Mass Diffusion Coefficients of Dimethyl Carbonate in Heptane and in Air at T = (278.15 to 338.15) K

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The mass diffusion coefficients of dimethyl carbonate in heptane and in air were measured at T = (278.15 to 338.15) K under atmospheric pressure. The experiments were carried out using a digital holographic interferometry system that was constructed by our group. The mass diffusion coefficient of KCl in standard aqueous solution at a temperature of 298.15 K and condensation of 0.33 mol·L^{-1} was measured to verify the accuracy and reliability of the system. The experimental uncertainties in temperature and mass diffusion coefficient are estimated to be no greater than ± 0.16 K and ± 0.2 %, respectively.

Introduction

Recently, with the gradual reduction of conventional energy reserves such as coal and petroleum, the research and promotion of new energy are becoming more urgent.[1] Among all of the research, the use of mixed fuel is considered to the most convenient and simple way to solve the problem of the worldwide energy crisis. Mixed fuel is a mixture of conventional liquid fuel (gasoline, diesel fuel, etc.) and some fuel additives. Fuel additives are used to accelerate the process of combustion, to improve the efficiency of combustion, and to reduce the off-gas pollution. Research shows that dimethyl carbonate (DMC) is a well-reproducible oxygenated fuel additive for the promotion of mixed fuel.[2] The addition of DMC to diesel oil will shorten the combustion time in the internal combustion engine, greatly improve the combustion performance, and effectively reduce the soot and NO_x emissions of the diesel engine.

The mass diffusion coefficient of the fuel additive is an important thermophysical property for experimentally researching the spray, atomization, and combustion processes of the substitute fuel in a combustion engine, and it is also a key parameter for the numerical simulation of the combustion process.[3] Therefore, the theoretical prediction and experimental research of mass diffusion coefficients of fuel additives are of great importance. A literature review indicated that there is a dearth of accurate data on mass diffusion coefficients of DMC in diesel fuel and in air. The motivation of this article is to conduct a detailed experimental investigation on the diffusivity of this kind of fuel additive.

In this work, an experimental system based on digital holographic interferometry for measuring the mass diffusion coefficients of fluid was constructed. By uncertainty analysis and experimental verification, the accuracy of this system is validated. On this basis, the mass diffusion coefficients of DMC in heptane (the standard substances substituted for diesel oil in the fuel research field of the world) and in air at T = (278.15 to 338.15) K were measured, and the experimental data can be referenced for engineering application.

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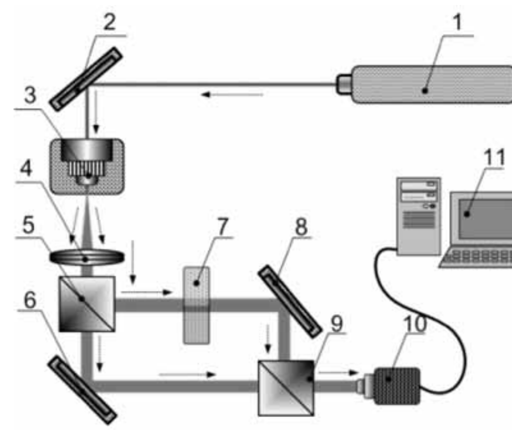

Figure 1. Optical system of digital image holographic interferometry. 1, He−Ne laser; 2, mirror; 3, spatial filter; 4, achromatic doublets lens; 5, beam splitter prism; 6, mirror; 7, diffusion cell; 8, mirror; 9, beam splitter prism; 10, CCD camera; and 11, computer.

Experimental Section

Apparatus and Procedure. The experimental system used in this work is a holographic interferometric system that is similar to the system reported in our previous work,[4] and this kind of experimental system has recently been widely used in measuring mass diffusion coefficients.[5−7] The experimental system is shown in Figure 1.

From the above Figure, we can see that the laser beam was emitted from a He−Ne laser and was reflected by a mirror, and it then went into a spatial filter in which it was expanded. Then, the expanded laser beam was collimated by an achromatic doublets lens into a parallel laser beam. The parallel laser beam was split into a reference beam and an object beam by a beam splitter. The object beam passed through the diffusion cell and recorded the diffusion information. Finally, both the object beam and the reference beam interfered to form the interference fringe, which was collected by a CCD camera and recorded on a computer.

All of the apparatus was required to be installed on the optical shockproof table to reduce the influence of the environmental shark. To make sure that the experiment was conducted in a

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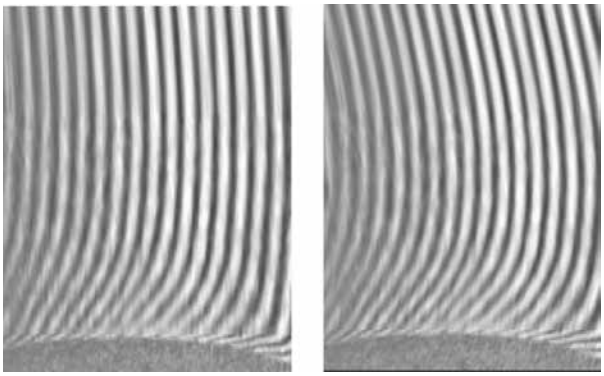

Figure 2. Interference fringe before and after the change in the solution's concentration.

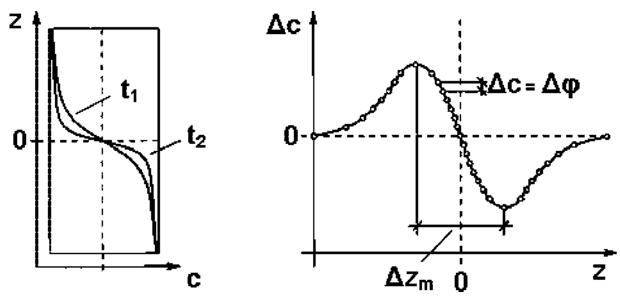

Figure 3. Distributions of the solution's concentration and its change.

stable temperature environment, we placed the diffusion cell in a thermostatic water bath whose temperature could be controlled from (0 to 80) °C with an uncertainty of ± 0.2 °C. With this experiment system, we can get interference fringe images of the diffusion liquid (as shown in Figure 2), and by analyzing the interference fringes of different moments, we can finally calculate the mass diffusion coefficient.

The basic theory of the experimental system is the second Fick's law of one-dimension diffusion,[8−11] which can be written as

$$\left(\frac{\partial c}{\partial t}\right) = D_{12}\left(\frac{\partial^2 c}{\partial z^2}\right) \quad (1)$$

where D_{12} is the mass diffusion coefficient, z is the direction of diffusion, t is the elapsed time of diffusion, and c is the concentration of the liquid, which is a function of z and t.

The solution of eq 1 for two binary fluid mixtures at $t = 0$ and $z = 0$ with concentrations c_1 and c_2 can be represented as[12,13]

$$c(z,t) = \left(\frac{c_1 + c_2}{2} + \frac{c_1 - c_2}{2}\right)\frac{2}{\sqrt{\pi}}\int_0^{\frac{z}{2\sqrt{Dt}}} \exp(-t^2)\,\mathrm{d}t \quad (2)$$

For dilute solution, the solution's refractive index n is a linear function of the solution's concentration and can be written as[14]

$$n(z,t) = mc(z,t) + n_0 \quad (3)$$

In the above equation, m and n_0 are specific constants for different fluids. The phase difference $\Delta\varphi$ of the object beam is also a linear function of the refractive index change, as shown in the following equation

$$\Delta\varphi(z,t) = \frac{2\pi l}{\lambda}\Delta n(z,t) \quad (4)$$

Therefore, the phase differences of the object beam for two different instances of time t_1 and t_2 ($t_2 > t_1$) can be written as

$$\Delta\varphi(z,t_1,t_2) = \Delta\varphi(z,t_2) - \Delta\varphi(z,t_1) = \frac{m\pi l(c_1 - c_2)}{\lambda}\frac{2}{\sqrt{\pi}} \times \left[\int_0^{\frac{z}{2\sqrt{Dt_2}}} \exp(-t^2)\,\mathrm{d}t - \int_0^{\frac{z}{2\sqrt{Dt_1}}} \exp(-t^2)\,\mathrm{d}t\right] \quad (5)$$

The distribution of $\Delta\varphi$ (z, t_1, t_2) has two extreme points, as shown in Figure 3, and the positions of the two points can be determined by the following formula

$$\frac{\mathrm{d}}{\mathrm{d}z}\Delta\varphi(z,t_1,t_2) = 0 \quad (6)$$

The two extreme points can be written as

$$z_{c_1} = \sqrt{\frac{2D\ln(t_2/t_1)}{(1/t_1) - (1/t_2)}}, \quad z_{c_2} = -\sqrt{\frac{2D\ln(t_2/t_1)}{(1/t_1) - (1/t_2)}} \quad (7)$$

The vertical distances between the two extreme points of concentration difference, Δz_m, can be written as

$$\Delta z_m = \sqrt{8D_{12}\frac{\ln(t_2/t_1)}{t_2^{-1} - t_1^{-1}}} \quad (8)$$

Transfigure the above equation, and the final equation for calculating D_{12} can be written as

$$D_{12} = \Delta z_m^2\frac{t_1/t_2 - 1}{8t_1\ln(t_1/t_2)} \quad (9)$$

From eq 9, we can see that as long as t_1, t_2, and Δz_m are obtained, we can calculate the mass diffusion coefficient; t_1 and t_2 may be read from the computer timer, and Δz_m may be extracted from the interference fringe image by the image processing method. The interference fringe image processing method used in the present work is shown in Figure 4.

The mass diffusion coefficient of KCl in aqueous solution at a temperature of 298.15 K and condensation of 0.33 $\mathrm{mol \cdot L^{-1}}$ was measured to verify the accuracy and reliability of the system. When the experimental results are compared with literature values,[15] the average of the relative deviations is within 1.30 %. The results are shown in Table 1.

Materials. Dimethyl Carbonate (CAS no. 616-38-6, molecular formula: $C_3H_6O_3$, molecular weight: 90.07, relative density: 1.0694, mass purity: ⩾ 99.5 %) and heptane (CAS no. 142-

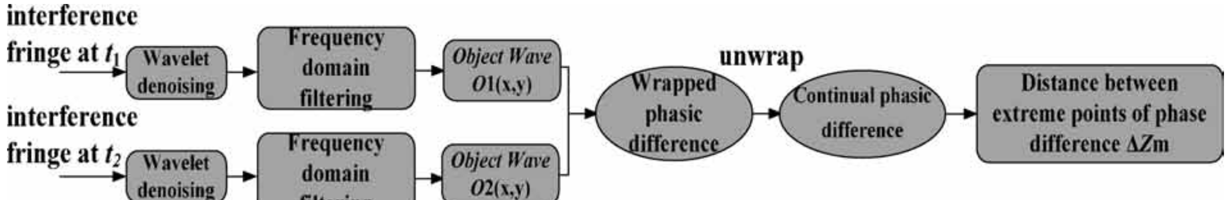

Figure 4. Flowchart of interference fringe image processing.

Table 1. Mass Diffusion Coefficients of KCl Solution at Condensation of 0.33 mol·L^{-1} in Water at 298.15 K[a,b]

Δz_m / mm	t_1 / s	t_2 / s	$10^5(D)$ / cm^2·s^{-1}
4.36	900	1800	1.876
4.91	900	3000	1.882
5.33	900	5100	1.833
5.89	900	9000	1.886
6.09	900	10200	1.848
	$10^5(D^*)$/cm^2·s^{-1}		1.865
	$10^5(D')$/cm^2·s^{-1}		1.841
	$100(D^* - D')/D'$		1.30

[a] D is experimental results, D^* is the average of experimental results, and D' is literature value. [b] Uncertainties: D, ± 0.2 %; t_1, ± 0.002 s; t_2, ± 0.002 s; Δz_m, ± 0.1 %.

Table 2. Experimental Uncertainty of Temperature and Mass Diffusion Coefficient

Temperature	
platinum resistance thermometer, u_1	± 0.01 K
data collection and process detector equipment, u_2	± 0.025 K
temperature control system, u_3	± 0.05 K
temperature stability of constant temperature cabinet, u_4	± 0.05 K
combined standard uncertainty, u_c	± 0.08 K
Mass Diffusion Coefficient	
time of getting hologram, u_1	± 2.22 ppm
distance between two extreme points of concentration, u_2	± 0.1 %
combined standard uncertainty, u_c	± 0.1 %

Table 3. Experimental Mass Diffusion Coefficients D_{12} of DMC in Heptane from T = (278.15 to 338.15) K[a]

T / K	$10^5(D_{12})$ / cm^2·s^{-1}	T / K	$10^5(D_{12})$ / cm^2·s^{-1}	T / K	$10^5(D_{12})$ / cm^2·s^{-1}
278.15	4.929	299.15	5.326	320.15	5.899
281.15	4.971	302.15	5.391	323.15	5.994
284.15	5.012	305.15	5.475	326.15	6.085
287.15	5.069	308.15	5.554	329.15	6.202
290.15	5.133	311.15	5.635	332.15	6.294
293.15	5.193	314.15	5.711	335.15	6.406
296.15	5.251	317.15	5.797	338.15	6.523

[a] Uncertainties: D_{12}, ± 0.2 %; T, ± 0.16 K.

82-5, molecular formula: C_7H_{16}, molecular weight: 100.21, relative density: 0.68, mass purity: ⩾ 99.5 %) were obtained from Sinopharm Chemical Reagent. The two components were used without further purification in the experiments.

Results and Discussion

The mass diffusion coefficient is described by temperature, the moment interference fringe was received, and the distance between two extreme points of concentration change. To determine the experimental uncertainty in the measurement, we use the following uncertainty equation[16]

$$U = ku_c = k\sqrt{\sum (u_i)^2} \quad (10)$$

where, subscript i is the influencing factor of the mass diffusion coefficient, u_i is the uncertainty for each variable, u_c is the compound uncertainty composed by each variable, and k is the confidence coefficient, which is usually taken to be 2 or 3. When $k = 2$, the degree of confidence is 95 %; when $k = 3$, the degree of confidence is 99 %. In this study, the confidence coefficient of the compound uncertainty is taken to be 2.

The result shows that the experimental uncertainties in temperature and the mass diffusion coefficient in this work are estimated to be no greater than ± 0.16 K and ± 0.2 %, respectively. (See Table 2.)

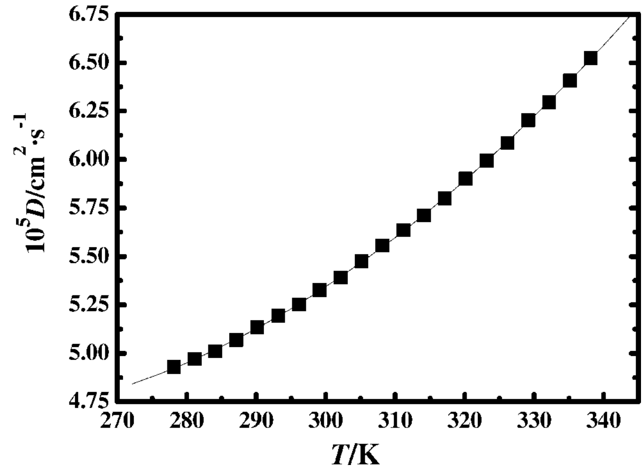

Figure 5. Plot of mass diffusion coefficients of DMC, D_{12}, in heptane against temperature. ■, experimental data; —, polynomial fit of experimental data.

Table 4. Experimental Mass Diffusion Coefficients D_{12} of DMC in Air from T = (278.15 to 338.15) K[a]

T / K	$10^5(D_{12})$ / cm^2·s^{-1}	T / K	$10^5(D_{12})$ / cm^2·s^{-1}	T / K	$10^5(D_{12})$ / cm^2·s^{-1}
278.15	8.257	299.15	8.802	320.15	9.929
281.15	8.301	302.15	8.916	323.15	10.14
284.15	8.340	305.15	9.074	326.15	10.32
287.15	8.419	308.15	9.211	329.15	10.57
290.15	8.503	311.15	9.379	332.15	10.79
293.15	8.598	314.15	9.548	335.15	11.03
296.15	8.693	317.15	9.727	338.15	11.33

[a] Uncertainties: D_{12}, ± 0.2 %; T, ± 0.16 K.

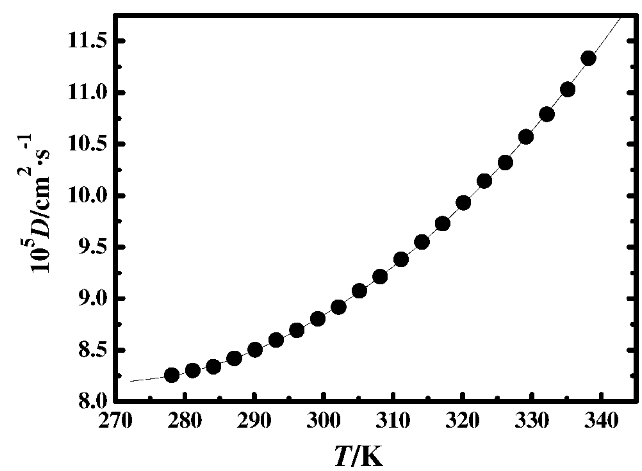

Figure 6. Plot of mass diffusion coefficients of DMC, D_{12}, in air against temperature. ●, experimental data; —, polynomial fit of experimental data.

The experimental results of the mass diffusion coefficients of DMC in heptane at T = (278.15 to 338.15) K are listed in Table 3 and Figure 5.

The polynomial of the mass diffusion coefficients of DMC in heptane calculation was fit by the experimental data at T = (278.15 to 338.15) K under atmospheric pressure, as follows

$$D_{12}/\text{cm}^2\cdot\text{s}^{-1} = 1.567\cdot 10^{-4} - 9.234\cdot 10^{-7}(T/\text{K}) + 1.931\cdot 10^{-9}(T/\text{K})^2 \quad (11)$$

The experimental results of the mass diffusion coefficients of DMC in air at T = (278.15 to 338.15) K are listed in Table 4 and Figure 6.

The polynomial of the mass diffusion coefficients of DMC in air calculation was fit by the experimental data at $T = (278.15$ to $338.15)$ K under atmospheric pressure, as follows

$$D_{12}/\mathrm{cm}^2\cdot\mathrm{s}^{-1} = 5.318\cdot10^{-4} - 3.364\cdot10^{-6}(T/\mathrm{K}) + 6.286\cdot10^{-9}(T/\mathrm{K})^2 \quad (12)$$

Conclusions

In the present work, an experimental system based on the theory of digital image holographic interferometry was constructed. With the experimental system, the mass diffusion coefficients of oxygenated fuel additives of DMC in heptane and in air were measured at $T = (278.15$ to $338.15)$ K; 42 data of mass diffusion coefficients have been obtained from the present measurements. The experimental uncertainties of temperature and mass diffusion coefficient are estimated to be no greater than $\pm$ 0.16 K and $\pm$ 0.2 %, respectively. Finally, the polynomial was fit by the experimental data, which are convenient for engineering application.

Supporting Information Available:

Properties of dimethyl carbonate and heptane. This material is available free of charge via the Internet at http://pubs.acs.org.

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