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Mutual diffusion coefficients, density, and viscosity of aqueous solutions of new polyamine CO_2 absorbents

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ABSTRACT

The mutual diffusion coefficients of aqueous solutions of new polyamine CO_2 absorbents, namely 3-(methylamino)propylamine, diethylenetriamine, N,N,N′,N′-tetramethylethylenediamine, and tetramethyl-1,3-diaminopropane at different concentrations were measured at temperatures from 303.15 to 323.15 K using the Taylor dispersion technique. Empirical and semi-theoretical models such as a modified Snijder et al. equation, UNIDIF equation, and a free-volume relation based on the rough hard-sphere theory were used to represent the experimental diffusion coefficient data as function of temperature and amine concentration. Densities and viscosities of the aqueous solutions, which were used in the calculation of diffusion coefficients, were also measured. The obtained density and viscosity data were correlated with temperature and amine concentration using a Redlich–Kister-type and Vogel–Tamman–Fulcher equation, respectively. The predicted density, viscosity, and diffusion coefficient data were in reasonable agreement with the experimental data, suggesting that the measured properties were satisfactorily represented by the applied models.

1. Introduction

Aqueous polyamine solvents are interesting candidate absorbents for CO_2 capture. Recent studies showed that the additional amine groups present in polyamines have properties similar to those of alcohols, which make them viable alternatives to alkanolamines [1]. It has also been reported that due to these added amine functionalities, aqueous solutions of several polyamines have higher CO_2 absorption capacity and faster reaction kinetics, compared with commonly used alkanolamine absorbents [2–5].

In the present work, we considered four polyamines, which are among the potential solvents for CO_2 absorption: 3-(methylamino)propylamine (MAPA), diethylenetriamine (DETA), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), and tetramethyl-1,3-diaminopropane (TMPDA). MAPA has been reported by Svendsen et al. [6,7] to have higher reaction rate compared with methyldiethanolamine (MDEA), and suggested it as an effective activator in aqueous MDEA and dimethylmonoethanolamine (DMMEA) solutions. On the other hand, we have shown in a recent work [8] that the triamine DETA in aqueous solution (30 wt%) has higher CO_2 loading than aqueous monoethanolamine (MEA) and aqueous MDEA (at the same concentration). Some studies also reported that compared with aqueous MEA, aqueous DETA have higher cyclic capacity and a much higher reaction rate with CO_2 [2,3]. Furthermore, MAPA and DETA were shown to have lower vapor pressures (lower volatility) than MEA [9,10]. In another study, the diamines TMEDA and TMPDA were shown to have superior degradation stability than MEA in the presence of CO_2 or O_2 [1].

Although some thermodynamic and physical properties namely heat capacity, enthalpy of fusion and vaporization, ideal-gas enthalpy of formation, density, and viscosity have already been reported by some authors [10,11], to our knowledge, the diffusion of any of the studied polyamines in aqueous solutions has not yet been investigated; hence, the absence of diffusion coefficient data for such systems in the literature. Diffusion coefficient is one of the most important transport properties that is indispensable in the design of any absorption process including that involved in CO_2 capture operations. Thus, in this work we measured the binary mutual diffusion coefficients, D_{12}, of MAPA, DETA, TMEDA, and TMPDA in water at concentrations $w_1 = (0.0–0.40)$ amine and temperatures from 303.15 to 323.15 K. The measured diffusion coefficients were then correlated with temperature and amine concentration using various models such as a modified Snijder et al. equation [12], UNIDIF equation [13], and that based on the rough hard-sphere theory [14]. Additional measurements of the densities, ρ, and viscosities, η, of the studied systems, which were used in the estimation of diffusion coefficients were also conducted.

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Table 1
Description of chemicals used in this work.

Polyamine	Source	Purity (wt%)	Purification done
MAPA	Alfa Aesar	>99	None
DETA	Acros Organics	>98	None
TMEDA	Alfa Aesar	>99	None
TMPDA	Tokyo Chemical Co. Ltd.	>98	None
Ethylene glycol (EG)	Tedia Company, Inc.	>99.9	None

2. Experimental

2.1. Materials

MAPA and TMEDA (purities > 99 wt%) were purchased from Alfa Aesar, DETA (purity > 98 wt%) was supplied by Acros Organics, and TMPDA (purity > 98 wt%) was from Tokyo Chemical Co. Ltd. These amines were used in the experiments without further purification. The description of the chemicals used is given in Table 1. The aqueous solutions were prepared by dissolving the amines in high-purity distilled deionized water (resistivity = 18.3 mΩ), which was processed in a Barnstead Thermolyne (model Easy Pure 1052) water purification system. The aqueous samples were prepared by mass using a digital balance (Mettler Toledo model AL204) with an accuracy of $\pm 1 \times 10^{-4}$ g. The uncertainty of the concentration of the samples was estimated to be ±0.02 wt%.

2.2. Measurements of density

The density of each sample was measured using an SVM 3000 Stabinger viscometer (Anton Paar GmbH), which also consisted a vibrating tube density meter. The equipment had a measurement cell made of a U-shaped borosilicate glass tube. It was equipped with an integrated thermostat with cascaded Peltier elements and Pt thermometer, and a low-thermal mass measuring cell, which enabled rapid changes and exact adjustments to the measuring temperature. The temperature was controlled to ±0.005 K, and the accuracy of the measured value was ±0.02 K. The densitimeter was calibrated as per manufacturer's recommendation using dry air and distilled deionized water as standard fluids. The overall uncertainty of the density measurement was estimated to be $\pm 5 \times 10^{-4}$ g cm^{-3}. All measurements were done in three to five replicate runs.

2.3. Measurements of viscosity

The viscosity of each sample was measured using an automated falling ball microviscometer (Anton Paar GmbH, model AMVn), which allowed measurements in a wide viscosity range (0.3–2500 MPa s) depending on the measuring system used. In this work, measurements were performed using the two capillaries (diameter d = 1.6 and 1.8 mm), which covered the whole range of viscosities of the studied systems. Each capillary was calibrated at various angles using appropriate certified standard calibration fluids (Canon N2 and N100) prior to use. The experimental method was described in detail in our recent work [15]. The viscometer had a built-in Pt-100 temperature sensor for temperature measurement and control. The uncertainties of the measured temperature and viscosity were estimated to be ±0.05 K and ±1.0%, respectively. All measurements were done in three to five replicate runs.

2.4. Measurement of diffusion coefficient

The measurements were performed using the Taylor dispersion technique [16,17], which was carried out on the basis of the analysis given by Alizadeh et al. [18]. Detailed descriptions of the experimental setup and design criteria were provided in our earlier works [19–21]. The setup was consist of a diffusion tube with length and inside radius (R_c) of 50.218 m and 0.254 mm, respectively, and was arranged as a helical stack of horizontal coils with radius (r_c) 300 mm. The diffusion tube was placed in a water bath whose temperature was controlled to ±0.01 K of the desired value using a Hart Scientific thermometer (model 1502). The estimated uncertainty of the temperature measurement was ±0.1 K. The sample, as well as the carrier fluid, was made to flow into the diffusion tube through a six-point injection valve (Rheodyne, model 7725i), and the fluid flow (laminar) was maintained constant by using an isocratic pump (Young Lin Instrument, model Acme 9000). A fluid flow rate of 0.15 mL min^{-1} was maintained to ensure that $Re^2\omega^{-1}Sc \le 100$, where Re and Sc are Reynolds and Schmidt numbers, respectively, and $\omega = R_c/r_c$; hence, preventing the secondary flow in the helical coil [18]. The measured densities and viscosities were used in the estimation of Re and Sc.

For each measurement, 1.0–1.5 μL of the sample was introduced to the carrier fluid. The concentration of the injected solution was usually only a small concentration, 0.03–0.1 kmol m^{-3}, greater than that of the carrier fluid. For the measurements at infinite dilution, the injected samples contained even smaller amounts of solute in solution (0.004–0.006 kmol m^{-3}). Based on the correction equation for the carrier solution composition due to the injected sample (according to Alizadeh et al. [18]), the contribution of the correction term is usually less than 0.1% of the solution composition. Consequently, the correction term for the solution concentration due to the injected sample can be said to be negligible. The concentration gradient in the system was determined using a differential refractometer (Precision Instruments, model IOTA 2), which was positioned at the tube exit. The analog output was then acquired, processed, and analyzed using a chromatograph data system (YL-Clarity Chromatographic Station). The signals were collected and plotted as a function of time, and a least squares procedure based on the method proposed by Deng and Leaist [22] was applied to determine the binary diffusion coefficients. Taking into account the validation performed (using ethylene glycol (EG) + water at x_1 = 0.2 as reference solution), the overall uncertainty of diffusion coefficient measurement was estimated to be within ±2%. All measurements were done in three to five replicates.

3. Results and discussion

Prior to the measurement of densities, ρ, viscosities, η, and diffusion coefficients, D_{12}, of the studied systems, the validity of the experimental setups and methods used were tested by measuring the ρ of a standard oil (APS3), η of water and the D_{12} of ethylene glycol in water (x_1 = 0.2) in the temperature range 303.15–323.15 K. The results obtained from the validation experiments are summarized in Table 2. As indicated in the table, the experimental data are in reasonable agreement with standard and literature values [23–26] at average percent deviations (APDs) of 0.01%, 0.7%, and 1.2% for ρ, η, and D_{12}, respectively. These values, which are all within the reported uncertainties of the measurements, suggest that the methods employed in this work would be expected to give accurate results.

3.1. Density

Density and viscosity are physical properties of a liquid solution, which are necessary in the estimation of the diffusion coefficient of the solvent; hence, they were measured for the studied binary systems. The experimental density data are listed in Table 3. For all polyamine systems, a decreasing trend in the values of the density