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Thermodynamic properties and sPC-SAFT modeling of 2-ethoxyethanol, 2-propoxyethanol and 2-butoxyethanol from $T = (293.15–413.15)$ K and pressure up to 30 MPa

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New experimental $P\rho T$ data of three glycols ethers, namely, 2-ethoxyethanol, 2-propoxyethanol and 2-butoxyethanol were measured in a wide range of temperatures (293.15–413.15) K and pressures (0.1–30) MPa with a vibrating-tube densimeter. The experimental $P\rho T$ data were correlated with the modified Tait equation. The study is completed with modeling in terms of the simplified perturbed-chain statistical associating fluid theory (sPC-SAFT) equation of state. The pure compound parameters of the sPC-SAFT equation are generally determined by fitting the equation to experimental saturated vapor pressure and liquid density data. In this work, by simultaneously minimizing the total objective function of temperature, pressure and density new correlation were developed to estimate the sPC-SAFT equation parameters with two association scheme for three glycols ethers including, 2-ethoxyethanol, 2-propoxyethanol and 2-butoxyethanol by using $P\rho T$ data and with a fitting AAD% of 0.17 on average. The validity of the parameters and the employed association scheme were tested by the evaluation of densities and derivative properties such as isobaric thermal expansion coefficients, α_P, isothermal compressibility, κ_T, isobaric heat capacities, C_P, and speed of sound, u. All correlated/predicted results were compared with the modified Tait equation and experimental literature data. The obtained results showed that the sPC-SAFT equation of state, along with the proposed correlations, presents good results for modeling these glycols ethers.

1. Introduction

The study of properties of pure glycol ethers is very important from both theoretical and industrial points of view. 2-Alkoxyethanols are used as a solvent for many different purposes such as varnishes, dyes, resins and brake fluid. Short-chain polyethylene glycol monoalkyl ethers are used in various biotechnical and biomedical applications, constituting a simple model of biological systems [1]. On the other hand, glycol ethers are nonionic amphiphilic molecules, very effective as surfactants with a large number of applications [2]. 2-Alkoxyethanols are avery interesting class of solvents owing to the presence of the oxy and hydroxyl groups in the same molecule. Hence the formation of intra-and intermolecular hydrogen bonds between the —O— and —OH groups of the same or different molecules have been observed [3–6]. The density of 2-ethoxyethanol at $T = (283.15–328.15)$ K and at atmospheric pressure and at $T = (293.15–353.15)$ K and pressures up to 60 MPa were reported in the literature [7–15]. For 2-propoxyethanol, the density at $T = (283.15–303.15)$ K and atmospheric pressure has been found in the literature [12,13,16–18]. $P\rho T$ data of 2-butoxyethanol at temperatures $T = (283.15–348.15)$ K and ambient pressures [11–13,19–24] and at $T = (288.15–348.15)$ K and pressures up 380 MPa were investigated in the literature [25]. Advances in applied statistical mechanics in recent years have resulted in a number of equations of state (EoS's) for real complex fluids with strong theoretical basis. Two of the most successful and widely used families of such models are based on Wertheim's first-order thermodynamic perturbation theory [26–29] and lattice theory [30]. PC-SAFT [31] is one of the most successful models of the first family, while a simplified version of the model, sPC-SAFT [32] reduces the computing time without compromising its performance. Glycol ethers are interesting candidates for testing sPC-SAFT equations of state for intra-and intermolecular association. It was presented in the Ph.D thesis by Avlund [33] and in a recently

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published paper [34]. In the present work, we report new experimental $P\rho T$ data for pure, 2-ethoxyethanol, 2-propoxyethanol and 2-butoxyethanol at T = (293.15–413.15) K and pressure P = (0.1–30) MPa. $P\rho T$ of pure component were correlated with the modified Tait equation and thermodynamic properties such as isobaric thermal expansion coefficients, α_P, isothermal compressibility, κ_T, internal pressure, P_{int}, and the difference in the isobaric and isochoric heat capacities, C_P - C_V were calculated. The study is completed with modeling in terms of the simplified perturbed-chain statistical association fluid theory (sPC-SAFT) equation of state with two association scheme. The validity of the parameters and the employed association scheme were tested by the evaluation of densities and derivative properties such as isobaric thermal expansion coefficients, α_P, isothermal compressibility, κ_T, isobaric heat capacities, C_P, and speed of sound, u. All correlated/predicted results were compared with the modified Tait equation and experimental literature data. The obtained results showed that the sPC-SAFT equation of state along with the proposed correlations, presents good results for modeling of these glycols ethers. The good agreement with experimental data indicates that this equation of state can be used to correlate the $P\rho T$ data of these glycols ethers.

2. Experimental

2.1. Materials

The source and purities of chemicals were: 2-ethoxyethanol (Merck, > 99.0%), 2-propoxyethanol (Sigma-Aldrich, > 99.4%), 2-butoxyethanol (Merck, > 99.0%), benzene (Merck, > 99.4%) and deionized distilled water. Substances were used without further purifications. The purity grade, densities, thermal expansion coefficient, isothermal compressibility and speed of sound of the solvents along with the literature data are given in Table 1. They were in good agreement with those reported in the literature data [12,13,18,35].

2.2. Apparatus and calibration procedure

Densities of the pure solvents at atmospheric pressure were measured using an Anton Paar density and sound velocity analyzer (DSA 5000) provided with automatic viscosity correction. The density determination is based on measuring the period of oscillating a vibrating U-shaped tube filled with the fluid sample. Since density is extremely sensitive to temperature, the temperatures were adjusted to $\pm 1 \times 10^{-2}$ K by a built-in solid-state thermostat. Before each series of measurements, the apparatus was calibrated with double distilled degassed water and dry air at the atmospheric pressure. The uncertainty in density at the atmospheric pressure was $\pm 2 \times 10^{-3}$ kg.m^{-3}. The density of high pressure measurements was obtained using an Anton Paar (model DMA HP) vibrating densimeter connected to a model DMA 4500 master instrument. DMA HP measures the period of harmonic oscillation of a built-in U-tube containing the sample. The pressure was created using a handing pump. Pressures were measured simultaneously with a pressure transducer (Gems, 3100, England, accuracy of 0.25% FS) and digital manometer (KELLER, LEO 2, Swiss, accuracy of <0.1 %FS). The reproducibility of the pressure measurements was checked by comparing two different pressure measurements [36]. The relative uncertainty of pressure measurements was $u_r(P) = \pm 3 \times 10^{-3}$. The temperature of the measuring cell is controlled with an integrated Peltier thermostat. The uncertainty of the temperature measurement was ±0.05 K. Double distilled water and benzene were used to calibrate the apparatus (DMA-HP) at the experimental domain of temperature and pressure. Calibration fluids were selected in order to the differences between the sample viscosities and those of the calibrating fluids to be quite small and the density of experimental solvent lies between densities of two calibrating fluid. The density data used for the calibration were taken from values reported in the manual of DMA HP [37], literature [38,39]. The reference data were used to correlate the density of solvents at the above-mentioned temperature and pressure ranges using the following equation [41,42]:

$$\rho = \sum_{i,j,k} a_{ijk} \tau^i T^j P^k, \qquad (1)$$

where ρ is the reference density (kg.m^{-3}), τ is the oscillation period (µs), T is the temperature (°C), P is the pressure (bar) [37], and a_{ijk} are the fitting parameters, with $i = 0, 2, j = 0, 1, 2$, and $k = 0, 1, 2$, the average absolute deviation (AAD) between the reference and calculated data was 0.01% based on the following equation:

$$AAD = \frac{100}{N} \sum_{i}^{N} \left| \frac{\rho_{i,ref} - \rho_{i,cal}}{\rho_{i,ref}} \right|, \qquad (2)$$

here N denotes the number of experimental point, $\rho_{i,ref}$, is the reference density data and, $\rho_{i,cal}$, is the density calculated by Eq. (1). In order to validate the calibration procedures, the densities of the pure solvents obtained with DMA HP at 0.1 MPa and different temperature were compared with those measured by DMA 4500 provided with automatic viscosity correction. They were in very good agreement with respect to uncertainty of density measurement. Anton Paar DMA HP does not operate on the built-in correction system for the viscosity effects. Such a correction has been advised by many authors for density measurements obtained by vibrating tube densimeter to account for the differences between the viscosity of the samples and those of the calibrating fluids [36,43–45]. However, these corrections depend upon the availability of viscosity data and accurate equations that would correlate the viscosity and the damping of the oscillation. Also there is no correlation mentioned in the literature to evaluate the viscosity corrections for Anton Paar DMA HP [36,41]. Unfortunately, we found no viscosity data in the literature for the systems studied at the above-mentioned temperature and pressure ranges. Also the viscosity of the studied solvents varies between about (1.846 and

Table 1
Purity, densities, ρ, thermal expansion coefficient, α_P, isothermal compressibility, κ_T, and speed of sound, u, for pure components with their literature values at atmospheric pressure and $T = 298.15$ K.[a]

Solvent	Purity	ρ/kg.m^{-3}		α_P.10^4/K^{-1}		κ_T .10^4/MPa^{-1}		u/m.s^{-1}	
		Exp	Lit	Exp	Lit	Exp	Lit	Exp	Lit
2-ethoxyethanol	≥0.99	925.64	925.23 [12]	9.84	9.82 [13]	7.92	7.73 [13]	1305.65	1301.73 [13]
2-propoxyethanol	≥0.994	907.23	907.15 [12]	9.62	9.67 [13]	8.19	7.86 [13]	1298.84	1298.58 [13]
2-butoxyethanol	≥0.99	896.17	896.29 [12]	9.24	9.37 [13]	8.12	7.83 [13]	1304.72	1304.92 [13]

[a] The standard uncertainty, u is $u(T) = \pm 1 \times 10^{-2}$ K and the combined expanded uncertainties u_c are $u_c(\rho) = \pm 2 \times 10^{-3}$, $u_c(u) = 3$ m.s^{-1}, $u_c(\alpha_P) = \pm 2 \times 10^{-6}$ K^{-1} and $u_c(\kappa_T) = \pm 2 \times 10^{-6}$ MPa^{-1} (095 level of confidence).