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Density, viscosity and spectroscopic studies of the binary system 1,2-ethylenediamine + 1,4-butanediol at $T = (293.15 \text{ to } 318.15)$ K

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ABSTRACT

Densities and viscosities were measured under atmospheric pressure over the entire concentration range for the binary system 1,2-ethanediamine (EDA) + 1,4-butanediol (BDO) at $T = 293.15$, 298.15, 303.15, 308.15, 313.15, and 318.15 K as a function of composition. Based on density and viscosity data, excess molar volumes (V_m^E) and dynamic viscosity deviations ($\Delta\nu$) were calculated. V_m^E and $\Delta\nu$ values were correlated by a Redlich–Kister type function to obtain the coefficients and to estimate the standard deviation between the experimental and calculated quantities. Based on FTIR and UV–vis spectral results, the intermolecular interaction between EDA and BDO was discussed.

1. Introduction

Global warming and climate change caused by greenhouse gases have become critical issues of global concern in recent years [1–3]. Carbon dioxide (CO_2), a major greenhouse gas produced by burning of fossil-fuels, contributes to over 60% of global warning [4,5]. Various CO_2 capture technologies have been developed, including absorption, adsorption, membrane separation, and biological methods [6–18]. Among these technologies, absorption with amine solutions such as monoethanolamine [19,20], diethanolamine [21], triethanolamine [22], *N*-methyldiethanolamine [23], and diglycolamine [24], is most widely used [25–29]. However, this method is limited by relatively high energy consumption due to high volatilization of amines in the absorption and desorption processes [30,31].

Our recent work showed that 1,2-ethylenediamine (EDA) had a high CO_2 absorption capability of approximately 0.46 mol CO_2 per mol EDA. However, the use of EDA was restrained because EDA with relatively high volatility can produce several negative effects in the gas treating unit, including higher operating cost and higher capital expenditures caused by the loss of EDA. One way to reduce the volatility of amines was to combine with an alcohol component to form a binary mixed solvent [32,33]. It was suggested that hydrogen bonding interactions and hydrogen bonded structures in amine–alcohol mixed solvent were the contributing factors for minimizing the loss of amines. With regard to the alcohol component, ethylene glycol (EG) and its derivatives were evaluated in our previous studies due to their favorable properties such as low vapor pressure, low toxicity, and low melting temperature [38,39]. EG and its derivatives have native hydrogen bonding sites and therefore the potential for scrubbing acid gases. Based on these considerations, a binary system of 1,4-butanediol (BDO) and EDA was studied for capturing CO_2 by our group. Approximately 40 g of the equimolar binary system absorbed 7.75 g CO_2 at room temperature and atmospheric pressure, which showed high absorption of CO_2 in this system.

The present study deals with the fundamental aspects of the EDA/BDO system derived from physical properties such as density (ρ), viscosity (η), and excess properties over a wide temperature range. We started by measuring density, viscosity, and excess properties for the system EDA/BDO over the whole composition range. Absorption and desorption properties of CO_2 in the system EDA/BDO/H_2O were then studied and intermolecular interactions in the system EDA/BDO/H_2O/CO_2 were investigated. Finally, intermolecular interactions of EDA with BDO were discussed based on the FTIR and UV–vis spectra. It is expected that this fundamental study can provide deeper understanding of the amine–alcohol system and thus a basis for improvements.

2. Experimental

2.1. Materials

EDA with a mass fraction purity of 0.99 was purchased from Tianjin Sheng Ao Company (Tianjin, China). BDO with a mass fraction purity of 0.99 was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). EDA and BDO were used after drying over molecular sieves (type 4A). All chemicals were degassed before use. Double-distilled water and high performance liquid chromatography (HPLC) grade ethanol were used. Specifications of all chemical samples are

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listed in Table 1. Density and viscosity data in the literatures are listed in Table 2 as references [40–59].

2.2. Measurements

The binary mixtures were prepared by mass using an analytical balance with a precision of ±0.0001 g (Sartorius BSA224S). The uncertainty of the mole fraction for each of the two components in the binary mixture was less than ±0.0001. Densities of neat liquids and their mixtures were measured using a bicapillary pycnometer with a bulb volume of 25 cm^3. The volume of pycnometer was calibrated as a function of temperature using the HPLC grade ethanol at $T = (293.15, 298.15, 303.15, 308.15, 313.15, \text{and } 318.15)$ K. The pycnometer filled with liquid was kept in a well-stirred and thermostatically controlled water bath to ±0.01 K. The water bath was used for all density and viscosity measurement over the time period required for achieving thermal equilibrium (20 to 25 min). The reported density value was an average of at least three measurements. The uncertainty of density measurements was estimated to be $\pm 0.0002\ \text{g}\cdot\text{cm}^{-3}$.

The dynamic viscosity values of both the neat liquids and their mixtures were determined using an Ubbelohde type viscometer with a capillary diameter of 1.1 mm. The principle of measurement for this type of viscometer is based on the time between two points as a result of gravity fall. The viscometer was calibrated using double-distilled water and ethanol (HPLC grade) in the experimental temperature range, respectively. A thoroughly cleaned and perfectly dried viscometer, filled with experimental solution samples, was placed exactly vertically in an insulated jacket, wherein constant temperature was maintained by circulating water from a thermoelectric controller at the required temperatures. After thermal stability was attained, the flow time was determined with a hand-held digital stopwatch capable of measuring time accurate to ±0.01 s. At least 16 repetitions of each data point were obtained, in addition to every flow time that does not exceed ±0.05 s. The time used to calculate the dynamic viscosity is the averaged result of 16 flow times.

The v values are calculated from Eq. (1),

$$v = At–B/t \tag{1}$$

where A and B are the viscometer contents, and t is flow time in the viscometer. Respectively, A and B are determined from measurements with the calibration fluids of double-distilled water and ethanol (HPLC grade).

The absolute viscosity (η) value was calculated from Eq. (2),

$$\eta = \rho v \tag{2}$$

where ρ is the density value of the binary system.

3. Results and discussion

3.1. Density

The measured density values of BDO and EDA, and their mixtures are listed in Table 3 and plotted in Fig. 1.

Table 3 and Fig. 1 show that the density values gradually decrease with increasing temperature at the same concentration, and the density values decrease with increasing concentration of EDA at the same temperature.

The V_{m}^{E} values of the solutions were calculated at $T = (293.15, 298.15, 303.15, 308.15, 313.15, \text{and } 318.15)$ K from the densities of the neat liquids and their mixtures according to the following equation,

$$V_{\text{m}}^{E} = (x_1M_1 + x_2M_2)/\rho - (x_1M_1/\rho_1 + x_2M_2/\rho_2) \tag{3}$$

where ρ_{m} represents the density of mixtures; x_1, ρ_1, and M_1 denote the mole fraction, density, and relative molecular mass of pure EDA, respectively; and x_2, ρ_2, and M_2 denote the mole fraction, density, and relative molecular mass of pure BDO, respectively. The V_{m}^{E} values are listed in Table 4 and shown in Fig. 2.

Table 4 and Fig. 2 show that the V_{m}^{E} values of the binary mixture become larger along with increasing temperature. The minimum was found at about $x_1 = 0.34$, which means that the volume of the binary mixture is minimum.

The experimental results were fitted in the Redlich–Kister polynomial equation,

$$V_{\text{m}}^{\text{E}} = \frac{x_1M_1 + x_2M_2}{\rho_m} - \left(x_1\frac{M_1}{\rho_1} + x_2\frac{M_2}{\rho_2}\right) \tag{4}$$

where x_1 represents the mole fraction of EDA, x_2 represents the mole fraction of BDO, A_i is the polynomial coefficients which were evaluated from the least-squares method, and n is the polynomial degree.

The calculated excess molar volume ($V_{\text{m}}{}^{\text{E}}{}_{\text{cal}}$) values and the calculated density (ρ_{cal}) values were correlated by the Redlich–Kister type polynomial,

$$Z = x_1(1-x_1)\sum_{i=0}^{n} B_i(2x_1-1)^i \tag{5}$$

where Z denotes ρ_{cal}, $V^E{}_{\text{cal}}$, η_{cal} or $\Delta\nu_{\text{cal}}$, x_1 represents the mole fraction of EDA, A_i is the polynomial coefficients which were evaluated from the least-squares method, and n is the polynomial degree. The smaller deviation ($\rho_{\text{cal}}–\rho_{\text{exp}}$) values between experimental and calculated results are shown in Fig. 3. In order to investigate the fitting efficiency for V_{m}^{E}, the standard deviation values, σ, between the calculated and experimental data points are obtained by the following equation,

$$\sigma = \left[\sum_{i=1}^{N}\left(Y^E_{\text{exp},i} - Y^E_{\text{calc},i}\right)^2 \Big/ (N-m)\right]^{\frac{1}{2}} \tag{6}$$

where N is the total number of experimental points and m is the number of A_i coefficients considered. Table 5 presents the values of the parameters A_i together with the standard deviation σ.

3.2. Viscosity

The dynamic and absolute viscosity values for EDA and BDO and their mixtures are listed in Table 6 and shown in Figs. 4 and 5 as a function of the mole fraction of EDA (x_1).

Table 1
Specification of chemical samples.

Chemical name	Source	Initial mass fraction purity[b]	Purification method
1,2-Ethanediamine	Tianjin Reagent Co., Ltd., China	≥0.99	Desiccation[c] and degasification[d]
1,4-Butanediol	Shanghai Reagent Co., Ltd., China	≥0.99	Desiccation[c] and degasification[d]
Ethanol[a]	Beijing Tongguang Industry of Fine Chemicals Co., Ltd., China	≥0.997	Desiccation[c] and degasification[d]

[a] Chromatographic grade.
[b] Declared by the supplier.
[c] Molecular sieve type 4A.
[d] Ultrasound.