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SHORT ARTICLE

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Mutual Diffusion Coefficients of Dimethyl Carbonate and Heptane Binary Mixtures in Air

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Supporting Information

ABSTRACT: The mutual diffusion coefficients of dimethyl carbonate (DMC) and heptane binary mixtures in air were measured with different mass fractions for DMC (0.00, 0.05, 0.10, 0.15, 0.20) and at temperatures ranging from (278.15 to 338.15) K. The experimental results show that, with the increase of mass fraction of DMC in heptane, the mutual diffusion coefficients of DMC + heptane binary mixtures in air have a slight increase.

INTRODUCTION

With the rapid depletion of petroleum-based fuels and ever-increasing serious automobile-related air pollution, more researchers worldwide are encouraged to research on their clean alternatives. It is commonly accepted that clean combustion of diesel engines can be fulfilled only if engine development is coupled with diesel fuel reformulation or additive introduction.[1,2] In this way, the methods to reduce particulate matter and NO_x emissions include high-pressure injection, turbocharging, and exhaust after treatments or using fuel additives, which is known as one of the most attractive solutions.[3−5] Oxygenated fuels have been proven to be the most promising substitutes for the fossil fuels to significantly reduce diesel engine exhaust emissions.[6−8] Ester substances as one kind of the oxygenated fuels, due to its features such as high oxygen content, lower boiling point, and prominent combustion and emission characteristics, becomes one of the effective additives for diesel engines. Dimethyl carbonate (DMC) is an ester substance, and it has been validated to be a suitable additive or a component of the blended fuel for diesel.[9−11]

The mutual diffusion coefficient plays an important role in determining the small-scale structures and dissipation in high-pressure turbulence and in determining flame structures.[12,13] It is also useful for investigations in atomization, spray, and combustion process of the combustion engine.

In this paper, the experimental apparatus based on the real time digital image holographic interferometry technique was used to measure the mutual diffusion coefficients of DMC and heptane binary mixtures in air, with different mass fractions for DMC (0.00, 0.05, 0.10, 0.15, 0.20) and at the temperatures ranging from (278.15 to 338.15) K. Here, it should be noted that heptane is regarded as the standard substance substituted for diesel oil in the fuel research field.

EXPERIMENTAL SECTION

Measurement Method and Equipment. The digital image holograph interferometry system was used to measure the mutual diffusion coefficients. References 14 to 16 represent the measuring principle and the experimental apparatus in detail, so the measurement theory was depicted as follows briefly. The fundamental mutual diffusion coefficient measurement is based on Fick's second law for one-dimension diffusion,[17−20] which can be written as:

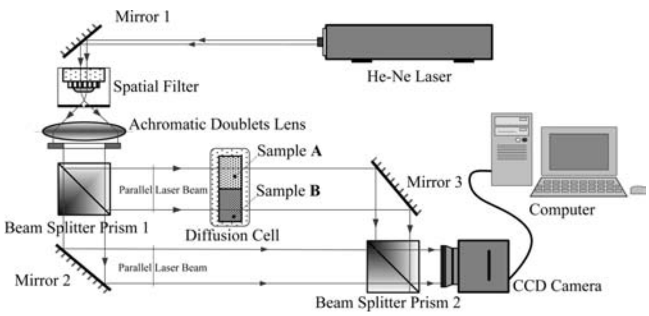

Figure 1. Optical system of digital image holographic interferometry.

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

where D_{12} is the mutual diffusion coefficient, t is the time, c is the concentration of sample, and z is the direction of diffusion.

From an analysis of the linear relationship between the variations of the object beam phase with the concentration, the D_{12} can be obtained from:

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

where t_1 and t_2 are the times of getting two adjacent holograms and Δz_m is the distance between two extreme points of concentration changes, which is obtained from digital image processing. From eq 2, it can be seen that the value of Δz_m is the key point for determining of the mutual diffusion coefficient.

Figure 1 shows the optical system of digital real-time holographic interferometry. Utilizing a spatial filter and an achromatic

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doublet lens, the laser was expanded and collimated into a parallel laser beam. The parallel laser beam was split into a reference beam and an object beam by a beam splitter. After passing through the diffusion cell and recording the diffusion information, the object beam and the reference beam interfered at the beam splitter to form the interference fringe, which was collected by a charge-coupled device (CCD) camera and recorded on a computer. All optical parts are required to be installed on the optical shockproof apparatus to reduce the influence of the environment shock.

Figure 2 shows the diffusion cell. A thermostatic water bath was used whose temperature could be controlled ranged from (273.15 to 353.15) K with an uncertainty of ± 0.2 K. As the work published before,[14,15] the experimental system was verified with the absolute average of relative deviations within 1.20 %. The total expanded experimental uncertainties in temperature and mutual diffusion coefficient were estimated to be not greater than ± 0.16 K and ± 0.2 %, respectively.

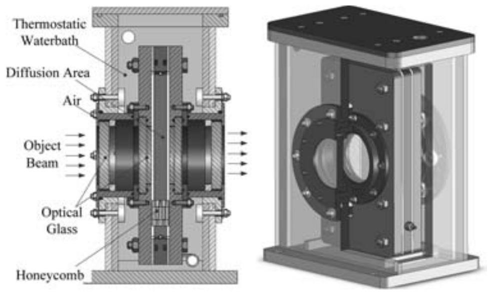

Figure 2. Diffusion cell.

Materials. DMC is considered as an oxygenated fuel additive; heptane (the standard substances substituted for diesel oil in the fuel research field) is used as a reference fluid for diesel oil because of the closed cetane number between heptane and diesel oil. The mass fraction purities of DMC and heptane were better than 0.99 and 0.97, respectively, and they were used without further purification. The DMC + heptane binary mixtures (0.00, 0.05, 0.10, 0.15, 0.20 mass fractions for DMC) were prepared by a weighing method, and the precision of balance used is 0.1 mg.

EXPERIMENTAL RESULTS AND DISCUSSION

The mutual diffusion coefficients of DMC + heptane binary mixtures in air were measured with different mass fractions of DMC (0.00, 0.05, 0.10, 0.15, 0.20). The experimental temperature ranged from (278.15 to 338.15) K. The experimental results are listed in Table 1. At each temperature, the mutual diffusion coefficients of the experimental liquid were measured at least three times, and the average value is reported. The uncertainties u of the mutual diffusion coefficient of each experimental point are also given in Table 1.

According to the experimental results, the mutual diffusion coefficients of DMC + heptane binary mixtures in air were fit to the following equation:

$$D_{12} = [71.38 - 0.6577(T/\mathrm{K}) + 1.892 \cdot 10^{-3}(T/\mathrm{K})^2 - 1.303 \cdot 10^{-6}(T/\mathrm{K})^3]\exp(0.096x) \quad (3)$$

Table 1. Mutual Diffusion Coefficients D_{12} and Uncertainties u for DMC + Heptane Binary Mixtures in Air at Temperature T

	mass fractions of DMC									
	0.00		0.05		0.10		0.15		0.20	
T	$10^5 D_{12}$	$10^5 u_{D_{12}}$	$10^5 D_{12}$	$10^5 u_{D_{12}}$	$10^5 D_{12}$	$10^5 u_{D_{12}}$	$10^5 D_{12}$	$10^5 u_{D_{12}}$	$10^5 D_{12}$	$10^5 u_{D_{12}}$
K	$\mathrm{cm^2 \cdot s^{-1}}$	$\mathrm{cm^2 \cdot s^{-1}}$	$\mathrm{cm^2 \cdot s^{-1}}$	$\mathrm{cm^2 \cdot s^{-1}}$	$\mathrm{cm^2 \cdot s^{-1}}$	$\mathrm{cm^2 \cdot s^{-1}}$	$\mathrm{cm^2 \cdot s^{-1}}$	$\mathrm{cm^2 \cdot s^{-1}}$	$\mathrm{cm^2 \cdot s^{-1}}$	$\mathrm{cm^2 \cdot s^{-1}}$
278.15	6.674	±0.0025	6.798	±0.0025	6.900	±0.0026	6.906	±0.0025	6.932	±0.0025
281.15	6.985	±0.0025	7.090	±0.0025	7.191	±0.0025	7.202	±0.0024	7.222	±0.0025
284.15	7.296	±0.0024	7.393	±0.0024	7.495	±0.0023	7.510	±0.0024	7.524	±0.0024
287.15	7.612	±0.0025	7.709	±0.0025	7.811	±0.0025	7.823	±0.0024	7.838	±0.0024
290.15	7.947	±0.0023	8.038	±0.0025	8.140	±0.0024	8.151	±0.0025	8.165	±0.0024
293.15	8.271	±0.0025	8.380	±0.0024	8.482	±0.0024	8.496	±0.0025	8.505	±0.0024
296.15	8.642	±0.0024	8.736	±0.0025	8.837	±0.0025	8.846	±0.0024	8.858	±0.0024
299.15	9.021	±0.0024	9.105	±0.0025	9.206	±0.0025	9.216	±0.0025	9.224	±0.0024
302.15	9.394	±0.0025	9.488	±0.0024	9.587	±0.0024	9.594	±0.0024	9.604	±0.0025
305.15	9.785	±0.0025	9.884	±0.0024	9.983	±0.0024	9.992	±0.0025	9.998	±0.0024
308.15	10.196	±0.0024	10.294	±0.0024	10.391	±0.0024	10.399	±0.0024	10.406	±0.0024
311.15	10.626	±0.0025	10.717	±0.0025	10.813	±0.0024	10.821	±0.0025	10.827	±0.0025
314.15	11.067	±0.0024	11.154	±0.0024	11.248	±0.0025	11.254	±0.0024	11.262	±0.0024
317.15	11.504	±0.0025	11.602	±0.0024	11.696	±0.0024	11.707	±0.0024	11.711	±0.0025
320.15	11.969	±0.0024	12.063	±0.0025	12.156	±0.0024	12.166	±0.0025	12.172	±0.0025
323.15	12.453	±0.0025	12.535	±0.0024	12.627	±0.0024	12.639	±0.0025	12.646	±0.0024
326.15	12.927	±0.0025	13.017	±0.0025	13.108	±0.0024	13.119	±0.0025	13.131	±0.0025
329.15	13.425	±0.0025	13.509	±0.0024	13.598	±0.0025	13.617	±0.0025	13.627	±0.0024
332.15	13.923	±0.0024	14.007	±0.0025	14.097	±0.0025	14.118	±0.0024	14.133	±0.0025
335.15	14.425	±0.0024	14.512	±0.0024	14.602	±0.0024	14.635	±0.0024	14.648	±0.0025
338.15	14.936	±0.0025	15.020	±0.0024	15.112	±0.0025	15.147	±0.0025	15.169	±0.0024

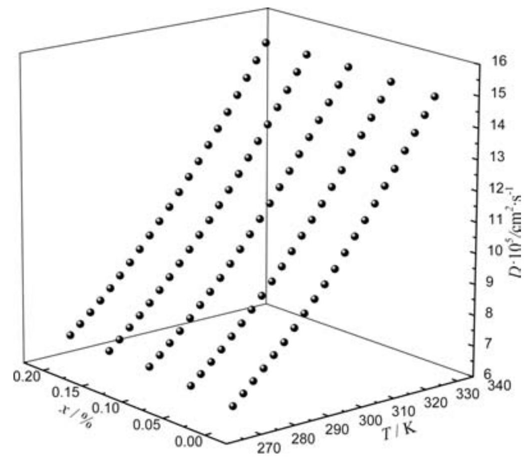

Figure 3. Mutual diffusion coefficients D_{12} for heptane and DMC mixtures in air at temperature T and mass fractions of DMC x. ●, experimental data.

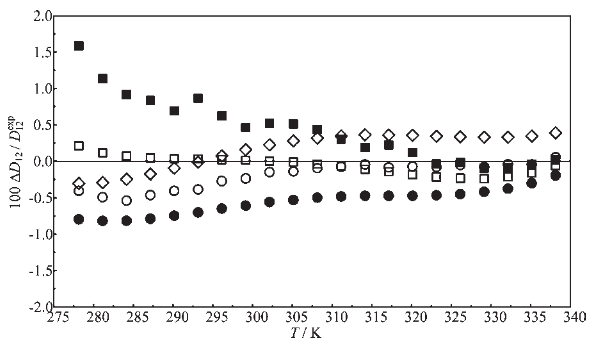

Figure 4. Fractional deviations $\Delta D_{12} = D_{12}(\text{expt}) - D_{12}(\text{calc})$ of the experimental mutual diffusion coefficients of heptane and DMC binary mixtures. ■, pure heptane in air; □, 0.05 DMC + 0.95 heptane in air; ●, 0.10 DMC + 0.90 heptane in air; ○, 0.15 DMC + 0.85 heptane in air; ◇, 0.20 DMC + 0.80 heptane in air.

where D_{12} is the mutual diffusion coefficient of DMC + heptane binary mixtures in air, T is the absolute temperature, and x is the mass fraction of DMC in DMC + heptane binary mixtures.

Figure 3 shows the variations of the mutual diffusion coefficients with temperature and mass fraction of DMC. Figure 4 shows the fractional deviations of the experimental data from that calculated with eq 3.

The experimental results show that, with the increase of mass fraction of DMC in heptane, the mutual diffusion coefficient of DMC + heptane binary mixtures in air has a slight increase. With the temperature ranging from (278.15 to 338.15) K and the mass fractions of DMC ranging from 0.05 to 0.20, the mutual diffusion coefficient of DMC + heptane binary mixtures in air increased less than 2 %, so the influence of DMC on the mutual diffusion coefficient of heptane in air could be ignored in the engineering project.

CONCLUSIONS

In the present work, adopting the real time digital image holograph interferometry method, the mutual diffusion coefficients of DMC + heptane binary mixtures in air were measured with the mass fractions for DMC (0.05, 0.10, 0.15, 0.20) at temperatures ranging from (278.15 to 338.15) K, and 84 experimental points are obtained. With the increase of mass fractions of DMC in heptane, the mutual diffusion coefficient of DMC + heptane binary mixtures in air has a slight increase.

ASSOCIATED CONTENT

Supporting Information. Table A: the physical properties of DMC and heptane. This material is available free of charge via the Internet at http://pubs.acs.org.

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