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 $^1$. 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 $47.3^\circ$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 $^2$ where it is shown that the reciprocal of the proton spin-lattice relaxation time, $1/T_{1,a}$, 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

$$
1/T_{1,a} = f_A (1/T_{1,A}) + f_B (1/T_{1,B}) + f_A f_B \left[ (1/T_1)^{trans,AB} + (1/T_1)^{trans,BA} - (1/T_1)^{trans,A} - (1/T_1)^{trans,B} \right],
$$

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, \( (1/T_1)_{\text{trans,AB}} \) and 
\( (1/T_1)_{\text{trans,BA}} \) 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 Eisner in several li­quid mixtures \(^{3, 4}\); 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), 
\( (1/T_1)_{\text{rot, A}} \), \( (1/T_1)_{\text{rot, B}} \), \( (1/T_1)_{\text{trans, A}} \), and 
\( (1/T_1)_{\text{trans, B}} \) 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 
\[
(1/T_1)_{\text{trans}} = \frac{2}{3} \pi^2 \gamma^2 \hbar^2 (\rho \eta/kT), \tag{2}
\]
\( \rho \) and \( \eta \) 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 \( c^2 \tau < 1 \), is 
\[
(1/T_1)_{\text{trans}} = \frac{8}{15} \pi^2 \gamma^2 \hbar^2 (\rho/a D),
\]
where \( D = kT/6 \pi a \eta \) 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 
\[
(1/T_1)_{\text{trans}} = \frac{8}{15} \pi^2 \gamma^2 \hbar^2 \left( \frac{Q \eta}{kT} \right) \left( 1 + \frac{5}{12} \frac{\langle r^2 \rangle}{a^2} \right). \tag{3}
\]
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 
\[
\frac{6}{5} \left( 1 + \frac{5}{12} \frac{\langle r^2 \rangle}{a^2} \right) \text{ near 17/10.}
\]
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
teractions 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 ($f_0 \approx 0.45$); 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.

Fig. 1. Experimental variation of the reciprocal of the observed proton spin-lattice relaxation time, as a function of concentration, for the water-ethylene glycol monobutyl ether systems at various temperatures.
by the equation
\[ \eta = B \frac{T^{1/4}}{T - T_0} \exp\left( K/(T - T_0) \right) \] (4)
deduced from the Cohen-Turnbull\(^9\) 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>
<thead>
<tr>
<th>(f_B)</th>
<th>(T_c) (°C)</th>
<th>((\Delta\eta/\eta)) x 100 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>47.8</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 \(T_c\), 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 \( (T_1)_{\text{trans}, AB} = (T_1)_{\text{trans}, BA} \) we obtain the results shown in Table 2.

As can be seen, the values of \( (T_1)_{\text{trans}, AB} = (T_1)_{\text{trans}, BA} \) in the considered region are about two times smaller than \( (T_1)_{\text{trans}, B} \) and about five and a half times smaller than \( (T_1)_{\text{trans}, A} \); 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

\[
(1/T_1)_{\text{trans}, AB} = (1/T_1)_{\text{trans}, BA} \propto \eta_{AB} \tag{5}
\]

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 \( (T_1)_{\text{trans}, AB} = (T_1)_{\text{trans}, BA} \), 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

\[
\eta = \frac{c_A}{\eta_A} + \frac{c_B}{\eta_B} + 2 \frac{c_{AB}}{\eta_A} \tag{6}
\]

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\(^1\) 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:

\[
1/T_{1,a} = f_A (1/T_1)_{\text{rot}, A} + f_B (1/T_1)_{\text{rot}, B} + \frac{f_A}{f_B} [ (1/T_1)_{\text{trans}, A} + (1/T_1)_{\text{trans}, BA} ] + \frac{f_B}{f_A} [ (1/T_1)_{\text{trans}, B} + (1/T_1)_{\text{trans}, AB} ] \tag{1'}
\]

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

\[
\eta = A \exp \{ C/T \} \tag{7}
\]

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
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

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

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 $(1/T_1)_{trans, B}$ in the region near $f_B = 1$ and corresponding to the values of $(1/T_1)_{trans, AB} = (1/T_1)_{trans, BA}$ shown in Table 2. Since the diagrams of Fig. 3 show that the anomalous behaviour of the viscosity starts from about $42 \degree C$, the values of $(1/T_1)_{trans, AB} = (1/T_1)_{trans, BA}$ calculated by Eq. (1), in the region near $f_B = 0$ at $30.6 \degree C$, $36.2 \degree C$ and $38.9 \degree C$, refer to absence of the critical phenomena, 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 $(1/T_1)_{trans, AB} = (1/T_1)_{trans, BA}$ one would obtain in the region near $f_B = 0$, at $43.4 \degree C$, $45.8 \degree C$ and $47.8 \degree C$, if the critical phenomenon did not occur.

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

\[R = \frac{2f_A/\beta_a[(1/T_1)_{trans', AB} - (1/T_1)_{trans', BA}]}{f_A(1/T_1)_{trans', A} + f_B(1/T_1)_{trans', BA} + 2f_A/\beta_a(1/T_1)_{trans', AB}}\]

has a negligible weight in the same region, since in Eq. (1') it appears only in the term with $f_B^2$.

The most reliable values of $R$ determined, for $f_B = 0.045$ and $f_B = 0.063$, at $43.4 \degree C$, $45.8 \degree C$ and $47.8 \degree C$, are given in Table 3 together with the corresponding values of $\Delta \eta/\eta$.

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>$f_B = 0.045$</th>
<th>$f_B = 0.063$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R \times 100$</td>
<td>$\Delta \eta/\eta \times 100$</td>
</tr>
<tr>
<td>43.4</td>
<td>48</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>45.8</td>
<td>70</td>
<td>1.7</td>
</tr>
<tr>
<td>47.8</td>
<td>187</td>
<td>7.1</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 $43.4 \degree C$, $38\%$ at $45.8 \degree C$ and $15\%$ at $47.8 \degree C$. 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
\[
(1/T_1)_{\text{trans}} = \frac{3}{2} \pi^2 \gamma^4 \bar{h}(Q \eta/kT),
\]
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 $A_B$, 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 $T_{1,a}$ 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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