



Correlations for the prediction of the density and viscosity of 1-alcohols at high pressures



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ABSTRACT

We present a correlation for the 1-alcohols density at high pressure based upon the Tait equation. The new equation includes a generalized correlation for the calculation of the density of 1-alcohols at atmospheric pressure and correlates the density of methanol to 1-decanol from (173.15 to 373.15) K at pressures up to 279 MPa within an average absolute percentage deviation of 0.11% from the experimental density values. Also, we use this equation to obtain a model to correlate the liquid viscosities of 1-alcohols. The new model correlates the viscosity at atmospheric pressure within an average absolute percentage deviation of 2.14% from the experimental values. At high pressures (up to 423 MPa), the new model correlates the viscosity of 1-alcohols (methanol through 1-hexadecanol) at temperatures from (293 to 423) K within an average absolute percentage deviation of 3.38%.

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1. Introduction

Generalized correlations for the prediction of the thermodynamic properties such as density and viscosity at high pressures are important for the design of unit operations equipment [1]. However, it is not always possible to find experimental data in the literature for the thermodynamic properties of interest, consequently many researchers have developed models to predict the properties of different homologous series [2,3].

Assael et al. [4] develop a correlation as a function of the reduced temperature and the number of atom carbons for the prediction of 1-alcohol densities at high pressures. Their correlation is valid for 1-alcohols from ethanol to 1-decanol at pressures up to 100 MPa and from (278 to 374) K.

For the prediction of the viscosities of 1-alcohols, Teja et al. [5] developed a generalized model using the corresponding states principle (GCSP). This model can be used to predict the viscosity of pure components and binary mixtures of liquids. They applied this correlation to 1-alcohols successfully. Nhaesi et al. [6] used the three-body McAllister equation to predict the kinematic viscosity of multicomponent mixtures of *n*-alkanes at atmospheric pressure. Later, Shan et al. [7] showed that this equation can be used to predict the kinematic viscosity of multicomponent mixtures of 1-alcohols

within an average percentage deviation of 1.20% from the experimental viscosity measurements. This model requires the kinematic viscosity of the pure components of the mixture at each temperature.

Sun and Teja [8] extended the model based upon rough hard sphere (RHS) theory for the calculation of the viscosity of many components including 1-alkanols. The rough-hard-sphere concept was originally proposed by Chandler [9] and extended by Assael et al. [4]. They expressed the reduced viscosity in terms of the reduced molar volume and parameters that account for deviations of the transport properties of the fluid from those of smooth hard spheres. Xuan et al. [10] used the Tait equation to predict the viscosities of *n*-alkanes, aromatics and 1-alcohols at high pressures. Unfortunately, their equation is not a generalized correlation since it requires two characteristic parameters for each fluid at each temperature.

In this work, we propose a generalized correlation for the prediction of the density and viscosity at high pressures for 1-alcohols. For the density, the new correlation is based upon the Tait equation and for the viscosity we propose a simple relationship between the viscosity and the density. The new correlations use the temperature and the number of carbon atoms as variables.

2. Methodology

2.1. Compressed liquid density

Previously, Assael et al. [4] reported a successful equation for the correlation of the density of 1-alcohols. They used the Tait

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Chemical Engineering Thermodynamics

Densities and viscosities of binary mixtures of *n*-decane + 1-pentanol, + 1-hexanol, + 1-heptanol at temperatures from 293.15 to 363.15 K and atmospheric pressure[☆]



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ABSTRACT

Densities (ρ) and dynamic viscosities (η) for three binary mixtures of *n*-decane with 1-pentanol, 1-hexanol and 1-heptanol are presented at temperatures from 293.15 to 363.15 K and atmospheric pressure over the entire composition range. The density and viscosity are measured using a vibrating tube densimeter and a cylindrical Couette type rotating viscometer, respectively. Excess molar volumes (V^E), viscosity deviations ($\Delta\eta$) and excess Gibbs energy of activation of viscous flow (ΔG^E_{vis}) are calculated from the experimental measurements. Intermolecular and structural interactions are indicated by the sign and magnitude of these properties. Partial molar volumes and infinity dilution molar partial volumes are also calculated for each binary system. These results are correlated using Redlich-Kister type equations.

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1. Introduction

A complete knowledge of thermodynamic and transport properties of liquid mixtures is essential for numerous industrial processes, in particular for chemical engineering industries. These properties are necessary in the modeling, design, construction, and optimization of process equipment such as condensers, heat transfer equipment, and distillation columns.

There has been a systematic study of the excess thermodynamic and transport properties for 1-alcohol + *n*-alkane mixtures. These properties have been extensively analyzed from both of experimental and theoretical points of view. From the experimental point of view, the analysis is important because it provides information about composition related changes, hydrogen bonding, and effects of size and structure of the molecules. This information allows the understanding of the molecular structure and the ruling intermolecular interactions. This knowledge can be used to develop models and theories about the mixtures behavior. In the last years there have been several efforts to develop models for excess properties such as enthalpy [1–6] and heat capacity [2,7–10]. Also, it is worth to mention the association models [1,4,11–13] and the group contribution methods [14–17] for the molar volume.

For 1-alcohol + *n*-alkane there are numerous reports on experimental data for excess molar volume or density [18–30] and viscosity [31–39]. Different thermodynamic properties for the binary mixtures with *n*-decane and 1-pentanol, 1-hexanol, or 1-heptanol have been reported in the literature. These properties are the excess enthalpy [40] and the heat capacity [41]. Density and excess volume data have been reported by different authors. The excess volumes for *n*-decane + 1-pentanol have been reported by Yun *et al.* [42]. Al-Dujaili and Awwad [28] and Kaur *et al.* [43] at 298.15 K. Densities at other temperatures are measured by Al-Dujaili and Awwad [28] at 288.15, 308.15 and 318.15 K. Experimental densities for the mixture of *n*-decane + 1-hexanol are measured at 298.15 K by Treszczanowicz and Berson [24], Kaur *et al.* [43] and Dubey and Sharma [26]. Dubey and Sharma [26] reported densities for this mixture at 303.15 and 308.15 K. To the best of our knowledge, density measurements for the binary *n*-decane + 1-heptanol do not exist in the literature.

In recent years there has been an increasing interest on the viscosities of liquid mixtures. For example, the study of the viscosity of *n*-alkane + 1-alcohol mixtures, together with other thermodynamic properties, will allow us to know the molecular interactions and structure of these liquid mixtures. Some of these systems exhibit a peculiar behavior [31,34,44–46] which cannot be explained in terms of traditional approaches that have been observed experimentally. Experimental viscosities have been only measured for the mixture *n*-decane + 1-hexanol at 298.15, 303.15, and 308.15 K [26].

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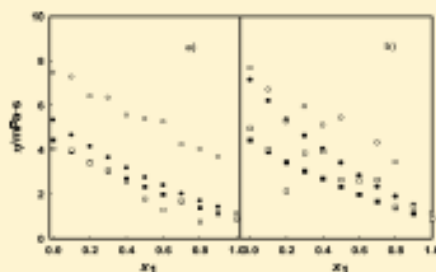
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Density and Viscosity of Binary Liquid Mixtures of Ethanol + 1-Hexanol and Ethanol + 1-Heptanol from (293.15 to 328.15) K at 0.1 MPa

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ABSTRACT: This paper presents experimental viscosity and density measurements for two binary mixtures of ethanol with 1-hexanol and 1-heptanol that cover the complete composition range from (293.15 to 328.15) K at 0.1 MPa. A vibrating tube densimeter provides density measurements, whereas viscosities come from a pellet microviscometer. The excess molar volumes calculated from the experimental data have positive deviations from ideality over the temperature range. Calculated viscosity deviations from the experimental data show negative deviations from a mole fraction weighted average of the pure component viscosities over the temperature range. A Redlich–Kister type equation correlates the data satisfactorily. We have correlated the three-body McAllister to the experimental kinematic viscosity. Comparison of the experimental viscosity data to predictions from a generalized three-body McAllister and a generalized corresponding states principle (GCSP) equation shows that the generalized McAllister equation is superior predicting the kinematic viscosity within an average absolute percentage deviation of 1.24%. Finally, molecular dynamics was performed to compare density and viscosity results with those obtained experimentally. Results for density agree with the experimental measurements, whereas viscosity calculations are beyond the experimental error.



1. INTRODUCTION

The viscosities for liquid binary mixtures of alcohols are important in chemical engineering applications, such as flow in pipes, in heat and mass transfer operations, and in the design of cryogenic systems. The need for a database of accurate properties such as densities and viscosities is essential to develop predictive models. Mixtures of ethanol + 1-hexanol or + 1-heptanol are used as solvents in liquid–liquid extraction therefore thermodynamic properties of these systems are needed. Recently, Rahamn et al.¹ have shown that ethanol extraction from aqueous solutions can be done with 1-hexanol as solvent. This will replace common solvents such as ethers, acetates, or ketones. In addition, these mixtures have been used as additives to gasoline. 1-Hexanol allows more ethanol in the diesel blend,² improving blend tolerance for water and keeping the blend fuel stable with time. Thermodynamic properties of 1-alcohols in the liquid phase are strongly influenced by the influence of hydrogen bonding; however, the conformation of small alcohol molecules³ in the thermodynamic properties has been studied in pure alcohol mixtures, but it has not been done with 1-alcohol mixtures with a large chain.

In recent years, an effort has evolved to develop predictive models for viscosities, and several models are available in the literature. Raut⁴ et al. report equations for the dynamic viscosity of ethanol + 1-heptanol from (288.15 to 323.15) K.

Unfortunately, they did not report their experimental values. Few authors have measured the densities and viscosities of the mixtures considered in this work. Faria et al.⁵ used a vibrating tube densimeter and a Cannon–Fenske viscosimeter to measure the density and viscosity of the ethanol + 1-heptanol at (283.15 to 313.15) K. Ali et al.⁶ measured the densities and viscosities of ethanol + 1-hexanol at 303.15 K. They used a Pyrex glass pycnometer and a Cannon–Ubbelohde viscosimeter to measure the densities and viscosities of this mixture.

An alternative method to know the density and viscosity of a mixture is to use molecular dynamics simulation with an adequate description of the potential energy of the system. Previously, we have shown that density calculations⁷ agree with the experimental density measurements for hydrocarbon mixtures. Molecular dynamic calculations have been performed for ethanol,^{8–12} 1-hexanol,^{8,13,14} and 1-heptanol.^{8,13} Molecular dynamics simulation of liquid density for pure alcohols from (288 to 338) K have been performed by Kulschewski and Pleiss.¹⁵ They found out that their density calculations agree with the experimental measurements within an average absolute percentage deviation of less than 0.6% for ethanol, 1-hexanol, and

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DENSITY OF PURE AND BINARY MIXTURES OF IONIC LIQUIDS BASED ON SULFONIUM, IMIDAZOLIUM AND PYRROLIDINIUM CATIONS AND BIS(TRIFLUOROMETHYLSULFONYL)IMIDE ANION WITH 1-PROPANOL

(Densidades de líquidos iónicos puros y sus mezclas con 1-propanol, basados en los cationes imidazolium, sulfonium y pyrrolidinium y el anión bis[trifluorometil sulfonil]imide)

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ABSTRACT

One of the main problems when designing processes or searching new applications containing ionic liquids (ILs) is the absence of a reliable database of thermodynamic and thermophysical properties of pure and their mixtures with other solvents. In this context, thermophysical properties of pure ionic liquids and mixtures could provide information not only about the structure of the fluid, but also about the intermolecular interactions, which are the basis for the improvement of thermodynamic models for the representation of the behavior of the ILs in any of their applications. The objective of this work is to investigate the densities of pure ionic liquids and excess properties in mixtures with 1-propanol, based on bis(trifluoromethylsulfonyl)imide anion and pyrrolidinium, sulfonium and imidazolium cations. Density of pure ILs and mixtures was determined by measuring the oscillation period of the U-shaped tube by an Anton Paar vibrating tube densimeter in a temperature range from 278.15 to 343.15 K at atmospheric pressure. The experimental data of pure ionic liquids were adjusted to Gardas and Coutinho equation and mixtures were adjusted to Redlich-Kister model. The excess molar volumes for $[\text{Et}_3\text{S}][\text{NTf}_2]$, $[\text{Amim}][\text{NTf}_2]$ and $[(\text{OH})_2\text{Im}][\text{NTf}_2]$ with 1-propanol are positive at all the ranges of composition and at all studied temperatures. Whereas $[(\text{OMe})_2\text{Im}][\text{NTf}_2]$ + 1-propanol system shows positive values at $x_{IL} > 0.7$. Gardas and Coutinho model exhibit an average absolute percentage error of 2.8156×10^{-6} , 1.4607×10^{-4} , 1.4402×10^{-4} , 1.4442×10^{-4} and 1.4905×10^{-4} for $[\text{Bmpyrr}][\text{NTf}_2]$, $[\text{Et}_3\text{S}][\text{NTf}_2]$, $[\text{Amim}][\text{NTf}_2]$, $[(\text{OMe})_2\text{Im}][\text{NTf}_2]$ and $[(\text{OH})_2\text{Im}][\text{NTf}_2]$, respectively.

Keywords: ionic liquid, density, mixtures, correlations.

RESUMEN

Actualmente, uno de los principales problemas que se presentan en el diseño de procesos o para determinar nuevas aplicaciones de los líquidos iónicos (LIs), es la falta de sus propiedades termofísicas tanto para líquidos iónicos puros como sus mezclas con diferentes solventes. En este sentido, las propiedades de los LIs puros y sus mezclas pueden proporcionar información no solo acerca de la