

# Thermal diffusivity of transparent liquids by photon correlation spectroscopy—III. Measurements in binary mixtures with large differences in the refractive index of the pure components

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**Abstract**—The measurement of thermal diffusivity by the photon correlation technique is limited so far to pure liquids and to such binary mixtures, for which the difference in the refractive index of both components is smaller than 5%. For the first time results for a binary mixture with a refractive index difference larger than 5% are presented (acetone/carbon tetrachloride with  $\Delta n = 7.4\%$ ). For the determination of the thermal diffusivity the exact knowledge of the diffusion coefficient is necessary. The thermal diffusivity and the diffusion coefficient are measured using the same apparatus.

## 1. INTRODUCTION

THE PHOTON correlation technique is a well-established method for the measurement of the thermal diffusivity of pure liquids [1–3]. For a mixture the situation is more complex. The spectrum of the scattering light arising from entropy (or temperature) fluctuations is superposed by the spectrum arising from concentration fluctuations. Under the ‘heterodyne condition’ [4] the intensity correlation function becomes a superposition of two nearly independent exponentials with different decay times, one of them controlled by the thermal diffusivity, the other controlled by the diffusion coefficient. The amplitude of the diffusion term depends on the difference of the refractive indices of both components. In a previous paper we have shown [4], that this exponential function can be substituted by a linear term under the condition, that the difference of the refractive indices is smaller than 5%. In this case the thermal diffusivity can be determined independently of the diffusion coefficient. The measurement accuracy depends obviously on the difference of the refractive indices. The diffusion term must be taken into account more accurately, when the refractive index difference becomes larger than 5%. In order to determine the thermal diffusivity, one needs the diffusion coefficient, which can also be measured by photon correlation spectroscopy using the same apparatus. This will be shown for the mixture acetone/carbon tetrachloride with  $\Delta n = 7.4\%$ .

## 2. THEORY AND EXPERIMENTAL PROCEDURE

The local fluctuations of the dielectric constant  $\epsilon$  in a liquid give rise to light scattering, which can be analysed by the photon correlation technique. In general the intensity correlation function of the scattered light can be expressed by [6]

$$\begin{aligned} \Gamma(\tau) = & (I_0 + \bar{I}_{s1} + \bar{I}_{s2})^2 + \bar{I}_{s1}^2 \exp(-2\tau/\tau_{c1}) \\ & + 2\bar{I}_{s1}I_0 \exp(-\tau/\tau_{c1}) + \bar{I}_{s2}^2 \exp(-2\tau/\tau_{c2}) \\ & + 2\bar{I}_{s2}I_0 \exp(-\tau/\tau_{c2}) \\ & + 2\bar{I}_{s1}\bar{I}_{s2} \exp(-\tau(1/\tau_{c1} + 1/\tau_{c2})) \end{aligned} \quad (1)$$

where  $\bar{I}_{s1}$  and  $\bar{I}_{s2}$  indicate the mean values of the intensity of the scattered light arising from the temperature and from the concentration fluctuations, respectively, and  $I_0$  the intensity of the reference light, which is the light scattered from the optical windows of the test cell. Under the ‘heterodyne condition’, i.e.  $I_0 \gg \bar{I}_{s1}$  and  $I_0 \gg \bar{I}_{s2}$ , equation (1) is reduced to

$$\begin{aligned} \Gamma(\tau) = & (I_0 + \bar{I}_{s1} + \bar{I}_{s2})^2 + 2\bar{I}_{s1}I_0 \exp(-\tau/\tau_{c1}) \\ & + 2\bar{I}_{s2}I_0 \exp(-\tau/\tau_{c2}). \end{aligned} \quad (2)$$

The thermal diffusivity  $a$  and the diffusion coefficient  $D_{12}$  can be obtained from the measured decay times  $\tau_{c1}$  and  $\tau_{c2}$  by

$$a = \frac{1}{\tau_{c1}q^2}; \quad D_{12} = \frac{1}{\tau_{c2}q^2} \quad (3)$$

with the modulus of the scattering vector  $q$

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

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## NOMENCLATURE

$a$	thermal diffusivity	Greek symbols	
$B$	constant	$\Gamma(\tau)$	correlation function
$C$	constant	$\Delta\tau$	correlator sample time
$D_{12}$	mutual diffusion coefficient	$\varepsilon$	dielectric constant
$I_0$	intensity of reference light	$\theta_e$	external scattering angle
$\bar{I}_{s1}$	intensity of scattered light arising from temperature fluctuations	$\tau$	time
$\bar{I}_{s2}$	intensity of scattered light arising from concentration fluctuations	$\tau_{c1}$	characteristic decay time of the correlation function for temperature fluctuations
$q$	modulus of scattering vector	$\tau_{c2}$	characteristic decay time of the correlation function for concentration fluctuations.
$x$	mole fraction.		

Because  $\tau_{c2}$  is in general one to two orders of magnitude larger than  $\tau_{c1}$ , the diffusion term (third term in equation (2)) can be substituted by a linear term under the condition that  $\bar{I}_{s2} \leq \bar{I}_{s1}$ , which implies that the difference in the refractive indices of the two components is smaller than approximately 5% [4]. This simplification leads to unacceptable errors, when  $\bar{I}_{s2}$  becomes larger than  $\bar{I}_{s1}$ , that is, the difference of the refractive indices becomes larger than 5%. For example, when  $\bar{I}_{s2} = 3\bar{I}_{s1}$  and  $a/D_{12} = 50$ , the error would be 2.5%. In order to obtain accurate values of the thermal diffusivity, one must directly use equation (2), and exact knowledge on the decay time  $\tau_{c2}$  or on the diffusion coefficient is necessary.

The measured intensity correlation function could be fitted to equation (2) and thus  $\tau_{c1}$  and  $\tau_{c2}$  or the thermal diffusivity and the diffusion coefficient could be determined simultaneously. This procedure requires, however, the determination of the intensity correlation function over a large time domain, because  $\tau_{c2}$  is of the order of 100–1000  $\mu\text{s}$ . It also requires a high time resolution (small sample time), so that a  $\tau_{c1}$  of about 10  $\mu\text{s}$  can be determined accurately. This is only possible, if the correlator has a large number of channels, which however is not available commercially and would be very expensive. The correlator used in our laboratory has 100 channels. The described measurement difficulty has been overcome through two independent measurements of the intensity correlation function in two different time domains.

First the intensity correlation function was measured in a large time domain with a relative large sample time. Because  $\tau_{c2}$  is one to two orders of magnitude larger than  $\tau_{c1}$ , the second term in equation (2) for the thermal diffusivity can be neglected and the intensity correlation function is reduced to

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

from which  $\tau_{c2}$  can be determined. The influence of the thermal diffusivity is limited to the first channels and can be eliminated by omitting these channels in

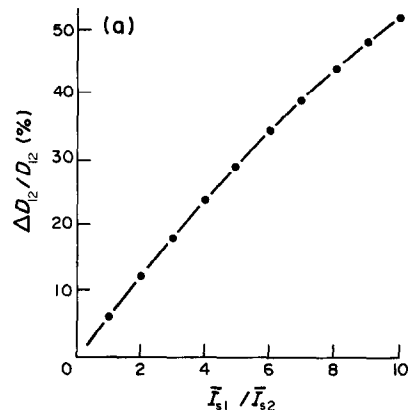


FIG. 1(a). The relative error of the diffusion coefficient due to the simplification from equation (2) to equation (5) as a function of intensity ratio, fit domain: channel 1–channel 84.

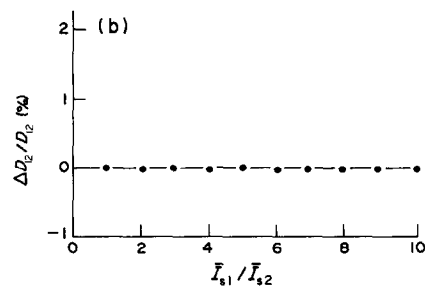


FIG. 1(b). The relative error of the diffusion coefficient as a function of intensity ratio, fit domain: channel 5–channel 84.

the data fit procedure as described in refs. [4, 5] and shown in Figs. 1(a) and (b). Figure 1(a) shows the large error due to the simplification which leads from equation (2) to equation (5) for the determination of the diffusion coefficient  $D_{12}$  or of the decay time  $\tau_{c2}$ , when the data are fitted from channel 1 to channel 84 for nearly all  $\bar{I}_{s1}/\bar{I}_{s2}$ . This error can almost be eliminated completely, when the fit domain starts only

from channel 5 instead of channel 1, i.e. omitting the first four channels (Fig. 1(b)).

When the quantity  $\tau_{c2}$  has been determined, a second measurement of the intensity correlation function with much smaller sample time gives  $\tau_{c1}$ . The decay time  $\tau_{c1}$  or the thermal diffusivity is obtained by fitting the measured data to equation (2) with the known  $\tau_{c2}$  value.

### 3. RESULTS AND DISCUSSIONS

The thermal diffusivity and the diffusion coefficient of the binary mixture acetone/carbon tetrachloride have been measured. The difference of the refractive indices of both pure components is 7.4%.

The ratio of the intensities  $\bar{I}_{s2}$  and  $\bar{I}_{s1}$  was measured and is presented in Fig. 2 as a function of the weight fraction of acetone. It shows that the ratio depends on the concentration. Therefore, for dilute solutions the concentration background can be always treated as a linear term [4]. In Fig. 3 the diffusion coefficient is plotted as a function of the weight fraction of acetone. The diffusion coefficient for each concentration value was determined before the measurement of the thermal diffusivity was performed. The results for the thermal diffusivity  $a$  are plotted in Fig. 4. The measurement was carried out at atmospheric pressure and for a temperature of 23°C. No literature values could be found for the concentration dependence of either the thermal diffusivity or the diffusion coefficient. For a temperature of 20°C the diffusion coefficients were measured by Czwozniak *et al.* [6]. For comparison with these values the diffusion coefficients have been measured additionally at this

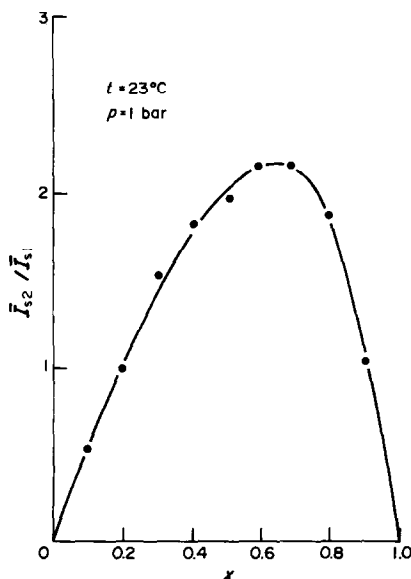


FIG. 2. Mean intensity ratio  $\bar{I}_{s2}/\bar{I}_{s1}$  due to concentration and temperature fluctuations as a function of the carbon tetrachloride mole fraction.

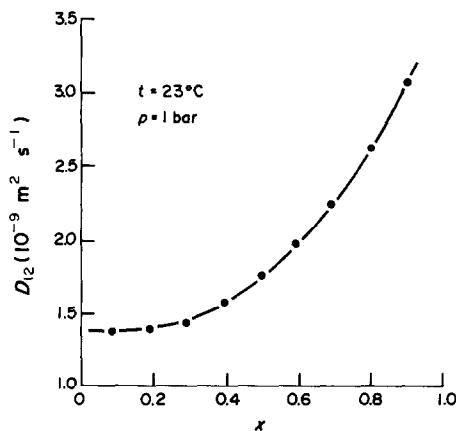


FIG. 3. The diffusion coefficient of the binary mixture acetone/carbon tetrachloride as a function of carbon tetrachloride mole fraction.

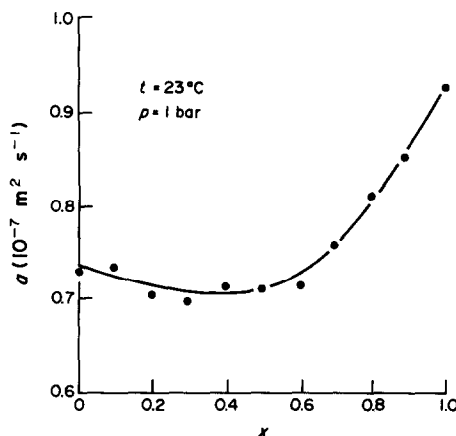


FIG. 4. The thermal diffusivity of the binary mixture acetone/carbon tetrachloride as a function of carbon tetrachloride mole fraction.

temperature and are shown in Fig. 5. The agreement is good.

The components of the acetone/carbon tetrachloride mixture have a refractive index difference, which is not too large for this study and allows therefore the measurement of the thermal diffusivity. For mixtures with a very large difference,  $\bar{I}_{s2}$  becomes much stronger than  $\bar{I}_{s1}$  and the heterodyne condition  $I_0 \gg \bar{I}_{s2}$  is not met. The homodyne term (fourth term in equation (1)) can therefore not be neglected. So far we cannot take into account the homodyne term appropriately in the data fit procedure. Of course one could reduce the intensity  $\bar{I}_{s2}$  so that the homodyne term can be neglected. But simultaneously the signal  $\bar{I}_{s1}$  for temperature fluctuations would also be reduced and the signal/noise ratio would increase. The necessary measurement time would become much longer. Binary mixtures with a very large difference of the refractive indices are still under study.

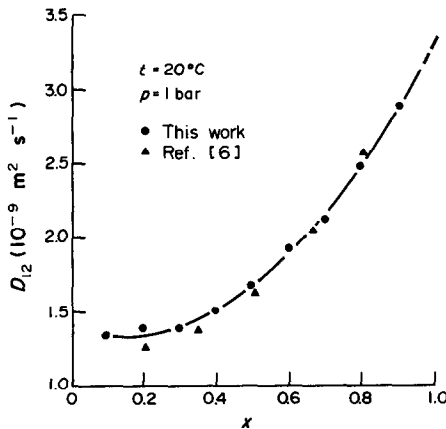


FIG. 5. The diffusion coefficient  $D_{12}$  of the binary mixture acetone/carbon tetrachloride as a function of carbon tetrachloride mole fraction at a temperature of 20°C.

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## DIFFUSIVITE THERMIQUE DES LIQUIDES TRANSPARENTS PAR SPECTROSCOPIE DE CORRELATION PHOTONIQUE—III. MESURES DANS DES MELANGES BINAIRES AVEC GRANDE DIFFERENCE DANS LES INDICES DE REFRACTION DES COMPOSANTS PURS

**Résumé**—La mesure de la diffusivité thermique par la technique de corrélation photonique était limitée jusqu'ici aux liquides purs et à des mélanges binaires pour lesquels la différence dans les indices de réfraction des deux composants est inférieur à 5%. Pour la première fois on présente des résultats pour un mélange binaire avec une différence d'indices supérieure à 5% (acétone/tétrachlorure de carbone avec  $\Delta n = 7,4\%$ ). Pour la détermination de la diffusivité thermique, la connaissance exacte du coefficient de diffusion est nécessaire. La diffusivité thermique et le coefficient de diffusion sont mesurés en utilisant le même appareil.

## ERMITTLUNG DER TEMPERATURLEITFÄHIGKEIT TRANSPARENTER FLÜSSIGKEITEN MITTELS PHOTONEN-KORRELATIONS-SPEKTROSKOPIE—III. MESSUNGEN IN BINÄREN GEMISCHEN BEI SEHR UNTERSCHIEDLICHEN BRECHZAHLEN DER REINEN KOMPONENTEN

**Zusammenfassung**—Die Messung der Temperaturleitfähigkeit durch die Photonen-Korrelations-Technik ist bisher auf reine Flüssigkeiten und binäre Gemische beschränkt, bei welchen die Differenz der Brechzahlen beider Komponenten kleiner als 5% ist. Zum ersten Mal werden Ergebnisse für ein binäres Gemisch vorgestellt, dessen Brechzahl-Differenz größer als 5% ist (Aceton/Kohlenstofftetrachlorid mit  $\Delta n = 7,4\%$ ). Für die Bestimmung der Temperaturleitfähigkeit ist die genaue Kenntnis des Diffusionskoeffizienten notwendig. Die Temperaturleitfähigkeit und der Diffusionskoeffizient werden mit der gleichen Apparatur gemessen.

## ОПРЕДЕЛЕНИЕ ТЕМПЕРАТУРОПРОВОДНОСТИ ПРОЗРАЧНЫХ ЖИДКОСТЕЙ МЕТОДОМ ФОТОННОЙ КОРРЕЛЯЦИОННОЙ СПЕКТРОСКОПИИ—III. ИЗМЕРЕНИЯ В БИНАРНЫХ СМЕСЯХ С СИЛЬНО ОТЛИЧАЮЩИМИСЯ КОЭФФИЦИЕНТАМИ ПРЕЛОМЛЕНИЯ ЧИСТЫХ КОМПОНЕНТОВ

**Аннотация**—В настоящее время применение фотонного корреляционного метода для измерения температуропроводности ограничивается чистыми жидкостями и такими бинарными смесями, в которых различие коэффициентов преломления обоих компонентов не превышает 5%. Впервые представлены результаты для бинарной смеси с разницей коэффициентов преломления более 5% (ацетон/тетрахлорид углерода с  $\Delta n = 7,4\%$ ). Для определения температуропроводности необходимо знать точный коэффициент диффузии. Температуропроводность и коэффициент диффузии измеряются с помощью одного и того же устройства.