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Transport Properties of Transparent Liquids by Photon-Correlation Spectroscopy[1]

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Photon-correlation spectroscopy can be used for the fast and accurate determination of the transport properties thermal diffusivity a, mutual diffusion coefficient D, and viscosity η of transparent liquids over a wide range of temperature and pressure. Different detection techniques (homodyne, heterodyne) have to be used within the critical region and far away from it. Using optical arrangements with small scattering angles, the application of the heterodyne technique is recommended in order to assure a high measurement accuracy. The inaccuracy for a single measurement, which can be proved by a certain criterion, is estimated to be better than $\pm 2\%$ for a and probably $\pm 1\%$ for D and η. The principle of the measurement technique is presented in some detail on the basis of the heterodyne detection method. Selected measurements are shown for the determination of a in pure liquids and in binary liquid mixtures, where the measurement situation is more complex, depending on the difference of the refractive index of both pure components. The determination of D in binary liquid mixtures is treated in its context with the measurements of a and also in a critical separation system typical for measurements within the critical region. Finally, the first results for η are given for atmospheric measurements in pure water near room temperature.

KEY WORDS: diffusion; light scattering; photon-correlation spectroscopy; thermal diffusivity; viscosity.

1. INTRODUCTION

For many technical processes, the exact knowledge of the transport properties of working fluids is of great importance, e.g., for the design of chemical or power plants. Those data are rare, however, in particular at high tem-

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peratures and pressures. Some of the reasons for that may be found in the difficulties of conventional measurement techniques which are directly related to the transport equations and thus make use of macroscopic gradients of temperature, concentration, and velocity for the determination of the thermal conductivity λ, the thermal diffusivity a [1, 2], the mutual diffusion coefficient D [3], and the viscosity η [4], respectively. Sometimes those gradients give rise to several possible disturbances which cannot easily be taken into account appropriately.

Alternatively to the conventional techniques, spectroscopic methods may be used without employing any macroscopic gradient and thus avoiding all the problems which are related to them. The frequency spectrum of the light scattered from liquids by temperature and concentration fluctuations contains information on the transport properties a and D [5, 6]; see Fig. 1. Seeding the liquid with small spherical particles of a known diameter, additionally, the particle diffusion coefficient can be measured, providing information on the viscosity η of the liquid by using the Stokes–Einstein equation [7]. While the spectral resolution of conventional analyzing techniques such as Fabry–Perot interferometers is usually not high enough to determine the line width of the Rayleigh line from which the required information can be obtained, this is possible by using the photon-correlation spectroscopy (PCS) technique.

During the last years, PCS has been used successfully for the study of critical phenomena [8–11], of macromolecular dynamics similar to the

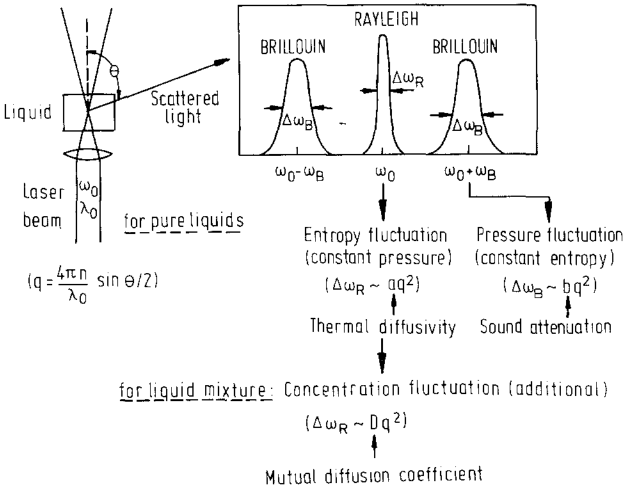

Fig. 1. Schematic of the frequency spectrum of light scattered from liquids. The Rayleigh linewidth contains information on the transport properties a and D.

determination of η [12–14], and of mass diffusion in liquid mixtures [11, 15–18]. Only a few attempts were made to measure the thermal diffusivity far away from the critical point [17, 19]. Compared to the other diffusion processes, temperature diffusion is much faster, and the signal arising from temperature fluctuations in the liquid is weak when working far away from its critical point. Using a modified experimental apparatus, our group has successfully expanded the application region of the PCS technique to measurements of the thermal diffusivity and of the mutual diffusion coefficient over a wide range of temperature and pressure [11, 20–23]. For binary liquid mixtures, the Rayleigh line arising from temperature fluctuations is superposed by contributions resulting from concentration fluctuations (see Fig. 1). Hence, the spectrum is more complex for the mixture than for a pure liquid, and whether both transport properties a and D can be determined from the PCS measurement or not depends on the difference of the refractive index of both pure components. This is shown in some detail in this paper.

In order to obtain a high measurement accuracy, different detection techniques—the homodyne or heterodyne technique—have to be used for measurements in the critical region, due to the strong signals when approaching the critical point, and for those performed far away from it. Its influence on the measurement accuracy is shown in the measurement of the diffusion coefficient D in a binary critical mixture. Very recently, we also performed some first viscosity measurements in pure water near room temperature. These results are presented in Section 5.

2. PRINCIPLE OF THE MEASUREMENT TECHNIQUE

The theory of light scattering, which is caused by the local statistical fluctuations of the dielectric constant ε and thus by temperature and concentration fluctuations of the fluid, is given in much detail elsewhere, see, e.g., the textbooks of Berne and Pecora [6], of Cummins and Pike [24], and of Chu [25]. Its application to the determination of transport properties can be found, e.g., in Refs. 5, 11, and 20–23, related mostly to the measurement of the thermal diffusivity a and the mutual diffusion coefficient D. Viscosity measurements are treated in this paper separately.

Using PCS, the measured intensity correlation function

$$G(\tau) = \langle I(0)\, I(t) \rangle = \lim(1/T) \int I(t)\, I(t+\tau)\, dt \qquad (1)$$

can in general be expressed by the superposition of two different intensity contributions: light scattered at the hydrodynamic fluctuations in the liquid

(I_s) and light scattered at solids, e.g., at particles in the liquid or at the optical windows of the test cell (I_o), which is superposing coherently the signal from the liquid. For pure liquids, the correlation function can be expressed by [25]

$$G(\tau) = (I_o + I_{s1})^2 + I_{s1}^2 \exp(-2\tau/\tau_{c1}) + 2I_{s1}I_o \exp(-\tau/\tau_{c1}) \qquad (2a)$$

and for a binary liquid mixture by

$$\begin{aligned} G(\tau) = {} & (I_0 + I_{s1} + I_{s2})^2 + I_{s1}^2 \exp(-2\tau/\tau_{c1}) \\ & + 2I_{s1}I_o \exp(-\tau/\tau_{c1}) + I_{s2}^2 \exp(-2\tau/\tau_{c2}) \\ & + 2I_{s2}I_o \exp(-\tau/\tau_{c2}) + 2I_{s2}I_{s1} \exp(-\tau/\tau_{c1} - \tau/\tau_{c2}) \end{aligned} \qquad (2b)$$

where I_{s1} and I_{s2} indicate the mean values of the intensity of the scattered light arising from temperature and concentration fluctuations, respectively. Detecting only the signal intensities I_s ($I_o \simeq 0$), the homodyne detection technique is employed, which is advantageous for high signal applications, e.g., for measurements near the critical point. However, in general, $I_o \simeq 0$ is not true. Experimentally, one can easily obtain the condition that $I_o \gg I_{s1}$ and $I_o \gg I_{s2}$. For this condition, the homodyne terms in Eqs. (2a) and (2b) with decay time $\tau_{c1}/2$ and $\tau_{c2}/2$ and the cross term with $\tau_{c1}\tau_{c2}/(\tau_{c1} + \tau_{c2})$ can be neglected. For this heterodyne detection condition the govering equations for pure liquids read

$$G(\tau) = (I_o + I_{s1})^2 + 2I_{s1}I_o \exp(-\tau/\tau_{c1}) \qquad (3a)$$

and those for binary mixtures read

$$\begin{aligned} G(\tau) = {} & (I_o + I_{s1} + I_{s2})^2 + 2I_{s1}I_o \exp(-\tau/\tau_{c1}) \\ & + 2I_{s2}I_o \exp(-\tau/\tau_{c2}) \end{aligned} \qquad (3b)$$

The characteristic decay times τ_{c1} and τ_{c2} contain the thermal diffusivity a and the diffusion coefficient D, which then can be calculated from the measurements by

$$a = 1/(q^2\tau_{c1}); \qquad D = 1/(q^2\tau_{c2}) \qquad (4)$$

Here, q is the modulus of the scattering vector, which is governed by the scattering angle θ and the refractive index of the fluid n for the laser wavelength λ_o:

$$q = (4\pi n/\lambda_o) \sin \theta/2 \qquad (5)$$

For a fixed concentration $I_{s2} \sim \Delta n$, Δn being the difference between the refractive indices of the two pure components of the mixture [22, 26]. Equation (3b) holds in general and in particular also for mixtures with $\Delta n \geqslant 5\%$. This is the most complicated situation. In order to isolate the thermal diffusivity in τ_{c1} from the diffusion coefficient in τ_{c2}, one has to have exact information on the magnitude of D first. This can be found by a measurement within the time period $0 \leqslant \tau \leqslant (2\text{–}3)\tau_{c2}$, neglecting the influences of τ_{c1} in the first channels of the correlation function, Eq. (3b). This is allowed because usually $a \gg D$. In a second measurement within the time domain $0 \leqslant \tau \leqslant (2\text{–}3)\tau_{c1}$ and with the knowledge of τ_{c2} (or D), τ_{c1} can be found by fitting the measured correlation function to Eq. (3b).

For most binary mixtures with $\Delta n < 5\%$, the intensity correlation function can be reduced to

$$G(\tau) = A \exp(-\tau/\tau_{c1}) + B\tau + C \tag{6}$$

Computer simulation shows that the error due to this simplification is smaller than 0.5% [27]. Because of the narrow range of the refractive indices of organic liquids and, in particular, also of working fluids, a great number of those mixtures can be studied by using Eq. (6). On the other hand, for those mixtures it may happen that $I_{s2} \ll I_{s1}$. In this situation the contribution of the concentration fluctuation cannot be isolated appropriately and thus the determination of D is not possible. This happens, vice versa, for the determination of a, if $I_{s2} \gg I_{s1}$, which can be expected for $\Delta n > 10\text{–}15\%$, depending on the investigated liquid mixture.

3. EXPERIMENTAL APPARATUS AND DATA ANALYSIS

On the basis of the heterodyne detection technique a modified PCS probe has been assembled in accordance with the two-photomultiplier tube (PMT) setup in Ref. 28, avoiding problems from afterpulse and dead-time effects of the PMTs. Its electrooptical part is shown schematically in Fig. 2 and described in detail elsewhere [21, 27–29].

Monochromatic light ($\lambda_o = 488$ nm) of an Ar^+ laser (300 mW) irradiates the transparent liquid to be investigated. The scattered light, which is observed at typical scattering angles of 3–6°, is superposed coherently with laser light scattered from the windows of the test cell (I_0) to assure the heterodyne condition. Two pin holes of 1.4-mm diameter in the collection optics fix the observation direction and the scattering angle.

Inaccuracies in the evaluation procedure may be due to errors in the determination of q and of τ_c; see Eq. (4). The estimated inaccuracy of q is better than $\pm 1\%$ [21, 29].

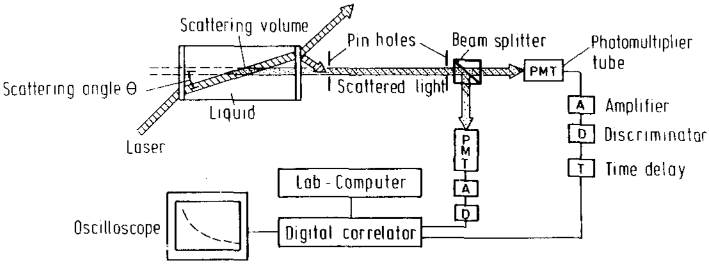

Fig. 2. Schematic of the electrooptical part of the probe assembly.

For the determination of τ_c, a nonlinear least-squares fit method is used in order to fit the measured data points to the correlation function of Eq. (3b) or (6). For pure liquids, $B=0$ in Eq. (6) due to Eq. (3a). Several possible error sources are discussed in detail in Refs. 27, 29, and 30. Possible systematical deviations of the correlation function from the theoretical model can be recognized by shifting the fit domain over the time domain of $(2\text{–}3)\tau_c$, and this, for our understanding, gives a clear criterion for the recognition of such deviations and errors in our measurements.

4. SELECTED EXPERIMENTAL RESULTS

In order to test the PCS technique and to apply it for data compilation, several pure liquids and selected liquid mixtures have been investigated over an extended range of temperature, pressure, and concentration. Most of the results have already been published elsewhere [11, 20–23]; some are presented here.

4.1. Thermal Diffusivity of Pure Liquids

Measurements were performed in several pure liquids [20, 21] over an extended range of temperature and pressure, proving the usability of the PCS technique. Figure 3 shows as an example the results for the two pure refrigerants R12 and R114 in the temperature range 0–120°C. These results are given in connection with the a data for the mixture R12/R114 for a weight fraction of $x=0.5$ measured in the same temperature range.

4.2. Thermal Diffusivity and Diffusion Coefficient of Binary Liquid Mixtures

In binary liquid mixtures, the applicability of the PCS probe depends on Δn of both pure components. For $\Delta n < 5\%$, only data for a and no D

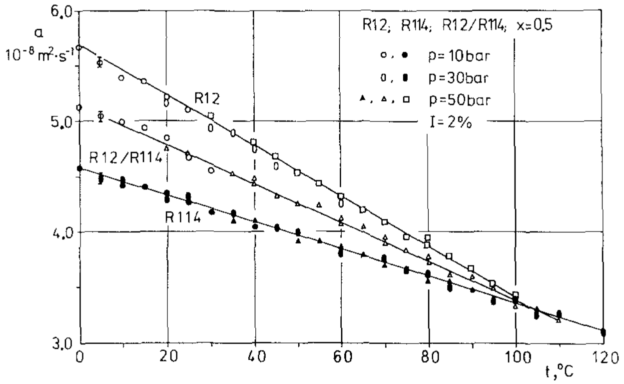

Fig. 3. Temperature dependence of the thermal diffusivity of the pure refrigerants R12 and R114 and of the binary mixture R12/R114 for a weight fraction of $x = 0.5$.

data can be obtained by using the simplified Eq. (6). As an example for such measurements, the mixture data of R12/R114 are shown in Fig. 3.

The situation is more complicated for mixtures with $\Delta n \geqslant 5\,\%$. Here, in general, the complete Eq. (3b) has to be used for the evaluation procedure. In order to isolate both contributions (*a* and *D*), first the intensity correlation function has to be measured in the large time domain of $(2\text{–}3)\tau_{c2}$ with a large sample time. Because τ_{c2} is one or two orders of magnitude larger than τ_{c1}, the second term in Eq. (3b), which accounts for the thermal diffusivity *a*, can be neglected, giving

$$G(\tau) = (I_0 + I_{S1} + I_{S2})^2 + 2 I_{S2} I_0 \exp(-\tau/\tau_{c2}) \qquad (3c)$$

from which τ_{c2} can be determined. The influence of *a* is limited to the first channels and can be eliminated by omitting these channels in the data fit procedure [23] similar to the elimination of the influences of Brillouin scattering on the Rayleigh–PCS measurements [28, 31, 32]. When τ_{c2} has been determined, a second measurement of $G(\tau)$ with a much shorter sample time gives τ_{c1}, which is obtained by fitting the measured data to Eq. (3b) with the known τ_{c2} value. As an example, Fig. 4 gives the results of the binary mixture acetone/carbon tetrachloride with $\Delta n = 7.4\,\%$ for $t = 23^\circ\mathrm{C}$ as a function of the mole fraction of acetone. For each mole fraction, *D* was determined first (Fig. 4a) before *a* was measured in a second run (Fig. 4b). Comparison with earlier measurements was possible only for the pure substances, with data from Refs. 33 and 34 indicating a deviation to higher values for the more conventionally measured data in the compilation works. This tendency was found in general and may be due to

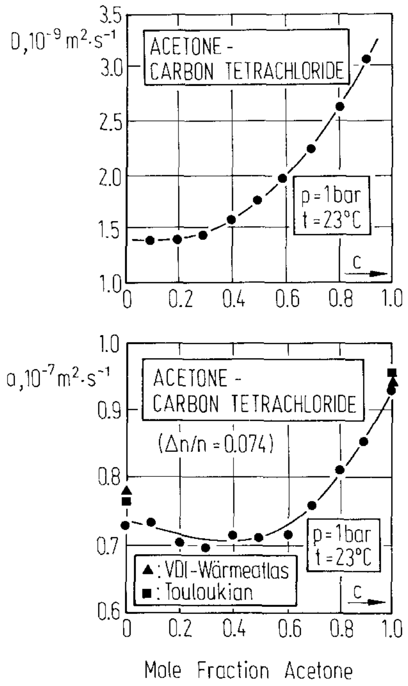

Fig. 4. (a) Measured mutual diffusion coefficient of the mixture acetone/CCl_4 as a function of the acetone mole fraction. (b) Measured thermal diffusivity of the mixture acetone/CCl_4 as a function of the acetone mole fraction.

influences of convective and radiative contributions to the conduction value using conventional gradient measurement techniques which have not been corrected appropriately.

For mixtures with a very large Δn, $I_{s2} \gg I_{s1}$ and the heterodyne condition $I_0 \gg I_{s2}$ is not met. The homodyne term [fourth term in Eq. (2b)] can therefore not be neglected. So far we have not been able to separate both contributions appropriately, and only D measurements are possible.

4.3. Diffusion Coefficient in a Separation System

The measurement of the binary diffusion coefficient was discussed in the last section. In a separation system, the diffusion coefficient should become close to zero when approaching the critical separation point. This situation is similar to the measurement of a, when approaching the critical point of a pure liquid. The separation system *N*-hexane/nitrobenzene has been used in order to prove the applicability and accuracy of homodyne and heterodyne detection techniques for the measurement near the critical separation point and far away from it. We have applied both techniques using the same apparatus [11].

Figure 5 shows the results for D as a function of temperature that we have obtained for the equimolar ($C = 0.5$) and for the critical ($C = 0.577$) concentration in comparison to the measurements of Siry [35]. Close to the critical separation point the signal intensities become large and the homodyne technique may be applied. In the temperature range 19.7–25°C those measurements were done with a scattering angle of 90°. Due to the strongly decreasing intensities for higher temperatures, in the temperature range 25–35°C heterodyne measurements were performed with a scattering angle of 13.5°. In order to prove both techniques, at 25°C both methods were applied.

For the critical concentration and close to the critical point, the diffusion coefficient could be expressed as a function of the reduced temperature difference $\varepsilon = (T - T_c)/T_c$ by an elementary exponential relation, $D = D_0 \varepsilon^{\psi}$. The exponent ψ was found to be 0.64.

Most of the PCS measurements published in the literature have been performed using homodyne techniques neglecting the heterodyne con-

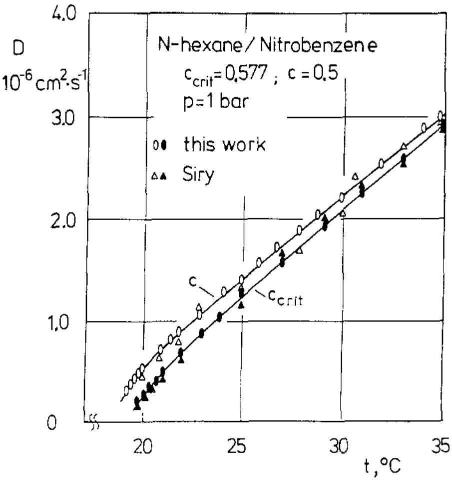

Fig. 5. Measured temperature dependence of the mutual diffusion coefficient of the separation system *N*-hexane/nitrobenzene for two different concentrations in comparison to data of Siry [35].

tribution to the signal, the terms with factor I_0 in Eq. (2). The influence of these heterodyne terms on the homodyne measurement has been investigated in some detail in the D measurement at 25°C [11, 27], indicating that the simplification of neglecting these heterodyne contributions is allowed only for large-scattering angle assemblies ($\theta = 90°$). Already for the relatively large angle of 13.5°, the deviations between both evaluation techniques may easily become several percent (5–10%) with an increasing tendency for smaller angles. Thus, the application of the heterodyne technique must strongly be recommended for small-angle measurements even when approaching the critical point.

5. VISCOSITY MEASUREMENTS

Seeding the fluid with particles, particle diffusion takes place due to Brownian motion and the particle diffusion coefficient D_p can be measured using PCS. The scattering intensities are large and the diffusion process is slow. Thus, from the experimental point of view, the situation is similarly simple as for the measurements close to the critical point: even low-power HeNe lasers may be used in a 90° arrangement applying the homodyne technique.

Using spherical particles of known diameter d, the viscosity η can be calculated from the measurement of D_p using the Stokes–Einstein relation [7]

$$\eta = kT/(6\pi D_p d) \tag{7}$$

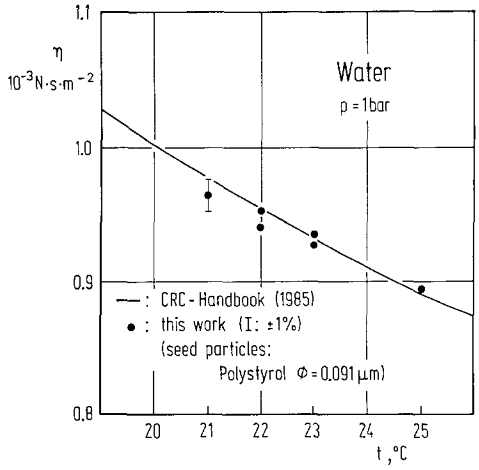

Fig. 6. Measured viscosity of pure water near room temperature in comparison to data taken from a compilation book [36].

Here, k is the Boltzman constant and T is the fluid temperature. Near room temperature, first measurements in pure water have been performed recently using small spheres of Polysterol with diameter $d = 0.091\ \mu\text{m}$. Figure 6 gives our results in comparison to the data published in a compilation book [36]. The agreement is quite good and well within the estimated inaccuracy of our measurements of about ±1%. Although these first measurements seem to be of a good quality, there are still some problems to be solved before the PCS technique can be considered to be suitable for routine use. These problems are related mostly to the seed particles, e.g., the seeding density, the size distribution, and its influence on the measurement accuracy and particle material. They are the subject of further investigations.

6. CONCLUSIONS

The photon-correlation spectroscopy (PCS) technique has been used successfully for the measurement of the thermal diffusivity (a) and the mutual diffusion coefficient (D) of transparent liquids over an extended range of temperature (0–200°C) and pressure (0.1–10 MPa). Its application to the determination of the viscosity (η) has been proved by first atmospheric measurements in pure water near room temperature.

Working in macroscopic equilibrium, the PCS technique avoids all the measurements problems which are related to the macroscopic gradients usually employed when using the conventional techniques. It provides absolute values within relatively short measurement times and without any calibration procedure. The high measurement accuracy obtainable can be proved by the certain criteron which is given by the exponential behavior of the correlation functions. For all three transport properties, the inaccuracy is better than ±2% for a single measurement and probably better than ±1% for D and η. While η can be measured in every transparent liquid, the determination of a and D is limited. In pure liquids, only a can be obtained. In binary liquid mixtures, the situation is more complex, depending on the difference Δn of the reflective index of both pure components: (i) for $\Delta n \leqslant 5\%$, a can be measured independently of D, and D cannot be determined; (ii) for $\Delta n \simeq 5\text{–}15\%$, a can be measured only with the exact knowledge of D, which can and must be measured first; and (iii) for $\Delta n \geqslant 10\text{–}15\%$, only D can be measured. The measurement time spans from 1–2 h (determination of a far away from the critical point) down to several seconds (viscosity determination and measurement of a and D very close to the critical point; here also the employment of low-power lasers is possible using homodyne conditions). Using small-scattering angle arrangements, the application of the heterodyne detection technique is highly recommended in order to assure the high measurement accuracy stated above.

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