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Interfacial properties of the ionic liquid [bmim][triflate] over a wide range of temperatures

José L. Rivera,^{a,b} Luis Molina-Rodríguez,^b Mariana Ramos-Estrada,^b Pedro Navarro-Santos^c and Enrique Lima^d

We carried out molecular dynamics simulations of the liquid/vacuum equilibrium of the ionic liquid [bmim][triflate] in a wide range of temperatures (323.15 to 573.15 K). The results showed liquid phases with high densities even at temperatures close to the decomposition temperature of the liquid. The density and surface tension behaviors are linear across this wide range of temperatures, which is an extension of the behaviors of these systems at low temperatures, where these properties have been experimentally measured. The interfacial region shows peaks of adsorption of the ions; they are ordered, with the alkyl chains of the [bmim] cations pointing out of the liquid, and the tailing angle of the chains becomes 90° at higher temperatures. The alkyl chains are part of the outermost interfacial region, where intra- and intermolecular tangential forces are in equilibrium; thus, they do not contribute to the total surface tension. Unlike simpler organic liquids, the surface tension is composed of positive normal contributions of intermolecular interactions; these are almost in equilibrium with the negative normal contributions of intramolecular interactions, which are mainly vibrations of the distance and the angle of valence. The pressure profiles show that the molecules are in 'crushed' conformations internally in the bulk liquid and even more so in the normal direction at the interface. The total pressure profiles show values with physical meaning, where the tangential peaks show higher values than normal pressures and give rise to the surface tension. Short cutoff radii for the calculation of intermolecular forces (less than 16.5 Å) produce a system that is not mechanically stable in the region of the bulk liquid (confirmed by radial distribution function calculations); this produces a difference between the normal pressure and the average of the tangential pressures, which affects the calculation of the surface tension due to overestimation by up to 20% when using the global expression, which is extensively used for the calculation of surface tension. The use of a sufficiently long cutoff radius avoids these mechanical balance problems.

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Introduction

Ionic liquids combine relatively large organic cations and organic and inorganic anions; this prevents the formation of ordered crystals over a wide range of temperatures, including room temperature. These liquids are more complex than ordinary organic liquids, and it is thought that they can be best described as fluids that self-assemble into amphiphilic nanostructures.^{1–8} Simulations of molecular dynamics in the liquid/vacuum equilibrium using 368 pairs of ions with a simulation

area of ~20 nm² and 5 ns for sampling indicate the presence of amphiphilic interfaces. This is due to ordering in the interfaces because the alkyl chains of diverse ionic liquids based on imidazole leave the bulk liquid, pointing towards the vacuum; this is similar to the behavior of complexes that form water bridges with amphiphilic molecules.⁹ Other simulations, with smaller samples (216 pairs of ions), a smaller surface area (~17 nm²), and 2 ns for sampling, produce similar results.⁹

On the other hand, the thermophysical properties of ionic liquids are unique. Their vapor pressure is extremely low, and the dependence of their surface tension, γ , on temperature is different from that of most organic liquids ($\gamma \propto T^{1/3}$). Ionic liquids behave almost linearly with respect to temperature; therefore, the linear van der Waals-Guggenheim equation, which describes the behavior of molten metals, also accurately describes the behavior of many ionic liquids.⁸ Some exceptions to this linear behavior have been attributed to problems arising during the preparation of the liquids, such as insufficient purification.^{8,7} The behavior of γ with respect to the

^aGraduate School of Physical Engineering, Universidad Michoacana de San Nicolás de Hidalgo, Morelia, C.P. 58000, Michoacán, Mexico. E-mail: jrivera@umich.mx

^bFaculty of Chemical Engineering, Universidad Michoacana de San Nicolás de Hidalgo, Morelia, C.P. 58000, Michoacán, Mexico

^cInstituto de Química y Biología, Universidad Michoacana de San Nicolás de Hidalgo, Morelia, C.P. 58000, Michoacán, Mexico

^dLaboratorio de Física Química y Reactividad de Superficies (LaFReS), Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior S/N, CU, Del. Coyoacán, Ciudad de México, México

Densities and Viscosities for Binary Liquid Mixtures of *n*-Undecane + 1-Heptanol, 1-Octanol, 1-Nonanol, and 1-Decanol from 283.15 to 363.15 K at 0.1 MPa

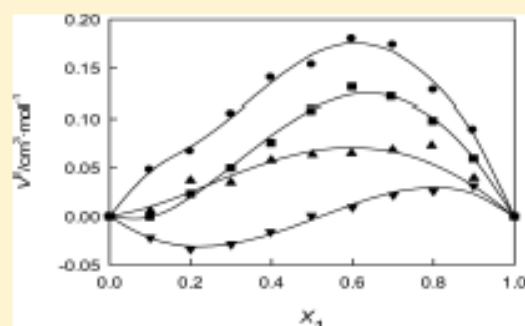
Adriana Guzmán-López, Gustavo A. Iglesias-Silva,*¹ Fátima Reyes-García, and Alejandro Estrada-Baltazar

Departamento de Ingeniería Química, Instituto Tecnológico de Celaya, Celaya, Guanajuato CP 38010, México

Mariana Ramos-Estrada

Facultad de Ingeniería Química, Universidad Michoacana de San Nicolás de Hidalgo, Morelia, Michoacan CP 58030, México

ABSTRACT: This paper presents densities and viscosities of binary mixtures of *n*-undecane with 1-alcohols with carbon atoms from C₇ to C₁₀ from 283.15 to 363.15 K at 0.1 MPa. Densities are measured using a vibrating tube densimeter, while viscosities are from a pellet microviscometer. Excess molar volumes and viscosity deviations are calculated from the experimental data. The excess molar volumes present positive deviations for the binary mixtures with 1-heptanol, 1-octanol, and 1-nonanol. The excess molar volumes of *n*-undecane + 1-decanol present negative deviations at lower temperatures. The viscosity deviations show negative deviations from ideality over the entire temperature range. Also we present a correlation for the kinematic viscosity based upon the activation Gibbs energy.



1. INTRODUCTION

Densities and viscosities of mixtures are used in industrial applications of mass and heat transfer. Currently, the mixtures of *n*-alkanes + alcohol have become relevant because of their applications as additives and solvents in the fuel and petrochemical industries.¹ This work is a continuation of our previous report of *n*-alkanes + 1-alcohols.^{2,3} Densities and viscosities of binary mixtures of *n*-undecane + 1-alcohols have been measured by Peleteiro et al.⁴ and Iglesias-Silva et al.⁵ Densities and viscosities with *n*-undecane + 1-heptanol, + 1-octanol, + 1-nonanol, and + 1-decanol do not exist in the literature.

This work reports the densities and viscosities for mixtures of *n*-undecane with 1-heptanol through 1-decanol at 0.1 MPa from 283.15 and 363.15 K over the entire composition range. A Redlich–Kister⁶ type equation has been used to correlate excess molar volume and viscosity deviations. The Nava-Rios et al.⁷ equation is used to correlate the experimental kinematic viscosities. This equation is a semi-theoretical equation based upon the McAllister⁸ principles.

2. EXPERIMENTAL SECTION

Samples. The samples are from SAFC for *n*-undecane (99.4% in mass fraction), Fluka for 1-heptanol (99.98% in mass fraction), Aldrich for 1-octanol (99.54% in mass fraction), Fluka for 1-nonanol (99.3% in mass fraction), and Aldrich for 1-decanol (99% in mass fraction). Samples are prepared using an analytical balance (Ohaus model AS120S) with an accuracy of 0.1 mg. Substances are used as received and kept in airtight

Table 1. Sample Information

chemical name	source	CAS No.	initial purity mass fraction	purification method	analysis method ^a
<i>n</i> -undecane	SAFC	1120-21-4	0.994	none	GC
1-heptanol	Fluka	111-70-6	0.9998	none	GC
1-octanol	Aldrich	111-87-5	0.9954	none	GC
1-nonanol	Fluka	143-08-8	0.993	none	GC
1-decanol	Aldrich	112-30-1	0.99	none	GC

^aGas chromatography provided by the supplier.

containers. Table 1 shows the specifications for all of the substances. Mixtures are prepared using an analytical balance (Ohaus model AS120S) with an accuracy of 0.1 mg. We have a standard uncertainty in the mole fraction of less than 0.0002.

Apparatuses and Procedures. Densities are measured using a vibrating tube densimeter (Anton Paar, DMA 5000). Details of the densimeter have been reported previously.³ The densimeter has a stated reproducibility by the manufacturer of 1×10^{-6} g·cm⁻³ for the density and 0.001 K for the temperature. The densimeter was calibrated by the manufacturer using two reference fluids: ultrapure water and dry air.⁸ The standard

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