Correlation and prediction of thermodynamic properties of binary mixtures from perturbed chain statistical associating fluid theory

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HIGHLIGHTS

- Densities and viscosities of the mixtures (DEA + 2-alkanols) were measured.
- PC-SAFT model was applied to predict some thermodynamic properties of mixtures.
- Compatibility between experimental data and predicted values by PC-SAFT model is satisfactory.

ARTICLE INFO

ABSTRACT

Densities and viscosities for binary mixtures of Diethanolamine (DEA) + 2 alkanol (2 propanol up to 2 pentanol) were measured over the entire composition range and temperature interval of 293.15–323.15 K. From the density and viscosity data, values of various properties such as isobaric thermal expansibility, excess isobaric thermal expansibility, partial molar volumes, excess molar volumes and viscosity deviations were calculated. The observed variations of these parameters, with alkanols chain length and temperature, are discussed in terms of the intermolecular interactions between the unlike molecules of the binary mixtures. The ability of the perturbed chain statistical associating fluid theory (PC-SAFT) to correlate accurately the volumetric behavior of the binary mixtures is demonstrated.

1. Introduction

Equations of state are powerful tools for the prediction of thermodynamic properties and phase equilibria. These properties are fundamental in design of the industrial processes. Alkanolamines find extensive applications in pharmaceutical industries, because they have the combined physical and chemical characteristics of both alcohols and amines in one molecule. Also their aqueous solutions are widely used in the industrial treatment of acid gas streams containing H_2S and CO_2. Diethanolamine (DEA) is a common solvent for removal of CO_2. So its physical properties such as density and viscosity are necessary to design the acid gas treatment equipment and for measuring other physical properties such as liquid diffusivities, free-gas solubility, and reaction rate constants [1].

Macroscopic properties of liquid and liquid mixtures can provide valuable informations to understand the types and nature of molecular interactions occurring in the mixtures. Volumetric data and derived volumetric properties in combination with molecular theories of solutions can be used to extend our understanding of molecular interactions occurring in these mixtures and to deduce a more detailed picture of solute–solvent interactions. Present paper deals with the study of molecular interactions of DEA with 2-alkanols over the entire composition range by density and viscosity measurements.

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Nomenclature

A	Helmholtz energy
a	Molar Helmholtz energy (total, res, seg, bond, assoc, etc.)
hs	Hard sphere
a_0	Segment molar Helmholtz energy (seg), per mole of segments
d	Temperature-dependent segment diameter
k	Boltzmann's constant
m	Effective number of segments within the molecule
mv^{00}	Volume occupied by 1 mol of molecules in a closed packed arrangements
m	Number of association sites on molecule
T	Temperature, K
u/k	Temperature-dependent dispersion energy of interaction between segments
u_0/k	Temperature-independent dispersion energy of interaction between segments
v^0	Temperature-dependent segment volume
v^{00}	Temperature-independent segment volume, mL/mol of
X^A	Monomer mole fraction (mole fraction of molecules *not* bonded at site A)
κ^{AB}	Volume of interaction between sites A and B
Δ^{AB}	"Strength of interaction" between sites A and B
$\in^{AB}$	Association energy of interaction between sites A and B
σ	Lennard-Jones segment diameter

The objective of the paper is to provide the density and viscosity values to investigate the effect of temperature and carbon chain length of alcohol molecules on the thermodynamic properties of these mixtures. Also prediction or correlation of thermodynamic characteristics with perturbed chain statistical associating fluid theory (PC-SAFT) is other background of this work. Recently there is an increasing demand for models that are suitable for simple and complex fluids. These models (such as PC-SAFT) have been successfully applied to the simple fluids, large polymeric fluids and their mixtures. Our scientific literature survey shows that a few studies have been conducted on the mixtures presented in this work.

2. Experimental section

In this work, the following materials were used with the highest purity available: Diethanolamine, 2-propanol, 2-butanol, 2-pentanol (Merck with mass purity > 0.99) Materials were used without further purification. Density and viscosity measurements were performed with a fully automated SVM 3000 Anton-Paar rotational Stabinger viscometer. The viscometer is based on a modified Couette principle with a rapidly rotating outer tube and an inner measuring bob which rotates more slowly. Uncertainty for density measurements is 1×10^{-4} g cm^{-3} and for viscosity measurements is 1%. All the mass measurements were performed on an electronic balance (Mettler AE 163, Switzerland) accurate to 0.01 mg and perfectly homogenized before the measurements. The possible error in the mole fraction is estimated to be less than $\pm 1 \cdot 10^{-4}$. Data of density and viscosity along with other thermodynamic properties are reported in Appendix A.

3. Results and discussion

3.1. Densities and viscosities

The density values have been used to calculate excess molar volumes, V_m^E, from the following equation

$$V_m^E = \sum_{i=1}^{N} x_i M_i (\rho^{-1} - \rho_i^{-1}). \tag{1}$$

Here x_i is the mole fraction of component i, in the liquid mixture; M_i its molecular weight, ρ_i and ρ and are the densities of the pure component i, and mixture, respectively. The V_m^E values were correlated with Redlich–Kister polynomial equation [2]

$$Y^E = x_1(1 - x_1) \sum_{k=0}^{N} A_k (1 - 2x_1)^k \tag{2}$$

where Y^E represents the excess molar volumes or viscosity deviations and x_1 is the mole fraction of Diethanolamine. A_k is fitting parameter and k is the number of parameters. Standard deviation σ is defined by the equation

$$\sigma = \left[\sum (Y - Y_{\text{cal}})^2 / (n - p) \right]^{1/2} \tag{3}$$

where Y and Y_{cal} are the experimental and calculated values of the property Y, respectively.