
<td>12.4</td>
</tr>
<tr>
<td>0.069</td>
<td>48.1</td>
<td>8.3</td>
</tr>
<tr>
<td>0.074</td>
<td>48.2</td>
<td>6.4</td>
</tr>
</tbody>
</table>

4. Discussion

The hypothesis of the existence of micro-domains whose dimensions increase as the temperature approaches \(T_c\) is consistent with light-scattering measurements\(^1\) and allows us to explain the anomalous behaviour of the viscosity near \(T_c\). According to the modified lattice theory of FLORY\(^14\), a length-to-diameter ratio, which for an assembly of domains is greater than a given value, is expected to cause a spontaneously ordered anisotropic phase. The ratio required for the formation of the anisotropic phase increases with dilution of the domains. Because of the dimensions that the domains can attain near \(T_c\)\(^1\), it is quite probable that a value of the length-to-diameter ratio is reached that is favourable for spontaneous ordering of the domains; this is consistent with the non-Newtonian behaviour of the viscosity, which can generally be observed at low shear rates.
Our question is whether the forces related to the formation of the domains in the critical region involve prevalently interactions of type AA and BB rather than AB. The viscosity and proton spin-lattice relaxation measurements show that the strength of the interaction between glycol and water is greatest at a concentration value far from that of the critical region. This leads us to believe that interactions of type AA and BB appear in the critical region overlapping the interactions of type AB already present in solution. Actually, the behaviour of \( \eta \) and \( 1/T_{1,a} \) near \( T_c \) cannot be explained by the existence in the critical region of interactions essentially of type AB.

Let us denote by A and B, respectively, the quantities related to water and glycol. The knowledge of \( (1/T_1)^{\text{trans,}A} \) and \( (1/T_1)^{\text{trans,}B} \), which can be evaluated with the stated criteria, allows us, first of all, to calculate by means of Eq. (1) the mixed translational contributions near \( f_B = 1 \). Since the mixed translational contributions cannot be separated, by setting \( (1/T_1)^{\text{trans,}AB} = (1/T_1)^{\text{trans,}BA} \) we obtain the results shown in Table 2. As can be seen, the values of \( (1/T_1)^{\text{trans,}AB} = (1/T_1)^{\text{trans,}BA} \) in the considered region are about two times smaller than \( (1/T_1)^{\text{trans,B}} \) and about five and a half times smaller than \( (1/T_1)^{\text{trans,A}} \); therefore, the coupling of protons belonging to molecules of different types is remarkably stronger than that related to molecules of the same type. Assuming that the relation

\[
(1/T_1)^{\text{trans,}AB} = (1/T_1)^{\text{trans,}BA} \propto \eta_{AB}
\]  

is valid, \( \eta_{AB} \) being the mutual viscosity, the mixed translational contributions indicate an increase in the mutual viscosity, that is a decrease in the reciprocal mobility, compared with the values of the pure components. These results are in agreement with the existence of an association process between water and glycol, which involves an “interaction of approach” between the components. The increase in the value of \( (1/T_1)^{\text{trans,}AB} = (1/T_1)^{\text{trans,}BA} \), which follows the temperature increase, is related to the increase in the reciprocal mobility that occurs when the temperature rises.

As is well-known, some theoretical relations have been proposed to describe the viscosity of binary liquid mixtures\(^{15-17}\). These relations contain three terms that take into account the contributions arising from AA, BB and AB interactions. We refer specifically to a relation such as

\[
\eta = \eta_A c_A + \eta_B c_B + \eta_{AB} + 2 \eta_A c_A + \eta_B c_B + \eta_{AB} + 2 \eta_A c_A + \eta_B c_B + \eta_{AB} + 2 \eta_A c_A + \eta_B c_B + \eta_{AB} + 2 \eta_A c_A + \eta_B c_B + \eta_{AB}.
\]  

where \( \eta_A \) and \( \eta_B \) are the viscosities of the pure liquids, and \( c_A \), \( c_B \) and \( c_{AB} \) are three suitable coefficients. Equation (6) is formally equal to the Hill relation\(^{17}\) whose coefficients \( c_A \), \( c_B \) and \( c_{AB} \), however, were calculated for polar molecules in solution in a non-polar solvent. Nevertheless, it seems reasonable to assume, for the viscosity of the mixtures tested by us, a relation of type (6) where the coefficients have suitable values different from those calculated by Hill.

Notice the analogy between Eq. (6) and Eq. (1), which can be rewritten:

\[
1/T_{1,a} = f_A (1/T_{1})_{\text{rot},A} + f_B (1/T_{1})_{\text{rot},B} + f_A (1/T_{1})_{\text{trans,A}} + f_B (1/T_{1})_{\text{trans,B}} + f_A f_B (1/T_{1})_{\text{trans,AB}} + (1/T_{1})_{\text{trans,BA}}.
\]  

The use of Eq. (6) implies that outside the critical region the temperature-dependence of each of the quantities \( \eta_A \), \( \eta_B \) and \( \eta_{AB} \) is described by a relation of type (4) or by the equation

\[
\eta = A \exp\{C/T\}
\]  

in a limited temperature range. Because of the relation (5), the temperature-dependence of

\[
(1/T_1)^{\text{trans,AB}} = (1/T_1)^{\text{trans,BA}}
\]  

outside the critical region must also be expressible by a relation of type (7) in a limited temperature range. This conclusion is confirmed by the straight
line a) of Fig. 4, which refers to the values of \((1/T_1)^{\text{trans}, AB} = (1/T_1)^{\text{trans}, BA}\) calculated by Eq. (1) in the region near \(f_B = 1\) and corresponding to the values of \((T_1)^{\text{trans}, AB} = (T_1)^{\text{trans}, BA}\) shown in Table 2. Since the diagrams of Fig. 3 show that the anomalous behaviour of the viscosity starts from about 42 °C, the values of \((1/T_1)^{\text{trans}, AB} = (1/T_1)^{\text{trans}, BA}\) calculated by Eq. (1), in the region near \(f_B = 0\) at 30.6 °C, 36.2 °C and 38.9 °C, refer to absence of the critical phenomenon, so that the corresponding experimental points must also lie on a straight line. Hence, the straight line b) of Fig. 4, to which these points give rise, allows us to determine by extrapolation the mixed translational contributions \((1/T_1)^{\text{trans}, AB} = (1/T_1)^{\text{trans}, BA}\) one would obtain in the region near \(f_B = 0\), at 43.4 °C, 45.8 °C and 47.8 °C, if the critical phenomenon did not occur.

If we denote by \((1/T_1)^{\text{trans}, AB}\) and \((1/T_1)^{\text{trans}, BA}\) the mixed translational contributions which one would obtain if the critical phenomenon were related essentially to interactions of type AB, the quantity

\[
R = \frac{2f_A f_B [(1/T_1)^{\text{trans}, AB} - (1/T_1)^{\text{trans}, BA}]}{f_A^2 (1/T_1)^{\text{trans}, A} + f_B^2 (1/T_1)^{\text{trans}, B}} + 2f_A f_B (1/T_1)^{\text{trans}, AB}
\]

may be assumed to give the viscosity per cent deviation due to the critical phenomenon, considering this to be mainly related to interactions of type AB. Its value may be compared with the per cent deviation \(\Delta\eta/\eta\), of the measured viscosity. The quantity \(R\) appears to be adequate also in view of the fact that the coefficients \(c_A\), \(c_B\) and \(c_{AB}\) may be considered of the same order of magnitude, as in the Hill formula.

The mixed translational contributions

\[
(1/T_1)^{\text{trans}, AB} = (1/T_1)^{\text{trans}, BA}
\]

can be calculated by Equation (1). The calculation requires that the rotational and translational contributions of the components be assumed to be equal to those of the pure liquids. One may agree with this statement since the molecular interaction that arises from the critical phenomenon does not involve the formation of true complexes but implies only spatial correlations between the positions of the molecules able to rotate and translate as individual molecules. In addition, regarding the translational contributions, one must note that the water structure in the region near \(f_B = 0\) is certainly not deeply modified by glycol and that \((1/T_1)^{\text{trans}, B}\)

may be used to determine by extrapolation the mixed translational contributions \((1/T_1)^{\text{trans}, AB} = (1/T_1)^{\text{trans}, BA}\) one would obtain in the region near \(f_B = 0\), at 43.4 °C, 45.8 °C and 47.8 °C, if the critical phenomenon did not occur.

Table 3. Comparison between the values of \(R\) and \(\Delta\eta/\eta\), at various temperatures, at \(f_B = 0.045\) and \(f_B = 0.063\). \(\Delta\eta/\eta\) is the per cent deviation of the measured viscosity, \(R\) the viscosity per cent deviation one would expect were the critical phenomenon essentially related to interactions of type AB.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>(R\times100)</th>
<th>(\Delta\eta/\eta\times100)</th>
<th>Temperature °C</th>
<th>(R\times100)</th>
<th>(\Delta\eta/\eta\times100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>43.4</td>
<td>48</td>
<td>&lt;0.1</td>
<td>43.4</td>
<td>56</td>
<td>0.5</td>
</tr>
<tr>
<td>45.8</td>
<td>70</td>
<td>1.7</td>
<td>45.8</td>
<td>85</td>
<td>3.0</td>
</tr>
<tr>
<td>47.8</td>
<td>187</td>
<td>7.1</td>
<td>47.8</td>
<td>229</td>
<td>12.4</td>
</tr>
</tbody>
</table>

responding values of \(\Delta\eta/\eta\). Taking into account the scatter of the experimental points in the diagrams of Fig. 1 and the error in the \(T_{1,A}\) and \(T_{1,B}\) measurements, the values of \(R\) are given with an accuracy estimated to be better than 24% at 43.4 °C, 38% at 45.8 °C and 15% at 47.8 °C. Comparison between the two sets of values shows that they are of a quite different order of magnitude.
We calculated the change in the values of $R$, which results from the adoption in Eq. (2) of a numerical factor lower than $3/2$. Since in this case higher values of $R$ than those shown in Table 3 are obtained, the discrepancy between the two sets of values becomes even greater. For instance, the values of $R$ obtained by calculating the translational contributions of the pure components with the equation

$$(1/T_1)_{\text{trans}} = \frac{9}{16} \pi^2 \gamma^4 \hbar^2 (q \eta/k T),$$

deduced by Abragam and obtainable from Eq. (3) for $\langle x^2 \rangle \ll a^2$, are higher than the values of $R$ shown in Table 3 by about 15%.

5. Conclusions

The hypothesis of the existence in the critical region of molecular interactions essentially of type AA and BB appears to be consistent with our experimental data. This conclusion is in agreement with the results of Anderson and Gerritz, who have tested aniline-cyclohexane systems. In view of this fact, the separation, beyond $T_c$, of the mixture into A-rich and B-rich liquid phases may be reasonably regarded as a process that follows the formation of two classes of domains, $A_A$ and $A_B$. The former is related to interactions mainly of type AA and is formed by A-rich ordered regions; the latter is related to interactions prevalently of type BB and is formed by B-rich domains. The increase in the dimensions of the domains that takes place when the temperature approaches $T_c$, may be ascribed to an increase in the strength of the interactions of type AA and BB. In this way, the liquid system near $T_c$ is assumed to contain an assembly of domains $A_A$ and $A_B$, which are associated because of presumable interactions $A_A A_A$, $A_B A_B$ and $A_A A_B$. The last correlation should determine the stability of the mixture. The strength of the interaction of type AB decreases as the temperature increases, as shown by the $T_{1,8}$ measurements, while the interactions of type AA and BB become stronger as the temperature approaches $T_c$. At the temperature $T_c$ the state of aggregation of the domain is destroyed; consequently, a separation into A-rich and B-rich phases takes place because of the interactions $A_A A_A$ and $A_B A_B$.

The characteristic behaviour of the viscosity near $T_c$ is analogous to that of a liquid crystal in correspondence with the nematic-isotropic phase transition. This is consistent with the existence near $T_c$ of an ordered anisotropic phase, in agreement with the lattice model of Flory, and leads us to believe that the separation at $T_c$ of the mixture into two phases is accompanied by an order-disorder transition. These statements must be confirmed by suitable experiments.

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