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Mutual Diffusion Coefficient and Dynamic Viscosity Near the Critical Consolute Point Probed by Dynamic Light Scattering[1]

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The possibility of applying dynamic light scattering to simultaneous determination of the mutual diffusion coefficient and the viscosity of binary liquid systems was studied near the critical consolute point. When seed particles are added to the system, the particle diffusion coefficient is measured, and the viscosity is obtained using the Stokes–Einstein relation. Since the amplitude of light scattered from concentration fluctuations is low in a mixture with a small difference between the refractive indices of the pure components, this approach allowed the determination of the viscosity of a critical mixture of nitroethane and isooctane, without a signal component from mutual diffusivity superimposed. In contrast, particle aggregation prevented the determination of the viscosity of a critical mixture of triethylamine and water. Despite this difficulty, and an unidentified contribution in the signals obtained, the mutual diffusion coefficient and the critical exponent ν could be determined in this system without a noticeable influence from the addition of seed particles.

KEY WORDS: binary mixture; critical consolute point; dynamic light scattering; mutual diffusion coefficient; nitroethane–isooctane; triethylamine–water; viscosity.

1. INTRODUCTION

The determination of transport and other thermophysical properties in the vicinity of critical points requires suitable experimental techniques which do not influence the system under investigation. To obtain the transport

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coefficients, any applied external gradient must be large enough to obtain data with a low uncertainty and small enough to cause little perturbation. This is the reason why optical techniques which work in equilibrium, and require only low-power illumination, have advantages in this field [1–3].

The mutual diffusion coefficient D_{12}, which vanishes at the critical consolute point of a binary liquid mixture, has been measured by various techniques, including Taylor dispersion [4] and dynamic light scattering [5]. Both for the determination of the correlation length ξ of critical fluctuations from the diffusion coefficient and for the direct measurement of the weak critical enhancement of the dynamic viscosity η, an accurate technique for the determination of η is needed. Conventionally, capillary viscometers and oscillatory techniques are employed. Alternatively, dynamic light scattering has been used successfully for the measurement of liquid viscosity via the determination of the diffusion coefficient of dispersed seed particles [6–8].

It is the aim of this paper to investigate whether the viscosity of a binary fluid mixture can also be determined by dynamic light scattering (DLS) in the vicinity of a critical consolute point. As this technique offers the possibility of a simultaneous determination of mutual diffusion and viscosity [7, 9], a further goal of the work is to check if such simultaneous measurements can be performed near a critical consolute point. This possibility would be highly desirable, because both the mutual diffusion coefficient and the viscosity could be obtained for truly identical boundary conditions, namely, temperature and composition, and in a cost-effective and time-saving way.

2. THEORETICAL BACKGROUND

2.1. Mutual Diffusion and Viscosity Near the Critical Consolute Point

This section is restricted to a brief survey of the behavior of mutual diffusivity and viscosity near a critical consolute point. A rigorous and comprehensive treatment may be found in several reviews [10, 11].

The mutual diffusion coefficient D_{12} may be separated into a background contribution $\bar{D}$ and a critical part ΔD_c near a critical point according to

$$D_{12} = \bar{D} + \Delta D_c \tag{1}$$

The critical part can be represented by a Stokes–Einstein relation,

$$\Delta D_c = \frac{R k_B T}{6 \pi \eta \xi} \tag{2}$$

with a universal amplitude R close to unity, Boltzmann's constant k_B, and temperature T. In the limiting case of wave numbers $q \to 0$ for the fluctuations investigated, the critical part vanishes at the critical point, dominated by the power-law behavior of the correlation length ξ,

$$\xi = \xi_0 \varepsilon^{-\nu} \tag{3}$$

where ξ_0 is a system-dependent amplitude, ε is the reduced temperature $\varepsilon = |T - T_c|/T_c$, T_c is the critical temperature, and ν is a universal exponent with $\nu = 0.63$. Since light-scattering investigations cannot probe a system in the true $q = 0$ limit, modifications to Eq. (2) will become relevant, which may have substantial implications for the decay rates of the fluctuations observed. This generalization is discussed in Section 2.2. An evaluation of the background contribution reveals that this term is most important at large wave vectors q [12]. In practical light-scattering investigations, however, it turns out that this contribution is small [12], i.e., of the order of a few percent, and may be neglected close to the critical point, i.e., in the range $q\xi > 1$.

The dynamic viscosity η displays only a weak enhancement at the critical point, which may be expressed in the form of a multiplicative expression,

$$\eta = \bar{\eta}(Q\xi)^z \tag{4}$$

where $\bar{\eta}$ is the background viscosity, which may be represented by the Andrade equation $\bar{\eta} = \bar{A} \exp(B/T)$, Q is a system-dependent amplitude, and z is a universal exponent, where the currently adopted theoretical value is $z = 0.063$ [11]. Combining Eqs. (3) and (4) results in a power-law behavior of the viscosity $\eta \propto \varepsilon^{-0.040}$. Although a crossover function must be introduced in the domain between normal and critical behavior of the viscosity for correct description of the dependence of viscosity on temperature, it is found that even the simple form of Eq. (4) is adequate for determination of the exponent z [12].

2.2. Dynamic Light Scattering

Dynamic light scattering analyzes the fluctuations of light scattered from a sample. This may be conveniently done by photon correlation, which means that an autocorrelation function (ACF) is computed from the signal fluctuations. If these fluctuations are due to an isolated diffusive process, the normalized correlation function of the electric field takes the form of a simple exponential decay,

$$\hat{g}^{(1)}(t) = c \exp(-\Gamma t) \tag{5}$$

with a characteristic decay rate Γ (the inverse of a decay time τ_c) and an experimental constant c which takes into account effects such as a deviation from a perfectly coherent registration. The decay rate is proportional to the desired diffusivity D,

$$D = \Gamma / q^2 \tag{6}$$

where q is the modulus of the scattering vector, with

$$q = \frac{4\pi n}{\lambda_0} \sin \frac{\Theta}{2} \tag{7}$$

which determines the wave number of the fluctuations investigated and which depends on the refractive index n of the sample investigated, the laser wavelength *in vacuo* λ_0, and the scattering angle Θ.

The diffusivity D can be identified with the mutual diffusion coefficient D_{12} from concentration fluctuations in a binary mixture with differing refractive indices or with the particle diffusion coefficient D_p of suspended particles. For the determination of the viscosity, nearly monodisperse and spherical particles of radius r are dispersed in a liquid or liquid mixture, and the viscosity is obtained using the Stokes–Einstein relation

$$D_p = \frac{k_B T}{6\pi\eta r} \tag{8}$$

in analogy with Eq. (2).

When seed particles are suspended in a binary mixture, the general correlation function is a superposition of the signals from both fluctuations,

$$\hat{g}^{(1)}(t) = c_{12} \exp(-\Gamma_{12} t) + c_p \exp(-\Gamma_p t) \tag{9}$$

As indicated in the previous section, the determination of the exponent ν of the correlation length of the critical fluctuations cannot be deduced from a combination of Eqs. (2), (3), and (6) in a straightforward manner. It has been observed in light-scattering investigations [13] that the critical part $\Delta\Gamma_{c,12}$ of the decay rate does not vanish close to the critical point but approaches a fairly constant value. The reason is that with increasing correlation length in the vicinity of the critical point, there is a deviation from the true $q\xi \to 0$ limit implicit in these simplified relations. For the critical part $\Delta\Gamma_{c,12}$ of the decay rate, a generalized Stokes–Einstein formula has to be used, which is given by [13]

$$\Delta\Gamma_c = \frac{R k_B T q^2}{6\pi\eta\xi} K(q\xi) \left[1 + \left(\frac{q\xi}{2} \right)^2 \right]^{z/2} \tag{10}$$

where $K(x)$ is the Kawasaki function

$$K(x) = \frac{3}{4x^2}\left[1 + x^2 + (x^3 - x^{-1})\, atan\, x\right] \tag{11}$$

As $K(q\xi) \to 1$ for $q\xi \to 0$ in this limiting case, the simplified equations hold. This is the underlying reason why in light-scattering investigations [5] at small scattering vectors, yet not too close to the critical point, the diffusion coefficient exhibits a simple behavior according to Eqs. (2) and (3).

3. EXPERIMENTAL

3.1. Materials and Sample Preparation

To test the possibility of measuring viscosities from the particle diffusion coefficient near a critical consolute point, a mixture of nitroethane (NE) and isooctane (IO, 2,2,4-trimethylpentane) was selected as the first system for investigation. This system was studied in an earlier work by Lyons et al. [14]. Since the refractive indices of these substances are close together ($n^{D}_{20°C,\,NE} = 1.3915$, $n^{D}_{20°C,\,IO} = 1.3917$) and thus the signal from binary diffusion is weak, it is possible to measure the particle diffusion coefficient for a wide range of temperatures without the interfering influence of an additional signal. The system exhibits an upper critical consolute point at a concentration $c_{NE,\,wt} = 0.465$ and a temperature $T_c \approx 303$ K. Both substances had a specified purity of 99.8% and were used as delivered. Since the system is sensitive to humidity, all glass containers used were filled with a protective argon atmosphere and closed immediately.

To test the simultaneous determination of mutual diffusion and viscosity, a mixture of triethylamine (TEA; purity, 99.9%) and water (deionized by a Millipore Milli-Q system; conductivity below 1 $\mu S \cdot cm^{-1}$) was used. The system exhibits a lower consolute point at a concentration $c_{TEA,\,wt} = 0.321$ and a temperature $T_c = 291$ K.

In both cases, industrially produced silica particles with a standard deviation in particle size below 10% were used as a seed. In the case of the NE–IO system, the particles were surface-modified by grafted methylacrylate chains. For the TEA–water system, native particles were used. Particle diameters were determined by DLS in ethanol or water to be 216 and 215 nm, respectively. A defined quantity of particles was dispersed in pure components, the dispersions were then submitted to ultrasonic treatment and filtered through syringe filters with a 0.45-μm pore size to remove possible residual agglomerates and dust. Mixtures were directly prepared in sample cuvettes by adding defined volumes, calculated from known liquid densities, of the individual components with a precision pipette.

3.2. Light-Scattering System and Experimental Procedure

The light-scattering system is based on a newly developed scattering cell which utilizes a symmetrical setup and is described in detail elsewhere [15]. With the symmetrical setup, the cuvette is tilted from the usual position, where the exit window is perpendicular to the axis of observation, by an angle $\Theta_i/2$, where Θ_i is the angle between the incident laser beam and the axis of observation. This approach makes the determination of the scattering vector feasible without having to know the refractive index of the sample; only the refractive index of the surrounding medium must be known.

A commercial square cuvette is placed inside a thermostated scattering cell and aligned symmetrically. The cell contains an oil, which serves as a thermostating medium and which has a refractive index closely matching that of the cuvette and the cell windows. The sample temperature is measured directly by a calibrated Pt-100 resistance probe with an absolute uncertainty of better than 0.05 K. The oil is thermostated via an external computer-controlled water or oil circuit. The temperature stability of the sample during an experimental run is better than ± 0.01 K, whereas the external lab thermostat could be regulated only in steps of 0.1 K. Although temperature control is thus only marginally suitable for exact measurements in the vicinity of a critical point, it may be considered sufficient for these initial tests.

At each temperature, normally six experimental replications were made, with a typical integration time of 10 min for each run. In the case of the NE–IO system, the signal from particle diffusion clearly dominated so that a single exponential could be fit well by a nonlinear fit algorithm described previously [16]. With the TEA–H_2O system, a nonlinear fit to a sum of exponentials was applied to the field ACF. Measurements were performed at different angles of incidence (30, 60, and 90°) with symmetrical geometry (denoted "s") and additionally with "conventional" rectangular geometry (90r), where refractive index data were taken from the literature.

4. RESULTS AND DISCUSSION

4.1. Nitroethane–Isooctane System

With the NE–IO system, a basic test for the applicability of the technique was performed. To check for possible systematic effects of adding seed

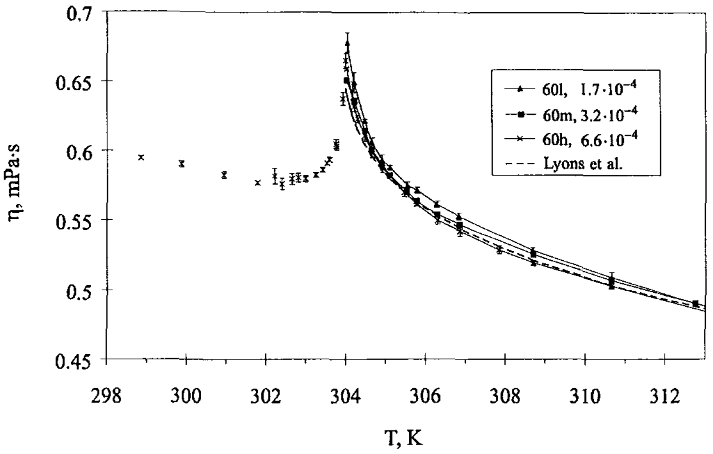

Fig. 1. Apparent viscosities measured in the nitroethane–isooctane system for various particle concentrations.

particles to any fluid, and especially to binary mixtures near the critical point, a variation of particle concentration is essential. At an angle of incidence of 60° three particle volume fractions Φ, 1.7×10^{-4} (denoted with "1"), 3.2×10^{-4} (m), and 6.6×10^{-4} (h), were used. The results are plotted in Fig. 1, from which it is apparent that the measured viscosity is essentially independent of particle concentration. The figure also includes the results of earlier DLS measurements by Lyons et al. [14]. For one measurement series, experimental data below the critical point are shown, where there is a separation into two phases, each with a different composition, which also exhibit critical behavior.

In the evaluation of the experimental results, the definition of viscosity requires some care. In Fig. 1 apparent viscosities are plotted, which were deduced from a straightforward application of the Stokes–Einstein law, Eq. (8), with a fixed particle radius. With the observation of particle motion near critical consolute points, there has been indication that the effective radius is increased due to effects of a correlated layer around the particles [17–19], where the thickness of the layer may be coarsely approximated by ξ, the characteristic length scale in critical systems. Accordingly, a modified radius $r + \xi$ has been used for further evaluation, where ξ has been calculated from Eq. (3) with a value $\xi_0 = 0.242$ nm taken from the literature [20]. These effective viscosity data were fit to a function of the form

$$\eta_{\mathrm{eff}} = A\left(\frac{T - T_{\mathrm{c}}}{T_{\mathrm{c}}}\right)^{-y} \exp\left(\frac{B}{T}\right) \tag{12}$$

with four free parameters, A, B, T_c, and y, with the final goal to determine $y = \nu z$. This approach turned out to be necessary, as a reliable determination of the background viscosity, unaffected by critical effects, would require study of a wide range of temperatures far away from the critical point. Moreover, factor A includes the amplitude Q, which is not known a priori. Yet, to improve the relevance of the fit regarding the background determination, a data point obtained in the 60h series at a temperature 20 K above critical was included in all fits. This auxiliary point was assigned a relative weight of 0.05, compared with a weight of unity for all other data points in the other series. The results of the fits are summarized in Table I.

The mean value of 0.037 obtained for the exponent y is below the expected theoretical value of 0.040. Accordingly, it is smaller than most experimental results on binary mixtures by other techniques [21, 22] and the value of approximately 0.043 obtained recently in a space experiment on xenon [23]. It is obvious, however, that a fit to four free parameters is highly sensitive to experimental error. Moreover, the exact thickness of the assumed correlated layer around the particle plays an important role in approaching the critical point. For example, the calculated thickness is more than 35 nm for $T - T_c = 0.1$ K and, thus, a significant portion of the particle radius. If the layer thickness were based on a value of $\xi_0 = 0.22$ nm, which may be deduced from experiments reported by Anisimov [10], a value of $y = 0.040$ would result.

Table I. Parameters Obtained for the Fits of Viscosities in the NE–IO System and Mutual Diffusion Coefficients in the TEA H_2O System to Eqs. (12) and (13), Respectively

η (NE–IO)[a]					D_{12} (TEA H_2O)[b]			
Series	A (mPa · s)	B (K)	T_c (K)	y	Series	C (10^{-15} N · K^{-1})	T_c (K)	r
30s	0.009	1221	303.74	0.028	60s	8.2	291.50	0.657
60sl	0.027	856	303.66	0.039	90pw	7.0	291.37	0.616
60sm	0.016	1035	303.71	0.024	90pl	8.1	291.43	0.649
60sh	0.022	919	303.60	0.037	90pm	7.3	291.45	0.628
90p	0.054	620	303.55	0.052	90ph	7.7	291.45	0.633
90s	0.027	853	303.46	0.041	90s	7.0	291.37	0.637
Mean	0.026	917	303.62	0.037	Mean	7.5	291.43	0.637
σ	0.016	201	0.11	0.010	σ	0.5	0.05	0.015

[a] Nitroethane isooctane.
[b] Triethylamine–water.

The presence of surface layers has been discussed in connection with aggregation effects of particle dispersions in mixtures near the critical point [19, 24]. In their DLS experiments, Gallagher et al. [24] found no evidence for the formation of a layer of significant thickness preceding the aggregation of polystyrene particles in a lutidine–water mixture. Although that study was devoted to the understanding of particle aggregation and carried out for a different system, generally, the questions for the existence and the actual thickness of a correlated layer in these types of system do not seem to be completely answered yet. If one did not take a surface layer into account, a value of $y = 0.066$ would result from a direct fit to Eq. (12).

In this context, it should be pointed out that we have not observed any signs of particle aggregation in the NE–IO system, which should result in slow components in the ACF (cf. next section). In fitting the experimental ACFs, increasing deviations from a single exponential became evident as the critical point was approached. A component with a faster decay evolved, which may be attributed to binary fluctuations. The amplitude of this component was low, however, namely, of order below 2% compared with the particle signal. Thus, the central problem with DLS viscosity measurements in the NE–IO system is connected with questions of a layer around the particles, which may be clarified by measurements with different particle sizes.

4.2. Triethylamine–Water System

For the TEA–H_2O system, the central question is the influence of the particles added on the diffusivities measured in the vicinity of the critical point. Thus, we start the discussion with the mutual diffusion coefficients measured as a function of the particle concentration, including a series without any particles added (90rw). Measurements were performed at particle volume fractions of 1.4×10^{-4} (l), 2.1×10^{-4} (m), and 3.8×10^{-4} (h). The data, shown in Fig. 2, exhibit a good agreement, especially approaching the critical point. Uncertainties and deviations are larger at lower temperatures due to the weak scattering amplitudes there.

In analyzing the field ACFs for both diffusivities and viscosities, however, we encountered a puzzling situation. Instead of the two components expected, there was a distinct third component. Fits clearly became worse when leaving out this additional term. The temperature dependence of the decay rates is shown in Fig. 3. Apart from the fastest component (rate 1), which could be clearly connected with the mutual diffusion coefficient, and the slowest component due to particle diffusion (rate 3), which of course did not exist in mixtures without particles added, a component with a medium decay rate (rate 2) evolved in all of our measurements,

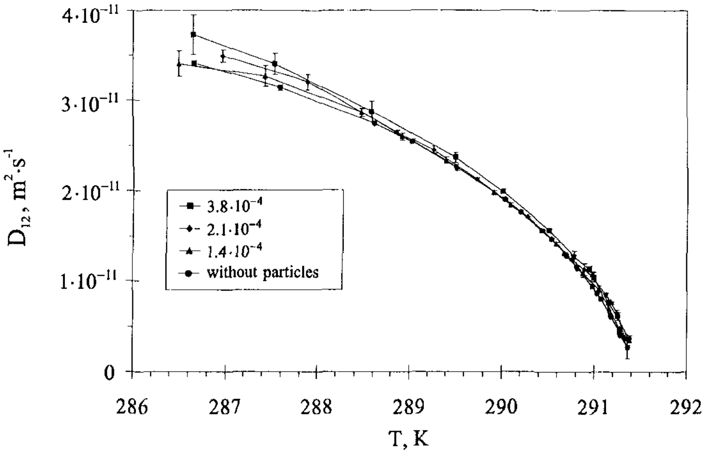

Fig. 2. Mutual diffusion coefficients measured in the trietylamine–water system for various particle concentrations.

including those without particles added. This contribution could also be observed for a wide range of system compositions, even in adding small amounts (a couple of %, v/v) of one component into the other. From Fig. 3 and the experiments without particles, it can be seen that the decay rate of this fluctuation is fairly constant with increasing temperature, until it shows

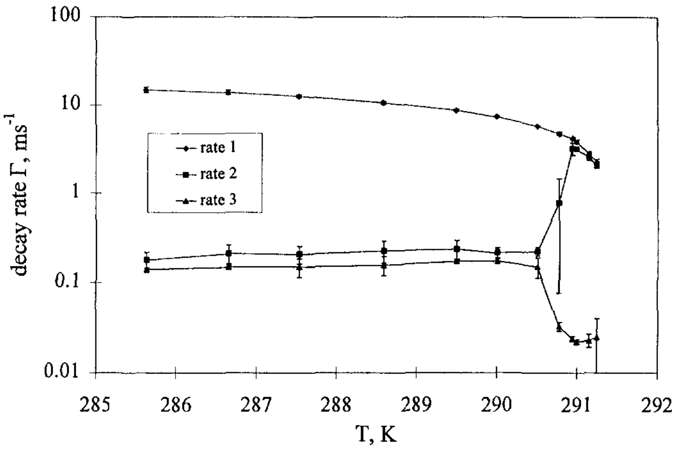

Fig. 3. Typical experimental decay rates observed in the trietylamine–water system. Rate 1 may be identified with mutual diffusion, and rate 3 with particle diffusion. Rate 2 of unknown origin is present also in a mixture without particles added.

a sharp increase, close to the critical temperature, where the additional component is hardly discernible from the diffusivity signal due to the low amplitude and a very similar decay rate. Regrettably, we cannot give an explanation for this experimental result, but can only rule out several possible interferences, such as a doubly scattered signal or impurities, as double scattering should result in larger decay rates [25] and no signals from other substances could be observed in the pure liquids.

In analyzing the signal from particle diffusion, we observe a fairly constant value a few Kelvins away from the critical point and a marked decrease in the vicinity of the critical point, until finally the component cannot be evaluated reasonably due to the low amplitude relative to the signal from fluctuations in concentration. The corresponding marked decrease in apparent viscosity is contradictory to the small critical enhancement expected. The effect may thus be better described in terms of a variation of an effective particle diameter and particle aggregation, which has also been observed in other systems near the critical point (e.g., Refs. 19 and 26]). From these experiments, it has been found that due to an increasing interaction of particles and a solvent component in approaching the critical point, there may be a solvent layer with increasing thickness and, finally, a reversible particle flocculation. Accordingly, we observed a fairly constant apparent diameter a few Kelvins away from the critical point, which could be reproduced after changing the temperature and giving the system time to equilibrate, and a marked increase in the apparent diameter when adding TEA to a dispersion of particles in pure water (the particles strongly aggregate in pure TEA).

Despite the problems in measuring the viscosity of the system and the unknown origin of the third decay rate, we attempted to evaluate the critical exponent of the decay rate in binary diffusion. Since our measurements are essentially in the range $q\xi < 1$, the evaluation did not have to take into account q-dependence of the decay rate according to Eq. (10), but could be restricted to a fit of the form (Table I),

$$\Delta D_{\mathrm{c}} = \frac{CT}{\bar{\eta}} \left(\frac{T_{\mathrm{c}} - T}{T_{\mathrm{c}}} \right)^{r} \tag{13}$$

where the data for the background viscosity were taken from the literature [27]. In the regime $q\xi < 1$, however, the background diffusivity may become relevant [14, 21], which we tried to account for by adding an additional term in the fit with a low adjustable amplitude and an additional fixed exponent, which should be close to 1.3 [4, 14, 21]. It was found, however, that this fit had too many parameters and that the values for r obtained were only marginally different from these without an additional background. Thus, we left out the background and obtained an average value of $r = 0.64$, which is close to the theoretically expected value of $\nu(1+z) = 0.67$, even though the difference is larger than the standard deviation of our results. Thus, even with particles aggregating in the vicinity of the critical point and a setup not especially designed for measurements in the vicinity of the critical point, the critical behavior of the mutual diffusivity may be reasonably measured.

Finally, from the amplitude $C = Rk_B/[6\pi\xi_0(Q\xi_0)]^z$ we may obtain an estimate for $\xi_0(Q\xi_0)^z$ or, as $(Q\xi_0)^z \approx 1$, for the correlation length amplitude ξ_0. We find $\xi_0 = 0.10$ nm, which agrees with other reported values in the range between 0.09 and 0.13 nm [28].

5. CONCLUSION

Our preliminary attempt to determine both the dynamic viscosity and the mutual diffusion coefficient in binary liquid mixtures near the critical consolute point by various applications of dynamic light scattering has been only partly successful. We have demonstrated through measurements on the NE–IO system that, in principle, the viscosity may be determined via the measured particle diffusion coefficient, yet final statements cannot be made due to unknown effects of possible correlated layers around the dispersed particles. Thus, future work should focus on the use of particles of different size. Additionally, the employment of a setup especially designed for measurements in the vicinity of the critical point should be helpful. Determination of the viscosity in the TEA–H_2O system was not possible due to particle aggregation. Moreover, all measurements showed an additional component, for which no explanation can be given. These two points require further research. Despite these difficulties, the critical behavior of the mutual diffusivity could be described well and was not influenced over the range of concentrations of particles added. Confirmation of these findings closer to the critical point is of further interest.

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