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Tracer Diffusion of $^{65}$Zn$^{2+}$ in Binary Isobutyric Acid + Water Mixtures Near the Critical Point

Moncef Bouanz

Laboratoire de Diffusion, Département de Physique, Faculté des Sciences de Tunis, 1060 Tunis, Tunisia

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Abstract. — Tracer diffusion coefficients of $^{65}$Zn$^{2+}$ in mixtures of isobutyric acid water and $10^{-4}$ M ZnCl$_2$ have been measured over the composition range $0 < X < 95\%$ in acid; at $\theta_1 = T_1 - T_c = 0.547$ K and $\theta_2 = T_2 - T_c = 7.547$ K using the open-ended capillary method. The critical temperature was found to be: $T_c = 27.453$ °C. An important anomaly was detected in the neighbourhood of the critical point $X_c = 0.38$, $X$ being the weight percentage of the acid. The concentration dependence as the shear viscosity coefficients were evaluated at each $X$ value for the same temperatures. The results are discussed in terms of Einstein-Stokes law. Our analysis suggests three different behaviours of the diffusing entity in the mixtures and it is based on the preferential solvation phenomenon.

1. Introduction

Critical phenomena at equilibrium and phase transitions in binary mixtures have been widely studied for a long time [1] by means of light scattering experiments. Close to the critical point, the fluctuations of the order parameter $M = X - X_c = B((T - T_c)/T_c)^\beta$ strongly increase, leading to the divergence of the susceptibility $\chi$ and the correlation length $\xi = \xi_0((T-T_c)/T_c)^{-\nu}$ where $T_c$ is the critical temperature, and the time decay of the fluctuations goes to zero. The influence of a shear flow on the critical properties of fluids has also been studied [2]. Recently, we have developed a new experiment to study ion transport phenomena in critical binary mixtures [3-6]. The transport properties on ions in binary liquids exhibit intriguing anomalies near a consolute critical point, which are presumably due to the presence of the large critical fluctuations of concentration. We have used radioactive tracers to measure accurate ionic diffusion coefficients near critical solution points [7].

We have experimentally determined the variation of the self diffusion coefficient $D$ of cesium (137) [4], gadolinium (153) [5] and sodium (22) [6] in isobutyric acid-water critical mixtures as a function of temperature. These studies revealed two regions of different behaviour. Far from the critical point $(T - T_c > 5$ K), the logarithm of $D$ is linear in the reciprocal of the temperature according to the Arrhenius-Eyring formula for the self diffusion:

$$\ln(D) = \ln(D_0) - \frac{E_D}{RT}$$

(1)
\[ \ln(10^6 D)_{Cs^+} = 13.08 - 3252.6/T; \]
\[ \ln(10^6 D)_{Gd^{3+}} = 12.649 - 3519.8/T \]
\[ \ln(10^6 D)_{Na^+} = 19.497 - 5365/T; \]

where \( D \) is expressed in cm\(^2\) s\(^{-1}\). Here the activation energy of diffusion remains constant and depends only on the labeled element and on the structure of the medium. In the temperature domain \( T - T_c < (5-6) \) °C, i.e., near the critical point, the Arrhenius plot showed significant curvature. In order to interpret this anomaly, we have recently developed a new model [6]. The self-diffusion coefficient presented a critical behaviour in agreement with relative thermodynamic potential fluctuations obtained by using the Landau expansion developed for a second order phase transition. Accordingly, the activation energy of diffusion is analytically represented by

\[ E_D = A(T - T_c)^{2\beta+1} \]

where \( A \) is a constant and \( \beta \) is the universal exponent. However, it is now possible to form an explicit expression for the coefficient \( D \) in the vicinity of the critical point of a binary fluid and the Arrhenius law is modified as follows:

\[ \ln(D) = \ln(D_0) + \left( \frac{A}{RT} \right) (T - T_c)^{2\beta+1} \]

we found that \( \beta = 0.304 \pm 0.090 \) [6] which is in reasonable agreement with the theoretical value \( \beta = 0.325 \pm 0.0015 \) from renormalization group theory [8].

We present here the results of the tracer diffusion coefficients \( D_{2+} \) of labeled \(^{65}\)Zn\(^{2+} \) in a mixture of isobutyric acid, water and ZnCl\(_2\) [10\(-4\) M] as a function of the weight percentage \( X \) of the acid for two different temperatures: \( T - T_c = 0.547; 7.547 \) K. The diffusion process depends upon the viscosity \( \eta \) of the medium; the shear viscosity coefficients \( \eta \) have been determined for each \( X \) value of composition.

It will be recalled that Zn is the tenth ion in the transition metal series, and that aqueous solutions of transition salts are important in many branches of science. Of particular interest to biologists is the contrasting behaviour of Zn\(^{2+} \)(aq) which gives rise to the concept of the ionic pump across a cell membrane or a transfer study of elements from soils to plant.

2. Experiment

2.1. Sample Preparation. — Commercial isobutyric acid (> 99.50% pure) was used as received. The water that was used to prepare the solutions had a resistivity of 18 M\(\Omega\) cm. The critical mass fraction \( X_c \) of the acid is 0.389 according to references [6–9].

We chose an isobutyric acid-water (I-W) mixture for the following reasons:

(i) Since densities of the pure components are very close to each other, this mixture does not have large density gradients induced by gravity.

(ii) The critical temperature of this system which varies from (299.20 to 299.94 K [10–12]), is low. Moreover, since the use of isotopes as tracers was discovered, self-diffusion coefficient measurements in various mediums were undertaken around \( T = 298.15 \) K.

(iii) In this mixture the salt can be dissolved in totality.
The binary mixtures are prepared for various \( X \) in the acid by weighing the components directly in the experiment cell, with a resolution of 0.1 mg. The experimental method necessitates adding \((\text{Zn}^{2+}, 2\text{Cl}^-)\) salt to the binary mixture with a concentration of \(10^{-4}\) mol kg\(^{-1}\) of mixture. The \((\text{ZnCl}_2)\) salt (Merck product) at the concentration \(10^{-4}\) M constituted significant impurities and these represented a third component. However, various investigators have reported not only substantial shifts in the critical temperature \([13,14]\) but also changes in the critical composition \([15]\) and critical exponents. Investigators have also used impurities to move the critical point of binary liquids. Impurities have a significant impact on experimental and theoretical study of critical phenomena \([16,17]\).

2.2. Effect of Salt on the Mixture of (I-W). — In previous work \([17]\) we studied extensively the influence of the salts CsBr \([10^{-3}\) M\] and Gd(NO\(_3\))\(_3\) \([5 \times 10^{-4}\) M\] on the coexistence curve of a binary mixture of isobutyric acid and water (I-W). The data were obtained from refractive index measurements. The shifts in critical amplitudes (temperature, concentration, etc.) were determined. The critical exponent \( \beta \) of the coexistence curve is compatible with the Ising model in both I-W and in the I-W +CsBr\([10^{-3}\) M\] mixture. In the I-W +Gd(NO\(_3\))\(_3\) \([5 \times 10^{-4}\) M\] mixture, the exponent \( \beta \) is slightly larger and suggests an impurity induced Fisher renormalization value

\[
\beta^* = \frac{\beta}{(1 - \alpha)}
\]

where \( \alpha = 0.110 \) is the specific heat exponent.

Therefore, in order to have one homogeneous phase of the electrolyte, we must know with a good precision the critical temperature of the system. It appears necessary to determine the critical temperature shift caused by \((\text{ZnCl}_2)\). We have used a high-precision parallelepipedic cell filled with the electrolyte and immersed in a thermally stabilized water bath with an accuracy 2 mK. A slightly focused He-Ne laser beam (6328 Å, 5 mW power) was sent through the cell, and the temperature was lowered in steps. The critical temperature \( T_c \) was determined by the appearance of a ring of spinodal decomposition in the scattered light after a thermal quench of a few mK. The critical temperature was found to be \( T_c = 27.453 \pm 0.008 \) °C. We noted a positive shift of critical temperature given by

\[
\delta T_c(\text{ZnCl}_2[10^{-4}\) M\]) = 0.453 K.
\]

2.3. Radioactive Solution. — Radioactive \(^{65}\)Zn\(^{2+}\) was used to measure the self-diffusion coefficient of labeled \( \text{Zn}^{2+} \) in the mixtures of isobutyric acid + water + \text{ZnCl}_2[10^{-4}\) M\]. The \(^{65}\text{Zn}^{2+}\) was supplied by the “Commissariat à l’Énergie Atomique, Saclay France”. The half-life of the radioactive \(^{65}\text{Zn}^{2+}\) is 243.9 ± 0.2 days.

2.4. Tracer Diffusion. — The self-diffusion coefficient \( D_{2+} \) was determined with the capillary method. The quartz capillary of length \((l \approx 3 \) cm\) was filled with a labeled electrolyte by means of a thin micropipette, operated with a medical syringe. A small drop of radioactive solution was left on top in order to prevent evaporation during the time necessary to reach thermal equilibrium, and also to avoid, as far as possible, convection disturbances when the capillary was immersed in the unlabeled electrolyte. The whole system was submerged in a water bath giving a thermal stabilization of \(\pm 2 \times 10^{-3} \) °C over more than one day, as verified by a quarts thermometer. We estimate the precision of our diffusion results to be ±1%.

Two experiments at atmospheric pressure were carried out at each \( X \) composition for a fixed temperature.
The capillaries used had a uniform diameter of 0.08 cm. In filling the capillaries, the absence of any air bubbles was carefully ensured. The total radioactivity content in the capillaries was measured in the absence of diffusion (reference capillary) and after diffusion had taken place by means of a Packard Tri-Carb liquid scintillation spectrometer (model 33200). The γ emitter (65Zn2+) could be counter directly in the glass capillary. The number of counts was maintained at a level to make the error in the radioactivity measurements negligible compared to the error due to the filling and emptying of the capillaries. The time for diffusion was between 2 and 3 days. We denote by \( C(x, 0) \) the total activity in the capillary at the time \( t = 0 \). After a diffusion time \( t \) the final average activity will be \( C(x, t) \). By solving Fick’s equation with the proper limiting conditions, the ratio

\[
R = \frac{C(x, t)}{C(x, 0)}
\]  

(5)

can be related to the self-diffusion coefficient \( D \) by solving the equation

\[
R = \sum_{n=0}^{\infty} \frac{8}{\pi^2} (2n + 1)^2 \exp(\pi^2(2n + 1)^2Dt/4l^2).
\]  

(6)

In the case of an upper critical solution point, one phase is guaranteed only if the temperature is above \( T_c \). The experiments were performed in a thermostated room within ±0.2°C.

The solution of Fik’s law under the appropriate boundary conditions is given in reference [18]; the first term in the series expansion is

\[
D_{2+} = \frac{4l^2}{\pi^2 t} \ln \left( \frac{8}{\pi^2 R} \right)
\]  

(7)

where \( D_{2+} \) is the self-diffusion coefficient, \( l \) the capillary length measured with a traveling microscope, \( t \) the diffusion time, and \( R \) is given by equation (5). If \( D_{2+}t/l^2 > 0.24 \), which was realized in most of our experiments, the second term in the series expansion is \( 10^{-3} \) smaller than the first term and the other terms are still smaller. Only in a few cases, it was necessary to include the second term. \( D_{2+} \) is directly obtained from the measured radioactivities and the measured diffusion times. The experimental conditions employed in this work were such that \( 0.45 < R < 0.55 \), for which range Mckay’s equation has been shown to be valid [18].

2.5. Viscosity. — According to the Einstein-Stokes law the shear viscosity \( \eta \) is an important factor in the interpretation of the self-diffusion process. The coefficient \( \eta(\text{cP}) = \nu(\text{cSt}) \rho(\text{g cm}^{-3}) \) of the mixture at different compositions was determined by measuring the density \( \rho \) and the kinematic viscosity \( \nu \).

The densities were measured with a digital precision densimeter, DMA 46 (PAAR, Graz, Austria). The density was calculated from the electronically measured frequency of a mechanical oscillator filled with the solution. The oscillator was U shaped glass tubing (volume 0.7 cm³) placed in a metal block at a controlled temperature of about ±10⁻³ °C. The temperature was measured by a quartz thermometer. The precision of the density measurement was about ±0.1 mg cm⁻³.

The kinematic viscosity was calculated from the flow times using the following equation:

\[
\nu = k(t - t')
\]  

(8)

where \( t \) is the flow time, \( k \) is a constant for a given viscometer (AVS/N-Chott-Gerate), and \( t' \) is the correction time. The viscometer was calibrated with fluids of known density and viscosity.
Table I. — Composition dependence of the shear viscosity and of the tracer-diffusion coefficients of $^{65}\text{Zn}^{2+}$ in the isobutyric acid + water + ZnCl$_2$[10$^{-4}$ M] mixture; $\theta_1 = T - T_c = 0.547 \, K$; $\theta_2 = T_c = 7.547 \, K$.

<table>
<thead>
<tr>
<th>$X$ %</th>
<th>$D \times 10^6$ cm$^2$/s</th>
<th>$\eta$ (cP)</th>
<th>$D\eta$ ($10^{-8}$ cm g s$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\theta_1$ $\pm$ 0.15</td>
<td>$\theta_2$ $\pm$ 0.08</td>
<td>$\theta_1$</td>
</tr>
<tr>
<td>0</td>
<td>6.51 $\pm$ 0.15</td>
<td>7.50 $\pm$ 0.08</td>
<td>0.842</td>
</tr>
<tr>
<td>5</td>
<td>6.17 $\pm$ 0.07</td>
<td>7.26 $\pm$ 0.02</td>
<td>0.961</td>
</tr>
<tr>
<td>10</td>
<td>5.82 $\pm$ 0.08</td>
<td>7.20 $\pm$ 0.14</td>
<td>1.105</td>
</tr>
<tr>
<td>15</td>
<td>5.15 $\pm$ 0.10</td>
<td>6.10 $\pm$ 0.05</td>
<td>1.260</td>
</tr>
<tr>
<td>20</td>
<td>4.67 $\pm$ 0.17</td>
<td>5.66 $\pm$ 0.08</td>
<td>1.447</td>
</tr>
<tr>
<td>25</td>
<td>4.25 $\pm$ 0.10</td>
<td>5.24 $\pm$ 0.06</td>
<td>1.614</td>
</tr>
<tr>
<td>30</td>
<td>4.08 $\pm$ 0.10</td>
<td>4.71 $\pm$ 0.20</td>
<td>1.776</td>
</tr>
<tr>
<td>35</td>
<td>3.55 $\pm$ 0.10</td>
<td>4.60 $\pm$ 0.07</td>
<td>2.084</td>
</tr>
<tr>
<td>$X_c$ = 38</td>
<td>3.33 $\pm$ 0.09</td>
<td>4.42 $\pm$ 0.10</td>
<td>2.315</td>
</tr>
<tr>
<td>40</td>
<td>3.35 $\pm$ 0.12</td>
<td>4.25 $\pm$ 0.15</td>
<td>2.372</td>
</tr>
<tr>
<td>45</td>
<td>3.18 $\pm$ 0.12</td>
<td>4.05 $\pm$ 0.10</td>
<td>2.482</td>
</tr>
<tr>
<td>50</td>
<td>3.10 $\pm$ 0.10</td>
<td>3.85 $\pm$ 0.12</td>
<td>2.573</td>
</tr>
<tr>
<td>55</td>
<td>3.00 $\pm$ 0.25</td>
<td>3.95 $\pm$ 0.16</td>
<td>2.631</td>
</tr>
<tr>
<td>60</td>
<td>2.50 $\pm$ 0.05</td>
<td>3.55 $\pm$ 0.08</td>
<td>2.650</td>
</tr>
<tr>
<td>65</td>
<td>2.25 $\pm$ 0.15</td>
<td>3.35 $\pm$ 0.05</td>
<td>2.667</td>
</tr>
<tr>
<td>70</td>
<td>2.08 $\pm$ 0.05</td>
<td>3.14 $\pm$ 0.05</td>
<td>2.871</td>
</tr>
<tr>
<td>75</td>
<td>1.95 $\pm$ 0.10</td>
<td>2.95 $\pm$ 0.07</td>
<td>2.630</td>
</tr>
<tr>
<td>80</td>
<td>1.80 $\pm$ 0.08</td>
<td>2.70 $\pm$ 0.10</td>
<td>2.565</td>
</tr>
<tr>
<td>85</td>
<td>1.69 $\pm$ 0.10</td>
<td>2.75 $\pm$ 0.12</td>
<td>2.400</td>
</tr>
<tr>
<td>90</td>
<td>1.52 $\pm$ 0.08</td>
<td>2.71 $\pm$ 0.11</td>
<td>2.144</td>
</tr>
<tr>
<td>95</td>
<td>1.49 $\pm$ 0.22</td>
<td>2.62 $\pm$ 0.08</td>
<td>1.920</td>
</tr>
</tbody>
</table>

The composition dependence of the shear viscosity of isobutyric acid + water + ZnCl$_2$ [10$^{-4}$ M], was determined from $X = 0\%$ to 95\% in acid. The viscosity data are reported in Table I and Figure 1. In Figure 1, it appears that $\eta$ changes more slowly in the region very close to $X_c$ than in the region far away from $T_c$. The usual increase of $\eta$ near $T_c$ is observed; this effect is well known. Our results are in agreement with those of reference [10].
Fig. 1. — Plot of the shear viscosity as a function of $X$ composition in acid.

3. Results and Discussion

The experimental tracer-diffusion coefficients of $^{65}\text{Zn}^{2+}$ in various isobutyric acid, water and $\text{ZnCl}_2[10^{-4} \text{ M}]$ mixtures at two different temperatures $\theta_1 = T_1 - T_c = 0.547 \text{ K}$ and $\theta_2 = T_2 - T_c = 7.547 \text{ K}$ are plotted in Figure 2 as a function of the weight percentage $X$ of isobutyric acid. The reported coefficients are averages of eight separate measurements. These data are presented in Table II. Figure 2 shows three distinct domains for the temperature $\theta$:

Region 1 with $X < 25\%$ has a composition which is poor in acid, the coefficient $D_{2+}$ decreases in a linear manner as $X$ increases.

Region 2 with $25\% < X < 55\%$ is close to the critical point ($X_c = 38.9\%, T_1 - T_c = 0.547 \text{ K}$). The coefficient $D_{2+}$ shows an anomaly, because near the consolute point of binary liquids, the density fluctuations become increasingly larger and tend to infinity at $T_c$. This behaviour reflects the tendency of the $\text{Zn}^{2+}$ ions to dissolve, as a result of the strong correlation between the water and the isobutyric acid molecules. The amount of correlation near the critical point is described elsewhere [8] by the correlation length $\xi$ which diverges at $T_c$; $\xi$ being given by $\xi = \xi_0((T - T_c)/T_c)^{-v}$ where $v = 0.630$ is the universal exponent. The critical contribution is observed in this region. On the basis of this curve alone the anomaly is only immediately discernible at the temperature nearest $T_c$ as has been observed for the tracer diffusion of $^{137}\text{Cs}^{+}$ in an isobutyric acid + water + (CsBr)$[10^{-3}\text{ M}]$ according to reference [3]. The slow variation of $D_{2+}$ with $X$ is described by a straight line of slope 0.20.

Region 3 with $X > 55\%$ is rich in acid. The coefficient $D_{2+}$ decreases rapidly as $X$ increases.

For the temperature $\theta_2 = T_2 - T_c = 7.547 \text{ K}$, the system is well outside the critical region, and the density fluctuations become weak. Figure 2 shows that $D_{2+}$ decreases exponentially as $X$ increases without critical effect in the neighbourhood of $X_c = 38.9\%$ in acid. The coefficient $D_{2+}$ exhibits a regular behaviour as a results of the weak correlation between the water and isobutyric acid molecules.
The coefficient $D_{2+}$ is connected to $\eta$, according to the Stokes-Einstein law for the motion of spherical uncharged particles

$$D_{2+} = \frac{KT}{6\pi\eta r_{se}}$$

where $r_{se}$ is the radius of the particle and $\eta$ is the shear viscosity of the fluid in which the particles move. Then it is interesting to examine the viscosity effect, by plotting the product $(D_{2+}\eta)$ against the weight percentage $X$ of acid as shown in Figure 3. We have observed an important maximum of this product in region 2: for the temperature $\theta_1$, this effect is due to the anomalous behaviour of the shear viscosity around $X_c$. This phenomenon has been well established in binary fluids for a long time. However the product $(D_{2+}\eta)$ is constant for a given solvation structure, according to the Walden law. The Stokes-Einstein radius $r_{se}$ of diffusing particles versus weight percentage $X$ of isobutyric acid is plotted in Figure 4.

The starting point for discussing ionic mobility in electrolyte at infinite dilution under the influence of an electric field has long been the Stokes-Einstein law. That is, the ion is treated as a sphere moving in a continuous medium under the laws of classical mechanics. Deviations form the Stokes law have been attributed to the breakdown of macroscopic hydrodynamics on a molecular scale and to solvation effects [19]. Studied of ionic mobilities in mixed solvents have demonstrated that dielectric relaxation in polar solvent induced by ionic movement gives rise to frictional resistance to that motion. However, Robinson and Stokes [19] have proposed a correction to Stokes law to represent the size of the solvated ions in water. The empirical correction has been extended to small ions to provide a concordant set of radii for hydrated ions. The corrected Stokes law radius of the hydrated ion can then be used to estimate its volume.
Table II. — *Species radii r data.*

<table>
<thead>
<tr>
<th>( r_{se} ) (10^{-1} nm)</th>
<th>( r_H ) (10^{-1} nm)</th>
<th>( \bar{r} ) (10^{-1} nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \theta_1 )</td>
<td>( \theta_2 )</td>
<td>( \theta_1 )</td>
</tr>
<tr>
<td>4.024</td>
<td>4.039</td>
<td>4.561</td>
</tr>
<tr>
<td>3.720</td>
<td>3.828</td>
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</tr>
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<td>3.430</td>
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<td>3.264</td>
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</tr>
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<td>6.770</td>
<td>4.519</td>
<td>6.538</td>
</tr>
<tr>
<td>7.712</td>
<td>5.812</td>
<td>7.624</td>
</tr>
</tbody>
</table>

In order to interpret our data in terms of Zn\(^{2+}\) preferential solvation by water or by acid molecules, we have used the Stokes empirical correction [19] to obtain the effective radius \( r_H \) for investigating the structure of the diffusing species. We determine the mean radius \( r_H \) by using the following formula:

\[
 r_H = 2.613 + 0.636 r_{se} - 0.0808 r_{se}^2 + 0.01071 r_{se}^3 
\tag{10}
\]

with \( r_{se} < 5.3 \text{ Å} \). This is in agreement with the calibration curve proposed by Nightingale [20].

Figures 3a-b show the behaviour of the radius \( r_H \). In a qualitative manner, these figures show that for the region rich in water (\( X < 25\% \)), the diffusing entity is the Zn\(^{2+}\) solvated by water (hydrated ions) of radii \( r_H(\theta_1) = 4.561 \text{ Å} \); \( r_H(\theta_2) = 4.569 \text{ Å} \).
Fig. 3. — Walden product $D_{2+\eta}$ plotted versus $X$ at $\theta_1$ and $\theta_2$.

From these values of $r_H$, the volumes of the particles may be estimated. These volumes can be combined with the values:

$$V_{H_2O}(\theta_1) = \left(\frac{4}{3}\pi\right) 4.561^3 = 397.236 \text{ Å}^3$$

$$V_{H_2O}(\theta_2) = \left(\frac{4}{3}\pi\right) 4.569^3 = 399.330 \text{ Å}^3$$

corresponding to close-packed spherical molecules, this is called structure 1; see Figure 5a. For $25\% < X < 55\%$, the effective radius $r_H$ decreases and it reaches a minimum in this region. In terms of solvation analysis, we can qualitatively affirm in this region that the Zn$^{2+}$ ions have a tendency to dissolve in spite of the intensity of the electrostatic field due to the charge (+2e) of the ions. In the domain with $X > 55\%$, we are far away from the critical point, the effective radius increases with the increasing weight percentage $X$ of acid, showing a tendency to preferential solvation of Zn$^{2+}$ by isobutyric acid of limiting radii $r_H(\theta_1) = 6.500 \text{ Å}$; $r_H(\theta_2) = 6.330 \text{ Å}$; and with volume values

$$V_{\text{acid}}(\theta_1) = 1149.763 \text{ Å}^3$$

$$V_{\text{acid}}(\theta_2) = 1061.890 \text{ Å}^3$$

these are called structure 2 (Fig. 5b).
Fig. 4. — The Einstein-Stockes radius calculated from experimental viscosity and diffusion coefficients, equation (9).

We shall consider a more practical application of the self-diffusion data and describe one from interrelation between the self-diffusion coefficient and the structure of the medium. We wish to give a more detailed discussion of the equivalence of the effective size of the solvated ion to water or to isobutyric acid molecules.

If we denote by \( r_1 \) the effective radii of the two limiting entities, i.e., \( r_1(\theta_1) = 4.561 \, \text{Å} \) and \( r_2(\theta_2) = 4.569 \, \text{Å} \); the radii of the hydrated ion, and \( r_2(\theta_1) = 6.500 \, \text{Å} \) and \( r_2(\theta_2) = 6.330 \, \text{Å} \) the radii of the ion solvated only by isobutyric acid molecules, we can describe the mean value of the self diffusion coefficient for a given weight percentage \( X \) by the following equation:

\[
D = \frac{K T}{(6\pi \eta \tilde{r})}
\]

where \( \tilde{r} \) is defined by:

\[
\frac{1}{\tilde{r}} = \frac{N_1}{r_1} + \frac{N_2}{r_2}
\]

Here \( N_1 \) and \( N_2 \) are the molar fractions of the water and the acid, respectively, for each composition \( X \). The calculated values \( \tilde{r} \) across the entire composition range are displayed.
Fig. 5. — Diffusivity cage model, (a) structure 1 (hydrated ions \( W = H_2O \)); (b) structure 2 (solvation by isobutyric acid, labeled IA).

graphically in Figures 6a-b. These plots show a significant difference between the \( \bar{r}(X) \) and \( r_H(X) \), especially around \( 20\% < X < 60\% \).

It is obvious that in the electrolyte a molecule or ion may be located at different sites, corresponding to different translational mobilities. The self diffusion coefficients observed are therefore composites of the self-diffusion coefficients at the different sites. An analysis of the relationship between the “local” quantities and the measured self diffusion coefficient has been given by Hertz [19]. From the Hertz treatment, we can interpret this difference by adopting the following approximation formula

\[
\frac{1}{\bar{r}} = \frac{P_1}{r_1} + \frac{P_2}{r_2}
\]

In general, \( P_i (i = 1, 2) \) is the probability that a diffusing particle is found in environment \( i \), here \( P_1 \) and \( P_2 \) are the probabilities that a diffusing particle is found in the structural limits 1 and 2 respectively (Figs. 5a and 5b, respectively). The structural limits 1 and 2 are the \( ^{65}\text{Zn}^{2+} \) ions which prefer to be surrounded by water or by isobutyric acid molecules, respectively. In the critical region, the correlation with the molecular solvent is very strong, this phenomenon is the origin of the difference between \( \bar{r}(x) \) and \( r_H(x) \). In the diffusing medium, there are two competitive processes between the preferential solvation by water or by acid.
Fig. 6. — Radius $r$ as a function of $X$; $r = r_H$ (the hydrodynamic radius); $r = \bar{r}$ (the corrected radius); curves (a) for $\theta_1 = 0.547$ K; Curves (b) for $\theta_2 = 7.547$ K.
4. Conclusion

Precise tracer diffusion measurements in the single-phase region of binary fluid mixtures of isobutyric acid and water were combined with independent viscosity measurements of the same system to apply the Stokes-Einstein relation. From the product $D\eta$, we can have access to the diffusing entity structure of the divalent transition metal cation $^{65}\text{Zn}^{2+}$ in a binary fluid.

We have shown that the effective radius of the solvated ion in the critical region (i.e., region 2) is not a simple concentration-weighted mean of the water and acid-solvated species (as proposed in Eq. (12)). In contrast, the water of free (unsolvated) ion structure persists as the dominant species up to quite large mole fractions of acid (about 80%). This we ascribe to the preferential solvation of the $^{65}\text{Zn}^{2+}$ by water as opposed to solvation by acid molecules.

In future work, it would be interesting to study the structural properties of ions in a critical binary mixture by neutron and X-ray diffraction.

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References