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Ionic structure in a binary fluid

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Abstract. The tracer diffusion coefficient D_{3+} of the trivalent lanthanide cation $^{153}\text{Gd}^{3+}$ is studied in mixtures of isobutyric acid, water and 5×10^{-4} M $\text{Gd}(\text{NO}_3)_3$ using an open-ended capillary tube. These data are given over the complete composition range at $T - T_c = 0.171$ K. The coefficients D_{3+} are combined with the shear viscosity η of the electrolyte. The results are discussed in terms of the 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

Much attention has been recently [1–3] focused on the Arrhenius law form in the neighbourhood of the critical point of a binary fluid. We have experimentally determined the variation in the self-diffusion coefficient D ($\text{cm}^2 \text{s}^{-1}$) of caesium-137 [1], gadolinium-153 [2] and of sodium-22 [3] in an isobutyric acid–water critical mixture as a function of temperature. This study reveals two variation regimes of the coefficient D as a function of temperature $T - T_c > 5\text{--}6^\circ\text{C}$. Firstly far from the critical point the logarithm of D is linear with the reciprocal of the absolute temperature according to the Arrhenius–Eyring formula for self-diffusion:

$$\begin{aligned}\ln D &= \ln D_0 - E_D/RT \\ \ln(10^6 D)_{\text{Cs}^+} &= 13.08 - 3252.6/T \\ \ln(10^6 D)_{\text{Gd}^{3+}} &= 12.649 - 3519.8/T \\ \ln(10^6 D)_{\text{Na}^+} &= 19.497 - 5365/T\end{aligned}\quad (1)$$

where D is expressed in square centimetres per second. Here the activation energy of diffusion remains constant and depends only on the labelled element and on the structure of the medium. In the temperature domain $T - T_c < 5\text{--}6^\circ\text{C}$, i.e. near the critical point, the Arrhenius plot was characterized by a significant curvature. In order to interpret this anomaly, we have recently developed a new model [3]. 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 β 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:

$$\ln D = \ln D_0 + \frac{A}{RT}(T - T_c)^{2\beta+1}\quad (2)$$

where A is a constant and β is the universal critical exponent. In order to obtain more precision in the variation in D with temperature, the coefficient D can be related to $T - T_c$ through the relationship

$$D = D_0(T - T_c)^\beta. \quad (3)$$

We found that $\beta = 0.304 \pm 0.090$ [3] which is in reasonable agreement with the theoretical value $\beta = 0.325 \pm 0.0015$ from renormalization group theory [4].

The aim of this paper is to demonstrate another aspect of experiment. We present here the results of the tracer diffusion coefficients D_{3+} of labelled $^{153}\text{Gd}^{3+}$ in a mixture of isobutyric acid, water and 5×10^{-4} M $\text{Gd}(\text{NO}_3)_3$ as a function of the weight percentage X of the acid for a fixed temperature $T - T_c = 0.171$ K. It will be recalled that Gd is the eighth ion in the lanthanide series, and that aqueous solutions of lanthanide salts are important in many branches of science. Of particular interest to biologists is the contrasting behaviour of $\text{Gd}(\text{aq})$ which gives rise to the concept of the ionic pump across a cell membrane or a transfer study of elements from earth to plant. The diffusion process depends upon the viscosity η of the medium; the shear viscosity coefficients η have been determined here for each X -value.

2. Experimental details

The isobutyric acid–water mixture used in this investigation was the same as used in the previous study [3]. 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 the $(\text{Gd}^{3+}, 3\text{NO}_3^-)$ salt to the binary mixture with a concentration of 5×10^{-4} mol per kilogram of mixture. The $(\text{Gd}(\text{NO}_3)_3)$ salt (Johnson Matthey) contained significant impurities and these represented a third component. However, various investigators have reported not only substantial shifts in the critical temperature [5, 6] but also changes in the critical composition [7] and critical exponents [8, 9]. Investigators have also used impurities to move the critical point. Impurities have a significant impact on experiment and theoretical work in critical phenomena. By comparing the transmitted light intensities with and without the salt, we have deduced an apparent T_c change. The optical set-up for T_c determination is the same as already described in [3]. We noted a positive shift of the critical temperature given by

$$\delta T_c(5 \times 10^{-4} \text{ M Gd}(\text{NO}_3)_3) = 0.453 \text{ K}.$$

The critical temperature was measured to be $T_c = 300.603 \pm 0.008$ K. The radioactive ^{153}Gd (half-life, 242 d) was obtained from England Amersham as gadolinium chloride in 0.1 M HCl. Since ^{153}Gd emits high-energy γ , a Packard Tri-Carb liquid scintillation spectrometer was selected as the detector. The γ emission could be counted directly in the glass capillary. The number of counts was maintained at a level to make the error in the radioactivity measurements negligible compared with the error due to the filling and emptying of the capillaries. The time for diffusion was between 3 and 5 d. The whole system was submerged in a water bath, giving a thermal stabilization of $\pm 2\%$ over more than 1 d, as verified with a quartz thermometer. Two experiments at atmospheric pressure were carried out at each X -value for a fixed temperature $T = 27.624^\circ\text{C}$. According to the Einstein–Stokes law the shear viscosity η of the electrolyte is an important factor in the

interpretation of the tracer diffusion process. It is necessary to know the shear viscosity η of the electrolyte. The coefficient $\eta(cP) = \nu(cSt)$. ρ (g cm^{-3}) of the mixture at different X was determined by measuring the density ρ and the kinematic viscosity ν .

The densities were measured in a digital precision densimeter. The density of a solution 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 cm^3) placed in a metal block the temperature of which was controlled to about $\pm 10^{-3} \text{ }^\circ\text{C}$. The precision of the density measurement was better than $\pm 0.1 \text{ mg cm}^{-3}$.

The kinematic viscosity was calculated from the flow times using the following equation: $\nu = k(t - \theta)$, where t is the flow time, k is a constant for a given viscosimeter and θ is the correction time. The viscosimeter was calibrated with fluids of known density and viscosity.

We chose an isobutyric acid–water mixture for the following reasons.

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

(ii) The critical temperature of this system which varies from 299.20 to 299.20 K [10–12], is low. Moreover, since the use of isotopes as tracers was discovered, self-diffusion coefficient measurements in various media have been made at around $T = 298.15 \text{ K}$.

3. Results and discussion

The experimental tracer diffusion coefficients D_{3+} of $^{153}\text{Gd}^{3+}$ in various isobutyric acid–water mixtures and $5 \times 10^{-4} \text{ M Gd}(\text{NO}_3)_3$ at $T - T_c = 0.171 \text{ K}$ are plotted in figure 1 as a function of the weight percentage X of isobutyric acid. The reported coefficients D_{3+} are the average values of eight separate double measurements. We estimate the precision of our diffusion results to be of the order of $\pm 1\%$. Figure 1 shows, at a temperature $T = 27.624 \text{ }^\circ\text{C}$ (300.774 K) and at atmospheric pressure, three distinct domains.

Region 1 with $X < 25\%$ has a composition which is poor in acid; the coefficient D_{3+} decreases in a ‘quasi-linear’ manner when X increases.

Region 2 with $25\% < X < 55\%$ is very close to the critical point ($X_c = 0.389$; $T - T_c = 0.171 \text{ K}$). The coefficient D_{3+} shows an anomaly, because around $X_c = 38.9\%$ the density fluctuation becomes increasingly larger and tends to infinity at T_c . This behaviour D_{3+} reflects the tendency of the Gd^{3+} ions to dissolve, as a result of strong correlation between the water and the isobutyric acid molecules. The critical contribution is observed.

Region 3 with $55\% < X < 100\%$ is rich in acid. The coefficient D_{3+} decreases exponentially when X increases.

According to the Einstein–Stokes law the motion of spherical uncharged particles is given by the following equation:

$$D_{3+} = kT/6\pi\eta r_s \quad (4)$$

where r_s is the radius of the particle and η is the shear viscosity of the electrolyte in which the particles move. Then it is interesting to examine the viscosity effect by plotting the product $D_{3+}\eta$ against the weight percentage X of acid as shown in figure 2. We have observed an important maximum of $D_{3+}\eta$ in region 2; this effect is due to the anomalous shear viscosity. This phenomenon has been well established in binary fluid mixtures for a long time. However, the product $D_{3+}\eta$ must be constant for a given solvation structure, according to the Walden law. Figure 2 shows three solvation domains for Gd^{3+} ions. The

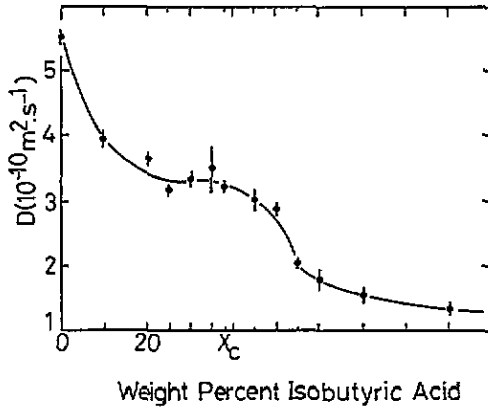


Figure 1. Plot of the tracer diffusion coefficients for $^{153}\text{Gd}^{3+}$ in a mixture of isobutyric acid, water and 5×10^{-4} M $\text{Gd}(\text{NO}_3)_3$ as a function of the weight percentage X of acid at $T - T_c = 0.171$ K.

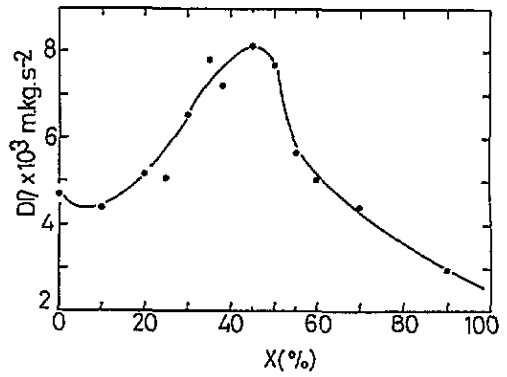


Figure 2. Walden product $D_{3+\eta}$ plotted versus X at 27.500°C .

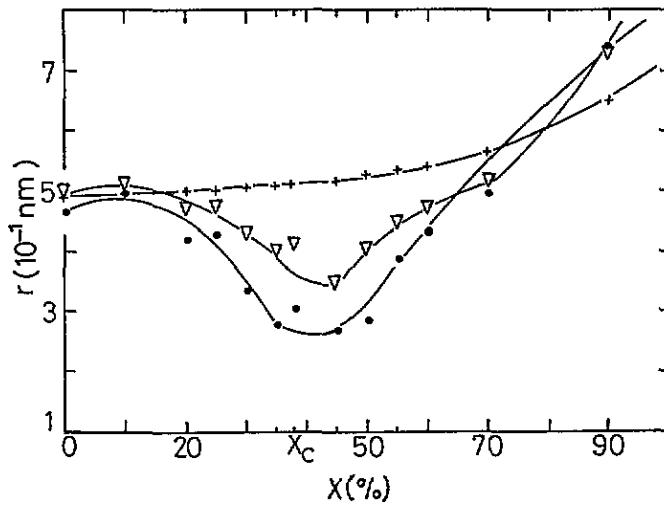


Figure 3. Radius r as a function of X ; \bullet , $r = r_s$ (the Stokes radius); ∇ , $r = r_H$ (the hydrodynamic radius); $+$, $r = \bar{r}$ (the corrected radius).

Einstein–Stokes radius r_s of diffusing particles versus weight percentage X of isobutyric acid is plotted in figure 3 as full circles.

The starting point for discussing the ionic mobility in the electrolyte at infinite dilution under the influence of an electric field has long been the Einstein–Stokes law. That is, the ion is treated as a sphere moving in a continuous medium under the laws of classical thermodynamics. Deviations from the Stokes law have been considered as due to the breakdown of macroscopic hydrodynamics on a molecular scale and to solvation effects [13]. The effect of the dielectric constant on the ionic mobility in mixed solvents has demonstrated importantly that the dielectric relaxation in polar solvent induced by ionic

movement gives rise to frictional resistance to that motion. However, Robinson and Stokes [13] have proposed a correction to the 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. Ions with a crystal ionic radius of about 2 Å exhibit a minimum hydrated radius of 3.3 Å corresponding to the maximum in the equivalent conductance. The corrected Stokes law radius of the hydrated ion can then be used to estimate, with good precision, its volume.

In order to interpret our data in terms of Gd^{3+} preferential solvation by water or by acid molecules, we have used the Stokes empirical correction [13] to obtain the effective radius r_H for investigating the diffusing entity structure. We determine the corrective radius r_H by using the following practical formula:

$$r_H = 2.613 + 0.636r_S - 0.0808r_S^2 + 0.01071r_S^3 \quad (5)$$

with $r_S < 5.3$ Å, r_S being the Stokes radius. This is in agreement with the calibration curve proposed by Nightingale [14].

Figure 3 (open triangles) shows the behaviour of the radius r_H . In a qualitative manner, this figure shows for the region rich in water ($X < 25\%$) that the diffusing entity is Gd^{3+} solvated by water (hydrated ions) of radius 4.917 Å. From this value of r_H we defined the volume of the particles that may be obtained. This volume can be combined with the value

$$V_{H_2O} = \frac{4}{3}\pi(4.917)^3 = 497.95 \text{ \AA}^3$$

corresponding to close-packed spherical molecules; this is called structure 1 (figure 4(a)). For $25\% < X < 55\%$, the effective radius decreases and it reaches a minimum for $X = 45\%$. In terms of solvation and analysis, we can qualitatively affirm in this region that the Gd^{3+} ions have a tendency to desolve in spite of the intensity of the electrostatic field due to the charge $+3e$ 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 Gd^{3+} by isobutyric acid of limiting radius 8.035 Å, and with a volume $V_{acid} = 2172.93 \text{ \AA}^3$; this is called structure 2 (figure 4(b)).

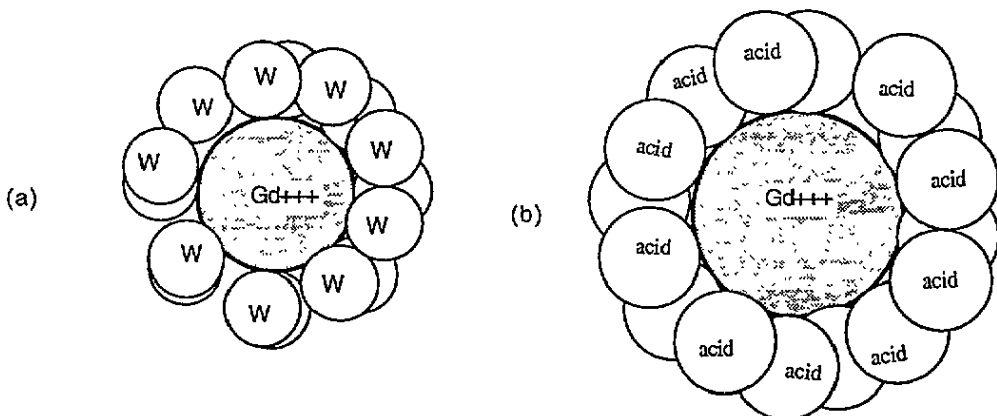


Figure 4. (a) structure 1 (hydrated ions $W \equiv H_2O$); (b) structure 2 (solvation by isobutyric acid, labelled acid).

We shall consider a more practical application of the self-diffusion data and describe one form of the 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 acid molecules.

If we denote by r_1 and r_2 the effective radii of the two limiting entities i.e. $r_1 = 4.917 \text{ \AA}$, the radius of the hydrated ion, and $r_2 = 8.035 \text{ \AA}$ the radius of the solvated ion 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:

$$\bar{D} = kT/6\pi\eta\bar{r} \quad (6)$$

where \bar{r} is defined by

$$1/\bar{r} = N_1/r_1 + N_2/r_2. \quad (7)$$

Here N_1 and N_2 are the molar fractions of the water and the acid, respectively, for each X . The calculated values r across the entire composition range are displayed graphically in figure 3 (+). This plot shows a significant difference between $\bar{r}(X)$ 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 [15]. From the Hertz treatment, we can interpret this difference by adopting the following rigorous expression:

$$\frac{1}{\bar{r}} = \frac{P_1}{r_1} + \frac{P_2}{r_2}. \quad (8)$$

In general, P_i ($i = 1, 2$) is the probability that a diffusing particle is found in the 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 (figures 4(a) and 4(b), respectively). The structural limits 1 and 2 are the $^{153}\text{Gd}^{3+}$ ions which prefer to be surrounded by water or by isobutyric acid molecules, respectively. In the two regions $0\% < X < 25\%$ and $25\% < X < 55\%$, $\bar{r}(X)$ coincides approximately with the radius $r_H(X)$. In the critical region, the correlation between 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.

4. Conclusion

Precise tracer diffusion measurements in the single-phase region of the binary fluid mixture of isobutyric acid and water were combined with independent viscosity measurements of the same system to apply the Einstein-Stokes relation. From the product $D\eta$, we can have access to the diffusing entity structure of the trivalent lanthanide cation $^{153}\text{Gd}^{3+}$ 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 equation (6)). In contrast, the water or 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 dissolution of the $^{153}\text{Gd}^{3+}$ of water as opposed to solvation by acid molecules.

As an important conclusion, the qualitative interpretation of ionic process in a binary fluid opens up a new field in phase transitions.

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