



# Mass connectivity index-based density prediction of deep eutectic solvents



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## ABSTRACT

Deep Eutectic Solvents (DES) are novel ionic liquid analogues that are gaining an increasing interest in the scientific community. Many novel applications have been reported for successfully using these solvents in diversity of fields. In this work, a new correlation is introduced for predicting their densities as a function of temperature. The concept of mass connectivity index (MCI) has been utilized for this purpose. The new correlation considers the molecular topology of the DES constituting molecules. The experimental density of a set comprising of 12 common DESs was used for optimizing the model. The new model was then validated using another set of 8 DESs. The new correlation attained an average relative deviation of around 0.07% for the two sets compared to that of more than 1% by the Rackett model. The MCI-based density model proved its superiority compared to the traditional Rackett density model as far as DESs are concerned.

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## 1. Introduction

One of the areas that deserves continuous focus and improvement is the prediction of liquids physical properties. Having efficient prediction methods will not only reduce the need for conducting experimental analysis to obtain these properties, but will also contribute in improving process simulators as well as process equipment design and sizing procedures. Developed predictions methods need to be simple as much as possible and need the least number of parameters and thermodynamic data [1].

Unfortunately, available efficient generalized prediction methods depend heavily on thermodynamic data that are usually not accessible in most cases or their accuracy is doubted. In the case of ionic liquids and their analogues, the scarcity of these data complicates the problem and makes application of such methods impractical. Thermodynamic properties such as acentric factor, normal boiling point, critical properties are scarce and their prediction methods are either not applicable or lack the needed accuracy [2–4].

Deep eutectic solvents (DES) are ionic liquids analogues that are gaining a surge of interest due to their similar favourable properties to those of ionic liquids as well as their low environmental

fingerprint and the ease of synthesis at high purity [5]. Many applications have been reported for these liquids in diverse scientific and industrial areas [6,7]. In addition, characterization of the most commonly used ones is also an area that showed increasing attention [8–11]. However, very little work has been reported on the prediction of their important physical data. In these studies, the main physical data were modelled with simple specific models that take the form of low order polynomials or exponential functions [5].

Density is one of the basic important physical properties for any liquid. It is needed in many thermodynamic calculations as well as in the design and sizing of process equipment. Studies on predicting this property have been reported for ionic liquids [20] and to less extent for deep eutectic solvents [12–15].

DES density is a fundamental physical property which plays a significant role in characterizing these liquids. Modelling of this property is reported for few common DESs and usually takes the form of relations based on the corresponding states principle and others based on group contribution methods [14,15]. The increasing number of DESs due to the inclusion of new salts and hydrogen bond donors (HBD) combinations makes predicting this property with a unique correlation a serious challenge [15].

The Rackett models was used by Shahbaz et al. [12] to model densities of type III DESs with temperature in the range 298.15–368.1 K. Later, the same group used the parachor parameter

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and surface tension data to predict DES density [13]. Atomic contributions and the Lorentz–Lorentz equation was also used for this purpose [14]. Mjalli et al. recently modified the Rackett model and used the new model to predict DES densities with an overall deviation error of 0.991% [15].

Randic [16] proposed to encode molecular bond contributions to the branching index and this allows to some extent partially quantify the extent of branching in a molecule. This concept was later expanded and improved by Kier and Hall [17]. Valderrama and Rojas [18] introduced the mass connectivity index which is defined as a function of the mass connectivity interactions. They used the mass connectivity index to model the heat capacity of ionic liquids.

In this work, the molecular structure explained by the mass connectivity index is proposed as a universal parameter to be used in a unified correlation for predicting the density of deep eutectic solvents. A selected set of commonly used type III DESs were used and their mass connectivity indices were calculated. The predictive capacity of the newly developed correlation is compared to the widespread Rackett correlation and a statistical analysis was performed for both methods.

## 2. DES density models

The simplest form for correlating the density of deep eutectic solvents with temperature was formed as a linear relationship of the general form:

$$\rho(T) = \rho_0 + \rho_1(T - T_0) \quad [1]$$

where  $\rho_0$  and  $\rho_1$  are two model parameters that are evaluated for each DES independently and  $T_0$  is a reference temperature. Despite the high predictive efficiencies of these correlations, their use is restricted for few number of systems and cannot be generalized for others. Some studies suggested correlating the second parameter  $\rho_1$  with structural molecular parameters or specific properties (group contributions, thermodynamic properties) [20,21].

In general, ionic liquids density was correlated using one of two methods namely: methods based on the corresponding state principle [22] and methods based on chemical functional group contributions [23]. Due to the intrinsic ionic nature of the liquids involved, these methods fail to capture the density variation with temperature efficiently [12]. Critical properties-based properties models are used in predicting thermos-physical and transport properties of liquids [22].

In a comparative study, Spencer and Danner [24] have compared different available methods for predicting saturated liquid densities as a function of temperature. Their study revealed that the best generalized methods for predicting the effect of liquid temperature on its density is by using the model proposed by Rackett [25]. The Rackett model was extensively used for many types of liquids due to its simplicity. It is based on the critical properties of the liquid and can be put in the form:

$$\rho_S = \rho_c Z_c^{-(1-T/T_c)^{2/7}} \quad (2)$$

where  $\rho_c$ ,  $T_c$ ,  $Z_c$  are respectively the critical density, temperature and compressibility factor. Other variations of this basic form have also been introduced. Due to the difficulty evaluating the critical properties of DESs (because one or both DES components may evaporate or decompose before reaching normal boiling temperature), they have been calculated using different prediction methods [26]. A modified form of Eq. (2) was used for predicting DES density data [15]. Recently, Eq. (2) was modified by including two adjustable parameters ( $a$  and  $b$ ) that need to be optimized to better capture the irregular variation of DESs molar volume with temperature.

$$\rho_S = \rho_{SR} Z_{RA}^{(1-T/T_c)^a - (1-T_R/T_c)^a} \quad (3)$$

where the compressibility factor is calculated from:

$$Z_{RA} = \left( \frac{V_{SR} P_c}{RT_c} \right)^{(b+T_R/T_c)^a} \quad (4)$$

Despite the good predictions of the abovementioned models, their dependence on the DES critical data (which are not available readily) make their application restricted to the accuracy of the thermodynamic methods used for calculating these critical data.

The concept of mass connectivity index (MCI) [19] can be utilized to encode the molecular structure branching. This offers a reasonable means to quantify the variation in molecular diversity of the DES and to utilize this factor in explaining the variation in their density as a function of temperature. The MCI of a particular molecule can be calculated from the mass connectivity interactions among the functional groups immediately connected in a molecule:

$$\lambda = \sum_{k=1}^{ij} \left( 1 / \sqrt{M_i M_j} \right) \quad (5)$$

The  $M_i$  and  $M_j$  are the masses of connected groups numbers ( $i$ ) and ( $j$ ). All combinations are considered in the summation. This parameter can be calculated for both components of the DES and then combined to get the corresponding index value of the DES. For example, to calculate the MCI for the Reline molecular structure, which is composed of 1 mole choline chloride (ChCl) + 2 moles urea, the MCI for ChCl and urea are calculated first. For ChCl, the type of functional groups connections composing the molecular structure are: ([–CH<sub>3</sub>] with [>N–]), ([>N–] with [–CH<sub>2</sub>–]), ([–CH<sub>2</sub>–] with [–CH<sub>2</sub>–]), ([–CH<sub>2</sub>–] with [–OH]), and ([–Cl] with [>N–]) and their corresponding numbers are: 3,1,1,1 and 1. Using the appropriate values of  $M_i$  and  $M_j$  reported by Valderrama et al. [19] and substituting in Eq. (5), the MCI of ChCl can be calculated as 0.9180. Similarly, the urea molecule contains two similar functional groups connections: ([–NH<sub>2</sub>] with [>C=O]) and the corresponding MCI is calculated as 0.1888. Multiplying the salt and HBD MCI by their molar quantities in the DES, the ChCl MCI is calculated as 1.2956.

The calculated MCI can then be incorporated in Eq. (1) to replace the  $\rho_1$  parameter and the new density model can be put as:

$$\rho(T) = \rho_0 + a_1 (n_{SALT} \lambda_{SALT} + n_{HBD} \lambda_{HBD})^{a_2} (T - T_0) \quad (6)$$

where  $n_{SALT}$  and  $n_{HBD}$  are the number of salt and HBD molecules in the DES and  $a_1$  and  $a_2$  are two model parameters than need to be estimated by optimizing the density model against experimental DES density data.

## 3. Density model formulation and testing

The proposed model in Eq. (6) has been considered in this work. A set of 20 DESs as given in Table 1, were selected from the literature for the purpose of identifying density model parameters. The table includes the molecular structure of each DES as well as the temperature and density used as reference values. These DESs are among the most commonly used type III DESs in the literature. The total number of experimental data points collected in the set is 189. The first 12 DESs were used to train the model and evaluate its parameters ( $a_1$  and  $a_2$ ). While the other 8 DESs were used to test the model generalization capability on density data which weren't part of the model training.

The MCI of each of the four salts and the eight HBD molecules

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