



Non-ideal behavior of ethanol + amines mixtures, modeling using the Peng-Robinson and PC-SAFT equation of state

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ABSTRACT

In this paper, experimental measurements of densities and viscosities of Ethanol + Diethylenetriamine (DETA) or Aminoethylethanolamine (AEEA) binary liquid mixtures are reported at temperatures of 298.15, 303.15 and 308.15 K and atmospheric pressure over the whole composition range. From the experimental data, excess molar volume, excess coefficient of thermal expansion, excess partial molar volume, isothermal coefficient of excess molar enthalpy, excess Gibbs free energy of activation and excess viscosity were calculated. The sign and magnitude of excess quantities were used to discuss about the nature and strength of molecular interactions in these solutions. The obtained excess molar volumes were correlated with Redlich-Kister polynomial equation. Moreover, the measured values of densities were predicted with Peng-Robinson and PC-SAFT equation of states and the experimental values of viscosities were correlated and predicted by different semi-empirical equations.

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1. Introduction

Recently, many researches have been deduced to the elimination of CO₂ from the exhausts systems because of the growth of CO₂ emission which is the main reason of global warming. One of the main promising method to decrease the CO₂ emission is the post-combustion capture using amine and alcohol mixtures in which large amount of volume gas can be cleaned [1–5]. Among the amines, Aminoethylethanolamine (AEEA) is considerable alternative solvents for acid gas treatment because of its acceptable absorption capacity, high carbon dioxide reactivity and energy efficiency [6,7]. Moreover, Diethylenetriamine (DETA) with three amine functionalities has higher capacity and faster absorption rate than single amine functionality [8]. Usage of alkanolamines are the most favorable but require high energy [6,9]. To reduce the cost of process, the mixture of different amines in aqueous or alcoholic systems is the more considerable. However, mixing of amine components with alcoholic systems may be interesting and promising approach for CO₂ treatment [10]. In addition to acid gas scrubbing application, alcohol and amine molecules have a noticeable trend to construct associated species due to the hydrogen bonding effect which is play a vital role in chemical, physical, and biological processes. From the practical point of view, study the thermodynamic and transport properties of mixtures are essential in design and operation of chemical plants and extend of models. Therefore, the reliable and accurate thermodynamic data of pure components and their mixtures, covering a wide range of temperature, pressure and composition, are necessary. Excess thermodynamic

properties and mixing deviation of binaries represent the information about the nature of molecular interactions in mixtures. This information is crucial in analysis and prediction of fluids behavior. This research is devoted to analysis the molecular interaction of ethanol + diethylenetriamine or aminoethylethanolamine mixtures using calculation of different excess thermodynamic properties. Several studies have been so far performed on the thermodynamic and transport properties of binary mixtures including the alcohols and amines. Excess molar enthalpies of ethylene diamine + methanol, ethanol, propanol and butanol binary mixtures were determined by Zarei et al. [11]. The reported excess enthalpies were negative for all mixtures, and the negative values of H_m^E were reported to increase with rising temperature. Negative excess viscosities and negative excess molar volumes were obtained for binary mixtures of diethylene glycol monobutyl ether with monoethanolamine, diethanolamine, and triethanolamine at temperatures of 293.15 to 333.15 K [12]. For these amine mixtures, excess molar volumes shift to more negative values and the excess viscosities shift to positive values with increasing temperatures. Using experimental measurements of density and viscosity, excess molar volumes and viscosity deviations of aqueous solutions of methylethanolamine, ethylethanolamine, dimethylethanolamine, 3-(dimethylamino)-1-propanol and 3-(Dimethylamino)-2-propanol were calculated by Chowdhury et al. [13]. These mixtures show the maximum viscosity values around the 0.5 water mole fraction. Moreover, positive viscosity deviation and excess molar volume were obtained for all aqueous amine mixtures. Kinart et al. [14] reported the negative values of excess molar volumes for 2-methoxyethanol + propylamine binaries over the whole composition range at $T = 298.15$ K. In similar research, experimental values of density, viscosity and refractive index of water + AEEA binary

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mixtures were reported by Mundhwa et al. [15]. Based on their measurements, density and viscosity pass over the maximum values at 0.3 and 0.6 AEEA mole fractions, respectively. Moreover, the obtained negative excess molar volumes shift to zero values when temperatures increase. In other research, negative excess molar volume and positive excess Gibbs free energy of activation of butylamine + 1-alkanol mixtures were reported and these results were ascribed to the predominance of the formation of NH–OH and OH–NH, bonds over the rupture of the OH–OH and NH–NH bonds present in pure alkanol and amine [16]. Similar to these results were observed for binary mixtures of 1-Alkanol + dipropylamine or dibutylamine at temperatures of 303.15 and 313.15 K [17].

In this study, the experimental measurements of densities and viscosities of ethanol (ET) and diethylenetriamine (DETA) or aminoethylethanolamine (AEEA) binary liquid mixtures are reported at temperatures of 298.15, 303.15 and 308.15 K and atmospheric pressure (0.1 MPa). Different thermodynamic properties including the thermal expansion coefficient, excess thermal expansion coefficient, excess molar volume, partial molar volume, excess partial molar volume, partial molar volume at infinite dilution, excess viscosity, excess Gibbs free energy of activation and isothermal coefficient of excess molar enthalpy are calculated. The density prediction capabilities of different equation of states were examined using the Peng–Robinson (PR) and perturbed-chain statistical associating fluid theory (PC-SAFT) models. The obtained results from thermodynamic calculation and modeling were used to analysis the molecular interaction in the mixtures. Moreover, McAlister, Arrhenius-like and Kendall–Monroe models have been used to reproduce the experimental viscosity data.

2. Experimental section

2.1. Chemicals

Ethanol (CAS no. 64-17-5) and aminoethylethanolamine (CAS no. 111-41-1) were purchased from Sigma–Aldrich and diethylenetriamine (CAS no. 111-40-0) was purchased from Merck. The purity of these chemicals was higher than 98% and their water content was <0.2%. All the chemicals were used without further purification and the purities were verified by measuring the normal boiling points of pure substances. The water content of the chemicals was measured with Kyoto mks-210 Karl Fischer instrument to be aware of the effect of water on temperature control. Molecular structures of the studied components are shown in Fig. 1.

2.2. Experimental procedures

All binary solutions were prepared by mass using a single pan Mettler Toledo AG204 balance with a standard uncertainty of 0.1 mg. The mixtures were freshly prepared and retained at desired temperature for some hours to ensure complete miscibility.

Densities of pure liquids and their mixtures were determined using an Anton Paar oscillation U-tube densitometer (model: DMA 500) with the standard uncertainty claim by the manufacture of $0.001 \text{ g}\cdot\text{cm}^{-3}$ and temperature standard uncertainty of 0.1 K calibrated at $T = 293.15 \text{ K}$ with pure water.

The kinematic viscosities of liquids were measured with Ubbelohde glass capillary tube viscometer with a Schott–Grate automatic measuring unit (model: AVS 400) immersed in a transparent thermostat water bath, which allows temperatures stabilization with a standard uncertainty of 0.01 K and the bath filled with distilled pure water. Different capillaries having various diameters were used depending on the sample viscosity. The kinematic viscosity ν and dynamic viscosity η were computed using equations: $\nu = k \cdot t$ and $\eta = \nu \cdot \rho$, where, t is the flow time and k is the capillary constant of viscometer. The viscosities were averaged from three measurements with the standard uncertainty of 0.01 mPa.s.

The experimental values of densities ρ and dynamic viscosities η of pure components are compared with the literature values at different temperatures and are reported in Table 1. The relative standard uncertainties for measured densities and viscosities are 0.002 and 0.1, respectively. From the Table 1, good agreement is observed between densities reported in this work with densities reported by Zhang et al. [18] and García-Abuín et al. [19] for ethanol at $T = 303.15 \text{ K}$ with pointwise absolute deviation percent $\text{PAD}\% \leq 0.01$. Moreover, minimum and maximum pointwise absolute deviation percent between experimental viscosities data and those reported in the literature are 0.020 [15] and 6.764 [20] for AEEA at $T = 298.15 \text{ K}$ and DETA at $T = 303.15 \text{ K}$, respectively. In this paper, the average absolute deviation percent $\text{AAD}\%$, between experimental and literature or models data is calculated using the following equation:

$$\text{AAD}\% = \left(\frac{100}{N} \right) \sum_{i=1}^N \left| \frac{A_i^{\text{exp}} - A_i^{\text{lit-cal}}}{A_i^{\text{exp}}} \right| \quad (1)$$

where N is the number of the experimental data points. The subscripts “exp” and “lit-cal” represent the values of the experimental and literature or calculated property, respectively. When $N = 1$, the pointwise comparison is desirable.

3. Results and discussion

The measured values of densities and viscosities of ET + DETA or AEEA binary mixtures and derived properties of thermal expansion coefficients, partial molar volumes and excess molar volumes are given in Tables 2 and 3.

Density is defined as the ratio of mass to volume of component and its variation against temperature and pressure represent the information about the phase behavior of fluids. The variation of densities against ethanol mole fractions for binary mixtures of ET + DETA or AEEA at all

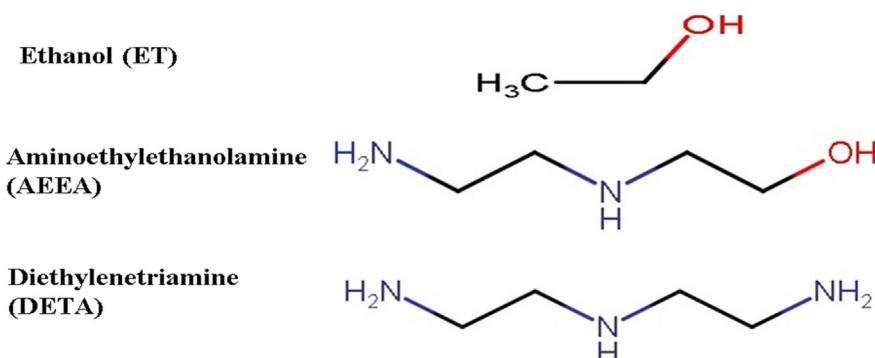


Fig. 1. The structure formulas of used components.

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