Effect of Temperature on Physical Properties for Binary Systems: Deep Eutectic Solvent and Alcohols.

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ABSTRACT

Compared with the conventional Ionic Liquids, Deep Eutectic Solvents (DES) are more biodegradable and biocompatible. Moreover, they are easily prepared with high purity at low cost. Because of this, an extensive study of both properties of pure DES and of their binary mixtures with alcohols, in function of temperature is very necessary and of considerable importance for the development and design of new processes using these solvents. Density, speed of sound, refractive index and viscosity of choline chloride and levulinic acid DES pure and their mixtures with alcohols have been studied at several temperatures and atmospheric pressure.

1. INTRODUCTION

The development of green chemistry caused the appearance of Ionic Liquids: melting salts with a melting point below the boiling point of water, therefore, under 100ºC [1]. These are considered green solvents by their physical properties: a negligible vapour pressure; high thermal and chemical stabilities; non-flammability; high solvent capacity [2]; and low viscosities of their mixtures [3-4]. However, the toxicity, difficult biodegradability and high cost are some of their disadvantages [5]. To overcome these limitations a new generation of solvents, named deep eutectic solvents (DES), have emerged. In 2003 was discovered that a choline compound and urea form a eutectic mixture, a homogenous liquid called deep eutectic solvent [6]. A DES is generally formed by two or three cheap and safe components which are capable of associating with each other through hydrogen bond interactions, to form a eutectic mixture. The resultant mixture have a melting point lower than each individual component, a very large depression of freezing point and are liquid at temperatures lower than 150ºC. To obtain a DES is necessary to mixer a quaternary ammonium salt with metal salts or a hydrogen bond donor (HBD). The HBD can form a complex with the halide anion of the quaternary ammonium salt [7]. DES can be expressed by the following general formula: $R^1R^2R^3R^4N^+ X^{-} \cdot Y^{-}$. There are three distinguishable types:

Type 1 DES Y = MCl_x, M = Zn, Sn, Fe, Al, Ga
Type 2 DES Y = $MCl_x \cdot yH_2O$, M = Cr, Co, Cu, Ni, Fe
Type 3 DES Y = R_5Z, Z = $-CONH_2$, -COOH, -OH

Note that the same group also defined a fourth type of DES which is composed of metal chlorides (e.g. ZnCl2) mixed with different HBDs such as urea, ethylene glycol, acetamide or hexanediol (type IV DES) [7-8].

In order to increases our knowledge of ILs behabior there already are a big amount of studies about the variation of physical properties of IL's binary mixtures with alcohols, alkanes, etc. Therefore, the purpose of this work is the determination of physical properties of the pure DES and their mixtures with alcohols such as ethanol and 1-Propanol in order to understand its behaviour. These physical properties are density, speed of sound and dynamic viscosity and refractive index.

2. EXPERIMENTAL

2.1. CHEMICALS

The quaternary ammonium salt selected to synthetizes the DES was choline chloride, which was purchased from Sigma-Aldrich with 99.5% purity. It was dried in a heater at 80ºC during two days to eliminate the water content of it, because it is a very hygroscopic compound. Levulinic acid was chosen as HBD, it was purchased from Sigma-Aldrich with 99% purity.

2.2. APPARATUS AND PROCEDURE

2.2.1. SYNTHESIS OF DES

The deep eutectic solvent used in this study was synthetized according to Florindo et al. [9]. This involves mixing a quaternary ammonium salt (choline chloride) and a hydrogen bond donor (levulinic acid) in relationship ratio 1:2 (choline chloride : levulinic acid).The eutectic mixture was prepared by stirring the two components at 333.15 K until a yellow homogenous transparent liquid was formed.

2.2.2. DENSITIES AND SPEED OF SOUND

The density and the speed of sound of the pure DES and their mixtures with alcohols were measured with an Anton Paar DSA 5000 M digital vibrating tube densimeter with an uncertaintly lower than $\pm(2\cdot10^{-3}$ and $3\cdot10^{-2})$ $Kg\cdot m^{-3}$ for density measures and ±(0.01 and 0.3) $m\cdot s^{-1}$ for the speed of sound, respectively. The DSA-5000 automatically corrects the influence of viscosity on the measured density. This equipment has a temperature controller that keeps the samples at working temperature with an uncertainty of ±0.01 K. Moreover, the equipment automatically detects the presence of bubbles in the cell. The apparatus was calibrated by measuring the density of Millipore quality water and ambient air according to the manual instructions.

2.2.3.REFRACTIVE INDEX

The refractive indices were determinated by the automatic refractometer ABBEMAT-WR Dr. Kernchen with a resolution of $\pm 10^{-6}$ and an uncertainty in the experimental measurements of $\pm 4 \cdot 10^{-5}$. This equipment also keeps the samples at working temperature with an uncertainty of ±0.01 K. The apparatus was calibrated by measuring the refractive index of Millipore quality water and tetrachloroethylene before each series of measurements, according to manual instructions. The calibration was also checked with known refractive index of pure liquids.

2.2.4.VISCOSITIES

To measure dynamic viscosities an Anton Paar Lovis 2000 ME microviscosimeter was used. This equipment has a viscosity range between 0.3 mPa·s and 10,000 mPa·s with a repeatability up to 0.1% and accuracy up to 0.5 %. Lovis 2000 M/ME is a rolling-ball viscometer which measures the rolling time of a ball through transparent and opaque liquids according to Hoeppler's falling ball principle. The samples were measured using a steel ball (1.5 mm diameter and ρ = 7690 Kg/m^3) and two capillary Lovis of 1.59 (0.3 – 90 mPa·s) and 1.8 (2.5 – 1700 mPa·s) mm of diameter according to the viscosity of the compound or mixture. The uncertainty of the capillary diameter is ±0.005 mm. The uncertainty in the experimental measurements has been found to be ±0.01 mPa·s. The calibration was also checked with known viscosity reference standard liquids.

3. RESULTS AND DISCUSSION

3.1. PURE DES

The physical properties: density (ρ), speed of sound (u), refractive index (n_D), dynamic (η) viscosity were experimentally determined for pure [ChCl]:[Lev] (1:2) DES at several temperature values (from 293.15 to 243.15) K at atmospheric pressure. The obtained results are shown in the figures 1 to 4. Once observed the results it is possible to conclude that all the properties decrease while the temperature increases. The temperature dependence of density, speed of sound and the refractive index was adjusted to a linear equation:

$$z = a + b \cdot T, \qquad (1)$$

where z is the property (ρ, n_D or u), T is the absolute temperature of each measure and a and b are adjustable parameters. This parameters are shown in Table 1 together with their standard relative deviations, σ:

$$\sigma = \left\{\sum_i^{n_{dat}} \left((z - z_{cal})/z\right)^2 / n_{dat}\right\}, \qquad (2)$$

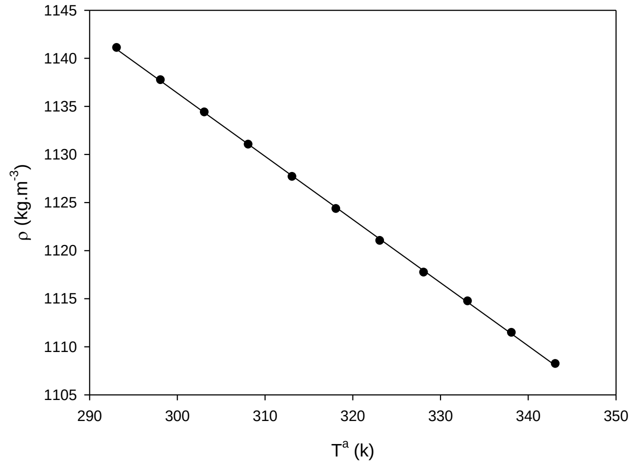

Figure 1: Density (ρ) experimental values (•) fitted using a linear equation (——).

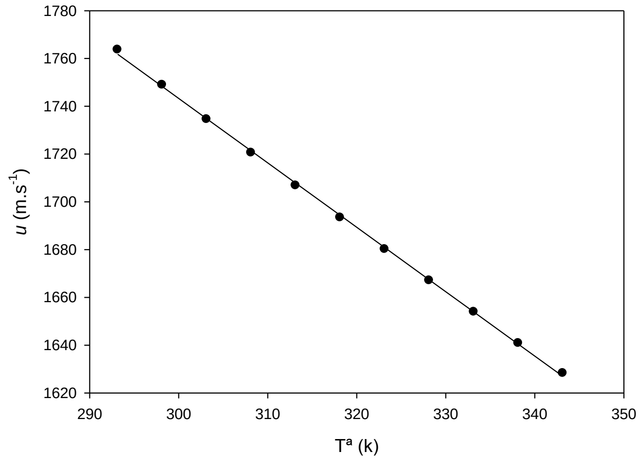

Figure 2: Speed of sound (u) experimental values (•) fitted using a linear equation (——).

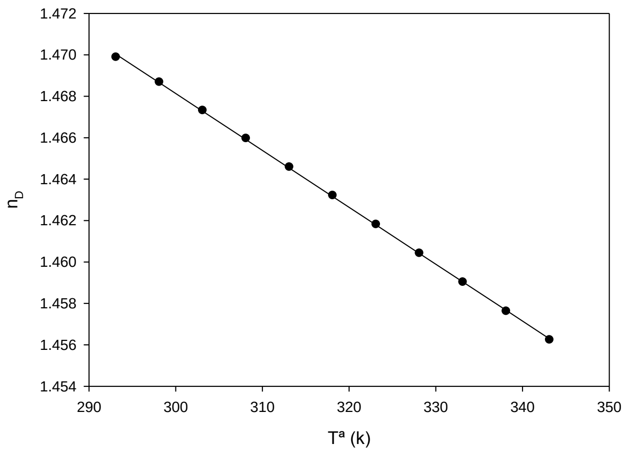

Figure 3: Refractive index (n_D) experimental values (•) fitted using a linear equation (——).

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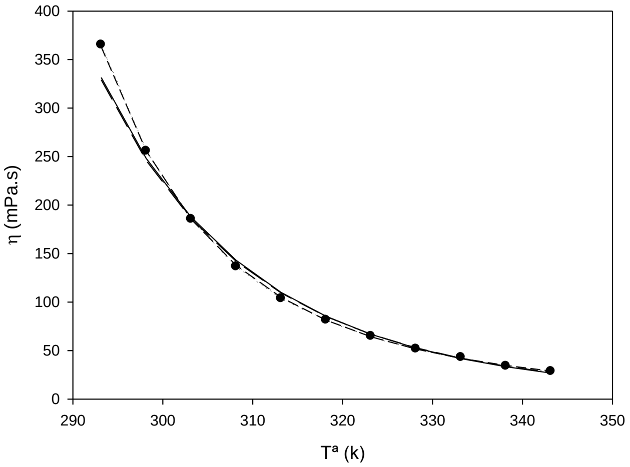


Figure 4: Dynamic viscosity (η) experimental values (•) fitted using Arrhenius (——), Voguel-Fulcher-Tamman (VFT) (— — —), mVFT (------) and Litovitz (············).

Table 1

Fitting parameters of equation (1) together for the density (ρ), speed of sound (u) and refractive index (n_D) with correlation coefficient squared (R^2), and standard relative deviations (σ).

	a	***b***	**R²**	**σ**
***ρ* (Kg·m⁻³)**	1.334	$-6.58\cdot10^{-4}$	0.9998	$1.19\cdot10^{-4}$
***u* (m·s⁻¹)**	2552.4	-2.697	0.9995	$5.34\cdot10^{-4}$
n_D	1.551	$-2.75\cdot10^{-4}$	0.9998	$3.93\cdot10^{-5}$

Figures 1 to 3 show the temperature dependence of density (Figure 1), Speed of sound (Figure 2) and refractive index (Figure 3), respectively. In these graphs is possible to observe the linear dependence between temperature and each physical properties. In the three cases the linear equation (1) is perfectly adjusted to experimental values which decreases while temperature increases.

However, dynamic viscosity values as was already commented were fitted using Arrhenius [10], Voguel-Fulcher-Tamman (VFT) [11-13], modified VFT (mVFT) and Litovitz [14].

Generally the Arrhenius equation is the most common used expression to correlate the variation of viscosity with temperature:

$$\eta = A\ exp\left(\frac{-B}{RT}\right), \qquad (3)$$

where A (mPa·s), and B (kJ·mol^{-1}) are adjustable parameters, R = 8.314 J·K^{-1}·mol^{-1} and T (K) is the temperature value of each measured viscosity value.

Voguel-Fulcher-Tamman (VFT) equation is also applicable to fit the dynamic viscosity:

$$\eta = A \cdot exp\left(\frac{B}{(T-T_0)}\right), \qquad (4)$$

where A (mP·s), B (K) and T_0 (K) are the three adjustable parameters.

A modification was introduced in the VFT expression. The resulting equation has been used by other authors with satisfactory outcomes [4-15]. mVFT can also be applied to fit the dynamic viscosity:

$$\eta = AT^{0.5} \cdot exp\left(\frac{B}{(T-T_0)}\right), \qquad (5)$$

where A (mP·s), B (K) and T_0 (K) are the three adjustable parameters and T (K) is the temperature value of each measured viscosity value.

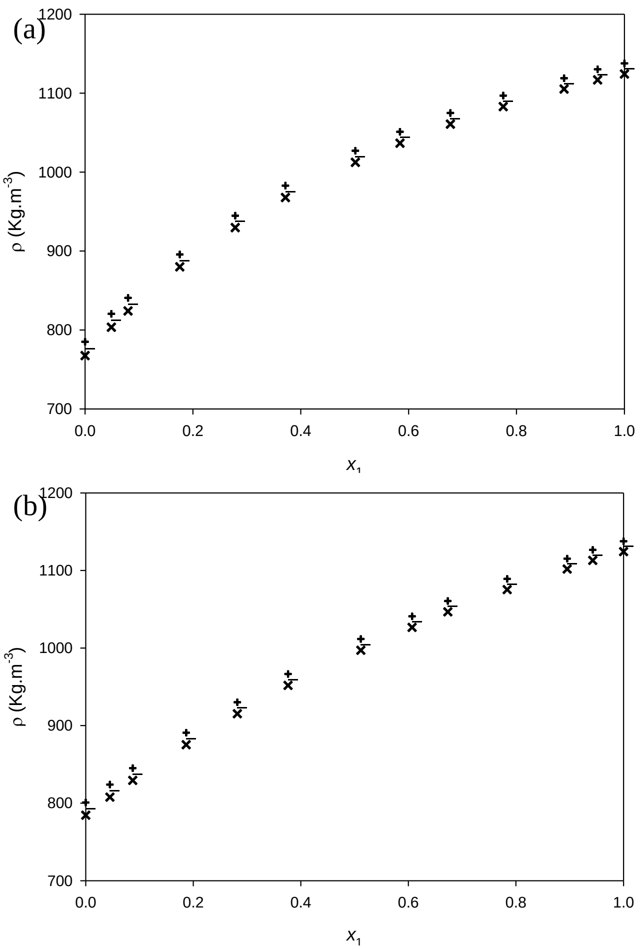


Figure 5: Density (ρ) experimental values for the binary mixtures {[ChCl:[Lev] (1) + alcohol (2)} at different temperatures: (a) ethanol; (b) 1-Propanol; and (+), (−) and (×) indicate T = (298.15, 308,15 and 318,15) K, respectively.

Finally, experimental determined dynamic viscosity values can be fitted also by Litovitz expression:

$$\eta = A \cdot exp\left(\frac{B}{(RT^3)}\right), \qquad (6)$$

where A (mPa·s) and B (kJ·mol^{-1}) are again adjustable parameters and T (k) are the temperature values.

Figure 4 shows the temperature dependence of the dynamic viscosity together with the fits obtained with the abovementioned equations. Through the graphical representation is possible to determine that the best fit is given by mVFT equation. There are not significant differences between the fits of Arrhenius, VFT and Litovitz expressions.

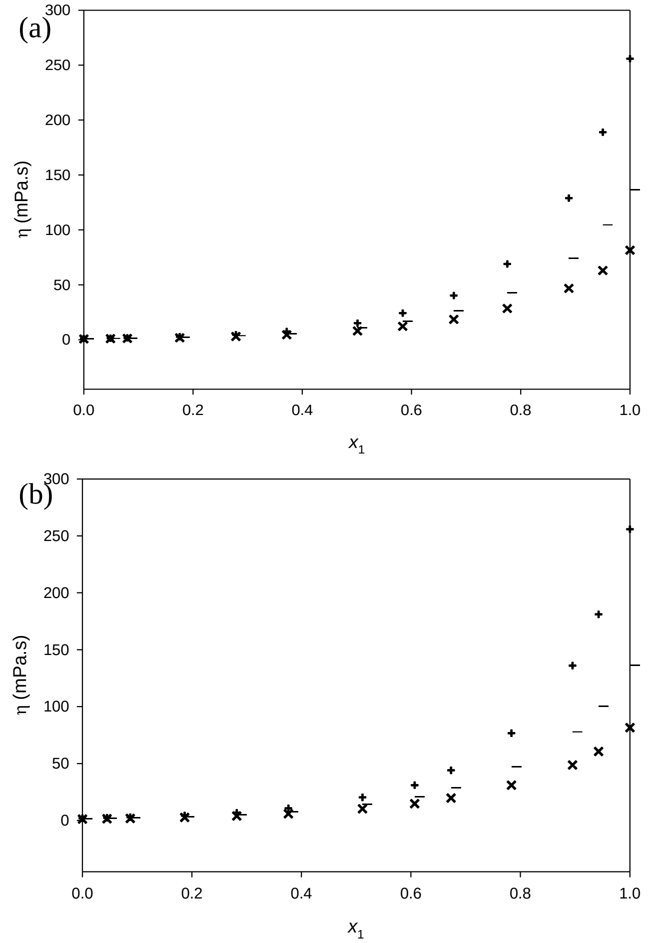


Figure 6: Dynamic viscosity (η) experimental values for the binary mixtures {[ChCl:[Lev] (1) + alcohol (2)} at different temperatures: (a) ethanol; (b) 1-Propanol; and (+), (−) and (×) indicate T = (298.15, 308,15 and 318,15) K, respectively.

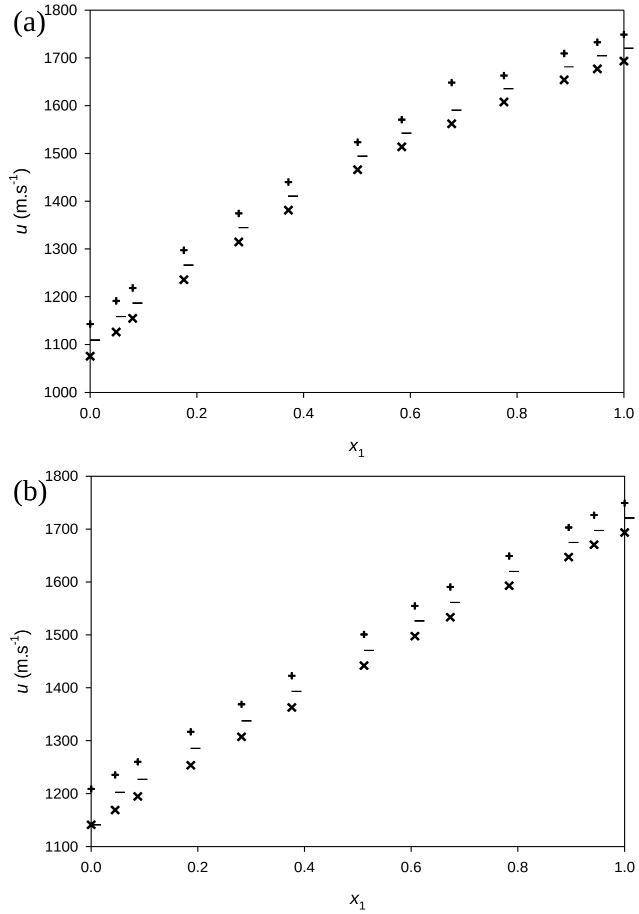


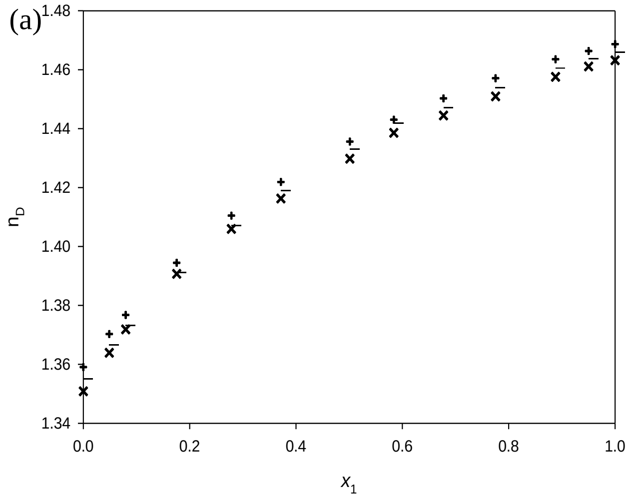
Figure 7: Speed of sound (u) experimental values for the binary mixtures {[ChCl:[Lev] (1) + alcohol (2)} at different temperatures: (a) ethanol; (b) 1-Propanol; and (+), (−) and (×) indicate T = (298.15, 308,15 and 318,15) K, respectively.

3.2. BINARY SYSTEMS

The experimental density (ρ), speed of sound (u), dynamic viscosity (η) and refractive index (n_D) were measured for the binary systems with ethanol and 1-propanol at T = (298.15, 308.15 and 318.15) K at atmospheric pressure.

Several mixtures were prepared to determine the physical properties of the binary systems at different mass fractions of DES. Also, these mixtures shows that [ChCl]:[Lev] (1:2) DES is completely miscible with both studied alcohols.

Figures 5 to 8 show the effect of the DES mole fraction (x_1) over the abovementioned physical properties together with the increase of the temperature. Figure 5 shows as density is progressively bigger as molar fraction of DES increases and temperature decreases. Dynamic viscosity values increases steeply after x_1 = 0.6 and decreases with high temperatures, as showed Figure 6. Speed of sound (Figure 7) and refractive index (Figure 8) exhibit the same behaviour as density.



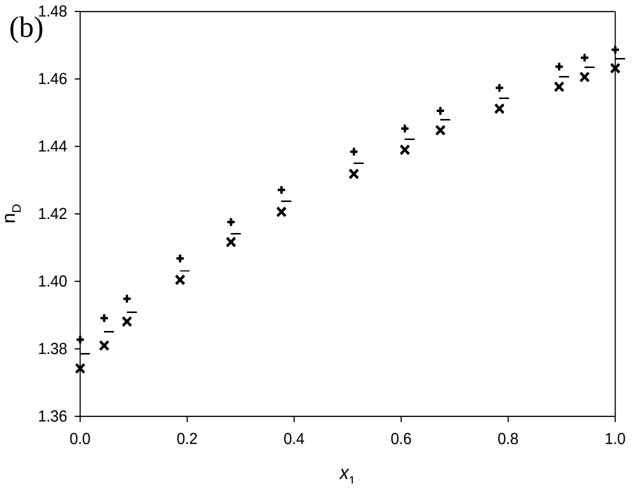


Figure 8: Refractive index (n_D) experimental values for the binary mixtures {[ChCl:[Lev] (1) + alcohol (2)} at different temperatures: (a) ethanol; (b) 1-Propanol; and (+), (–) and (✕) indicate T = (298.15, 308,15 and 318,15) K, respectively.

4. CONCLUSIONS

In this work density, refractive index, speed of sound and dynamic viscosity of pure [ChCl]:[Lev] (1:2) have been determined from T = (293.15 to 343.15) K at atmospheric pressure. As expected, these properties decrease as temperature increases. The mVFT equation was satisfactorily used to fit experimental viscosities while the rest of studied properties were fitted to a linear equation.

Furthermore, density, refractive index, speed of sound and dynamic viscosity were determined for the binary mixtures {[ChCl]:[Lev] (1) + alcohol (2)} over the whole composition range at T = (298.15, 308.15 and 318.15) K at atmospheric pressure where (2) ethanol and 1-propanol were used. These experimental data showed that these property values increases when DES molar fraction is bigger and temperature decreases.

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