MUTUAL DIFFUSION COEFFICIENT AND DYNAMIC VISCOSITY NEAR THE CRITICAL CONSOLUTE POINT PROBED BY DYNAMIC LIGHT SCATTERING[1]

S. Will[2,3] and A. Leipertz [2]

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2 Lehrstuhl für Technische Thermodynamik (LTT), Friedrich-Alexander-Universität Erlangen-Nürnberg, Am Weichselgarten 8, D-91058 Erlangen, Germany

3 Author to whom correspondence should be addressed.

ABSTRACT

The possibility of applying dynamic light scattering to a simultaneous determination of the mutual diffusion coefficient and the viscosity of binary liquid systems near the critical consolute point was studied. For the measurement of the viscosity seed particles are added to the system, for which the particle diffusion coefficient is obtained. In a critical mixture of nitroethane and isooctane with a small difference in refractive indices of the components this approach allowed a determination of the viscosity. In contrast, particle aggregation prevented a determination of the viscosity in 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 without an noticeable influence of 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 should not influence the system under investigation. An external gradient applied 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 thermal equilibrium and only rely on low-power illumination have found ample application in this field for a considerable time [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 a determination of the correlation length ξ of critical fluctuations from the diffusion coefficient and for a direct measurement of the weak critical enhancement of the dynamic viscosity η an accurate technique for the determination of this property is desired. Conventionally, for this goal capillary viscometers and oscillatory techniques are employed. Besides the fundamental problem that these methods require an external driving force, which may result in a non-negligible dissipation of energy, influences of shear rate and driving frequency may become relevant [6]. Alternatively, dynamic light scattering has been successfully used for the measurement of liquid viscosity via the determination of the diffusion coefficient of dispersed seed particles [7-9].

It is the aim of this paper to investigate if the viscosity of a binary fluid mixture in the vicinity of a critical consolute point can also be determined by dynamic light scattering (DLS). As this technique offers the possibility of a simultaneous determination of various properties, especially of mutual diffusion and viscosity [8, 10], a further goal of the work is to check if such measurements can be performed near a critical consolute point. This possibility would be an highly desirable achievement, because a direct connection between diffusivity and correlation length could be realised and the determination of either transport property, mutual diffusion coefficient and viscosity, could be performed for truly identical boundary conditions, namely temperature and composition, and in an cost- and time-saving

way. This work is intended only as a first step to investigate the basic possibilities and restrictions of such an approach.

2. THEORETICAL BACKGROUND

2.1. Mutual Diffusion and Viscosity Near the Critical Consolute Point

This section is restricted to a brief survey about the behaviour of mutual diffusivity and viscosity near a critical consolute point. A rigorous and comprehensive treatment may be found in several reviews [11, 12].

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

$$D_{12} = \overline{D} + \Delta_c D \,. \tag{1}$$

The critical part can be represented in form of a Stokes-Einstein law,

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

with an universal amplitude R close to unity, Boltzmann´s constant k_B and temperature T. In the limiting case of wave numbers $q \to 0$ of the fluctuations investigated the critical part vanishes at the critical point, dominated by the power-law behaviour 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 $\varepsilon = |T\text{-}T_c| / T_c$ with critical temperature T_c, and ν is an universal exponent with $\nu = 0.63$. As light scattering investigations cannot probe a system in the true q=0 limit, in general modifications to Eq. (2) will become relevant, which may have substantial implications for the decay rates of the fluctuations observed. This generalisation will be discussed in section 2.2. An evaluation of the background contribution reveals that this term is most important at large wave vectors q [13]. In practical light scattering investigations, however, it turns out that this contribution is small [13], i.e. of order 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 form of a multiplicative expression,

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

where $\overline{\eta}$ is a background viscosity, which in a simplest case can be given in form of an Andrade equation $\overline{\eta} = \overline{A}\exp(B/T)$, Q is a system-dependent amplitude and z is an universal exponent, where the currently adopted theoretical value is z=0.063 [12]. Combining Eqs. (3) and (4) results in a power-law behaviour of the viscosity $\eta \propto \varepsilon^{-0.040}$. Although in the domain between a normal and critical behaviour of the viscosity a crossover function has to be introduced for a correct description of the dependence of viscosity on temperature, it is found that even the simple form of Eq. (4) is adequate for a determination of the exponent z [13].

2.2. Dynamic Light Scattering

Dynamic light scattering analyses 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 normalised 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 like a deviation from a perfectly coherent registration. The decay rate is proportional to desired diffusivity D,

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

where q is the modulus of the scattering vector, with

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

which determines the wave number of the fluctuations investigated and which is given by 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 or with the particle diffusion coefficient D_p of suspended particles, respectively. For the determination of the viscosity η ideally

monodisperse and spherical particles of radius r are dispersed in a liquid or liquid mixture, where the viscosity follows from 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 either fluctuation,

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

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 [14] that the critical part $\Delta_c\Gamma_{12}$ of the decay-rate does not vanish in coming close to the critical point but approaches a fairly constant value. The reason is that with increasing correlation length ξ in the vicinity of the critical point there is a deviation from the true $q\xi\rightarrow 0$ limit underlying these simplified relations. For the critical part $\Delta_c\Gamma_{12}$ of the decay rate fluctuations a generalised Stokes-Einstein formula has to be used, which may be represented by [14]

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

where K(x) is the Kawasaki function

$$K(x) = \frac{3}{4x^2}[1 + x^2 + (x^3 - x^{-1})\,\mathrm{a}\tan x] \tag{11}$$

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

3. EXPERIMENTAL

3.1. Materials and Sample Preparation

In order to test the possibility of measuring viscosities via the particle diffusion coefficient near a critical consolute point a mixture of nitroethane (NE) and isooctane (IO, 2,2,4-trimethylpentane) was chosen as a first system of investigation, as it had been done in an early work by Lyons et al [15]. As the refractive indices of theses 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 for a wide range of temperatures to measure the particle diffusion coefficient without an 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≈303 K. Either substance had a specified purity of 99.8% and was used as delivered. As the system is sensitive to humidity, all glass containers used were filled with a protective argon atmosphere and closed immediately.

For a test of a simultaneous determination of mutual diffusion and viscosity a mixture if triethylamine (TEA, purity 99.9%) and water (milli-Q-quality) had been chosen. The system exhibits an lower consolute point at a concentration $c_{TEA,\ wt.}$= 0.321 and a temperature T_c= 291 K.

In either case industrially produced silica particles with a standard deviation in particle size of clearly below 10% were used as a seed. In the case of the NE-IO system the particles had been surface-modified by grafted methylacrylate chains, for the other system native particles were used. Particle diameters had been determined by DLS in ethanol or water with values of 216 nm 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 0.45µm pore size to remove possible residual agglomerates and dust. Mixtures were directly prepared in sample cuvettes by adding defined volumes of the individual cuvettes with a precision pipette.

2.2. Light-Scattering System and Experimental Procedure

The light-scattering system is based on a newly developed scattering cell which utilises the principle of a symmetrical setup and is described in detail elsewhere [16]. With a symmetrical setup the cuvette is tilted form 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 a determination of the scattering vector feasible without having to know the refractive index of the sample; only that 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 the refractive index of which closely matches that of the glass material used. The sample temperature is measured directly by a calibrated Pt-100-resistance probe immersed with an absolute uncertainty of better than 0.05 K. The oil is temperated 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 Another restriction is that the external lab thermostat could only be regulated 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 first basic tests.

At a given temperature usually six single experimental runs with a typical duration of ten minutes were carried through. In the case of the NE-IO system the signal from particle diffusion clearly dominated so that an single exponential could be well fitted by a non-linear fit algorithm described previously [17]. With the TEA-H_2O system a non-linear 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 with "s") and additional with a "conventional" rectangular geometry (90r), where refractive index data were taken from the literature.

3. RESULTS AND DISCUSSION

3.1. Nitroethane-Isooctane System

With the NE-IO system a basic test for the applicability of the technique was to be performed. In order to check for possible systematic effects of adding seed 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° we have used three different particle volume fractions Φ of 1.7×10^{-4} (denoted with "l"), 3.2×10^{-4} (m), and 6.6×10^{-4} (h). The results are plotted in Fig. 1, from which it may be inferred that the measured viscosity is essentially independent of particle concentration. The figure also includes the results of earlier DLS measurements by Lyons et al. [15]. For one measurement series also experimental data below the critical point are shown, which indicate that there is not a full separation into the individual components, but a mixture, naturally with a different composition, which exhibits critical behaviour, too. The data were fitted to a function of form

$$\eta = A\left(\frac{T - T_c}{T_c}\right)^{-y} \exp\left(\frac{B}{T}\right), \tag{12}$$

with four free parameters A, B, T_c, and y with the final goal of a determination of $y = \nu\cdot z$. This approach turned out to be necessary, as a reliable determination of the background viscosity unaffected by critical effects would require to cover a wide range of temperatures far away from the critical point. Moreover, the factor A includes the amplitude Q, which is not known a priori. The results of the fits are summarised in Table I. Although it is obvious that a fit to four free parameters is highly sensitive to experimental errors, the value obtained for the exponent y is clearly above the expected theoretical value of 0.040. The reasons for this discrepancy remain obscure. In fitting the experimental ACFs increasing deviations from a single exponential became evident in approaching the critical point. A component with a faster decay evolved, which may be attributed to binary fluctuations. The amplitude of this component was small, however, namely of order below two percent as compared with the particle signal. Additionally, for an explanation of an more pronounced enhancement of the viscosity an additional slow component would be necessary, which

might be due to effects like particle aggregation. Although a possible aggregation is conceivable (cf. next section), no distinct slow components in the ACF could be detected.

3.2. Triethylamine-Water System

For the TEA-H_2O system the central question is that for 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 particle concentration, where besides 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 in approaching the critical point, uncertainties and deviations are larger at lower temperatures due to the weak scattering amplitudes there.

In analysing the field ACFs for both diffusivities and viscosities, however, we encountered a puzzling situation. Instead of two components expected there was a distinct third component, and fits clearly became worse when leaving out this additional term. The temperature dependence of the decay rates observed 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 vanished in mixtures without particles added, a component with a medium decay rate (rate 2) evolved in all of our measurements, also in 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 one. From Fig. 3 and experiments without particles it can be seen that the decay rate of this fluctuation is fairly constant with increasing temperature, until it shows a sharp increase, where close to the critical temperature the additional component can be poorly determined and is hardly discernible from the diffusivity signal due to the small amplitude and a very similar decay rate. Regrettably, we cannot give an explanation for this experimental result, but only can rule out several possible interferences, like a doubly scattered signal or impurities, as

double scattering should result in larger decay rates [18] and no signals from other substances could be observed in the pure liquids.

In analysing the signal from particle diffusion we observe a fairly constant value a few K away from the critical point and a marked decrease in approaching the vicinity of the critical point, until finally the component cannot be evaluated reasonably due to the small amplitude as compared with 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, which has also been observed by different optical methods in other critical binary systems (e.g., [19, 20]). 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 an apparent diameter some tens of percent above the nominal value a few K 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 drawback 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. As 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 form (Table I)

$$\Delta D_c = \frac{CT}{\overline{\eta}}\left(\frac{T_c - T}{T_c}\right)^r , \qquad (13)$$

where the data for the background viscosity were taken from the literature [21]. 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 small adjustable amplitude and an additional fixed exponent, which should be close to 1.3 [4, 14, 21]. It was found, however, that this fit was clearly overparametrised and that the values for r obtained were

only marginally different from these without an additional background. Thus, we left out the background and resulted in an average value of r=0.64, which is close to the theoretically expected value of $\nu(1+z) = 0.67$, even when 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 behaviour of the mutual diffusivity may be reasonably measured.

Finally, from the amplitude $C = R\,k_B / [6\pi\xi_0(Q\xi_0)]^z$ 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, with $\xi_0 = 0.10$ nm, which agrees with other reported values in the range between 0.09 nm and 0.13 nm [22].

4. CONCLUSION

In our preliminary study the 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 only been partly successful. We have demonstrated through measurements in the NE-IO system that basically the viscosity may be determined via the particle diffusion coefficient measured, yet our data result in an critical exponent clearly above the value expected. Thus, future work here should try to reveal the reasons for this discrepancy. Both the employment of a setup especially designed for measurements in the vicinity of the critical point and including the crossover behaviour of the viscosity in the evaluation, which requires the knowledge of more system data, should be helpful. The determination of the viscosity in the TEA-H_2O system was prohibited by particle aggregation. Moreover, all measurements showed an additional component, for which no explanation can be given. These two points are the central topic of further research in this context. Despite these difficulties the critical behaviour of the mutual diffusivity could be described well and without a significant influence by various concentrations of particles added. A confirmation of these findings closer to the critical point is another point of further interest.

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Table I: Parameters obtained for the fits of viscosities in the NE-IO system and mutual diffusion coefficients in the TEA-H_2O to Eqs. (12) and (13), respectively.

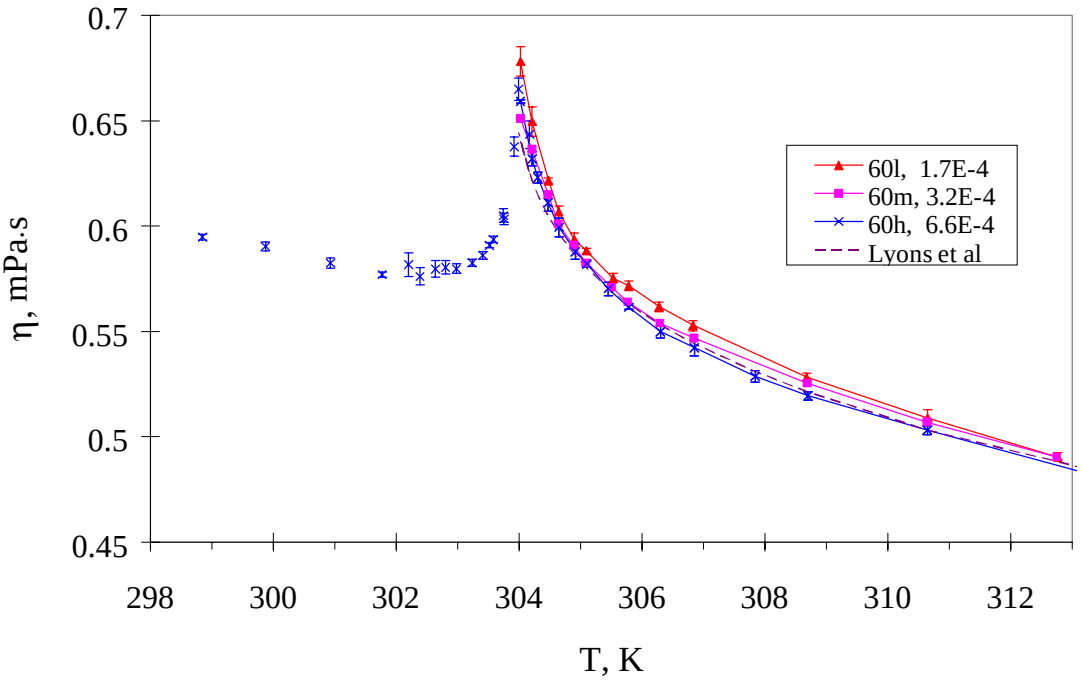
η NE-IO					D_{12} TEA-H_2O			
Series	A (mPa·s)	B (K)	T_c (K)	y	Series	C (10^{-15}N·K^{-1})	T_c (K)	r
30s	0.036	1014	303.89	0.068	60s	8.2	291.50	0.657
60sl	0.051	904	303.83	0.068	90pw	7.0	291.37	0.616
60sm	0.046	950	303.93	0.058	90pl	8.1	291.43	0.649
60sh	0.039	987	303.80	0.067	90pm	7.3	291.45	0.628
90p	0.047	924	303.81	0.071	90ph	7.7	291.45	0.633
90s	0.040	985	303.71	0.066	90s	7.0	291.37	0.637
mean	0.043	961	303.83	0.066	mean	7.5	291.43	0.637
σ	0.006	42	0.07	0.004	σ	0.5	0.05	0.015

FIGURE CAPTIONS

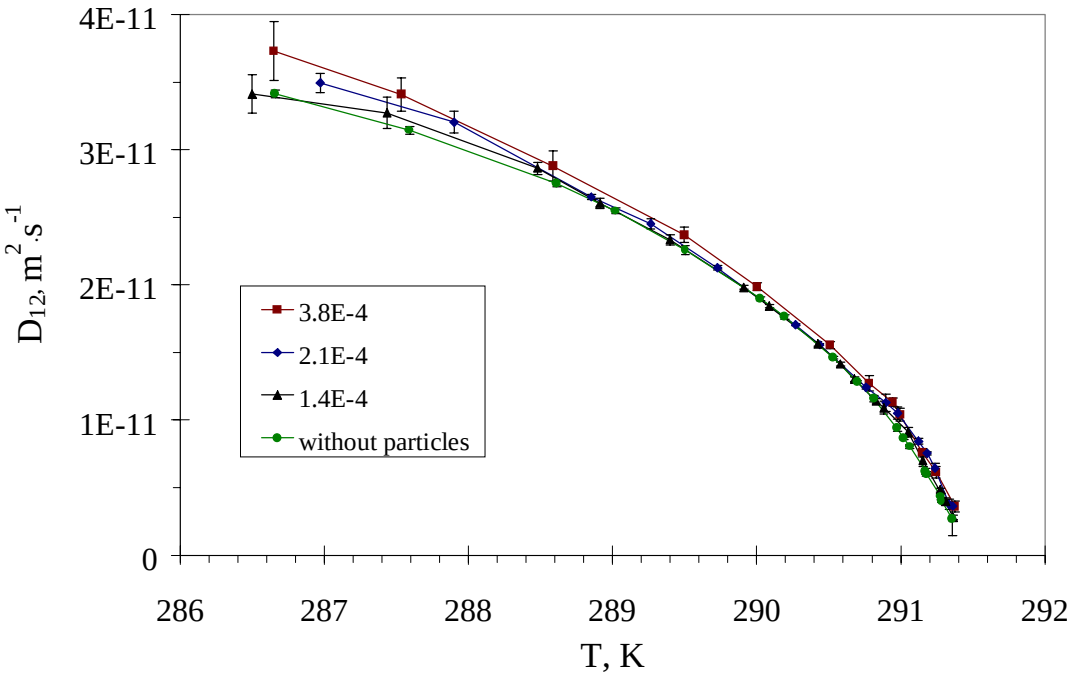
Fig. 1 Visosities measured in the NE-IO system for various particle concentrations.

Fig. 2 Mutual diffusion coefficients measured in the TEA-H_2O system for various particle concentrations.

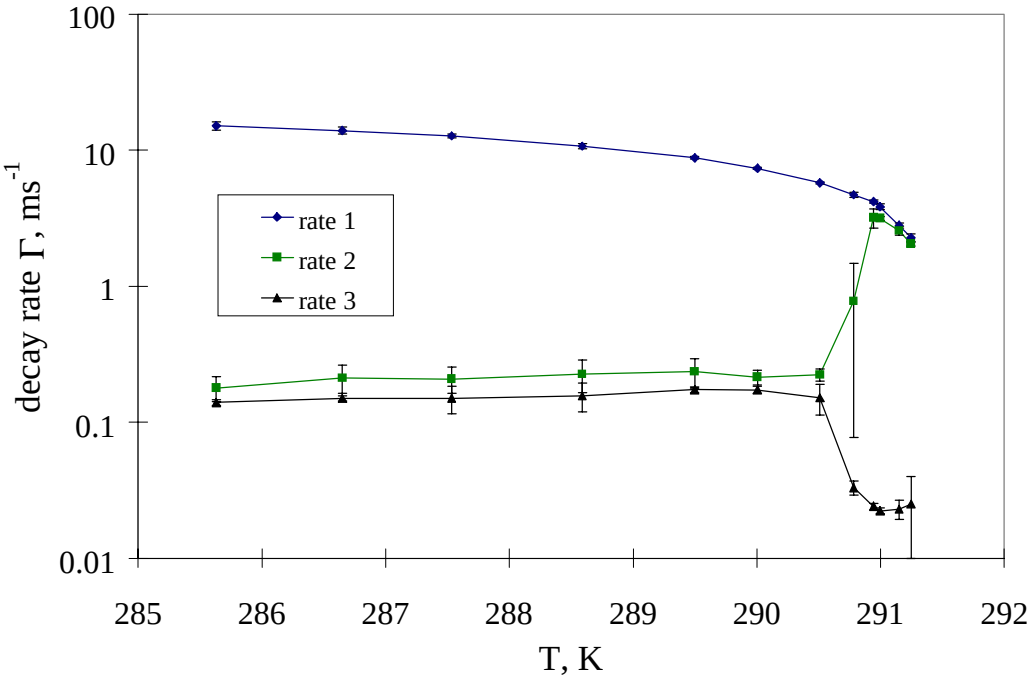
Fig. 3 Typical experimental decay rates observed in the TEA-H_2O system. Rate 1 may be identified with mutual diffusion, rate 3 with particle diffusion. Rate 2 of unknown origin is present also in a mixture without particles added.



Will, Leipertz, Fig. 1



Will, Leipertz, Fig. 2



Will, Leipertz, Fig. 3