International Journal of Heat and Mass Transfer 111 (2017) 559–569

Contents lists available at ScienceDirect

International Journal of Heat and Mass Transfer

journal homepage: www.elsevier.com/locate/ijhmt

Investigation of the mutual diffusion coefficients of [mmim]DMP/H_2O and [mmim]DMP/CH_3OH at atmospheric pressure

Wei Chen [*], Bin Zhang, Zhigang Liu, Minmin Zhao, Zhanli Miao

College of Electromechanical Engineering, Qingdao University of Science & Technology, Qingdao 266061, China

ARTICLE INFO

Article history:
Received 23 December 2016
Received in revised form 1 March 2017
Accepted 7 April 2017
Available online 12 April 2017

Keywords:
Mutual diffusion coefficient
Holographic interferometry
Modified group contribution model
Ionic liquid absorption system

ABSTRACT

The mutual diffusion coefficient (D_{12}) of [mmim]DMP (1-methyl-3-methylimidazolium dimethylphosphate)/H_2O and [mmim]DMP/CH_3OH at ionic liquid (IL) mass fraction (ω_1) of 0.005–0.995, atmospheric pressure of 101.5 kPa, and temperature (T) of 298.15–328.15 K were measured using the holographic interferometry. It is the first time to employ holographic interferometry to measure the D_{12} of binary solutions containing ionic liquid. The influence of the meniscus on the determination of the initial time for diffusion is discussed for the first time. And this influence is eliminated by using a fitting method. D_{12} of [mmim]DMP/H_2O and [mmim]DMP/CH_3OH increase with the increase of temperature, and decrease with the increase of the IL mass fraction. The experimental data of [mmim]DMP/H_2O and [mmim]DMP/CH_3OH were correlated using the modified group contribution model, with the total deviations below 4.7% and 4.2%, respectively. The relationship of the mutual diffusion coefficients is [mmim]DMP/CH_3OH > [mmim]DMP/H_2O > LiBr/H_2O on the same conditions. The studies on D_{12} establish the foundation for the design and optimization of the absorber of ionic liquid absorption systems.

1. Introduction

Absorption refrigeration and heat pump systems are the key technologies for waste heat recycling in the industry and use of low-grade energy, such as solar [1], geothermal [2,3], and biomass [4]. LiBr/H_2O and H_2O/NH_3 are the most extensively used traditional working fluids for absorption systems [5,6]. However, absorption systems that use traditional working fluids have several shortcomings [7]. For LiBr/H_2O system, the LiBr aqueous solution is easily crystallized at low temperature and is substantially corrosive at high temperature. For the H_2O/NH_3 systems, the use of the rectifier is unavoidable, thereby leading to the deterioration of thermal performances.

In this background, the investigations on absorption refrigeration systems using ionic liquids as absorbents have become a subject that undergoes intense study. Such interest can be attributed to the unique physical and chemical properties of IL, which is a salt liquid in form at room temperature. IL possesses good thermal and chemical stability and is miscible with most refrigerants. Therefore, IL is substantially suitable as an absorbent [8]. Compared with the LiBr/H_2O absorption system, the IL absorption systems have the advantages of non-corrosion and non-crystallization. Compared with the H_2O/NH_3 absorption system, the IL absorption systems avoid the utilization of a rectification device [9] and possess improved coefficients of performance (COP). Therefore, the development of absorption refrigeration using IL as absorbent has been significantly promoted [10].

To date, the vast majority of studies on the IL absorption refrigeration are focused on the screening of the IL working fluids. The screening process can be divided into three steps. First, the vapor–liquid equilibrium (VLE) for the binary solutions containing IL and refrigerant are investigated. Second, the thermal properties of binary working fluid, such as heat capacity and excess enthalpy, are conducted. Lastly, the thermal performances of the theoretical cycle of the IL absorption refrigeration are simulated and analyzed. Based on the simulation results, the working fluids with good thermal performances can be screened out. According to the above-mentioned research procedure, the investigation on the ionic liquid absorption systems using H_2O [11,12], CH_3OH [13,14], Freon [15,16], NH_3 [17,18] and CO_2 [19,20] have been conducted. In particular, absorption systems using [mmim]DMP (1-methyl-3-methylimidazolium dimethylphosphate)/H_2O and [mmim]DMP/CH_3OH as working fluids possess excellent thermal performances. Subsequent research should focus on the industry application of absorption systems using [mmim]DMP/H_2O and [mmim]DMP/CH_3OH as working fluids.

---

[*] Corresponding author at: Songling Road 99, Qingdao, China.
E-mail address: cw_19344616@aliyun.com (W. Chen).

http://dx.doi.org/10.1016/j.ijheatmasstransfer.2017.04.025
0017-9310/

Nomenclature

a, b, c, d	fitting parameters for MGC model
C	concentration
D	mutual diffusion coefficient
E	molecular activation energy (J/mol)
q	surface parameters of component
Q	surface parameters of group
r	volume parameters of component
R	volume parameters of group
T	temperature
u	uncertainty
v	number of group
x	mole fraction
z	vertical position

Greek symbols

α, β	fitting parameters for MGC model
ϕ	unwrapped phase
ϕ^*	wrapped phase
γ	activity coefficient
π	circumference ratio
τ	time
ψ	modified coefficient of MGC model

Subscript

cal	calculation
exp	experimental
id	ideal

The absorption and desorption processes in the absorber and generator are complex phase change processes with coupled heat and mass transfer [21]. The properties of thermal conductivities and mutual diffusion coefficients of [mmim]DMP/H_2O and [mmim]DMP/CH_3OH are essential to achieve the design and optimization of the IL absorption system. The thermal conductivities of [mmim]DMP/H_2O and [mmim]DMP/CH_3OH have been investigated in our previous study [22]. Therefore, the measurement and theoretical research of the mutual diffusion coefficients of [mmim]DMP/H_2O and [mmim]DMP/CH_3OH are urgently necessary.

Several methods are employed to measure the D_{12} of binary systems, such as the diaphragm cell [23], isotope [24], NMR [25], and holographic interferometry methods [26]. The measurement accuracy of the diaphragm cell method is considerably high. However, this method takes a long time (i.e., occasionally over 24 h) [23]. The measurement using the isotope and NMR methods are rapid and precise. However, the devices of the two methods are expensive [24,25]. The holographic interferometry method is a relatively good choice because of its speed, accuracy, and low cost [26]. He et al. [27] obtained the D_{12} of H_2, CH_4, and O_2 in air at temperature of 273.15 K and atmospheric pressure of 0.1 MPa through a holographic interferometric experimental system. Peng et al. [28] also used holographic interferometry to determine the D_{12} of several short-chain alcohols (ethanol, n-propanol, and n-butanol) with noctane mixtures at 283.2–313.2 K and different concentrations. Similarly, Zhu et al. [29] measured the D_{12} of L-ascorbic acid at 298.15 K under five varying concentrations with a real-time holographic interferometer. Their studies suggest that the D_{12} of binary gas mixtures and binary solutions can be accurately measured by holographic interferometry. Thus, holographic interferometry can be potentially used to determine the D_{12} of IL working fluids.

The holographic interferometry method requires different refractive indexes of the solute and solvent for binary solution. The refractive indexes of [mmim]DMP, H_2O, and CH_3OH are 1.468 [30], 1.333 [31], and 1.328 [32], respectively, at 298.15 K. Therefore, holographic interferometr can be used to measure the D_{12} of the [mmim]DMP/H_2O and [mmim]DMP/CH_3OH solutions. So far, the studies on using this method in such application have not been reported yet. And it is the first time to use the holographic interferometry method to measure the D_{12} of IL absorption refrigeration working fluids. The influence of the meniscus on determination of the initial time for diffusion is discussed for the first time. And this influence is eliminated by using a fitting method. In this study, the D_{12} of [mmim]DMP/H_2O and [mmim]DMP/CH_3OH with [mmim]DMP mass fractions of 0.005–0.995, T of 298.15–328.15 K, p of 101.5 kPa were measured using the holographic interferometry method. The modified group contribution (MGC) models were constructed by correlating with the D_{12} data. The D_{12} of [mmim]DMP/H_2O, [mmim]DMP/CH_3OH, and LiBr aqueous solution were also compared with one another.

2. Experiment materials and procedure

2.1. Materials

High-purity anhydrous potassium chloride (CAS No. 7447-40-7, KCl, purity ≥ 99.999%) was purchased from D. Chemical Co., Ltd. (Beijing, China). The IL [mmim]DMP (CAS No. 654058-04-5, $C_7H_{15}N_2O_4P$, purity ≥ 99.99%,) was purchased from C. J. Company (Shanghai, China). High-purity, anhydrous methanol (CAS No. 67-56-1, CH_3OH, purity ≥ 99.999%) and high-purity, deionized water (CAS No. 7732-18-5, H_2O purity ≥ 99.999%) were obtained from WEITE Industries (Beijing, China). Two samples with different mass fractions were prepared for each measurement. The suitable mass fraction differences for the [mmim]DMP/H_2O and [mmim]DMP/CH_3OH solutions were determined to be 0.12% and 0.08%, respectively. When the mass fraction difference is substantially large, the interference fringe becomes considerably dense. Consequently, undersampling occurs during CCD sampling. At considerably small mass fraction difference, the interference fringe rapidly changes and thus affects the accuracy of the measurement. The samples were prepared using an electronic scale with an uncertainty of ±0.0001 g.

2.2. Measurement system

Fig. 1 presents the optical schematic for the D_{12} measurement system using digital holographic interferometry. The measurement system is a classical Mach–Zehnder interferometer, which is extensively used in optical measurements. A beam emitted from a He–Ne laser (632.8 nm) is divided into two beams by a beam splitter. The two beams are expanded, filtered, and collimated through microscopic objective, spatial filter, and collimating lens. One of the collimated beams (i.e., object beam) then passes through the diffusion cell, whereas the other collimated beam (i.e., reference beam) does not pass through the diffusion cell. The object and reference beams are combined using a beam splitter to form a holographic interferogram, which is recorded by a CCD camera and saved in a computer. All optical components are fixed on a vibration isolation optical platform to avoid the effects of vibration.

Fig. 2 displays the structure of the diffusion cell system. The two optical glasses were assembled and attached to the diffusion cell element with liquid glue. Two sealed cells are formed by the