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Thermal diffusivity of di-isopropyl ether (DIPE) in the temperature range 298–530 K and pressure up to 10 MPa from dynamic light scattering (DLS)

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ABSTRACT

Transport properties of di-isopropyl ether are so scarce that it prevents the further studies of di-isopropyl ether as an alternative fuel additive. For this purpose, dynamic light scattering method is used to investigate the thermal diffusivity of di-isopropyl ether (purity: >98%) in the temperature range from 298 to 530 K and at the pressure up to 10 MPa, including saturated liquid and vapor, compressed liquid and the supercritical region. It is estimated that the standard uncertainties are: $u(T) = 0.01$ K under saturated condition; $u(T) = 0.02$ K, $u(p) = 0.015$ MPa for $p < 5.5$ MPa, $u(p) = 0.03$ MPa for $p > 5.5$ MPa under compressed liquid and supercritical conditions; and the relative expanded uncertainty U_r in the thermal diffusivity is $U_r(a) = 0.03$ with a coverage factor of $k = 2$. Moreover, the reference relations of thermal diffusivities for saturated liquid, vapor and compressed state are presented by employing the experimental results for interpolation with the average absolute deviation of 0.92%, 1.28% and 0.75%, respectively.

1. Introduction

As the number of vehicles worldwide surpasses one billion, large quantities of oil additives are being consumed all over the world. However, several kinds of additives have been proved to damage the catalytic converter or contaminate underground water, such as tetraethyl lead (TEL), methyl tert-butyl ether (MTBE) and so on. These additives are now outlawed in many countries. Recently, di-isopropyl ether (DIPE) was suggested as an alternative additive for the engine fuel since it has a low blending Reid vapor pressure and low water solubility, and especially it is environmentally benign [1]. In addition, di-isopropyl ether is frequently used as an extractant to extract polar organic compounds from aqueous solutions, e.g. phenols, ethanol and acetic acid.

It is very important to investigate the thermodynamic properties and transport properties of DIPE as an alternate fuel additive. In recent years, many scientists studied the thermophysical properties in binary or ternary mixtures of DIPE with alcohols [2–5], ethers [6], ionic liquid [7], carbon dioxide [8] and other organic fluids [9–11]. Few thermophysical data about pure DIPE can be found, although they are the foundations of binary and ternary system which is composed of DIPE. Christian [12] measured the compressed liquid densities of DIPE from 273 to 473 K with vibrating tube densimeter system. Meng [13] measured the viscosity and density of DIPE in the temperature range from 243.15 to 373.15 K and the pressure up to about 20 MPa using the vibrating-wire method. Li [14] measured the thermal conductivity of liquid DIPE from 233 to 373 K at the pressure up to 30 MPa. Páramo investigated the heat capacities between 277 and 337 K for saturated liquid DIPE [15]. Thermal diffusivity is one of the most important transport properties, which is necessary in almost all industry design of fluid energy transfer. However, thermal diffusivity of DIPE has not been measured directly up to now. In this work, we measured the thermal diffusivity of DIPE in a wide temperature range using the dynamic light scattering (DLS) method.

DLS is an effective method to investigate the thermal diffusivity of fluids. In 1965, N.C. Ford and G.B. Benedek [16] observed the spectrum of light scattered from SF_6 near its critical point, which represents the first measurement of thermal diffusivity using DLS. In the 1980s and 1990s, this method was widely used to measure the thermal diffusivities of refrigerants because of the development of photomultiplier technology and digital correlator technology [17–21]. Almost at the same time, some other light scattering methods related to DLS were used to investigate the other

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thermophysical properties such as speed of sound [22–24], viscosity [25–28], surface tension [25–28], mutual diffusion coefficient [29–31] and Soret coefficient [32,33]. In recent years, more and more attention was paid to DLS method, because it has some unique advantages:

(1) Do not need the macro temperature gradient to decrease the influence of heat convection and radiation.
(2) Measure the thermal diffusivity directly instead of thermal conductivity.
(3) It is a noninvasive method which can avoid contaminating the reagents.
(4) It is possible to measure several properties in a single experimental system simultaneously.

In the present work, the principle of DLS method and the experiment system will be described in Sections 2 and 3, respectively. In Section 4 and Section 5, we will give the measurement results and discussion. The thermal diffusivity of DIPE is measured by DLS method in the temperature range from 298 to 499 K for saturated liquid and from 465 to 499 K for saturated vapor. In addition, the isothermal thermal diffusivities in the temperature from 390 to 525 K and at pressure up to 10 MPa are also measured. At last, Section 6 will make a summary about the present work.

2. Principle of dynamic light scattering method

R.D. Mountain is one of the earliest scientists to establish the relations between the spectrum of scattered light and the physical property of fluids [34]. The DLS principle has also been detailedly represented in some classical books by B. Chu [35] and B.J. Berne et al. [36]. Thermal diffusivity is related to the half width at half maximum (HWHM) of Rayleigh peak of the scattered light. The electric field power spectrum of Rayleigh peak is Lorentzian which cannot be measured directly, because the photomultiplier is a square-law detector and its output current is proportional to the square of the incident electric field strength. However, the corresponding time autocorrelation function of photocurrent from photomultiplier can be measured alternatively. Moreover, the photon correlation technique has been certified more efficient than the spectrum analyzing for the thermal diffusivity measurement. The photon autocorrelation function is an exponential decay function

$$G^{(2)}(\tau) = A + B\,\exp\left(-\frac{\tau}{\tau_R}\right) \tag{1}$$

where τ_R is the decay constant or decay time and A, B are the fitted constants. When the heterodyne mixing is employed, the decay constant as the reciprocal of the HWHM is connected with the thermal diffusivity as the following equation.

$$a = \frac{1}{q^2 \tau_R} \tag{2}$$

where a is the thermal diffusivity, q is the modulus of scattering vector and can be calculated from Eq. (3), which is related to fluid refractive index (n), laser wavelength in vacuum (λ_0), and scattering angle (Θ_s).

$$q = \frac{4n\pi}{\lambda_0}\sin\left(\frac{\Theta_s}{2}\right) \tag{3}$$

When the scattering angle Θ_s is small enough, $\sin(\Theta_s/2)$ is approximately equal to $\sin\Theta_s/2$. According to the law of refraction, $n\sin(\Theta_s) = \sin(\Theta_{EX})$ is satisfied with the assumption that the refractive index of the surrounding air is equal to 1, where Θ_{EX} is the out incident angle as shown in Fig. 1. Hence, the scattering vector modulus can be expressed by:

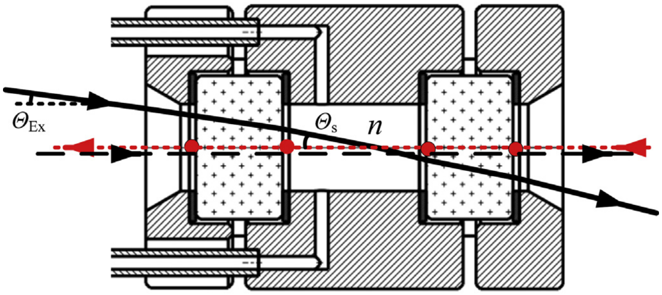

Fig. 1. The sample vessel and schematic of scattering angle.

$$q \approx \frac{2\pi}{\lambda_0}\sin\,\Theta_{EX} \tag{4}$$

It should be noted that the photon autocorrelation function $G^{(2)}(\tau)$ is obtained by the correlator with discrete data points as shown in Fig. 2, and the decay constant τ_R is determined by the nonlinear least-squares fitting (NLSF) from these points with Eq. (1). Then, the thermal diffusivity can be calculated by Eq. (2) and Eq. (4).

3. Experimental

3.1. Experimental apparatus

The optical setup in this work is shown in Fig. 3, which is similar to that was employed in literature [19,20]. Light from the high performance diode pumped solid state (DPSS) laser (λ_0 = 532 nm), which is operated in the CW single longitudinal mode, is divided into two beams by the beam splitter 1. The probe beam (the stronger one) with the vertical polarization passes though the Glan–Taylor prism and irradiates the sample in the cylindrical vessel to induce the scattered light. The Glan–Taylor prism is employed to improve the polarization ratio significantly. The reference beam (the weaker one) is not necessary when the measurement is operated in the region far away from the critical point, because the stray light from the inner wall and the quartz window of the sample vessel is sufficient for the heterodyne mixing. After combined in the beam splitter 2, the scattered light and reference light would be limited by two pin holes to make sure that only one coherence area

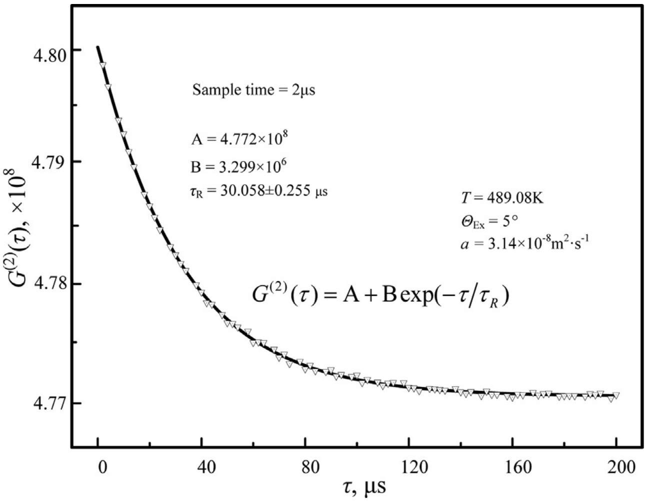

Fig. 2. A typical photon correlation function from DIPE: (▽) discrete points from digital correlator; (—) fitted autocorrelation function.