J. Chem. Eng. Data **2009,** *54,* 3101–3103

Mutual Diffusion Coefficients of Diethyl Carbonate and Diethyl Adipate in Heptane at T = (278.15 to 338.15) K under Atmospheric Pressure

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A method based on digital holographic interferometry for measuring the mutual diffusion coefficients of binary liquid is introduced. With uncertainty analysis and experimental verification, the uncertainties of temperature and mutual diffusion coefficient are estimated to be no greater than ± 0.16 K and ± 0.2 %, respectively. On this basis, the mutual diffusion coefficients for diethyl carbonate and diethyl adipate in heptane were measured from T = (278.15 to 338.15) K under atmospheric pressure, and a polynomial was fitted by the experimental data.

Introduction

Recently, with the gradual reduction of conventional energy reserves such as coal and petroleum, research and promotion of new energy is becoming more urgent.[1,2] Among all of the research, the use of mixed fuel is considered to be a convenient and simple way to alleviate the problem of the worldwide energy crisis. Mixed fuel is a mixture of conventional liquid fuel (gasoline, diesel oil, etc.) and fuel additives. Research shows that the addition of oxygenated fuel additive to gasoline or diesel oil will accelerate the process of combustion, shorten the combustion time in the internal combustion engine, greatly improve the combustion performance and efficiency, and effectively reduce the emissions of harmful off-gas such as NO_x, CO_x, HC, and soot, etc.[3,4] Since the late 20th century, thermophysical properties of fuel additives and mixed fuel have been studied, including the surface tension, viscosity, mutual solubility, stability, and optimal mixing ratio, etc. Fully understanding and utilizing the thermophysical properties have promoted the application of mixed fuel in engineering.[5,6]

The mutual diffusion coefficient of the fuel additive in liquid fuel is also an important thermophysical property to study the spray, atomization, and combustion processes of the mixed fuel in a combustion engine, and it is also a key parameter for the numerical simulation of the combustion process.[7] Therefore, theoretical predictions and experimental research on mutual diffusion coefficients of fuel additives are of great importance. A literature review indicated that there is a dearth of accurate data on mutual diffusion coefficients of oxygenated fuel additives in heptane (the standard substances used to substitute diesel oil in research). In this work, a detailed experimental investigation on the diffusivity of two kinds of oxygenated fuel additives in heptane was made.

Experimental methods of measuring mutual diffusion coefficients include: diaphragm cells, Taylor's dispersion, pulsed-field gradient nuclear magnetic resonance, dynamic light scattering, and holographic interferometry, etc. Compared with other methods, digital holographic interferometry is the newest method with the highest accuracy for measuring the mutual diffusion coefficient and has been widely used in recent years.[8,9] In this work, an experimental system based on digital holographic interferometry which was constructed by our group was used to measure the mutual diffusion coefficients of binary liquid. The mutual diffusion coefficients of fuel additives: diethyl carbonate (DEC) and diethyl adipate (DEA) in heptane were measured at different temperatures from (278.15 to 338.15) K under atmospheric pressure.

Experimental Section

Material. Diethyl carbonate (CAS No. 105-58-8, molecular formula: $C_5H_{10}O_3$, molecular weight: 118.13, relative density: 0.975, boiling point: 126.8 °C, mass purity: ≥ 99.7 %), diethyl adipate (CAS No. 141-28-6, molecular formula: $C_{10}H_{18}O_4$, molecular weight: 202.25, relative density: 1.026, boiling point: 240 °C, mass purity: ≥ 99.7 %), and heptane (CAS No. 142-82-5, molecular formula: C_7H_{16}, molecular weight: 100.21, relative density: 0.68, boiling point: 98.5 °C, mass purity: ≥ 99.5 %) were obtained from Sinopharm Chemical Reagent CO. Ltd., and they were used without further purification in the experiments.

Apparatus. The experimental system used in this work is a digital holographic interferometric system. The system includes three parts: Mach−Zehnder optical interference subsystem, the thermostatic water bath subsystem, and the diffusion cell subsystem. The first two parts were reported in our previous work.[10] The previously used diffusion cell has been improved as shown in Figure 1. A sealed cavity between two optical surfaces was added which eliminates interference of the thermostatic water on the object beam and permits operation at higher pressures. The whole diffusion cell was thermostatted in a thermostatic water bath.

The experimental uncertainties in temperature and diffusion coefficient are estimated to be no greater than ± 0.16 K and ± 0.2 %, respectively.[11] The mutual diffusion coefficient of KCl in aqueous solution at a temperature of 298.15 K and concentration of 0.33 $\text{mol} \cdot \text{L}^{-1}$ was measured to verify the accuracy and reliability of the system, and the absolute average deviations of experimental results with literature values[12] are within 1.30 %.[11]

Procedure. In the experiment, along with the progress of diffusion, the concentration of the solution changes continuously which induced the change of refractive index and the change of the object wave's phase, and it leads to the continuous change

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10.1021/je900193m CCC: $40.75

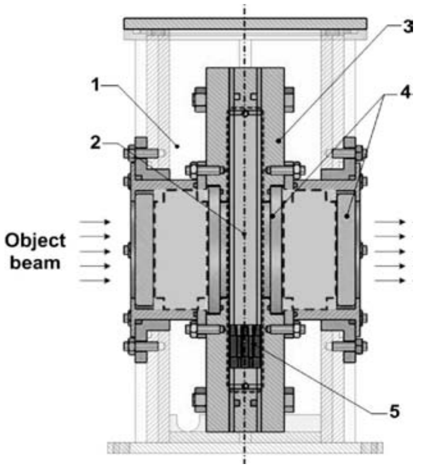

Figure 1. Diffusion cell subsystem. 1, thermostatic water bath; 2, diffusion zone; 3, diffusion cell; 4, optical glass; 5, honeycomb.

of an interference fringe on the hologram. By extracting the useful information of the object wave's phase from the interference fringe and using the relationship between the object wave's phase and diffusion coefficients, the diffusion coefficient can finally be determined.

The basic theory of the experiment is the second Fick's law of one-dimension diffusion, which can be written as[13]

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

The final equation for calculating D_{12} can be deduced as[14]

$$D_{12} = \Delta z_{\mathrm{m}}^2 \frac{t_1/t_2 - 1}{8t_1 \ln(t_1/t_2)} \tag{2}$$

where t_1 and t_2 are the moments of collecting the interference fringes which may be read from the computer timer and Δz_{m} is the vertical distance between the two extreme points of the solution's concentration difference which may be extracted from the interference fringe image by the image processing method. For a detailed description of the experimental theory and interference fringe processing method, see the work reported previously.[15]

Results and Discussion

The measured mutual diffusion coefficients of diethyl carbonate (DEC) and diethyl adipate (DEA) in heptane at T = (278.15 to 338.15) K under atmospheric pressure are listed in Table 1 and Figure 2.

Polynomial Fit. The polynomial of the mutual diffusion coefficients for DEC and DEA in heptane was fitted by the experimental data as follows

$$D_{12}/\mathrm{cm}^2\cdot\mathrm{s}^{-1} = C_1 + C_2\cdot(T/\mathrm{K}) + C_3\cdot(T/\mathrm{K})^2 \tag{3}$$

where T is the absolute temperature. C_1, C_2, and C_3 are fitted constants, and their values together with the root-mean-square deviations (rmsd) are listed in Table 2. The rmsd is defined as follows

$$\mathrm{rmsd} = \left[\frac{\sum_{j=1}^{N}(x_j^{\exp} - x_j^{\mathrm{cal}})^2}{N-1}\right]^{1/2} \tag{4}$$

where N is the number of experimental points; x_j^{cal} is the mutual diffusion coefficient calculated from eq 3; and $x_j^{\exp}$ is the experimental value of mutual diffusion coefficient.

Table 1. Experimental Mutual Diffusion Coefficients $D_{12}/(\mathrm{cm}^2\cdot\mathrm{s}^{-1})$ and Uncertainty $U_{D_{12}}/(\mathrm{cm}^2\cdot\mathrm{s}^{-1})$ for Binary Liquid DEC (1) + Heptane (2) and DEA (1) + Heptane (2) at T = (278.15 to 338.15) K under Atmospheric Pressure[a]

	DEC (1) + heptane (2)		DEA (1) + heptane (2)	
	$10^5 D_{12}$	$10^5 U_{D12}$	$10^5 D_{12}$	$10^5 U_{D12}$
T/K	$\mathrm{cm}^2\cdot\mathrm{s}^{-1}$	$\mathrm{cm}^2\cdot\mathrm{s}^{-1}$	$\mathrm{cm}^2\cdot\mathrm{s}^{-1}$	$\mathrm{cm}^2\cdot\mathrm{s}^{-1}$
278.15	3.929	± 0.0023	1.929	± 0.0023
281.15	3.956	± 0.0027	1.959	± 0.0021
284.15	3.988	± 0.0022	1.991	± 0.0021
287.15	4.025	± 0.0021	2.018	± 0.0022
290.15	4.084	± 0.0022	2.055	± 0.0025
293.15	4.144	± 0.0025	2.098	± 0.0021
296.15	4.192	± 0.0022	2.151	± 0.0023
299.15	4.266	± 0.0022	2.201	± 0.0022
302.15	4.325	± 0.0023	2.249	± 0.0022
305.15	4.399	± 0.0024	2.307	± 0.0022
308.15	4.469	± 0.0020	2.366	± 0.0021
311.15	4.539	± 0.0020	2.430	± 0.0024
314.15	4.619	± 0.0020	2.493	± 0.0025
317.15	4.705	± 0.0021	2.557	± 0.0026
320.15	4.796	± 0.0027	2.621	± 0.0026
323.15	4.881	± 0.0025	2.697	± 0.0027
326.15	4.972	± 0.0023	2.783	± 0.0025
329.15	5.068	± 0.0024	2.847	± 0.0023
332.15	5.153	± 0.0026	2.921	± 0.0022
335.15	5.251	± 0.0021	3.017	± 0.0025
338.15	5.352	± 0.0023	3.113	± 0.0027

[a] Uncertainties: $\delta(T)$ = ± 0.16 K.

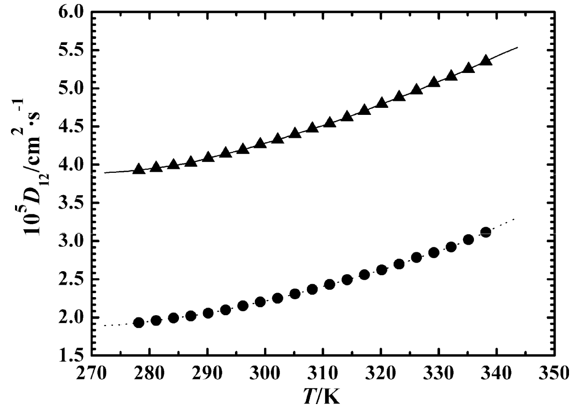

Figure 2. Plot of mutual diffusion coefficients for DEC and DEA in heptane against temperature. ▲, experimental data of mutual diffusion coefficients for DEC (1) + heptane (2); ●, experimental data of mutual diffusion coefficients for DEA (1) + heptane (2); —, polynomial fit of experimental data for DEC (1) + heptane (2); ····, polynomial fit of experimental data for DEA (1) + heptane (2).

Table 2. Parameters of Equation 3 for Polynomial Fit of Experimental Data

binary liquid	C_1	C_2	C_3	rmsd
DEC (1) + heptane (2)	$1.479\cdot10^{-4}$	$-9.124\cdot10^{-7}$	$1.874\cdot10^{-9}$	$8.871\cdot10^{-8}$
DEA (1) + heptane (2)	$1.239\cdot10^{-4}$	$-8.483\cdot10^{-7}$	$1.696\cdot10^{-9}$	$1.082\cdot10^{-7}$

From Figure 2, we can see that with the increase of temperature the mutual diffusion coefficient of these two fuel additives in heptane is increased, and the specific magnitude sequence is D_{12}(DEC + heptane) > D_{12}(DEA + heptane). This difference is mainly determined by the molecular size of these two fuel additives. For the liquid diffusion, the Stokes−Einstein equation[16] is

$$D_{12} = \frac{k_{\mathrm{B}}T}{6\pi\eta R_0} \tag{5}$$

where η is the solvent viscosity and R_0 is the radius of the solute sphere. From eq 5 we can see that under the same thermophysical conditions, the smaller the R_0 is, the bigger D_{12} is. This

Table 3. Fitted Parameters of Equation 7

binary liquid	C_4	C_5	10^4D_0 $\text{cm}^2\cdot\text{s}^{-1}$	E_D $\text{kJ}\cdot\text{mol}^{-1}$
DEC (1) + heptane (2)	−8.38334	−498.62084	2.2864	4.1458
DEA (1) + heptane (2)	−8.16713	−759.50259	2.8383	6.3149

reflected the inversely proportional relationship between the mutual diffusion coefficient and molecular volume.

Effect of Temperature. The effect of temperature on the mutual diffusion coefficient follows the Arrhenius type relationship.

$$D_{12} = D_0 \exp\left(\frac{-E_D}{RT}\right) \tag{6}$$

where D_0 is the pre-exponential factor; E_D is the activation energy for the diffusion process; R is the gas constant; and T is temperature in K.

To get D_0 and E_D, the linear equation in the form of the Arrhenius formula was fitted, as follows

$$\ln(D_{12}/\text{cm}^2\cdot\text{s}^{-1}) = C_4 + C_5/(T/\text{K}) \tag{7}$$

The fitted parameters in the temperature range studied in this work are summarized in Table 3. A plot of ln D_{12} against T^{-1} was shown in Figure 3, from which we can see the excellent correlation of the data to the Arrhenius relationship. In this work, the temperature range only covers 60 K up to 338.15 K, and in this temperature range the activation energy is independent of temperature. From the slope of this plot, diffusion activation energy can be calculated. From Table 3, we can see that, though the binary mutual diffusion coefficient D_{12}(DEC + heptane) > D_{12}(DEA + heptane), the magnitude of activation energy E_D is reversed: E_D(DEA + heptane) > E_D(DEC + heptane).

Conclusions

With the experimental system of digital holographic interferometry which was constructed in our previous work, the mutual diffusion coefficients of two kinds of oxygenated fuel additives, diethyl carbonate (DEC) and diethyl adipate (DEA), in heptane were measured at 21 different temperatures from (278.15 to 338.15) K under atmospheric pressure. The polynomial was fitted in the form of the Arrhenius equation, and its accuracy was validated by the analysis of root-mean-square deviations. The temperature effect on the diffusion coefficients follows the Arrhenius law, and the activation parameters have been obtained.

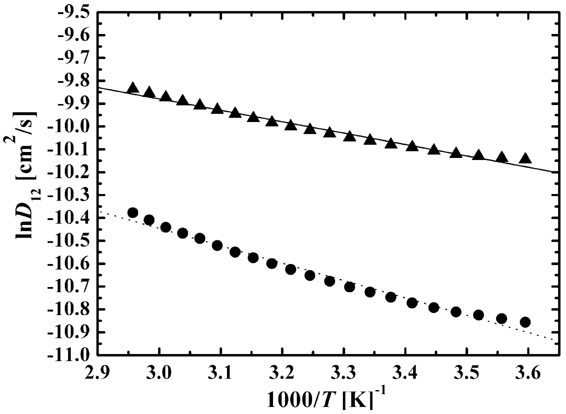

Figure 3. Arrhenius mutual diffusion coefficients plot of DEC and DEA in heptane against temperature. ▲, experimental data of mutual diffusion coefficients for DEC (1) + heptane (2); ●, experimental data of mutual diffusion coefficients for DEA (1) + heptane (2); —, best fit of experimental data for DEC (1) + heptane (2); ····, best fit of experimental data for DEA (1) + heptane (2).

Supporting Information Available:

Part 1. The physical and chemical properties of DEC, DEA, and Heptane are listed in table A.

Part 2. Derivation of the final equation to calculate the mutual diffusion coefficient used in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review February 18, 2009. Accepted May 31, 2009. We gratefully acknowledge the National Nature Science Fund Committee (NSFC nos. 50676069 and 50836004) for financial support of this work.

JE900193M