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Measurement of Diffusion in Ternary Liquid Mixtures by Light Scattering Technique and Comparison with Taylor Dispersion Data

D. A. Ivanov · J. Winkelmann

Abstract Results of diffusion coefficient measurements by dynamic light scattering (DLS) in the ternary liquid systems, glycerol–acetone–water (GAW), and cyclohexane–methanol–toluene (CMT), are reported. Data for the GAW system are compared with Taylor dispersion (TD) measurements in overlapping concentration regions close to the critical solution point at 298.15 K. A fit of the intensity autocorrelation function (ACF) could be used to predict values and explain the physical character of the corresponding diffusion coefficients. In the vicinity of the critical solution point, the DLS measurements reveal two and more hydrodynamic relaxation modes with well separated characteristic relaxation times. From the ACF, at least two effective diffusivities, D_1 and D_2, can be experimentally determined. Theoretical predictions reveal that they may result from pure mass diffusion and pure thermal diffusion transport processes. A possible physical meaning of the modes D_1 and D_2 in the ternary liquid mixtures is discussed. When we compare the transport modes from DLS with the Taylor dispersion results, only the slowest mode represents mass diffusion, and this mode agrees very well with one of the eigenvalues of Fick's diffusion matrix. There is no relation between the mass diffusion mode from DLS and any one of the four diffusion coefficients obtained by TD.

Keywords Diffusion coefficients · Dynamic light scattering · Taylor dispersion · Ternary liquid mixture

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1 Introduction

Dynamic light scattering (DLS) measurements have proven to be a powerful technique for studying the behavior of transport properties of liquid and liquid mixtures both in the vicinity of a liquid–liquid critical point and also far from it. Therefore, this type of measurement seems superior to classical methods of Fick's diffusion coefficients determination, like Taylor dispersion (TD), using macroscopic concentration gradients. Both the intensity and spectrum of scattered light can be related to the magnitude and the dynamics of fluctuations in thermodynamic variables. The time distribution of light scattered by density and concentration fluctuations in a dense, three-component liquid mixture is calculated from the density and concentration fluctuations predicted by the linearized hydrodynamic equations of irreversible thermodynamics.

In DLS experiments, we obtain the time-dependent intensity autocorrelation function (ACF). The ACF of the scattering light is a superposition of waves scattered from individual scattering centers. This intensity ACF, normalized to the average intensity of the signal, has the form [1],

$$G(q,t) = 1 + \beta_0 S(q,t)^2, \tag{1}$$

where β_0 is a constant depending on experimental conditions and S $(\vec{\mathrm{q}}, \mathrm{t})$ is the dynamic structure factor.

At the critical solution point of a multicomponent liquid mixture, the mass diffusion coefficient vanishes, whereas the thermal diffusivity should not exhibit a significant change in the immediate vicinity of the critical point. Fitting the experimental ACF, we could predict values and explain the physical character of diffusion coefficients. As subjects of the investigations, the systems glycerol (1) + acetone (2) + water (3) (GAW) and cyclohexane (1) + methanol (2) + toluene (3) (CMT) were selected. The GAW-system shows a strong asymmetry of the critical line on the ternary phase diagram as reported by Krishna et al. [2] from liquid–liquid equilibrium measurements of this system. The CMT-system has only a small and rather symmetric miscibility gap at 298.15 K.

The aim of the present study is to perform dynamic light scattering measurements in two ternary liquid mixtures in the vicinity of their respective critical solution points. The different transport modes yield diffusivities, the physical meaning of which has to be identified. Experimental Fick's diffusion coefficients were obtained from Taylor dispersion (TD) measurements in an overlapping range of concentration to compare diffusivity modes from DLS with macroscopic Fick's diffusion coefficient data.

2 Theory

2.1 Measurements of the Autocorrelation Function

The motion of solute molecules in a liquid mixture can be studied by real-time fluctuations in terms of the intensity time-correlation function $G^{(2)}(\tau)$ of the scattered light, which provides information about hydrodynamic transport properties of the solute, such as diffusion coefficients. The ACF of a quantity describes the time scales, on which changes in this quantity take place, and thus conclusions on the underlying transport behavior can be drawn. Basically, these fluctuations affect the ACF of the electric field $G^{(1)}(\tau)$, which may become a sum of two or even more exponential terms [1],

$$G^{(1)}(\tau) = A_{\mathrm{S}} \exp(-\tau/\tau_{\mathrm{T}}) + A_{\mathrm{C}} \exp(-\tau/\tau_{\mathrm{c}}) \tag{2}$$

The terms τ_{T} and τ_{c} are the characteristic decay times of the temperature and concentration fluctuations, and A_{S} and A_{C} are the corresponding amplitudes.

After normalization of the intensity, we find for the second-order ACF, $G^{(2)}(\tau)$,

$$G^{(2)}(\tau) = 1 + (I_{\mathrm{S}} \exp(-\tau/\tau_{\mathrm{T}}) + I_{\mathrm{C}} \exp(-\tau/\tau_{\mathrm{c}}))^2 \tag{3}$$

where I_{S} and I_{C} are the intensities due to scattering caused by entropy and concentration fluctuations, respectively. From Eq. 3, we can extract both the contributions from thermal diffusion and the mass diffusion coefficient by extrapolation to zero wave vector q:

$$D_{\mathrm{T}} = \lim_{q\to 0}\left(1/q^2\tau_{\mathrm{T}}\right) \quad \text{and} \quad D_{\mathrm{m}} = \lim_{q\to 0}\left(1/q^2\tau_{\mathrm{C}}\right) \tag{4}$$

2.2 Calculation of Dynamic Structure Factor

In the general case of a multicomponent liquid mixture, the fluctuations in the local dielectric constant are related to fluctuations in local thermodynamic quantities such as the pressure, concentration, and temperature. Our theoretical model is based on the linearized hydrodynamic equations and follows the methods, suggested by Landau [3], and later by Mountain and Deutch [4], for binary mixtures. We extend and generalize these equations to the ternary-liquid-mixture case [5].

Let us consider the special case of a system with uniform pressure, and consequently, only the temperature and concentration fluctuate. This model is described by the following set of equations:

$$\begin{cases} \frac{\partial c_1}{\partial t} = D_{11}\left(\Delta c_1 + \frac{D_{12}}{D_{11}}\Delta c_2 + \frac{k_{T1}}{T_0}\Delta T\right) \\ \frac{\partial c_2}{\partial t} = D_{22}\left(\frac{D_{21}}{D_{22}}\Delta c_1 + \Delta c_2 + \frac{k_{T2}}{T_0}\Delta T\right) \\ \frac{\partial T}{\partial t} - \frac{k_{T1}}{C_P}\left(\frac{\partial \mu_1}{\partial c_1}\right)_{C_2,P,T} \cdot \frac{\partial c_1}{\partial t} - \frac{k_{T2}}{C_P}\left(\frac{\partial \mu_2}{\partial c_2}\right)_{C_1,P,T} \cdot \frac{\partial c_2}{\partial t} = \kappa \Delta T \end{cases} \tag{5}$$

In these equations, T is the temperature, D_{ij}'s are the coefficients of Fick's diffusion matrix, k_{Ti} is the thermal diffusion ratio, C_P is the heat capacity at constant pressure, κ is the coefficient of thermal conductivity, and μ_i and c_i are the chemical potential and concentration of component i of the mixture, accordingly.

Rewriting the set of linearized hydrodynamic equations in terms of T, c_1, and c_2, and performing a Fourier–Laplace transform, we obtain this set in matrix form as an extension to the binary solution case developed by Mountain and Deutch [4];

$$M \cdot \hat{N}(q, z) = T \cdot N(q), \tag{6}$$

where $\hat{N}(q, z)$ is a column vector with elements $c_1(q, z), c_2(q, z), T(q, z)$.

The general structure of the solution of Eq. 6 is [5]

$$\hat{N}_i(q, z) = \frac{\sum_j P_{ij}(q, z) N_j(-q)}{\det\left(M(q, z)\right)}, \tag{7}$$

where P_{ij} is an algebraic function in i and j.

The equilibrium modes of the spectrum of scattered light are the roots of the dispersion equation; they will be obtained from $\det(M)$ (for details, see [5]). We can find approximate roots of the determinant when we consider the conditions of a typical light scattering experiment. With $\vec{q} \approx 10^5 \text{cm}^{-1}$ and the adiabatic speed of sound $\text{c} \approx 10^5 \text{cm} \cdot \text{s}^{-1}$, small dimensionless parameters $\left(\kappa q^2/c\right)$ and $\left(D_{ij} q^2/c\right)$ are of the order of 10^{-2} and 10^{-4}, respectively. In this approximation, when quadratic terms of the first quantity $\left(\kappa^2 q^4/c^2\right)$ and cross terms $\left(\kappa D_{ij} q^4/c^2\right)$ are retained, and terms with $\left(D_{ij}^2 q^4/c^2\right)$ are omitted, we obtain for the determinant of the matrix M,

$$\det\left(M\left(q, z\right)\right) = -c^2 (z + z_1)(z + z_{2,3})^2, \tag{8}$$

These three roots describe the width of the Rayleigh component of scattered light, which contains the combined effects of both temperature and concentration fluctuations of the solute component in a liquid mixture. From the results of Eq. 8, we derive a final expression for the dynamic structure factor, which can be written as (9)

$$S\left(q, t\right) = A_1 \mathrm{e}^{-z_1 t} + 2A_2 \mathrm{e}^{-z_{2,3} t}, \tag{9}$$

In general, the Rayleigh peak cannot be simply considered as the superposition of two Lorentzians, the first arising only from thermal diffusivity and the second only from mass diffusion. However, these equations are correct under the following conditions. First, the fluctuations can be described by the usual system of the linearized hydrodynamic equations. In the linearized theory, the deviations of thermodynamic variables about equilibrium are small. Second, the dimensionless parameters $\left(\kappa q^2/c\right)$, and $\left(D_{ij} q^2/c\right)$ are required to be small.

3 Results

Using the instrumental setup, as described in [6,7], we obtain the intensity ACF as a function of the lag time τ. In binary mixtures and some ternary systems, a single-exponential decay in the ACF was found and associated with a mass diffusion mode. For the first time in a ternary mixture, we observe in both GAW and CMT systems, a double-exponential decay in the ACF. We applied the discrete algorithm by Provencher

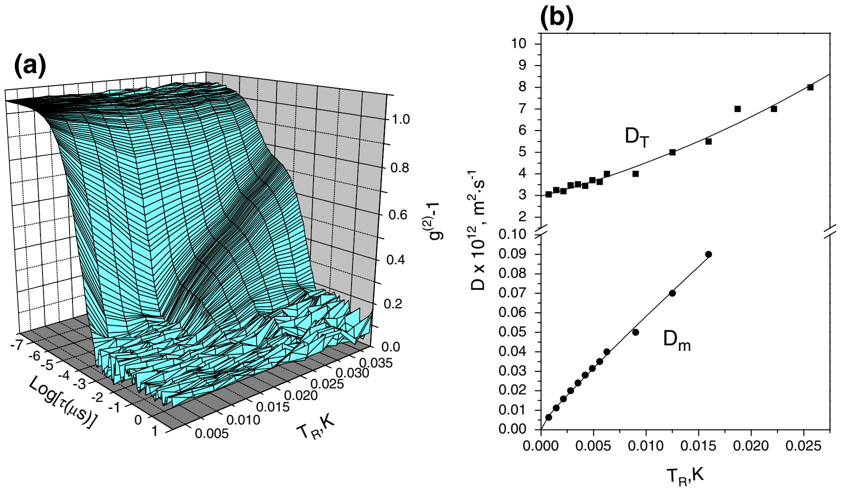

Fig. 1 Glycerol + acetone + water (GAW) system: (**a**) ACF versus temperature difference $T_R = T - T_c$ and lag time τ [6] and (**b**) two transport modes extracted from this ACF as a function of the temperature difference $T_R = T - T_c$ [5,6]

[8] to calculate the linewidth Γ of each mode and the corresponding diffusivities. For the GAW system, we find behavior as shown in Fig. 1a. The three-dimensional (3-D) plot clearly reveals that two separate modes with quite different dependencies on the reduced temperature are obtained. Far from the critical point, it shows double-exponential decay, while on approaching T_c, the second slow process disappears. This is the first time that in a ternary liquid mixture both fast and slow transport modes were found, well separated from each other and with different critical behavior.

In their studies, Anisimov et al. [9–11] show that in the asymptotic vicinity of the critical point, the mass diffusion coefficient reduces to

$$D_{\mathrm{ii}} = \frac{kT_{\mathrm{c}}}{6\pi \eta_{\mathrm{s}} \xi} \tag{10}$$

and vanishes at T_c as ξ^{-1}. From Eq. 10, it follows that both main terms of Fick's diffusion matrix in the asymptotic vicinity of the critical point will become equal.

Mixtures near a critical liquid–liquid consolute point are weakly compressible. Therefore, the thermodiffusion coefficient D_T tends to a finite value,

$$D_{\mathrm{T}} = D_0 \theta x_{\mathrm{c1}} x_{\mathrm{c2}} (1 - x_{\mathrm{c1}} - x_{\mathrm{c2}}) k_{\mathrm{T}}^0. \tag{11}$$

The parameter θ relates the diffusion coefficient D_{ij} far away from the critical point, where $\omega \cong 1$, to $D_{ij,0}$ as $D_{ij} = \theta D_{ij,0}$, and x_c is the critical mole fraction of a mixture.

We find two different transport modes that are associated with thermal diffusion (first time decay) and mass diffusion (second one). These two time exponential modes are defined by coefficients z_1 and $z_{2,3}$ given in Eq. 8. The diffusivity z_1 of the fast mode is associated with the thermal diffusivity D_2, and the diffusivity $z_{2,3}$ of the slow mode is associated with the mass diffusion coefficient D_1:

$$\begin{aligned} z_1 \rightarrow \quad D_2 &= D_{\mathrm{T}} = \frac{\kappa}{\rho_{\mathrm{i}} C_{\mathrm{P}}} \\ z_{2,3} \rightarrow \quad D_1 &= D_{11,22} = \frac{k_{\mathrm{B}} T}{6\pi \eta_{\mathrm{s}} \xi} \end{aligned}, \tag{12}$$

with $D_1 << D_2$ as $(T - T_{\mathrm{c}})/T_{\mathrm{c}} \rightarrow 0$. From Eq. 12, it follows that in the close vicinity of the critical point, the light scattered from a multicomponent liquid system is determined by the fast thermal diffusion mode with $z_1 = D_{\mathrm{T}}$ and amplitude A_1.

When we plot the experimental results for both D_1 and D_2 versus temperature T_{R}, we observe a completely different slope of these two diffusivities as shown in Fig. 1b for the critical composition of the GAW mixture. The $D_1 = D_{\mathrm{m}}$ has a steep descent toward the critical temperature, whereas the $D_2 = D_{\mathrm{T}}$ only slightly decreases towards a finite value. This behavior is very similar to that presented in [9] for the binary methane + ethane mixture.

In the framework of Fick's diffusion matrix for a ternary mixture, where one has two main and two cross diffusion coefficients, the physical meaning of the mass diffusion mode D_{m} obtained by DSL is still an open question. To identify the D_{m} mode, we performed Taylor dispersion (TD) measurements in an overlapping range of concentration [7,12], as shown in Fig. 2a. When comparing the results of the TD and the corresponding DLS measurements, we found that there is no relation between the mass diffusion mode and any one of the four diffusion coefficients obtained by

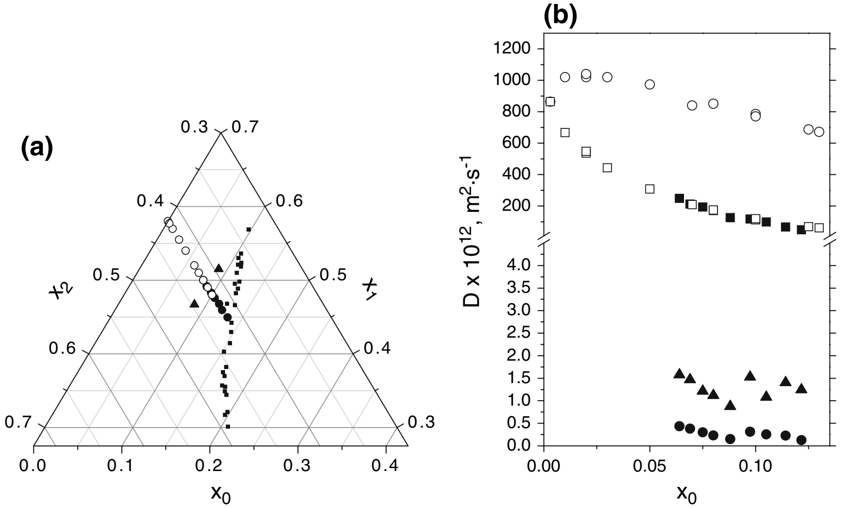

Fig. 2 Comparison of diffusion coefficients from Taylor dispersion and transport modes from DLS versus mole fraction of glycerol in the GAW ternary system: (**a**) fragment of the liquid–liquid phase diagram of the glycerol (0) + acetone (1) + water (2) system at 298.15 K with the concentration paths of the TD (open circles) and the overlapping DLS (full circles) measurements, and; (**b**) eigenvalues of Fick's diffusion matrix (open symbols) from TD and results of the DLS measurements: (■) mass diffusion mode and (▲) thermodiffusion mode

TD. But when we compared the corresponding eigenvalues of Fick's matrix with the transport modes, a striking agreement was observed between the eigenvalue D_1 and the mass diffusion mode D_m, as shown in Fig. 2b. Thus, for the GAW system we conclude that the D_m mode is identical with the lower eigenvalue D_1 of Fick's matrix.

At this stage, it was not clear whether these results are specific to the GAW system or it is part of a more general behavior. Therefore, the studies were extended to a second ternary mixture with liquid–liquid phase separation, cyclohexane (1) + methanol (2) + toluene (3). The corresponding phase diagram is shown in Fig. 3 along with the concentrations investigated by DLS. At concentrations close to the critical solution point, we performed DLS measurements. A temperature scan over a rather large range of $T_R = T - T_C$ revealed a behavior very similar to what was observed in the GAW system close to the critical temperature. Figure 4a shows the ACF, $G^{(2)}(\tau) - 1$, over a range of $0.8 \le T_R \le 2.50$ with two clearly separated transport modes. A numerical

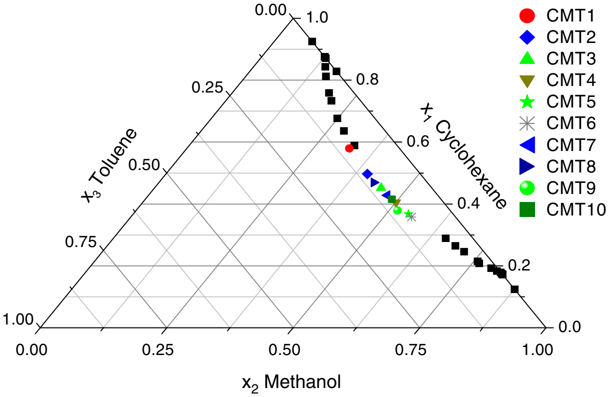

Fig. 3 Liquid–liquid phase diagram of the cyclohexane (1) + methanol (2) + toluene (3) system at 298.15 K

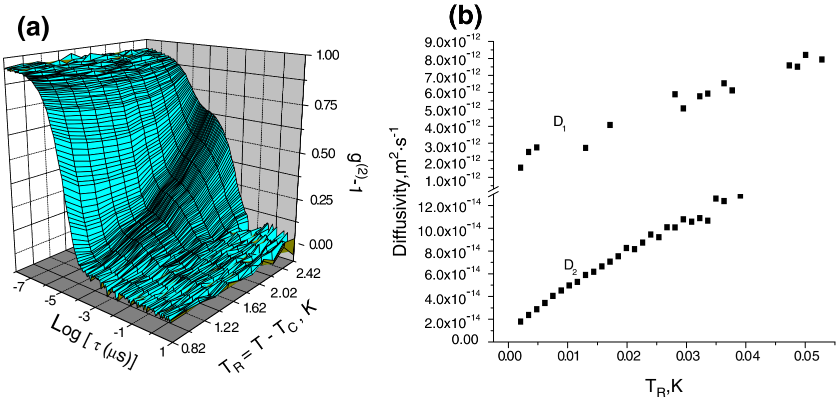

Fig. 4 Cyclohexane + methanol + toluene system: (**a**) intensity ACF versus temperature difference $T_R = T - T_c$ and lag time τ for CTM9 mixture, and (**b**) transport modes extracted from the ACF of the CMT10 mixture as a function of the temperature difference $T_R = T - T_c$

analysis of the modes results in two diffusivities (Fig. 4b), where the fast mode D_1 behaves like thermodiffusion and the slow mode D_2 tends toward zero with decreasing T_R. Therefore, we identify it as a mass diffusion mode. Thus, the CMT system is the second ternary system where we observed thermodiffusion and a mass diffusion mode. The important difference is the larger distance from the critical temperature, at which the double-exponential decay in the ACF appears. From these results, we conjecture that this might be a more general behavior, experimentally not yet detected due to the larger distance in T_R.

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