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Acoustic investigation of choline chloride based ionic liquids analogs

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ABSTRACT

Despite the surge in publications related to the characterization of deep eutectic solvents (DESs), the speed of sound of these liquids was not considered. This work represents the first study to report the acoustic properties of choline chloride-based DESs (Type III). Five different hydrogen bond donors were used to synthesize the DESs and the speed of sound was measured as a function of temperature within the range: 293.15–353.15 K. In general the speed of sound was affected by the nature and molecular structure of the DES considered. A general decrease in the speed of sound with temperature was noticed for all studied DESs. Three different models were attempted to correlate the speed of sound with some basic physical properties of these DESs as well as the temperature. The Gorbachev's model was able to correlate the speed of sound for the examined DESs with an overall relative error of 0.273%. Further work needs to be done on characterizing other types of DESs (Types I, II and IV) as well as relating the speed of sound data to other physical and thermodynamic parameters.

1. Introduction

Deep eutectic solvents (DESs) are being considered by many recent studies as a viable and cost effective alternative for ionic liquids. Many studies reported possible industrial applications for these solvents to gradually replace conventional solvents commonly used in the industry [1–5]. Due to this surge in possible industrial applications for these liquids, it is becoming necessary to investigate the physical and thermodynamic properties of deep eutectic solvents (DES). Different studies were reported for the basic physical properties of these solvents [6–9]. However, until now no data were reported for the speed of sound in these liquids. This triggers the attention to start filling this gap in this field.

Ultrasonic studies in fluids are of a paramount importance and have many applications in understanding the liquid mixtures physico-chemical properties. This involves understanding important phenomena such as intermolecular interactions, association, dissociation and complex formation [10]. Many studies have been conducted on mixtures to investigate the physico-chemical properties and the molecular interaction between the participating components using ultrasonic techniques [11–13].

Speed of sound along with other properties, can be used to estimate many thermophysical properties. Properties like isentropic and isothermal compressibilities, isobaric thermal expansion coefficient, thermal pressure coefficient, the Joule–Thomson coefficient, isobaric and isochoric heat capacities, ratio of isobaric and isochoric heat capacities, and the reduced bulk modulus have been estimated using such approach. This estimation provides valuable data necessary for the industrial process design and optimization [14].

When critical properties are not available, speed of sound in liquids can be measured with a high degree of accuracy, and can be used for the estimation of many thermodynamic parameters including the virial coefficients, the van der Waals constants, the Lennard–Jones potential parameters, and other equation of state constants [15,16].

Recently, Wu et al. [17] published a databased for the speed of sound in ionic liquids. This database involves 96 ILs which have a total of 51 cations and 23 anions.

Despite the fact that there has been a vast literature on applications of ILs in general and DESs in particular, the reported studies on predicting the speed of sound for such liquids are very limited, and hence, more efforts should be directed toward establishing a reliable source for the prediction of such important data. Moreover, the lack of these data at different operating conditions, increases the importance of developing highly accurate prediction methods for these data. Quite a few articles have been published on the theoretical and empirical means of predicting the speed of sound in ILs [18–20].

The current study reports, for the first time, the speed of sound data for some choline chloride based deep eutectic solvents at the temperature range of 298.15–353.15 K. The studied DESs involved

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five frequently used solvents namely: reline (1:2), glyceline (1:2), ethaline (1:2), fructoline (2:1) and glucoline (2:1). All of these DESs share choline chloride as the common salt in combination with a hydrogen bond donor (HBD). The temperature variation of speed of sound data for these liquids has been studied. Three different methods were used to correlate this property as a function of temperature. The correlation prediction results have been consolidated with the experimental data and proper recommendations were reported.

2. Theory of speed of sound prediction methods

The speed of sound (u) in m/s units can be estimated using the theoretical Auerbach's relation [21]

$$u = \left(\frac{\sigma}{6.33 \times 10^{-10}\rho}\right)^{a} \tag{1}$$

where $a = 2/3$, σ and ρ are the surface tension in mN m^{-1} units and density in kg m^{-3} units, respectively. This model was used by Oswal et al. to estimate speed of sound of alkyl alkanoates [22] and alkyl amines [23]. Additionally, Aminabhavi et al. [24] used the same model to estimate speed of sound of binary mixtures of 2-methoxyethanol with aliphatic alcohols. Blairs [26] modified this model to give better predictions for the sound velocities of metallic liquids. He plotted $\log u$ against $\log(\sigma/\rho)$ and got a linear relationship (with a correlation coefficient $R^2 = 0.9717$ at 95% confidence level) with the slope equal to 0.6199. The resulting linear correlation, can be expressed as:

$$\log(u) = 0.6199\ \log\left(\frac{\sigma}{\rho}\right) + 5.9447 \tag{2}$$

This model improved the performance of that of Eq. (1) to some extent. Model (2) was used by Blairs to correlate the sound velocities of ionic liquids. Gardas and Coutinho [14] adopted a similar approach using predicted values for surface tension and density data.

Alternatively, another way to model the speed of sound is by including the critical molar volume as another parameter in addition to density and surface tension. Gorbachev [27], modified the original models of Filippov [26], by including the effect of critical volume. Gorbachev [27] assumed that the highest effective radius molecular motion, which is possible in the investigated liquid phase for its separate molecule, will be proportional to $V_c^{1/3}$ and $(M/\rho)^{1/3}$, where V_c is the critical molar volume (m^3 mol^{-1}) and M is the molecular weight of this liquid (kg mol^{-1}).

The numerical value of the difference between the molecular radius and the highest effective radius of molecular motion in non-associated liquids describes the upper limit of the possible increase of the effective radius of molecular motion [27]. Consequently, Gorbachev's model takes the following form:

$$u = \xi\left[V_c^{1/3} - \left(\frac{M}{\rho}\right)^{1/3}\right]\left(\frac{\sigma}{M}\right)^{1/2} \tag{3}$$

where ξ is a constant for one mol of any liquid at constant temperature. This model assumes that the molecules of the liquid are spherical or close to spherical.

In its original form, Gorbachev assumed the temperature effect on ξ is expressed as:

$$\xi = \alpha \quad \ln\left(\frac{T}{\tau}\right) \tag{4}$$

where α and τ are two numerical constants for every type of liquid. Including this relation in Eq. (3), results in a temperature sensitive speed of sound model. However, in this work, it was found that the ξ–T relationship can be well approximated by a linear model and hence, Eq. (4) is written as:

$$\xi = a_1 T + a_0 \tag{5}$$

The critical molar volume for the considered DESs was calculated using the modified Lydersen–Joback–Reid method [29]. This method was adopted previously by Shahbaz et al. [28] to calculate the critical properties of a group of salts and hydrogen bond donors. They used these critical values in combination with the Lee–Kesler mixing rules to estimate the corresponding critical properties of few DESs composed of the original salts and hydrogen bond donors.

Based on the Modified Lydersen–Joback–Reid method, the critical volume can be calculated as:

$$V_c = E_M + \sum n\Delta V_m \tag{6}$$

where ΔV_m is a constant for the modified Lydersen–Joback–Reid method [29], n is the number of functional groups in the considered components of the DESs and $E_M = 6.75$. The calculated pure components critical volume was then used in the following Lee–Kesler mixing rule to estimate the DESs critical volume:

$$V_{cm} = \frac{1}{8}\sum_i\sum_j y_i y_j (V_{ci}^{1/3} + V_{cj}^{1/3})^3 \tag{7}$$

In this equation m refers to the mixture, i and j refer to the pure constituents and y refers to the mole fraction of the pure constituent i or j.

3. Experimental methodology

3.1. Chemicals used

Choline chloride ($C_5H_{14}ClNO$), and urea ($CO(NH_2)_2$), glycerol($C_3H_8O_3$), ethylene glycol ($C_2H_6O_2$), D-fructose anhydrous ($C_6H_{12}O_6$) and D-glucose anhydrous ($C_6H_{12}O_6$) were obtained from Merck Chemicals with high purity (>98%) and used for the synthesis of DESs without further purification. The water mass fraction of these chemicals as per the manufacturer's guide was less than 10^{-4}.

3.2. DES synthesis

The DES components (listed in Table 1) were dried in a vacuum oven overnight in order to ensure the absence of any traces of moisture. For every DES, an adequate amount of choline chloride was mixed with the corresponding hydrogen bond donor at the desired molar ratio. The two components quantities for every DES were measured using a Shimatzu AUW120D high precision balance with a precision of 0.01 mg. The average standard uncertainty in measuring the DES molar fractions is estimated to be 0.05%. The mixture was put in vials and loaded to a ThermoMixer (DITABIS MKR 13) operating at 353.15 K. Mixing was commenced for at least 1 h by which a homogenous transparent liquid was observed. The water content of the synthesized DESs was measured by Karl Fisher titration method. The average measured moisture content was less than 0.2 wt%.

3.3. DESs characterization

The melting points of the studied DESs were measured using TA-Q20 Differential Scanning Calorimeter (DSC) with an auto-sampler. The DSC was combined with a refrigerated cooling system RSC90. To ensure the measurement's accuracy and repeatability, the DSC was calibrated for its baseline as well as the temperature calibration using an indium post-transition metal standard. Density measurements were done using an Anton Paar DMA 4500 vibrating-tube