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Experimental investigation of density, viscosity and intermolecular interaction of binary system 1,3-butanediol + 1,2-ethanediamine for CO_2 capture

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ABSTRACT

In our recent work, the binary system of 1,3-butanediol (BTD) (1) + 1,2-ethanediamine (EDA) (2) shows strong solubility to CO_2 with 0.7551 mol CO_2 per mol EDA. In this work, as important thermodynamic properties, densities (ρ) and viscosities (η) of the binary system of BTD (1) + EDA (2) at $T =$ (298.15, 303.15, 308.15, 313.15, and 318.15) K were carefully measured as a function of composition over the whole concentration range under atmospheric pressure. Based on the experimental ρ and η data, the excess properties of the BTD (1) + EDA (2) mixtures, including excess molar volume (V_m^E) and viscosity deviation $\Delta\eta$, apparent molar volume ($V_{\varphi,1}$ and $V_{\varphi,2}$), partial molar volume ($\overline{V_1}$ and $\overline{V_2}$), and isobaric thermal expansion coefficient α_ρ were systemically investigated. Meanwhile, the Redlich-Kister equation was used to fit with V_m^E and $\Delta\eta$, the optimal fitting coefficients were obtained, and the standard deviations σ between the experimental and calculated quantities were evaluated. Additionally, the intermolecular interaction of BTD with EDA was expressed as the N···H hydrogen-bonding interaction with the form of ···HOCH(CH_3)CH_2CH_2O—H···$NH_2CH_2CH_2N(H_2)$··· on the basis of UV–vis, FTIR, ^{1}H NMR, and Fluorescence spectral results and electrical conductivity of BTD (1) + EDA (2) mixtures.

1. Introduction

The property of liquid mixtures draws practical interests in technological and theoretical applications. Specially, density and viscosity are seen as important thermodynamic properties in the field of chemical engineering region [1], including process development, process design, system simulation, and operation control.

Compared with monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA), which were often used to capture CO_2 in industrial processes [2], 1,2-Ethanediamine (EDA) presents a high CO_2 capacity with 0.46 mol CO_2/mol EDA with two amine-groups [3], thus a fact that EDA was used to absorb CO_2 has been developed [4,5]. On the other hand, 1,3-butanediol (BTD) was attributed to the label of "green solvent" because it is nonflammable, nonvolatile, nontoxic to living organisms, and biodegradable by bacteria in some specific environment. For this reason, a binary system of BTD + EDA was used to absorb CO_2, which showed a stronger absorption ability with 0.7551 mol CO_2 per mol EDA. Therefore, accurate prediction physicochemical properties of mixture are becoming increasingly importance.

To the best of our knowledge, the literatures about density and viscosity of the system of BTD (1) + EDA (2) was not reported; consequently, these density and viscosity data were systemically measured at various concentrations at the ambient pressure and temperature ranging from (298.15 to 318.15) K with a step of 5 K in this work. Furthermore, on the basis of the density and viscosity data, excess molar volume (V_m^E), viscosity deviation ($\Delta\eta$), apparent molar volume ($V_{\varphi,1}$ and $V_{\varphi,2}$), standard partial molar volume ($\overline{V_1}$ and $\overline{V_2}$), and isobaric thermal expansion coefficient (α_ρ) of mixtures were calculated. Especially, the V_m^E and $\Delta\eta$ values were fitted with the Redlich-Kister equation. Additionally, molecular interactions of binary system were also systemically discussed based on FTIR, UV, NMR, and Fluorescence spectral results and electrical conductivity.

2. Experimental section

2.1. Materials

The source and purity of all chemicals were listed in Table 1. Before measurements, the whole chemicals were dried through molecular sieves (type 4A) and also degassed using ultrasonic method. The conductivity of doubly distilled and deionized water was lower than

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Table 1
Specification of chemical samples.

Chemical name	CAS No	Source	Molecular weight ($g \cdot mol^{-1}$)	Mass fraction purity[b]
1,2-Ethanediamine	107-15-3	Tianjin Reagent Co., Ltd., China	60.10	≥0.99
1,3-Butanediol	107-88-0	Shanghai Biochemical Technology Co., Ltd., China	90.12	≥0.99
Ethanol[a]	64-17-5	Tianjin Guangfu Institute of Fine Chemicals Co., Ltd., China	46.07	≥0.997

[a] Chromatographic grade.
[b] Declared by the supplier.

0.1 μs·cm^{-1} at 25 °C. Meanwhile, the pycnometer and Ubbelohde viscometer were corrected using HPLC grade ethanol.

FTIR spectra were recorded on a Nicolet (Nexus 670) FTIR spectrometer with a resolution of 1 cm^{-1} in the range from (4000 to 400) cm^{-1}. The spectrometer possesses auto-align energy optimization and a dynamically aligned interferometer and is fitted with two constringent BaF_2 pellets for the measurement of aqueous solution. A baseline correction was made for the spectra recorded in air; and then 10 μL solution was used to perform on the FTIR spectrometer in each measurement and the thickness of sample layers was less than a typical thickness of 2 μm. All spectral experiments of BTD (1) + EDA (2) were performed at room temperature and atmospheric pressure.

UV spectra were recorded on a Shimadzu (UV-2450) UV–vis spectrometer with a resolution of 0.5 nm in the range of (190 to 400) nm at room temperature. The deionized water was used to make a baseline correction for the spectra.

Fluorescence spectra were acquired using an F-4500 fluorescence spectrophotometer employing a 500 W Hg—Xe high-pressure lamp. All liquid reagents were weighed by using Sartorius BS224S electric balance.

The ^{1}H NMR spectra were conducted by a 500 MHz Bruker Advance III spectrometer. The ^{1}H NMR experiments were performed with both internal and external references. For internal references, the sample was mixed in d6-DMSO. For external references, the samples and deuterated reagents were injected into capillary tubes (25 cm × 0.9 mm) and NMR tubes (17.8 cm × 5 mm), respectively. Then the capillary tube was inserted into the NMR tube to separate the samples from the solvents (deuterated regents).

2.2. Measurements

All mass measurements were performed using an electronic balance with an accuracy of 0.1 mg (Sartorius BS224S), and the uncertainty of mole fraction was estimated to be ±0.0001. Density data of pure liquids and their mixtures were determined using a bicapillary pycnometer with a bulb volume of 10 cm^3. The volume of pycnometer was calibrated using double-distilled water at T = (298.15 to 318.15) K, respectively. A thermostatically controlled and well-stirred water bath with a temperature control accuracy of ±0.01 K was used to provide constant temperature condition. The pycnometer filled with liquid was kept in water bath for 20 min to attain thermal equilibrium. Each experimental density value was an average of at least three measurements, and the uncertainty of density measurements was estimated to be ±0.0020 g/cm^3.

The kinematic viscosity (ν) values of pure liquids and their mixtures were measured using the Ubbelohde viscometer with a capillary diameter of 1.1 mm. Double-distilled water and ethanol (HPLC grade) was used to calibrate the Ubbelohde viscometer at T = (298.15 to 318.15) K, respectively. The viscometer was put in the water bath for 30 min to attain thermal equilibrium, and the flow time of liquid was measured with a hand-held digital stopwatch capable of measuring time within ±0.01 s. The average of sixteen flow times for each fluid was taken for the calculation of kinematic viscosity value, and the relative uncertainty of viscosity measurements was estimated to be ±0.028 m$^2 \cdot$s^{-1}.

The electrical conductivity values were measured at room temperature using a high sensitive DDSJ-308A conductivity meter.

3. Results and discussion

The experimental data was verified by comparing densities and viscosities obtained in this work with the corresponding literature values as seen in Table 2, and the agreement between the experimental and literature values was found to be satisfied.

3.1. Density

The measured densities of BTD, EDA, and their mixtures under atmospheric pressure at T = (298.15 to 318.15) K were presented in Fig. 1.

As shown in Fig. 1, the density values of BTD (1) + EDA (2) mixtures increased with the increasing concentration of BTD at the identical temperature, and finally the rising trend became gentle; at the same time, the density values gradually decreased with the increasing temperature at the identical concentration of BTD.

For forecasting densities over all concentrations, the measured densities were calculated by Eqs. (1) and (2) [23,24]. More specifically, Eq. (1) was used for deducing the correlation between density and

Table 2
Comparison of experimental densities and viscosities of BTD with EDA with literature values at different temperatures.

T/K	ρ/(g·cm^{-3})		η/(mPa·s)		ρ/(g·cm^{-3})		η/(mPa·s)	
	Exp BTD	Lit	Exp	Lit	Exp EDA	Lit	Exp	Lit
298.15	1.0004	1.00042 [6] 1.0003 [7]	96.7	97.250 [7] 97.2620 [9]	0.8941	0.8945 [8] 0.8948 [10] 0.8949 [12]	1.38	1.37 [3] 1.39 [11] 1.405 [13]
303.15	0.9973	0.99754 [14] 0.996895 [16]	69.7	69.8440 [9]	0.8881	0.8881 [15] 0.8888 [11]	1.18	1.16 [3] 1.21 [15] 1.24 [11]
308.15	0.9944	0.99420 [14] 0.99422 [7]	51.8	52.500 [7] 52.5420 [9] 52.55 [18]	0.8852	0.8849 [11] 0.8856 [8] 0.885616 [19]	1.08	1.0 5 [3] 1.07 [17] 1.12 [11]
313.15	0.9901	0.990116 [16] 0.9897 [20]	40.0	39.4180 [9]	0.8804	0.8800 [11] 0.880896 [19]	1.03	1.03 [11] 1.01 [21]
318.15	0.9870	0.98708 [22] 0.986665 [16]	29.9	30.487 [7] 30.5050 [9]	0.8757	0.8752 [11] 0.876153 [19]	0.930	0.95 [11] 0.953 [3]