Experimental study of mass diffusion coefficients of hydrogen in dimethyl phosphate and n-heptane

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Abstract. In this study, a laser holographic interferometer experimental system was developed for studying the gas-liquid mass diffusion coefficient. Then the experimental system's uncertainty was analyzed to be at most ±0.2%; therefore, this system was reliable. The mass diffusion coefficient of hydrogen in dimethyl phosphate and n-heptane was measured at atmospheric pressure in the temperature range of 273.15–338.15 K. Then, the experimental data were used to fit the correlations of the mass diffusion coefficient of hydrogen in dimethyl phosphate and n-heptane with temperature.

1. Introduction

The mass diffusion of hydrogen in liquid hydrocarbons plays an important role in many industrial applications. For example, hydrogen is used as a fuel for internal combustion engines [1]; during combustion, it diffuses into the lubricating oil in the engine. In chemical industries, various hydrogenation technologies such as hydrocracking [2] and hydrofining [3] are used to improve the base oil of lubricants to realize high viscosity, low volatility, and improved safety [4]. In the hydrogenation process, hydrogen diffuses into the base oil of the lubricants. Even in the thermal power industry, hydrogen used for cooling the generator rotor diffuses into the lubricating oil and sealing oil [5]. In some of these applications, the diffused mass transfer is advantageous, because hydrocracking improves the lubricant properties and diffusion can promote the lubricant upgrading process. However, diffusion can also be detrimental. For example, when hydrogen is used as a coolant, diffusion will increase hydrogen leakage. Therefore, it is important to study the diffusion coefficient of hydrogen in liquid hydrocarbons.

At present, experimental studies of hydrogen diffusion have mainly focused on hydrogen diffusion into solid materials [6-8]. Few studies have investigated hydrogen diffusion into liquids, especially liquid hydrocarbons. Some studies have used mathematical approaches to provide equations for predicting the diffusion coefficient of hydrogen in liquid hydrocarbons [9,10]. In this study, we have developed a laser holographic interferential experimental platform for studying the gas-liquid diffusion coefficient. Then, by using this experimental system, we have measured the mass diffusion coefficient of hydrogen in dimethyl phosphate and n-heptane, the main components of lubricating oil and seal oil, at atmospheric pressure in the temperature range of 273.15–338.15 K. Then, we used the experimental data to fit the correlations of the mass diffusion coefficient of hydrogen in dimethyl phosphate and n-heptane with temperature. These correlations can be used as a reference in future engineering applications.
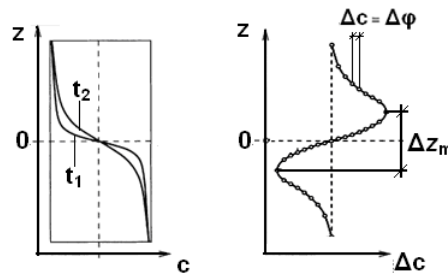
2. Experimental principle and experimental system

2.1. Experimental principle

For one-dimensional diffusion of two solutions in the vertical direction, the relation between concentration with time and space is given by equation (1) [11], and the concentration distribution curves with time and space are shown in figure 1.

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

Figure 1. Concentration distribution with time and space.

In equation (1), D_{AB} (unit: m^2/s) is the mass diffusion coefficient; c(unit: kg/m^3), the concentration; z (unit: m), the distance in the vertical direction; and t (unit: s), the time.

Upon substituting the initial and boundary conditions into equation (1) and performing a series of derivations [12], the final formula for calculating the diffusion coefficient D_{AB} for one-dimensional diffusion can be obtained as given in equation (2).

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

In equation (2), t (unit: s) is the time at which the two holograms are obtained, and ΔZm (unit: m) (figure 1) is the vertical distance between the two extreme points of concentration that can be obtained using interference fringe processing.

2.2. Experimental system

The experimental system for digital holographic interferometry consists of an optical interference system, a diffusion cell system, and a constant temperature water system.
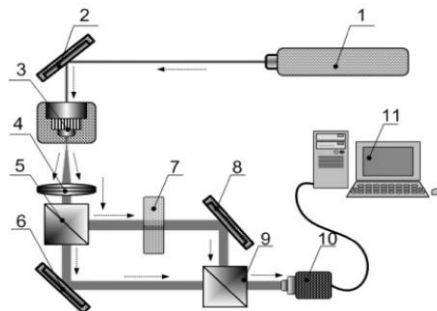
Figure 2. Optical interference system.
1, laser launcher; 2, reflector; 3, filter; 4, doublet lens; 5, light splitter prism; 6, reflector; 7, diffusion cell; 8, reflector; 9, light splitter prism; 10, image acquisition camera; 11, computer.

Figure 2 shows the laser holographic interferometry system used for measuring the diffusion coefficient. A 632.8 nm He-Ne laser is used in this experiment. The He-Ne laser beam is expanded into a parallel beam of light with ~50-mm diameter by using a spatial filter and a collimated lens. This parallel beam then passes through an aperture with 30-mm diameter such that its center uniform brightness is preserved. Then, the beam is split using a prism into the object light and reference light beams. The object light which contains the information of concentration is used to analyze diffusion, it interferes with the reference beam, and the resulting interference pattern is captured using a charge-coupled device CCD. In the experimental system, each component is placed on an anti-vibration platform to reduce the vibrations and improve the measurement accuracy.
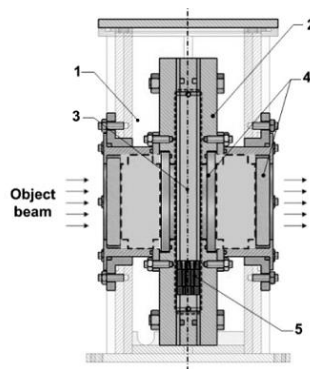

Figure 3. Diffusion subsystem.
1, water bath; 2, diffusion cell; 3, diffusion zone; 4, observation window; 5, honeycomb.

Figure 3 shows the diffusion system used for measuring the gas-liquid diffusion coefficient. This system consists of a thermostatic water bath, diffusion cell, diffusion zone, and observation window. The thermostatic water bath helps ensure that diffusion occurs under a constant temperature. The diffusion cell contains a diffusion zone within which the diffusion of two substances occurs. The observation window is the channel through which the object light is passed; it can also be used to monitor the injection process and to observe the diffusion process.

To test the gas-liquid diffusion coefficients at different temperatures, the diffusion resulting should be controlled accurately. Figure 4 shows the thermostatic water bath system used for controlling the diffusion temperature.
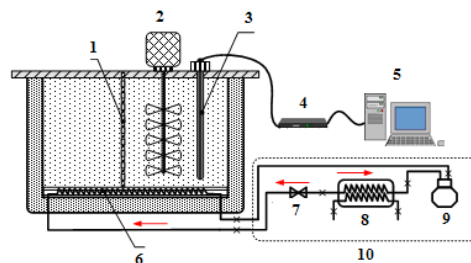

Figure 4. Thermostatic water bath subsystem.
1, rectifier grid; 2, stirrer ; 3, heating rod; 4, temperature controller; 5, computer; 6, evaporator; 7, throttle valve; 8, condenser; 9, compressor; 10, refrigeration system.

This system consists of a thermostatic environment box, a heating device, and a refrigeration device. The heating rod can be heated to a temperature of 80°C, and the evaporator of the refrigeration

system at the bottom of the box can reduce the temperature to 0°C. The stirrer and rectifier grid are used to mix the water to achieve a uniform temperature. The temperature controller connects the heating rod and the computer to control the heating temperature and record the water temperature on the computer. The system can be used to set a temperature in the range of 0–80°C with 0.1°C accuracy.

The temperature, pressure, and other operational data were collected using an NI-SCXI data acquisition system controlled by a data acquisition program written using Labview. This system consists of an SCXI-1000 universal case, an SCXI-1102 signal conditioning module, and an SCXI-1581 analog output module. Figure 5 shows the signal acquisition process.
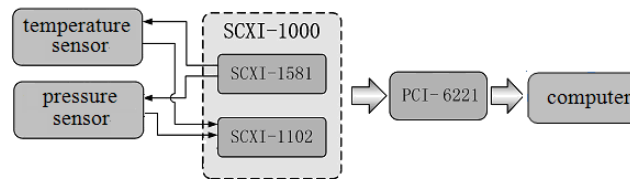
**Figure 5.** Experimental data acquisition system.

In order to evaluate the reliability of the experimental system, the mass diffusion coefficient of KCl in aqueous solution was measured, the relative deviations of the experimental results with literature values are within 1.30% [13]. The uncertainty of the physical quantities measured using this system are also determined. In this paper, the uncertainty of the mass diffusion coefficient measurement system depends on the temperature, time at which hologram is obtained, and the distance between two extreme points of concentration. According to the International Organization for Standardization [14], the combined experimental uncertainty of these three is given as

$$U = k \cdot u_c = k \sqrt{\sum (u_i)^2} \tag{3}$$

where u_i is the uncertainty of every variable in the experiment; u_c, is the synthetic uncertainty of all variables; and k is the confidence coefficient of the total uncertainty, set as 2 in this study, with the degree of confidence being 95%. Using equation (3), the uncertainty of temperature in this experiment can be calculated to be ±0.16 K, and the uncertainty of mass diffusion coefficient can be calculated as ±0.2% [13].

2.3. Interference fringe processing
Figures 6 and 7 show the interference fringe processing. The interference fringe recorded using the CCD was first denoised by the wavelet method, and then, a Fourier transform was used to obtain the frequency spectrum of the interference fringe, and then take out the first-order frequency form the spectrum with a rectangular window function and then the wrapped phasic difference can be obtained using the first-order frequency to reconstruct the object wave at two different moments. Then, it is unwrapped to obtain the continual phasic difference, from which the value of ΔZ_m can be determined to calculate the diffusion coefficient using equation (2). Details of the image processing principles and processes are given in reference [15].
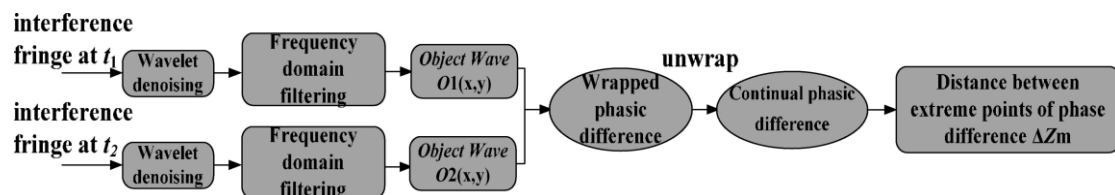
Figure 6. Flowchart of interference fringe processing.
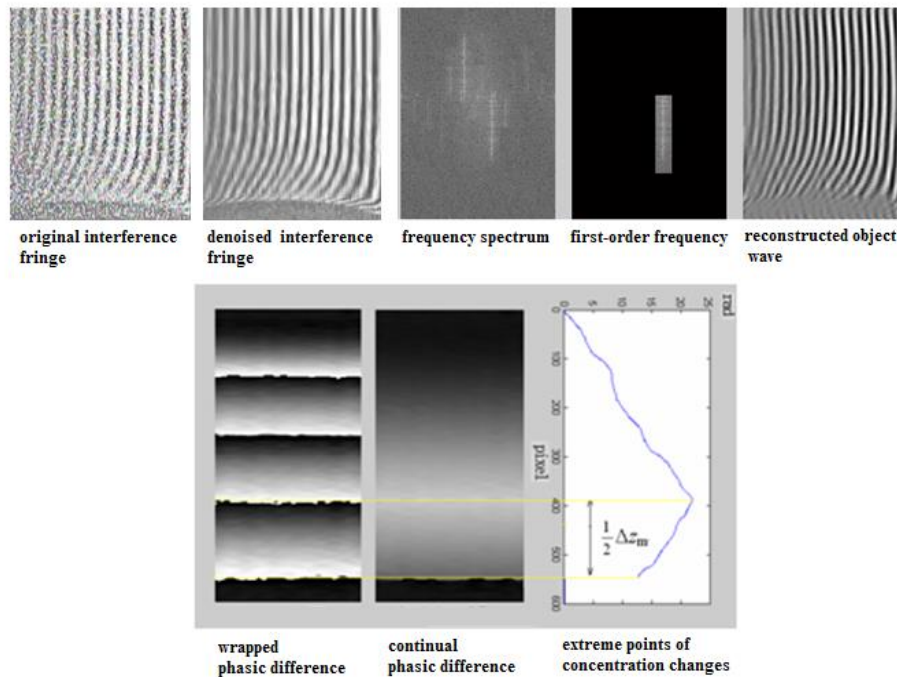
Figure 7. Interference fringe processing.

## 3. Experimental results and analysis

The mass diffusion coefficients of hydrogen in dimethyl phosphate and n-heptane were measured in the temperature range of 278.15–338.15 K and at atmospheric pressure of 0.1 MPa. Table 1 and figure 8 show the experimental results and uncertainty of all data.

Table 1. Experimental diffusion coefficients of hydrogen in n-Heptane and dimethyl phosphate.

T/K	Hydrogen (1) + n-Heptane (2)		Hydrogen (1) + Dimethyl Phosphate (2)	
	$10^5 D_{AB}/\text{cm}^2 \cdot \text{s}^{-1}$	$10^5/u_{D_{AB}}$ $\text{cm}^2 \cdot \text{s}^{-1}$	$10^5 D_{AB}$ $/\text{cm}^2 \cdot \text{s}^{-1}$	$10^5 u_{D_{AB}}$ $/\text{cm}^2 \cdot \text{s}^{-1}$
278.15	8.990	±0.0023	8.148	±0.0021
281.15	9.043	±0.0022	8.204	±0.0023
284.15	9.093	±0.0021	8.246	±0.0022
287.15	9.172	±0.0021	8.311	±0.0021
290.15	9.248	±0.0022	8.359	±0.0021
293.15	9.336	±0.0022	8.408	±0.0022
296.15	9.442	±0.0021	8.485	±0.0023
299.15	9.576	±0.0021	8.558	±0.0023
302.15	9.709	±0.0020	8.637	±0.0022
305.15	9.836	±0.0022	8.740	±0.0021
308.15	9.990	±0.0023	8.853	±0.0023
311.15	10.161	±0.0021	8.979	±0.0021
314.15	10.330	±0.0022	9.105	±0.0022
317.15	10.491	±0.0022	9.249	±0.0023
320.15	10.694	±0.0021	9.418	±0.0022
323.15	10.896	±0.0024	9.558	±0.0023
326.15	11.139	±0.0021	9.707	±0.0023
329.15	11.370	±0.0022	9.881	±0.0023
332.15	11.600	±0.0022	10.094	±0.0021

| 335.15 | 11.870 | ±0.0020 | 10.307 | ±0.0023 |
| 338.15 | 12.130 | ±0.0021 | 10.549 | ±0.0022 |

D_{AB} is the experimental result; $u_{D_{AB}}$ is the uncertainty of the diffusion coefficient.
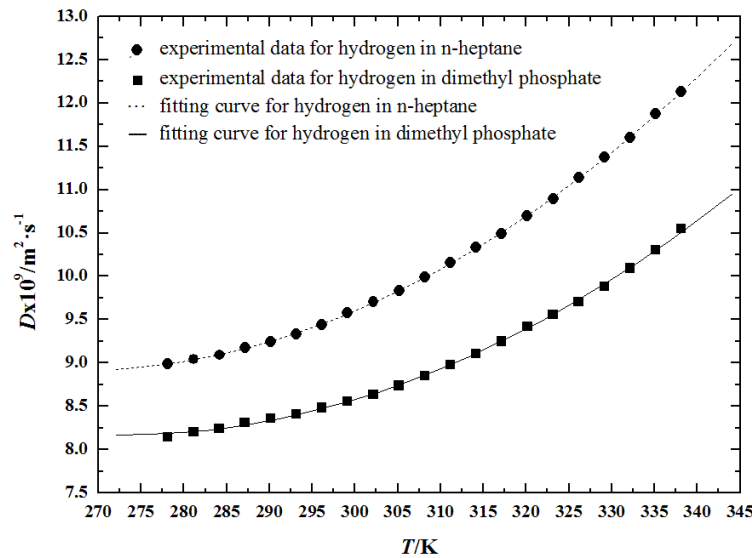
Figure 8. Experimental diffusion coefficients of hydrogen in n-heptane and dimethyl phosphate.

Figure 8 shows that as the temperature increases, the diffusion coefficients of hydrogen in the two liquid hydrocarbons increase. Under the same temperature condition, the mass diffusion coefficient of hydrogen in n-heptane is larger than that of hydrogen in dimethyl phosphate. This can be attributed to the inverse relation between diffusion coefficient and molecular size.

For engineering applications, a polynomial for calculating the mass diffusion coefficient of hydrogen in dimethyl phosphate and n-heptane was fitted as given by equation (4).

$$D_{12}/\text{cm}^2 \cdot \text{s}^{-1} = C_1 + C_2 \cdot (T/K) + C_3 \cdot (T/K)^2 \tag{4}$$

Where T is the absolute temperature; C_1, C_2, and C_3 are the fitting parameters; and the fitted values are shown in table 2.

Table 2. Parameters of polynomial (4) fitted by experimental data.

	C_1	C_2	C_3	RMSD
hydrogen in n-heptane	5.30553×10⁻⁴	-3.40312×10⁻⁶	6.37003×10⁻⁹	5.493×10⁻⁸
hydrogen in dimethyl phosphate	4.67295×10⁻⁴	-2.97017×10⁻⁶	5.44822×10⁻⁹	8.871×10⁻⁸

The root mean square deviation (RMSD) between the results calculated using equation (4) and the experimental values listed in table 3 is given by equation (5) as

$$\text{rmsd} = \left[\sum_{j=1}^{N} (x_j^{\text{exp}} - x_j^{\text{cal}})^2 / (N-1) \right]^{1/2} \tag{5}$$

Where N is the number of experimental points, x_j^{cal} is the diffusion coefficient calculated according to equation (4), and x_j^{exp} is the diffusion coefficient measured experimentally.

4. Conclusion

In this study, a laser holographic interferometer experimental system was developed for studying the gas-liquid mass diffusion coefficient. Each subsystem of the experimental platform is introduced in detail, and then, the reliability and the accuracy of the system were confirmed by uncertainty analysis and experimental verification. By using this experimental system, the mass diffusion coefficient of hydrogen in dimethyl phosphate and n-heptane was measured at atmospheric pressure in the temperature range of 273.15–338.15 K. Then, we used the experimental data to establish correlations of the mass diffusion coefficient of hydrogen in dimethyl phosphate and n-heptane with temperature. These correlations can be used as a reference in future engineering applications.

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