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Measurement of the Thermal Diffusivity of Aqueous Solutions of Alcohols by a Laser-Induced Thermal Grating Technique

J. Wang[1] and M. Fiebig[1,2]

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The thermal diffusivity of methanol, ethanol, and their aqueous solutions was measured at atmospheric pressure and temperature. The measurements were performed with a laser-induced thermal grating technique. The aqueous solutions have weight fractions of 20, 40, 60, and 80%. Systematic errors were taken into consideration, and corrections were made to the measured values. Focused laser beams were used, which notably intensify the diffracted signal, reduce the background to zero, and justify neglecting the heterodyne term of the diffracted signal, thus simplifying the data evaluation. Hence, the accuracy of the measurements was improved significantly. The overall accuracy of the measurements is estimated to be better than 1.5%.

KEY WORDS: aqueous solutions; diffraction; ethanol; laser-induced thermal grating; methanol; scattering; thermal conductivity; thermal diffusivity; water.

1. INTRODUCTION

Methanol and ethanol are very important industrial chemicals. Their aqueous solutions have found wide applications in breweries, chemical plants, and food-freezing plants. Recently, aqueous solutions of alcohols have become technically significant as heat transfer fluids.

Up to now, the thermal conductivity and the thermal diffusivity of aqueous solutions of alcohols have rarely been studied. Assael et al. [1] have measured the thermal conductivity of mixtures of alcohols with water with a hot-wire technique. Photon correlation spectroscopy (PCS), which has been successfully used for the measurement of the thermal diffusivity of

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[1] Institut für Thermo- und Fluiddynamik, Ruhr-Universität Bochum, D-44780 Bochum, Germany.

[2] To whom correspondence should be addressed.

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pure liquids and their binary mixtures, has also been tried. Unfortunately, this method can only be used for liquid mixtures whose difference between the refractive indices of both pure components is not too large [2, 3]. In addition, it was found that substances such as water and aqueous solutions, whose Landau–Placzek ratio is very large, cannot be investigated by PCS due to a large Brillouin contribution [4, 5].

The present work represents an experimental investigation of the thermal diffusivity of methanol, ethanol, and their aqueous solutions at atmospheric pressure and temperature. The measurements were performed with a laser-induced thermal grating technique, which can be applied to all liquids and liquid mixtures. Based on a systematic error analysis [6], error effects were taken into consideration and corrections were made to the measured thermal-diffusivity values. The overall accuracy of the measurements is estimated to be better than ±1.5%.

2. EXPERIMENTAL SETUP

The theory of the laser-induced thermal grating technique used for the determination of thermal diffusivity has been described by Eichler et al [7], Nagasaka et al. [8], and Wu et al. [5]. The experimental setup is shown schematically in Fig. 1. To excite the thermal grating, an argon-ion

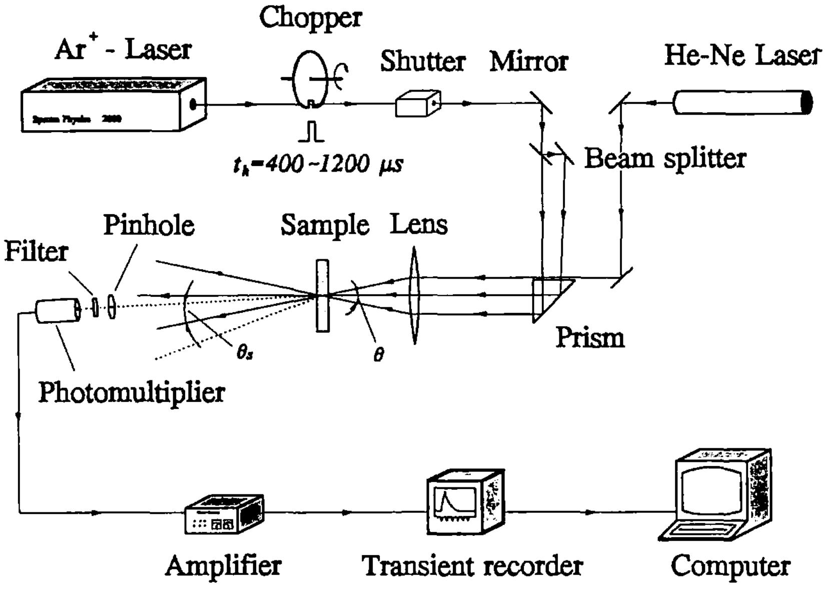

Fig. 1. Schematic of the experimental setup.

laser (Spectra Physics, Series 2000, $\lambda_h = 488$ nm) is employed as the heating laser. The heating laser beam is mechanically chopped into short light pulses, whose duration time t_h can be changed from 400 to 1200 μs. To avoid an excessive temperature rise in the heating region, we employ a shutter behind the chopper, which enables us to get a low heating pulse-repetition rate [6]. With a beam splitter the heating laser beam is split into two beams, which intrersect each other in the sample, to produce the interference pattern. As a result, a spatially sinusoidal temperature distribution, i.e., a thermal grating is induced by the absorbed laser energy. If the assumption of one-dimensional heat conduction in the modulation direction x is permissible, the thermal grating decays as

$$\delta T(x, t) = \Delta T_0 \cos(qx) \exp(-t/\tau_c) \tag{1}$$

after the heating pulse, where $\delta T(x, t)$ is the temperature fluctuation, ΔT_0 the initial temperature amplitude, q the modulus of the grating vector, t the time, and τ_c the relxation time.

To detect the thermal grating, a He–Ne laser (Aerotech Model OEM5P; $\lambda_p = 632.8$ nm) is used as the probing laser, which is diffracted by the grating. According to the theory of diffraction [8, 9], the intensity of the first-order diffracted beam can be expressed by

$$I_1(t) \propto \exp(-2t/\tau_c) \tag{2}$$

The thermal diffusivity of the sample a is then

$$a = (\tau_c q^2)^{-1} \tag{3}$$

The intensity of the first-order diffracted beam is measured in the homodyne scheme by a photomultiplier (Thorn EMI, Model B 271 F) in which a 400-μm pinhole and an interference filter are fitted. The output signal is amplified and subsequently displayed and recorded by a transient recorder (Iwatsu, DMS 6430, 8 bit). The sample consists of two glass windows separated by a thin spacer of 0.5 mm. Between the two windows is a film of liquids to be measured, which was slightly doped with methyl red, to obtain suitable absorption of the heating laser beam. The concentration of the dye is kept low enough to ignore the influence of addition of the dye on the thermophysical properties of the sample. In the measurements, we maintained the absorption coefficient α of the sample below 0.8 mm^{-1}.

It was mentioned in Ref. 6 that the diffracted intensity did not decay to zero after each heating light pulse due to the probing laser light scattered at the sample windows. This leads to great difficulties in data evaluation. Now we have succeeded in solving this problem by (a) focusing the laser beams to improve the signal-to-noise ratio significantly, (b) improving the optical quality of sample windows to reduce the scattered light on them notably, and (c) excluding the scattered and reflected light of the optical surfaces by an additional aperture before the photomultiplier. As a result, the background of the diffracted intensity decays to zero after each heating pulse. Hence, the heterodyne terms of the signal can be neglected and the data can be simply evaluated according to Eq. (2). Consequently, the accuracy of the determination of τ_c is notably improved.

According to Eq. (3), the modulus q of the grating vector q has to be determined besides the relaxation time τ_c, to get the thermal diffusivity a. By measuring the scattering angle θ_s instead of the intersection angle of both heating laser beams θ, q can be calculated using Eq. (4),

$$q = 2\pi \sin \theta_s / \lambda_p \tag{4}$$

where λ_p is the wavelength of the probing beam. However, as stated in Ref. 5, the scattered light signal, which corresponds to the first-order diffraction, has a narrow distribution centered at $q = (2\pi/\lambda_p) \sin \theta_s$. In the measurements, the scattering angle θ_s varied slightly about 0.76°. To determine θ_s accurately, we measure the intensity distributions of diffracted beams of $+1$ and -1 order with the photomultiplier, which is mounted on a two-dimensional adjustable optical bank. Both peaks of the intensity distributions can be determined by a computer, which gives the distance between the two peaks ΔX. Therefore, the scattering angle θ_s can be calculated from the geometrical relationship to an accuracy of $\pm 0.55\,\%$.

3. ERROR ESTIMATION

The systematic effects, which are considered in the estimation of errors, are (a) sample thickness, (b) intersection angle, (c) absorption, and (d) Gaussian beam intensity distribution and focusing of heating laser beam. These systematic effects, which result from the deviations from one-dimensional heat conduction, have been systematically analyzed in Ref. 6 by using a numerical simulation method. Based on this numerical error analysis, we can estimate the total systematic error with a given sample thickness (sum of the effects of intersection angle, absorption, and Gaussian beam intensity distribution and focusing of heat laser beam) and cancel this total systematic error from the measured thermal-diffusivity value. Therefore, we can estimate the accuracy of the measurements from Eq. (3). The scattering angle θ_s, or to be precise, the modulus q of the scattering vector q can be determined to an accuracy of $\pm 0.55\,\%$. The determination of the relaxation time τ_c due to the least-square fitting according to Eq. (2) is accurate to within about $\pm 1\%$. Hence, the overall uncertainty of the measurements is estimated to be better than $\pm 1.5\,\%$.

4. RESULTS

The experimental data for methanol, ethanol, and their aqueous solutions at 295 K and 0.1 MPa are listed in Table I. The methanol and ethanol samples had a purity of not less than 0.98%. Superpure water for high-performance liquid chromatography was used as the water sample. An electronic analytical balance with a sensitivity of ±10 mg was employed to determine the weight fractions of the aqueous solutions of methanol and ethanol. At least 100 g of each solution was prepared every time. Hence, the weight fractions of the solutions were known to an accuracy of better than ±0.06%. Figures 2 and 3 show the thermal diffusivity of the aqueous solutions of methanol and ethanol as a function of the weight fractions of the alcohols. The measured thermal-diffusivity value of methanol in this work agrees very well with the result obtained by Hendrix et al. [10] (within 0.04%), but it is about 2.3% smaller than the value recommended in the *VDI-Wärmeatlas* [11]. Similarly, the result for ethanol is also about 2.0%

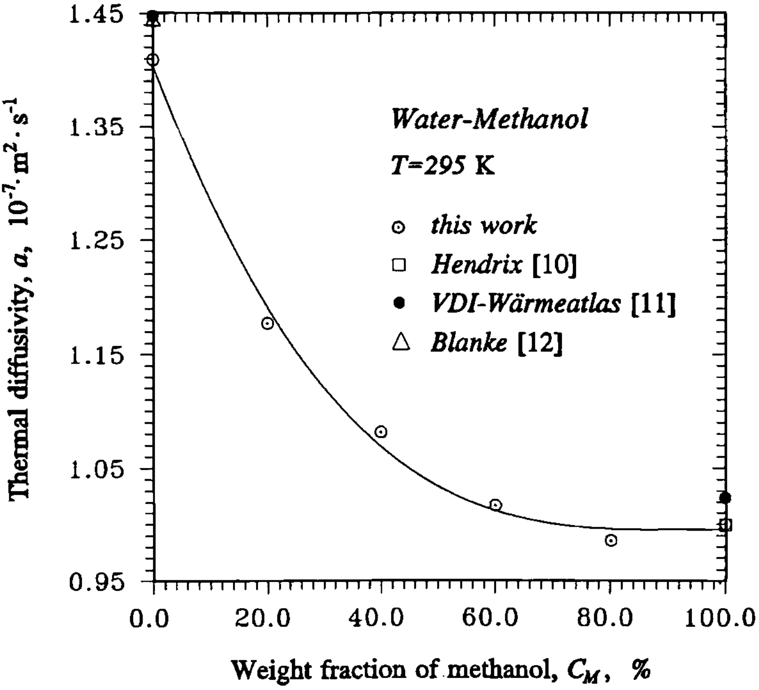

Fig. 2. Thermal diffusivity of aqueous solutions of methanol as a function of the weight fraction of methanol.

Table I. Experimental Data for Thermal Diffusivity and Derived Thermal Conductivity of Aqueous Solutions of Methanol and Ethanol

	a ($10^{-7}\,m^2 \cdot s^{-1}$)	λ ($mW \cdot m^{-1} \cdot K^{-1}$)
Methanol/water		
0%	1.4088	588.11
20%	1.1770	467.75
40%	1.0810	387.86
60%	1.0165	307.15
80%	0.9853	246.90
100%	0.9996	200.74
Ethanol/water		
0%	1.4088	588.11
20%	1.1737	488.09
40%	0.8771	337.94
60%	0.8340	267.55
80%	0.8175	209.87
100%	0.8519	162.38

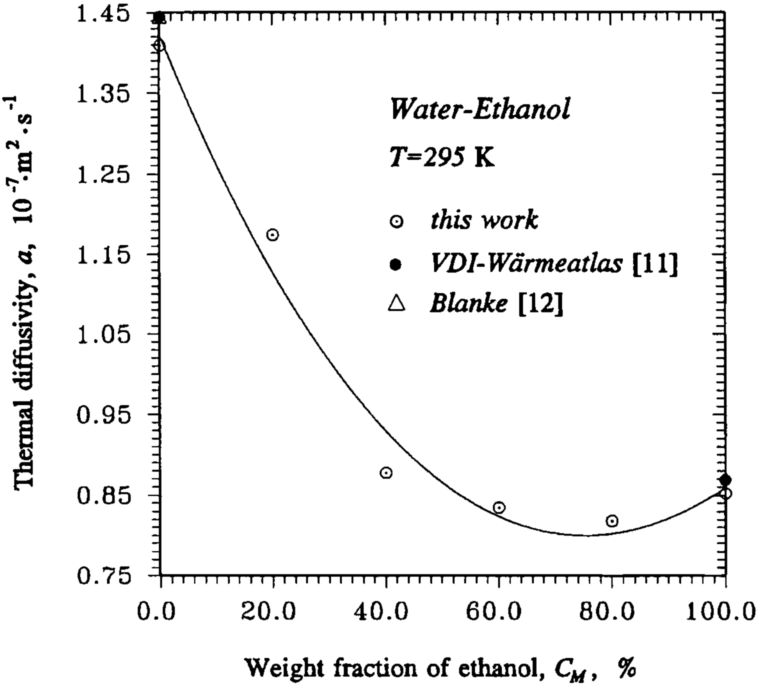

Fig. 3. Thermal diffusivity of aqueous solutions of ethanol as a function of the weight fraction of ethanol.

smaller than the value in [11]. The thermal diffusivity of water in the present work is around 2.7 and 2.3% smaller than the values reputed previously [11, 12].

Since no previous experimental data on the thermal diffusivity of the aqueous solutions of methanol and ethanol were available, we used the density and the specific heat capacity data in Ref. 13 and calculated the thermal conductivity of the aqueous solutions of methanol and ethanol from our thermal-diffusivity data (Table I). As shown in Figs. 4 and 5, the present thermal-conductivity results of the aqueous solutions of methanol and ethanol show a very good agreement with the experimental data in Refs. 12 and 1. The deviations of the derived thermal conductivity of aqueous solutions of methanol and ethanol from the resuts in Refs. 12 and 1 are within ±3%.

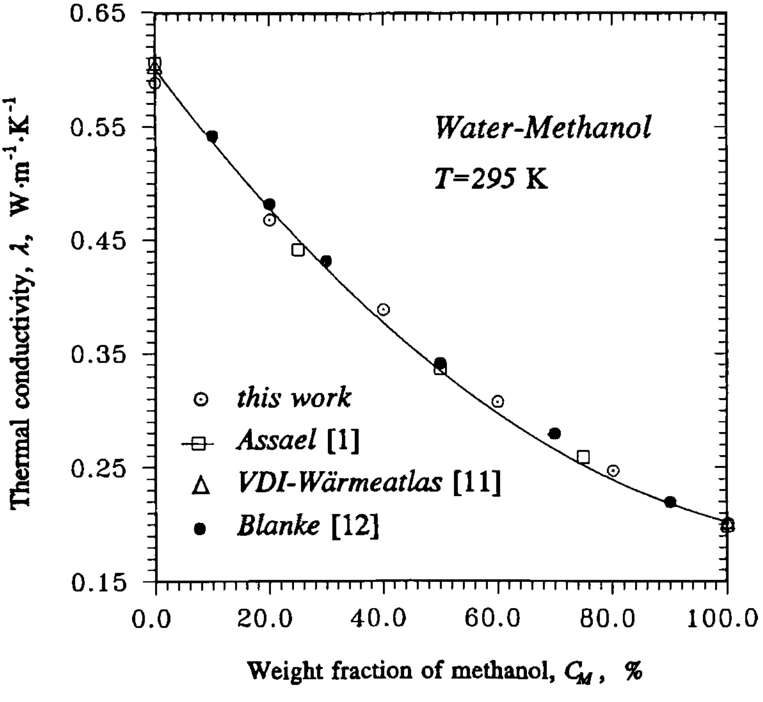

Fig. 4. Thermal conductivity of aqueous solutions of methanol as a function of the weight fraction of methanol.

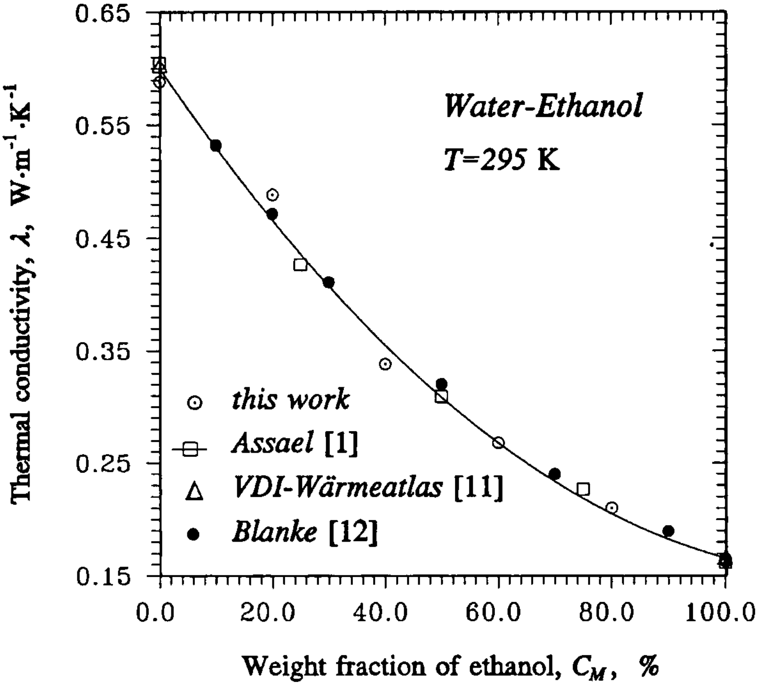

Fig. 5. Thermal conductivity of aqueous solutions of ethanol as a function of the weight fraction of ethanol.

5. CONCLUSIONS

The laser-induced thermal grating technique can be used for accurate determination of the thermal diffusivity of all liquids and liquid mixtures. In the measurements, only a very small sample volume is necessary (a few cubic millimeters). Because of the small temperature rise in the sample during the measurements and the very short measuring time, the influence of convective heat transfer is negligible. The excellent agreement of the measurements with data in the literature indicate that the laser-induced thermal grating technique is suitable for the fast determination of the thermal diffusivity of acqueous solutions of all kinds of chemicals. The systematic error, which results from the systematic effects, can be estimated and canceled. The overall uncertainty of the measurements is estimated to be better than $\pm 1.5\%$.

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