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Thermal diffusivity of transparent liquids by photon correlation spectroscopy—II. Measurements in binary mixtures with a small difference in the refractive index of both pure components

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Abstract—Photon correlation spectroscopy has been used successfully for the measurement of the thermal diffusivity of some selected binary liquid mixtures. Under the condition, that the difference of the refractive indices of both pure components is smaller than 5%, the thermal diffusivity can be determined independently on the diffusion coefficient, which in general also gives contributions to the measured signal. For room temperature and atmospheric pressure, the results for benzene–toluene, carbon tetrachloride–toluene, decalin–toluene, and bromobenzene–toluene systems are presented as functions of the weight fraction.

1. INTRODUCTION

DYNAMIC light scattering in combination with photon correlation spectroscopy has been proved to be a rapid and accurate technique for measuring the thermal diffusivity of transparent liquids [1]. It is based on analysing the Rayleigh spectrum of the light scattered from the probe, which is caused by entropy or temperature fluctuations. So far, the measurement of thermal diffusivities by this technique was limited to pure liquids. Liquid mixtures are however of great importance in industrial applications. For binary mixtures, the frequency spectrum arising from temperature fluctuations is superposed by the spectrum resulting from concentration fluctuations. Hence the spectrum of binary mixtures is much more complex than that of pure liquids.

In this paper we present results of the measurement of the thermal diffusivity of binary mixtures with a small difference in the refractive index of both pure components. The measurement in mixtures with a large difference in the refractive index (>5%) is more complicated and will be discussed in detail in a forthcoming paper.

2. THEORY

The fluctuations $\delta\varepsilon$ of the dielectric constant ε in a liquid give rise to light scattering. In pure liquids, these fluctuations are produced only by temperature and pressure fluctuations. In liquid mixtures, the statistical, local concentration fluctuations cause additional fluctuations of the dielectric constant. According to the hypothesis of Onsager [2], the dissipation of temperature fluctuations at a position **r** in the liquid obeys the Fourier heat equation

$$\frac{\partial}{\partial t}\delta T(\mathbf{r},t) = a\nabla^2\delta T(\mathbf{r},t). \qquad (1)$$

By the same argument, the dissipation of concentration fluctuations at a position **r** obeys the diffusion equation

$$\frac{\partial}{\partial t}\delta c(\mathbf{r},t) = D_{12}\nabla^2\delta c(\mathbf{r},t). \qquad (2)$$

Here D_{12} is the mutual diffusion coefficient.

Mountain and Deutch [3, 4] presented a more rigorous development for obtaining the time dependence of density and concentration fluctuations by using the linearized hydrodynamic equations—the continuity equation, the Navier–Stokes equation, the diffusion equation and the energy equation. They found, that the central Rayleigh component contains the combined effects of entropy (or temperature) fluctuations at constant pressure and of concentration fluctuations. They also found a cross term resulting from the cross effects between energy transport and diffusion. These cross effects are known in non-equilibrium thermodynamics as the Dufour effect and the Soret effect [5]. It also can be shown theoretically, that under the condition $a \gg D_{12}$ the separation of the contributions from the entropy (or temperature) and the concentration fluctuations is possible. This situation is true for most organic liquid mixtures.

For a mixture the spectral density of the fluctuations of the dielectric constant can be expressed by [4]

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NOMENCLATURE

a	thermal diffusivity
B	constant
C	constant
c	concentration, weight fraction
δc	statistical concentration fluctuations
c_1	weight fraction of toluene
c_p	heat capacity for constant pressure
D_{12}	mutual diffusion coefficient
k	Boltzmann constant
I_0	intensity of reference light
$\bar{I}_{s1}$	intensity of scattered light arising from temperature fluctuations
$\bar{I}_{s2}$	intensity of scattered light arising from concentration fluctuations
q	modulus of scattering vector $\mathbf{q}$
$\mathbf{r}$	position vector
$S(\mathbf{q}, \omega)$	spectral density
T	temperature
δT	statistical temperature fluctuations
t	time.

Greek symbols

$\Gamma(\tau)$	correlation function
ε	dielectric constant
θ_e	external scattering angle
λ	thermal conductivity
λ_0	wavelength of laser radiation
μ	chemical potential
ρ	density
τ	time
$\Delta\tau$	correlator sample time
τ_{c1}	characteristic decay time of the correlation function for temperature fluctuations
τ_{c2}	characteristic decay time of the correlation function for concentration fluctuations.

$$S(\mathbf{q}, \omega) \equiv \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}\tau\, \mathrm{e}^{-\mathrm{i}\omega\tau}\langle \delta\varepsilon^*(\mathbf{q}, 0)\delta\varepsilon(\mathbf{q}, \tau)\rangle$$
$$= \left(\frac{\partial\varepsilon}{\partial c}\right)^2_{p,T} \frac{kT}{(\partial\mu/\partial c)_{p,T}}\left(\frac{2D_{12}q^2}{(D_{12}q^2)^2+\omega^2}\right)$$
$$+\left(\frac{\partial\varepsilon}{\partial T}\right)^2_{p,c}\frac{kT}{c_p}\left(\frac{2aq^2}{(aq^2)^2+\omega^2}\right) \quad (3)$$

where q is the modulus of the scattering vector which can be calculated from

$$q = \frac{2\pi}{\lambda_0}\sin\theta_e. \quad (4)$$

The quantity of direct interest in photon correlation spectroscopy is the intensity correlation function of the scattered light, which under 'heterodyne detection' can be expressed for a mixture by [6]

$$\Gamma(\tau) = (I_0+\bar{I}_{s1}+\bar{I}_{s2})^2+\bar{I}_{s1}^2\,\mathrm{e}^{-2\tau/\tau_{c1}}$$
$$+2\bar{I}_{s1}I_0\,\mathrm{e}^{-\tau/\tau_{c1}}+\bar{I}_{s2}^2\,\mathrm{e}^{-2\tau/\tau_{c2}}$$
$$+2\bar{I}_{s2}I_0\,\mathrm{e}^{-\tau/\tau_{c2}}+2\bar{I}_{s1}\bar{I}_{s2}\,\mathrm{e}^{-\tau(1/\tau_{c1}+1/\tau_{c2})} \quad (5)$$

where $\bar{I}_{s1}$ and $\bar{I}_{s2}$ indicate the mean values of the intensity of the scattered light arising from temperature and concentration fluctuations, respectively, and I_0 is the intensity of the reference light, which is the light scattered from the optical windows of the cell. Under the 'heterodyne condition', i.e. $I_0 \gg \bar{I}_{s1}$ and $I_0 \gg \bar{I}_{s2}$, the so-called homodyne terms with decay times $\tau_{c1}/2$ and $\tau_{c2}/2$ and the cross term with decay time $\tau_{c1}\tau_{c2}/(\tau_{c1}+\tau_{c2})$ can be neglected. Equation (3) can therefore be reduced to

$$\Gamma(\tau) = (I_0+\bar{I}_{s1}+\bar{I}_{s2})^2+2\bar{I}_{s1}I_0\,\mathrm{e}^{-\tau/\tau_{c1}}+2\bar{I}_{s2}I_0\,\mathrm{e}^{-\tau/\tau_{c2}}. \quad (6)$$

The characteristic decay times τ_{c1} and τ_{c2} contain the thermal diffusivity a and the mutual diffusivity D_{12}

$$a = \frac{1}{\tau_{c1}q^2}; \quad D_{12} = \frac{1}{\tau_{c2}q^2}. \quad (7)$$

The intensity of the light scattered from concentration fluctuations can be expressed by

$$\bar{I}_{s2} \sim \left(\frac{\partial\varepsilon}{\partial c}\right)^2_{p,T}\frac{kT}{(\partial\mu/\partial c)_{p,T}}. \quad (8)$$

The rate of change of the mixture dielectric constant ε with mixture composition c can be quantitatively related to the difference in the refractive indices of the pure components [7]. Roughly speaking, for a fixed concentration value, the intensity $\bar{I}_{s2}$ is proportional to the difference in the refractive indices. It was found, that for many binary mixtures, for which the difference in the refractive indices is smaller than 5%, $\bar{I}_{s2}$ is smaller than $\bar{I}_{s1}$. Furthermore, for most binary mixtures the thermal diffusivity is one to two orders of magnitude larger than the diffusion coefficient. So the diffusion term $2I_0\bar{I}_{s2}\,\mathrm{e}^{(-\tau/\tau_{c2})}$ can be substituted approximately by $2I_0\bar{I}_{s2}(1-\tau/\tau_{c2})$. For such mixtures, the intensity correlation function is reduced to

$$\Gamma(\tau) = A\,\mathrm{e}^{-\tau/\tau_{c1}}+B\tau+C. \quad (9)$$

The error in the thermal diffusivity due to this simplification is shown in Fig. 1 in its dependence on the ratio of intensities of the scattered light $\bar{I}_{s1}$ and $\bar{I}_{s2}$, in

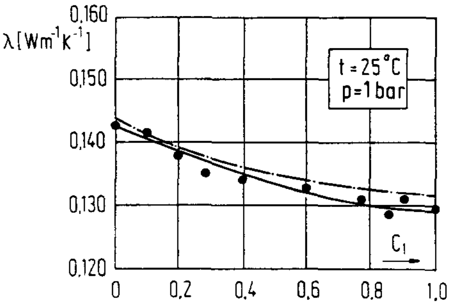

FIG. 3(b). Thermal conductivity of the binary mixture benzene–toluene (——, this work; — · —, ref. [10]).

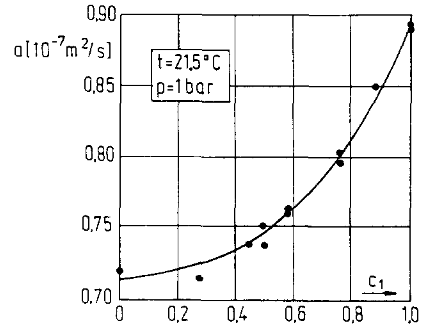

FIG. 4(a). Thermal diffusivity of the binary mixture carbon tetrachloride–toluene.

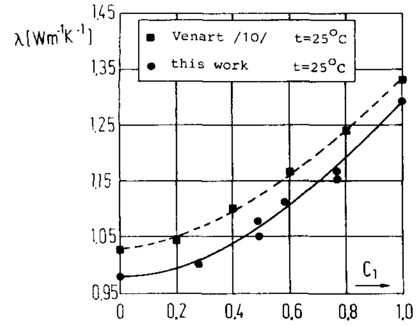

FIG. 4(b). Thermal conductivity of the binary mixture carbon tetrachloride–toluene.

determined by the stationary hot-wire method. The Venart values are about 2% larger than our results. This could be caused by convective and radiative contributions to the heat transfer in the liquid not corrected appropriately in the evaluation procedure of the hot-wire technique [1].

In Fig. 4(a) the results of the mixture carbon tetrachloride–toluene with a refractive index difference of 2.5% is shown. The thermal conductivity has been calculated with the data of c_p and ρ from the literature [11, 12] and is presented in Fig. 4(b) in comparison to the Venart data [10]. The comparison shows a good agreement for the concentration dependence, but again a 2% deviation in the absolute values.

In Figs. 5 and 6 the measured thermal diffusivity of the binary mixtures decalin–toluene ($\Delta n/n = 1.0\%$) and bromobenzene–toluene ($\Delta n/n = 4.2\%$) are presented. For these mixtures no literature data have been found for comparison.

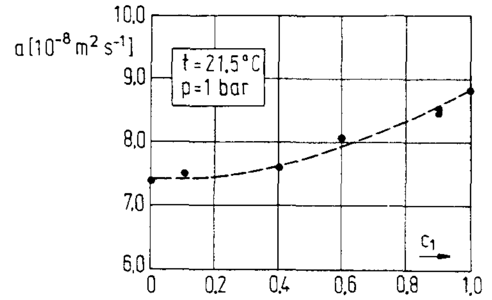

FIG. 5. Thermal diffusivity of the binary mixture decalin–toluene.

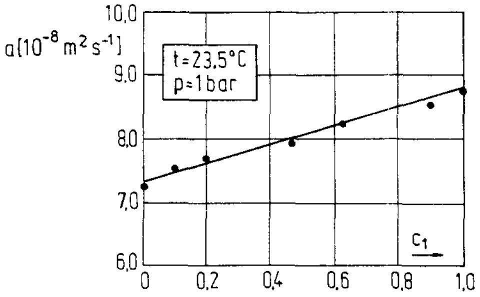

FIG. 6. Thermal diffusivity of the binary mixture bromobenzene toluene.

5. CONCLUSIONS

The application of the photon correlation technique to the measurement of the thermal diffusivity has been extended successfully to the investigation of liquid mixtures with differences in the refractive index of the pure liquids smaller than 5%. Under these conditions, the thermal diffusivity can be determined independently on the knowledge of the diffusion coefficient. For this procedure, a modified correlation function (equation (9)) is suggested, which also can be used for the investigation of any dilute mixture and of the influences of impurities in the probe. For binary mixtures with very large refractive index differences, the situation is more complicated. To determine the thermal diffusivity in such systems, the diffusion coefficient has to be known, which however can be determined with the same apparatus. This work is in progress, and will be presented in a forthcoming paper.

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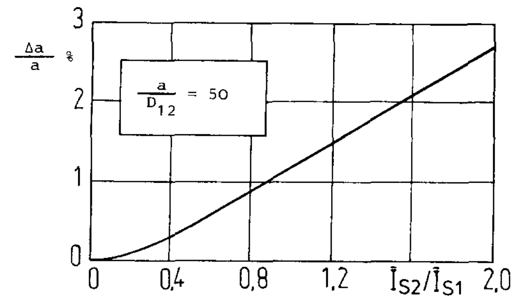

FIG. 1. Error in the determination of the thermal diffusivity due to the simplification of equation (9).

which the ratio a/D_{12} is assumed to be 50. For typical situations in this study, the error is smaller than 0.5%.

Because of the narrow range of the refractive indices of most simple organic liquids, a great number of organic mixtures can be studied using equation (9). This procedure can also be used to evaluate τ_{c1} for dilute mixtures, because $\bar{I}_{s2} < \bar{I}_{s1}$ when c_1 or c_2 is much smaller than the other one. Naturally this holds for chemical impurities too.

3. DATA REDUCTION

The correlation function (equation (9)) is a superposition of an exponential function and a linear term, which decays relatively slowly with time. Because of this long-time behaviour one must determine the correlation function in a broad time domain. In the experiments we split the function into two parts, one for the fast decaying domain, and one for the slow decaying domain by inserting a delay card between the correlator channels. In this way we can determine the correlation function over a large time domain. This allows an accurate determination of the time constant τ_{c1} and of the thermal diffusivity from equation (7).

A non-linear least square method was used to fit the measured data to equation (9). Possible systematical deviations of the correlation function from the theoretical model can be recognized by shifting the fit-domain from the short-time to the long-time region. Figure 2(a) shows a typical correlogram of the correlation function for the mixture carbon tetrachloride–toluene. The evaluated values of the thermal diffusivity from the different fit domains are indicated in Fig. 2(b). Each point represents the results of the fit of 45 channels starting with channel number NA. The dotted line represents the result from the fit domain from channel 3 to channel 84. It can be seen that the maximal deviation is smaller than 1%, which corresponds to the statistical error.

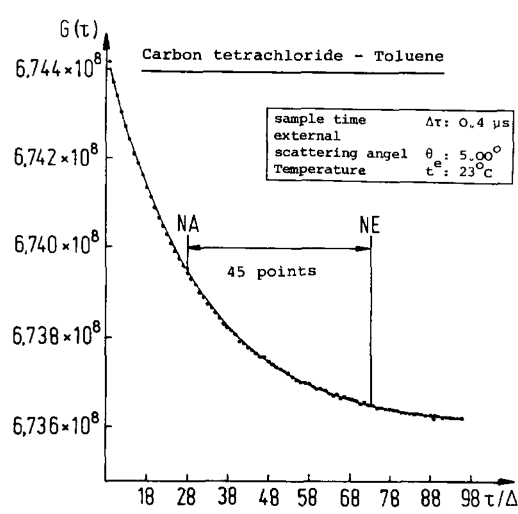

FIG. 2(a). Typical correlogram of the correlation function.

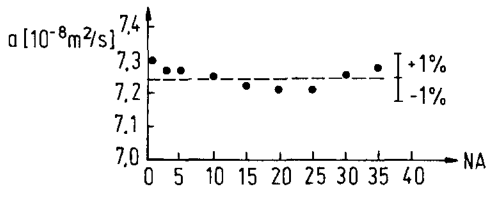

FIG. 2(b). Results from different fit domains.

4. RESULTS AND DISCUSSION

The thermal diffusivities of several binary liquid mixtures have been measured. The mixtures have been selected according to the differences in the refractive index of the pure components up to about 5%.

The results of the binary mixture benzene–toluene with a refractive index difference of 0.3% is plotted in Fig. 3(a) as a function of the weight fraction. The thermal diffusivity has been measured at room temperature (22.5°C). Error bars indicated are based on the standard deviation of the decay time τ_{c1} and of the error in determining the scattering vector. The thermal conductivities have been calculated from the measured thermal diffusivity a and the data of the specific heat capacity c_p and the density ρ from the literature [8, 9]. Because the values of the specific heat capacity and the density are given for the temperature $t = 25°\mathrm{C}$, the thermal diffusivities for this temperature were estimated from the measured values (22.5°C). The thermal conductivities are shown in Fig. 3(b) in comparison with the results of Venart [10], which were

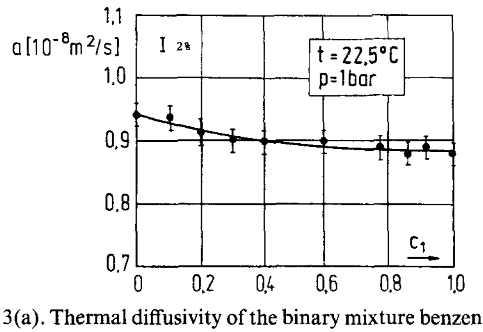

FIG. 3(a). Thermal diffusivity of the binary mixture benzene–toluene.

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DIFFUSIVITE THERMIQUE DES LIQUIDES TRANSPARENTS PAR SPECTROSCOPIE A CORRELATION PHOTONIQUE—II. MESURES DANS DES MELANGES BINAIRES DE COMPOSANTS AYANT UNE FAIBLE DIFFERENCE D'INDICE DE REFRACTION

Résumé—La spectroscopie à corrélation photonique est utilisée avec succès pour la mesure de la diffusivité thermique de quelques mélanges binaires de liquides. A la condition que la différence des indices de réfraction des deux composants purs soit inférieure à 5%, la diffusivité thermique peut être déterminée indépendamment du coefficient de diffusion qui généralement contribue au signal mesuré. A la température ambiante et à la pression atmosphérique, les résultats sont présentés en fonction de la fraction massique, pour les systèmes benzène–toluène, tetrachlorure de carbone–toluène, décalin–toluène, bromobenzène–toluène.

MESSUNG DER TEMPERATURLEITFÄHIGKEIT VON TRANSPARENTEN FLÜSSIGKEITEN MITTELS DER PHOTONEN-KORRELATIONS-SPEKTROSKOPIE—II. MESSUNGEN IN ZWEISTOFFGEMISCHEN BEI GERINGEM UNTERSCHIED ZWISCHEN DEN BRECHZAHLEN DER BEIDEN KOMPONENTEN

Zusammenfassung—Die Photonen-Korrelations-Spektroskopie wurde erfolgreich für die Messung der Temperaturleitfähigkeit bestimmter flüssiger Zweistoffgemische eingesetzt. Unter der Bedingung, daß der Unterschied zwischen den Brechzahlen der beiden reinen Stoffe kleiner als 5% ist, kann die Temperaturleitfähigkeit unabhängig vom Diffusionskoeffizienten bestimmt werden, der im allgemeinen auch einen Beitrag zum Meßsignal liefert. Die Ergebnisse für die Zweistoffsysteme Benzol–Toluol, Tetrachlorkohlenstoff–Toluol, Dekalin–Toluol und Brombenzol–Toluol werden bei Umgebungstemperatur und Atmosphärendruck als Funktion des Gewichtsanteils dargestellt.

ОПРЕДЕЛЕНИЕ КОЭФФИЦИЕНТА ТЕМПЕРАТУРОПОВОДНОСТИ ПРОЗРАЧНЫХ ЖИДКОСТЕЙ С ПОМОЩЬЮ ФОТОННОЙ СПЕКТРОСКОПИИ—II. ИЗМЕРЕНИЯ В БИНАРНЫХ СМЕСЯХ С МАЛОЙ РАЗНОСТЬЮ ПОКАЗАТЕЛЕЙ ПРЕЛОМЛЕНИЯ ЧИСТЫХ КОМПОНЕНТОВ

Аннотация—Фотонная спектроскопия успешно применялась для измерения коэффициента температуропроводности ряда жидких бинарных смесей. При условии, что разность показателей преломления чистых компонентов меньше 5%, коэффициент температуропроводности можно определить независимо от коэффициента диффузии, которая в общем случае также вносит вклад в измеренный сигнал. Для комнатной температуры и атмосферного давления результаты для смесей бензол–толуол, четыреххлористый углерод–толуол, декалин–толуол и бромбензол–толуол представлены как функции весовой концентрации.