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Prediction of deep eutectic solvents densities at different temperatures

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ABSTRACT

Predicting densities of nonconventional solvents like deep eutectic solvents (DESs) as a function of temperature is of considerable importance in the development and design of new processes utilizing these solvents. Because of the nature of bonding existing between the salt and the hydrogen bond donor, conventional methods result in very large deviations. In this study, the density of DESs based on three different salts was estimated using empirical method. Nine different salts:hydrogen bond donor combinations were selected to test this method. The densities of all DESs were measured at a temperature range (298.15–368.1 K). The critical properties of salt and hydrogen bond donor were estimated using the Modified Lydersen–Joback–Reid method, while that of the mixture were calculated using Lee–Kesler equation. The Rackett equation modified by Spencer and Danner was employed to predict the DES density. The values of measured and predicted densities were compared and the average of absolute relative error percentage (ARPE) for all DESs was found to be 1.9%. The effect of salt to HBD molar ratio on ARPE in predicted DESs densities was also investigated.

1. Introduction

One of the main obstacles preventing the widespread usage of ionic liquids in industry is their synthesis high cost. This is mainly due to expensive raw material chemicals and long preparation and purification procedures. Deep eutectic solvents (DESs) have been recognized as low cost alternatives of ILs. DESs are mixtures of two or more components which have low melting points compared to their constituting component. This depression of melting point causes the liquid state of DESs, whereby hydrogen bond interactions between an anion and a hydrogen bond donor are more energetically favored relative to the lattice energies of the pure constituents [1,2]. DESs share common solvation properties with ionic liquids. In addition, they have many advantages, e.g. they are prepared easily in high purity at low cost. Other advantages include its non-toxicity, no reactivity with water and being biodegradable [3]. Currently, DESs have mediated in many research areas and became attractive for many applications because of their potential use as alternative environment friendly solvents.Mixtures of quaternary ammonium salts with hydrogen bond donors such as amines and carboxylic acids were the first generation of deep eutectic solvents. The mixture of choline chloride and urea with 1:2 molar ratio showed its capability in dissolving many metal salts like lithium chloride and copper(II) oxide [2]. Abbott et al. [4] have shown that eutectic mixtures of salts were used to reduce the processing temperature for applications of molten salts. They have reported that the formation of the eutectic results as a consequence of the formation of complex anions e.g. $Al_2Cl_7^-$ and $Zn_2Cl_5^-$ thus decreasing the lattice energy and decreasing the freezing point of the system. Chen et al. [5] reported two methods of nucleophilic fluorination to prepare α-fluoroacetophenones from α-bromoacetophenones using KF with PEG-400 or TBAF with ZnF_2. Morrison et al. [6] used the DES to solubilize compounds with low solubility for increasing bioavailability in early drug development such as toxicology studies. Abbott et al. [7] have shown that glycerol based DES is an efficient extraction media for glycerol from biodiesel based on rapeseed and soy beans. Hayyan et al. [8] showed that a low cost quaternary ammonium salt–glycerol based DES can be successfully used as a solvent for extracting the byproduct glycerol from palm oil-based biodiesel. In addition, DESs have been utilized in many industrial applications such as electroplating, electrowinning and electropolishing [9].

The density is one of the important physical properties for ionic liquids in general and DESs in particular. The usual practice for evaluating densities is through experimental procedure. This is not practical and sometimes not possible for cases where it is required to estimate the densities as a function of temperature. Therefore a great need arises for developing estimation methods of acceptable accuracy to fulfill this requirement.

Two methods have been reported in the literature for estimating ionic liquids densities. The first method is based on the corre-

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sponding state principle [10,11] and the other method is related to group contribution methods [12,13]. Using such methods as they are results in high prediction errors because of the special ionic nature of ionic liquids and DESs.

The critical properties, normal boiling temperature and acentric factor are utilized in many cases for correlations and prediction methods to estimate thermophysical and transport properties [10]. Unfortunately, the critical properties needed to predict other physical properties are not available for deep eutectic solvents. DESs critical properties cannot be measured experimentally because the components making the DESs start to decompose before reaching boiling point temperature of the DES. In addition, the apparent boiling point of the DES is not a representative for the DES mixture. Because of the common behavior between ionic liquids and DESs, it is acceptable to develop prediction methods for DESs which are similar to those developed for ionic liquids.

Previous studies concentrated on predicting ionic liquid properties using group contribution methods. Recently, Valderrama and Robles [11] presented a group contribution method to calculate critical properties for ionic liquids with reasonable accuracy. They determined the critical properties (T_c, P_c and V_c), the normal boiling temperature and the acentric factor of ionic liquids using an extended group contribution method which was based on Lydersen and Joback and Reid method. Due to the absence of experimental critical properties of ionic liquids the consistency and accuracy of the method was tested by calculating the liquid density which is functional of normal boiling temperature, molecular mass and critical properties [14]. The results of calculated ionic liquid density were compared with measured values reported in the literature. The method was found to be sufficiently accurate. Jacquemin et al. [12] reported a group contribution method to predict the density (in the form of molar volume) of ionic liquids as a function of temperature, between 273 and 423 K at 0.1 MPa, by the addition of the effective molar volume of the component ions. The authors reported that the prediction uncertainty of their method was lower than 1% in the average, although some reported deviations were higher than 5% for several cases. Valderrama et al. [13] used artificial neural networks and the concept of group contribution method concurrently to estimate the density of ionic liquids. The proposed combined method follows the classical method of dividing the molecule into defined groups. However, in this case, instead of determining the value of the group contribution, an artificial neural network is trained to determine the relation between the dependent and independent variables. The predicted densities were compared with literature values of density of ionic liquids. The results verified that neural network plus group contribution method are able to predict the density of ionic liquids with satisfactory accuracy for engineering calculations. The application of such black box modeling method for the prediction of physical properties of ionic liquids is limited to the tested database of ILs. Moreover, this method may not be suitable for DESs where the salt molecule interacts with one or more hydrogen bond donor molecules.

To our best knowledge there are no studies dedicated for the estimation of DESs densities as function of temperature. In this work, nine DESs at different salts to HBD molar compositions were considered for estimating their densities as a function of temperature. An acceptable method for density prediction based on the DES chemical composition and structure is presented.

2. Materials and methods

2.1. Chemicals

Choline chloride ($C_5H_{14}ClNO$), methyl triphenyl phosphonium bromide ($C_{19}H_{18}PBr$), N,N-diethyl ethanol ammonium chloride ($C_6H_{16}ClNO$), glycerol ($C_3H_8O_3$), ethylene glycol ($HOCH_2CH_2OH$) and 2,2,2-trifluoroacetamide ($C_2H_2F_3NO$) were obtained from Merck Chemicals with high purity (>99%) and used for the synthesis of DESs without further purification. The water mass fraction of these chemicals as per the manufacturer's guide is $<10^{-4}$.

2.2. DES synthesis

There is no limit to the number or type of DESs that can be synthesized from the available chemicals because there are a huge number of salts and hydrogen bond donors which can be used to synthesize the DESs. In this work, three different salts namely; choline chloride, N,N-diethyl ethanol ammonium chloride and methyl triphenyl phosphonium bromide were selected. Glycerol, ethylene glycol and 2,2,2-trifluoroacetamide were selected as hydrogen bond donors. A jacketed vessel with a mechanical stirrer was used to mix each salt with different HBDs in different molar ratios at 343.15 K and 300 rpm agitation until a homogenous transparent liquid was observed.

The above procedure was conducted inside a glove box with humidity control of less than 1 ppm water. The different salt:HBD combinations are coded in Table 1. As can be seen in Table 1, all the synthesized DESs gave freezing points lower than constituting components which is consistent with the general behavior of deep eutectic solvents.

2.3. DESs characterization

Density measurements were done using an Anton Paar DMA 4500 vibrating-tube density meter. The adjustment of the density meter was checked using degassed bi-distillated water. The measured values were compared with the corresponding values in the density tables, and the accuracy was ±0.00003 g cm^{-3}. DESs densities measurements were repeated three times to obtain mean values at each temperature. Mettler Toledo Differential Scanning Calorimeter (DSC) was used for the determination of freezing temperatures. The equipment's measurement accuracy was tested by measuring samples of known freezing points.

Table 1
Synthesized DESs compositions and freezing points.

Salt	HBD	Molar ratio (salt:HBD)	Freezing point (K)	Abbreviation
Choline chloride	Glycerol	1:1	281.80	DES1
Choline chloride	Ethylene glycol	1:2	207.14	DES2
Choline chloride	2,2,2-Trifluoroacetamide	1:2	243.14	DES3
N,N-diethyl ethanol ammonium chloride	Glycerol	1:2	271.82	DES4
N,N-diethyl ethanol ammonium chloride	Ethylene glycol	1:3	250.9	DES5
N,N-diethyl ethanol ammonium chloride	2,2,2-Trifluoroacetamide	1:2	273.05	DES6
Methyl triphenyl phosphonium bromide	Glycerol	1:2	276.89	DES7
Methyl triphenyl phosphonium bromide	Ethylene glycol	1:4	223.81	DES8
Methyl triphenyl phosphonium bromide	2,2,2-Trifluoroacetamide	1:8	203.86	DES9

Table 2
Groups considered for Modified Lydersen–Joback–Reid method.

Group	ΔT_{bM}	ΔT_M	ΔP_M	ΔV_M
Without rings				
$-CH_3$	23.58	0.0275	0.3031	66.81
$-CH_2-$	22.88	0.0159	0.2165	57.11
>CH–	21.74	0.0002	0.114	45.7
>C<	18.18	−0.0206	0.0539	21.78
$=CH_2$	24.96	0.017	0.2493	60.37
=CH–	18.25	0.0182	0.1866	49.92
=C<	24.14	−0.0003	0.0832	34.9
=C=	26.15	−0.0029	0.0934	33.85
≡CH		0.0078	0.1429	43.97
≡C–		0.0078	0.1429	43.97
–OH (alcohol)	92.88	0.0723	0.1343	30.4
–O–	22.42	0.0051	0.13	15.61
>C=O	94.97	0.0247	0.2341	69.76
–CHO	72.24	0.0294	0.3128	77.46
–COOH	169.06	0.0853	0.4537	88.6
–COO–	81.1	0.0377	0.4139	84.76
HCOO–		0.036	0.4752	97.77
=O (others)	−10.5	0.0273	0.2042	44.03
$-NH_2$	73.23	0.0364	0.1692	49.1
>NH	50.17	0.0119	0.0322	78.96
>N–	11.74	−0.0028	0.0304	26.7
–N=	74.6	0.0172	0.1541	45.54
–CN	125.66	0.0506	0.3697	89.32
$-NO_2$	152.54	0.0448	0.4529	123.62
–F	−0.03	0.0228	0.2912	31.47
–Cl	38.13	0.0188	0.3738	62.08
–Br	66.86	0.0124	0.5799	76.6
–I	93.84	0.0148	0.9174	100.79
With rings				
$-CH_2-$	27.15	0.0116	0.1982	51.64
>CH–	21.78	0.0081	0.1773	30.56
=CH–	26.73	0.0114	0.1693	42.55
>C<	21.32	−0.018	0.0139	17.62
=C<	31.01	0.0051	0.0955	31.28
–O–	31.22	0.0138	0.1371	17.41
–OH (phenol)	76.34	0.0291	0.0493	−17.44
>C=O	94.97	0.0343	0.2751	59.32
>NH	52.82	0.0244	0.0724	27.61
>N–	52.82	0.0063	0.0538	25.17
–N=	57.55	−0.0011	0.0559	42.15
Other groups				
–B	−24.56	0.0352	0.0348	22.45
–P	34.86	−0.0084	0.1776	67.01
$-SO_2$	147.24	−0.0563	−0.0606	112.19

2.4. Properties estimation methods

Alvarez and Valderrama [15] presented a Modified Lydersen–Joback–Reid method which combined the best results of Lydersen method [16] and that of Joback–Reid [17]. The Modified Lydersen–Joback–Reid method demonstrated very good accuracy for estimating the critical properties of molecules with high molecular mass [10,11]. In this method the critical pressure and critical volume were calculated using the equations of the Lydersen method. The normal boiling temperature and the critical temperature were calculated using the equations of the Joback–Reid method. The authors modified the parameters of equations for the critical properties, but the normal boiling point equation was exactly the same equation used in the Joback–Reid method. In addition, the method was extended for ionic liquids by introducing three new groups (–B, $-SO_2$ and –P). The method for the determination of these new groups parameters was explained in Alvarez and Valderrama [15]. Table 2 shows the values of the three new groups as well as all other groups for this method.

In this study, the Modified Lydersen–Joback–Reid method was selected as the method of choice for estimating the critical properties of salts and hydrogen bond donors separately. One reason for using this method is that the salts which are used to synthesize the DESs are similar to ionic liquids in terms of ionic nature. T_b, T_c, P_c and V_c of the salts and HBDs were estimated using the following equations:

$$T_b = 198.2 + \sum n\Delta T_{bM} \tag{1}$$

$$T_c = \frac{T_b}{[A_M + B_M \sum n\Delta T_M - (\sum n\Delta T_M)^2]} \tag{2}$$

$$P_c = \frac{M}{(C_M + \sum n\Delta P_M)^2} \tag{3}$$

$$V_c = E_M + \sum n\Delta V_M \tag{4}$$

where ΔT_{bM}, ΔT_M, ΔP_M and ΔV_M are constants for the Modified Lydersen–Joback–Reid method given in Table 2 and $A_M = 0.5703$, $B_M = 1.0121$, $C_M = 0.2573$, $E_M = 6.75$.

The acentric factor of each component was calculated using the following equation which has been described by Valderrama and Robles [11].

$$\omega = \frac{(T_b - 43)(T_c - 43)}{(T_c - T_b)(0.7T_c - 43)} \log\left(\frac{P_c}{P_b}\right) - \frac{(T_c - 43)}{(T_c - T_b)} \log\left(\frac{P_c}{P_b}\right) + \log\left(\frac{P_c}{P_b}\right) - 1 \tag{5}$$

In this equation, T_c and P_c are the estimated critical properties and T_b is the normal boiling temperature at the normal boiling pressure ($P_b = 11{,}0132.5$ Pa).

After estimating the critical properties of DES components Lee–Kesler mixing rules equations recommended by Knapp et al. [18] were employed to calculate the mixing critical properties of DES.

$$T_{cm} = \frac{1}{V_{cm}^{1/4}} \sum_i \sum_j y_i y_j V_{cij}^{1/4} T_{cij} \tag{6}$$

$$V_{cm} = \sum_i \sum_j y_i y_j V_{cij} \tag{7}$$

$$\omega_m = \sum_i y_i \omega_i \tag{8}$$

$$T_{cij} = (T_{ci} T_{cj})^{1/2} k'_{ij} \tag{9}$$

$$V_{cij} = \frac{1}{8}(V_{ci}^{1/3} + V_{cj}^{1/3})^3 \tag{10}$$

$$P_{cm} = 0.2905 - 0.085\omega_m \frac{RT_{cm}}{V_{cm}} \tag{11}$$

In these equations 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. k'_{ij} is binary parameters, which are simplified to be of unit value because no published data are available [19].

2.5. Density estimation method

Several methods for estimating densities have been described by Kurtz [20], Li et al. [21], Reid et al. [19]. Spencer and Danner [22] have conducted an extensive evaluation of the available methods for predicting saturated liquid densities as a function of temperature. They concluded that the most accurate mean of predicting the effect of temperature on the saturated liquid densities is using the modified Rackett equation. The Rackett's equation [23] has been modified by Spencer and Danner [22] to predict the saturated liquid density as a function of temperature:

$$V_S = V' Z_{RA}^{(1-T/T_c)^{2/7}} \tag{12}$$

where V_S is saturated molar volume of liquid at reduced temperature, V' is a characteristic volume that in many cases its value is close to the critical volume and Z_{RA} is Rackett compressibility factor. Eq. (12) can be written in an equivalent form:

$$V_S = \left(\frac{RT_c}{P_c}\right) Z_{RA}^{(1+(1-T/T_c))^{2/7}} \tag{13}$$

where P_c and T_c are the critical pressure and critical temperature, respectively. If an experimental liquid molar volume (V_{S-R}) is available at a reference temperature (T_R), Eq. (12) can be written as:

$$V_S = V_{S-R} Z_{RA}^{\phi} \tag{14}$$

where

$$\phi = \left(1 - \frac{T}{T_r}\right)^{2/7} - \left(1 - \frac{T_R}{T_r}\right)^{2/7} \tag{15}$$

Z_{RA} can be determined using measured densities and substituted in Eq. (14). This method needs two experimental densities to calculate the Z_{RA}. In this work, we refer to this method as method 1.

However, Eq. (13) can be rewritten as follows [24]:

$$Z_{RA} = \left(\frac{V_S P_c}{RT_c}\right)^{(1/1)+(1-(T/T_c))^{2/7}} \tag{16}$$

The value of Z_{RA} can be calculated from Eq. (16) using one reliable value of the saturated molar volume (V_S). To reduce the dependency on experimental data, the value of V_S in Eq. (16) was assumed to be equivalent to the value of the experimental liquid molar volume (V_{S-R}) at the reference temperature. The value of Z_{RA} for each DES was calculated through Eq. (16) and substituted in Eq. (14) to calculate the density. In this case we refer to this modification as method 2.

3. Results and discussion

Nine DESs with different salt:HBD combinations were selected and synthesized to test the above mentioned method (method 2) for density estimation. The densities of all synthesized DESs were measured from 298.15 to 368.15 K at 10 K intervals with an average uncertainty of ±0.0001 g cm^{-3}. The density at 298.15 K for each DES was chosen as the reference density needed by the method to predict DESs densities at other different temperatures.

The measured densities of DESs were compared with predicted densities. The results of measured and predicted densities for choline chloride based salt (DES1, DES2 and DES3), N,N-diethyl ethanol ammonium chloride based salt (DES4, DES5 and DES6) and methyl triphenyl phosphonium bromide based salt (DES7, DES8 and DES9) are shown in Figs. 1–3, respectively. As can be seen in the figures, the densities of all DESs represent temperature-dependent behavior. Both experimental and predicted DESs densities gradually decrease with increase in temperature. Obviously, at high temperature molecules move faster and create more space. As a result, the density value goes down.

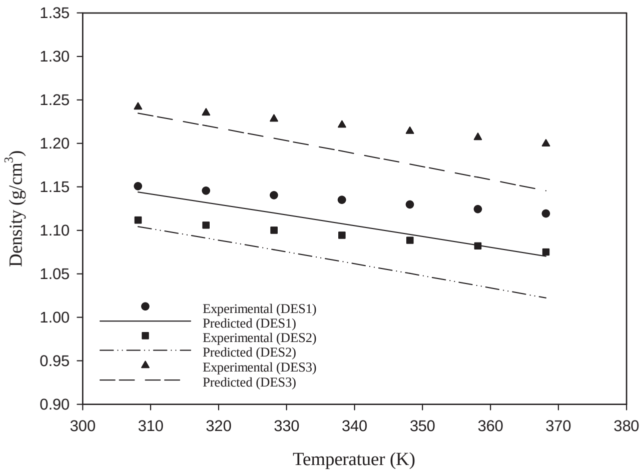

Fig. 1. Experimental and predicted (using method 2) density data comparison of choline chloride based DESs.

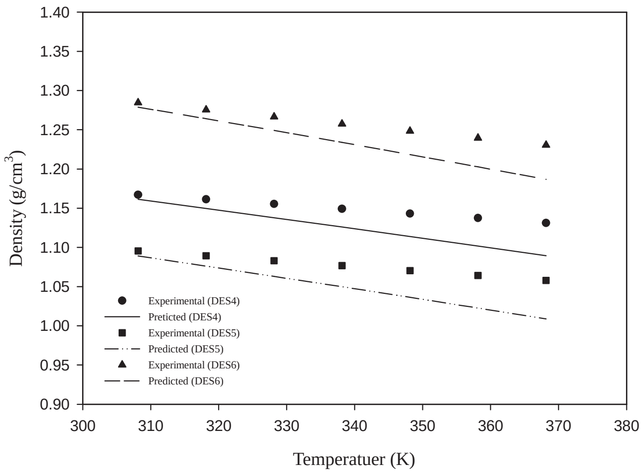

Fig. 2. Experimental and predicted (using method 2) density data comparison of N,N-diethyl ethanol ammonium chloride based DESs.

In addition, the difference between experimental and predicted DESs densities increases with rise in temperature. This means that DESs densities, which have been predicted by method 2, show more errors at higher temperatures than at lower temperatures. The range of absolute relative percentage error (ARPE) for predicted densities of DES1, DES2 and DES3 is (0.5–4.5%) in a temperature range from 298.15 K to 368.15 K. Similarly, the range of ARPE for DES4, DES5 and DES6 is (0.44–4.6%). The deviation between measured and predicted densities for DES7, DES8 and DES9 is slightly less than that for other DESs. The range of ARPE for predicted densities of methyl triphenyl phosphonium bromide based salt was the lowest among all tested DESs (0.16–2.6%). A probable reason for this behavior is that the density of methyl triphenyl phosphonium bromide salt is higher than that of N,N-diethyl ethanol ammonium chloride and choline chloride salts. As the value of density becomes higher, the relative prediction error becomes less because the absolute error is approximately the same. Since this method uses Modified Lydersen–Joback–Ried method to calculate the crit-

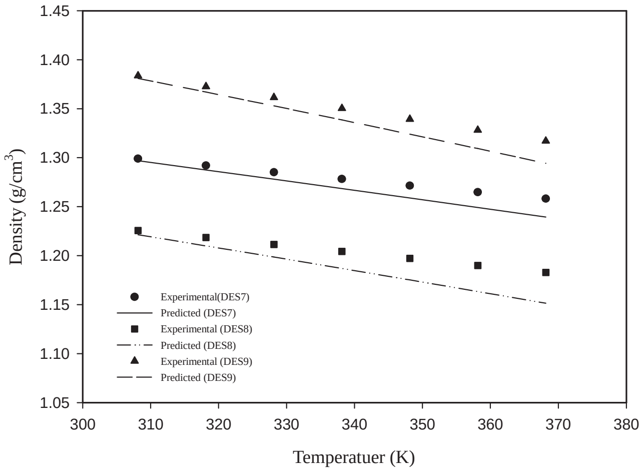

Fig. 3. Experimental and predicted (using method 2) density data comparison of methyl triphenyl phosphonium bromide based salt.

Table 3
Absolute relative percentage error (ARPE) in the predicted DESs densities using three different methods.

Methods	Temperature (K)							
	298.15	308.15	318.15	328.15	338.15	348.15	358.15	368.16
DES1								
1	0.000	0.000	0.007	0.022	0.035	0.058	0.089	0.138
2	0.000	0.579	1.173	1.783	2.401	3.037	3.691	4.373
3	17.769	17.384	17.418	17.235	17.057	16.874	16.685	16.480
DES2								
1	0.000	0.000	0.010	0.031	0.063	0.107	0.165	0.229
2	0.000	0.664	1.338	2.037	2.770	3.510	4.228	4.530
3	23.331	23.345	23.371	23.392	23.399	23.426	23.516	23.660
DES3								
1	0.000	0.000	0.003	0.009	0.037	0.053	0.093	0.132
2	0.000	0.586	1.188	1.806	2.455	3.112	3.802	4.508
3	28.878	28.856	28.840	28.831	28.808	28.810	28.805	28.813
DES4								
1	0.000	0.000	0.019	0.044	0.053	0.076	0.142	0.165
2	0.000	0.482	0.995	1.513	2.022	2.554	3.137	3.687
3	11.960	12.170	12.360	12.562	12.794	13.017	13.202	13.448
DES5								
1	0.000	0.000	0.006	0.027	0.055	0.100	0.157	0.230
2	0.000	0.596	1.210	1.848	2.506	3.194	3.905	4.346
3	14.479	14.771	15.071	15.369	15.675	15.979	16.288	16.601
DES6								
1	0.000	0.000	0.004	0.023	0.047	0.088	0.170	0.2541
2	0.000	0.443	0.901	1.381	1.877	2.400	2.974	3.562
3	22.326	22.502	22.688	22.872	23.067	23.260	23.424	23.606
DES7								
1	0.000	0.000	0.039	0.086	0.138	0.22	0.294	0.382
2	0.000	0.152	0.348	0.545	0.795	0.991	1.233	1.486
3	21.273	21.632	21.950	22.262	22.578	22.878	23.186	23.490
DES8								
1	0.000	0.000	0.004	0.014	0.030	0.057	0.087	0.128
2	0.000	0.345	0.698	1.063	1.440	1.835	2.238	2.658
3	0.934	0.512	0.080	0.358	0.803	1.251	1.711	2.177
DES9								
1	0.000	0.000	0.010	0.030	0.060	0.106	0.187	0.243
2	0.000	0.199	0.413	0.641	0.882	1.145	1.427	1.730
3	6.762	6.085	5.395	4.692	3.973	3.245	2.502	1.747

ical properties, it is more accurate in predicting density for DESs which have salts with higher molecular mass.

The effect of salt to HBD molar ratio on the predicted DESs densities was also investigated. Methyl triphenyl phosphonium bromide was selected in combination with ethylene glycol at different salt:HBD molar ratios (1:3, 1:3.5, 1:4, 1:4.5, 1:5 and 1:5.5). As indicated by Fig. 4, the value of the experimental and predicted densities for methyl triphenyl phosphonium bromide with ethylene glycol DES drops linearly with the increase in mole fraction of ethylene glycol. This is attributed to the fact that the value of the density of ethylene glycol (1.1132 g/cm^3) is less than the density of the corresponding DES for all its ratios (1.213–1.250 g/cm^3). This means that, as expected, the density of the DESs lies between the density of the salt and that of the HBD. Fig. 5 depicts the absolute relative percentage error (ARPE) for different molar ratios of methyl triphenyl phosphonium bromide to ethylene glycol DES. As can be seen from the figure, the ARPE in density predictions of the

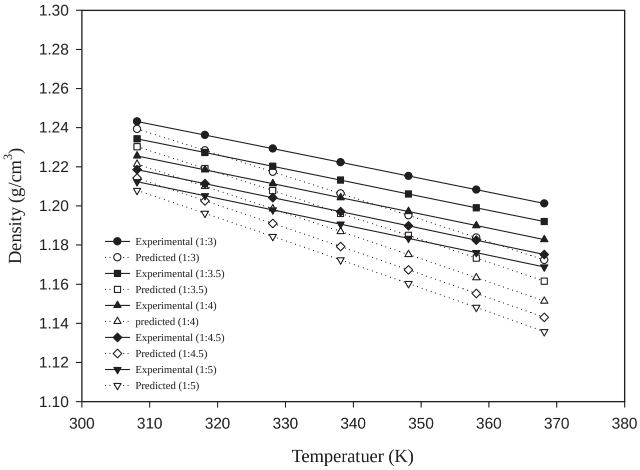

Fig. 4. Experimental and predicted (using method 2) density data for methyl triphenyl phosphonium bromide to ethylene glycol DES in different (salt:HBD) molar ratios.

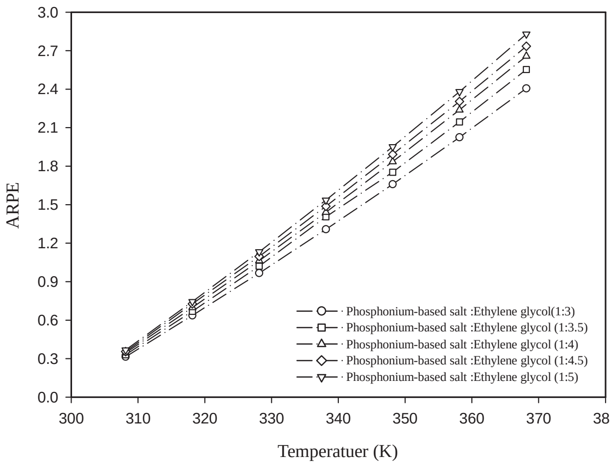

Fig. 5. Absolute relative percentage error (ARPE) for different molar ratios of methyl triphenyl phosphonium bromide to ethylene glycol DES.

phosphonium-based DES increased with the increase in DES molar ratio and temperature.

The two methods mentioned above for calculating the Rackett compressibility factor (Z_{RA}), were also compared. In the method 1, two reference densities were used to calculate the Z_{RA} while the method 2 requires only one reference density. In Table 3, for each DES the first row is the ARPE of predicted densities using method 1 while the second row corresponds to method 2. The ARPE values indicate the using the method requiring two experimental densities gives less prediction errors that the other method requires one experimental value. Nevertheless, the one experimental density based method has the merit of being able to predict the temperature dependency of DES densities without the need for an additional time consuming and sometimes impractical experimental value. Therefore, this approach simplifies the use of the prediction method.

In an attempt, The Modified Lydersen–Joback–Reid method (method 3) was tested to predict the DESs density in general and its results were compared with those using method 2. In this method, it is assumed that there is no hydrogen bond interaction between the molecules of DES components. This means that the combination of salt and HBD molecules in the DES is assumed to behave as one molecule. T_b, T_c, P_c and V_c of each DES (DES1–DES9) were estimated using Eqs. (1)–(4), respectively. The density of DESs was calculated using the following equation which was described by Valderrama and Robles [11]:

$$\rho_L = \left(0.01256 + \frac{0.9533M}{V_c}\right)\left[\left(\frac{0.0039}{M} + \frac{0.2987}{V_c}\right)V_c^{1.033}\right]^{\psi} \tag{17}$$

where

$$\psi = -\left[\frac{1 - T_r}{1 - T_{br}}\right]^{2/7} \tag{18}$$

where T_r is the reduced temperature ($T_r = T/T_c$), and T_{br} is the reduced temperature at the normal boiling point ($T_{br} = T_b/T_c$). This equation needs the molecular mass, the critical properties and the normal boiling temperature of the liquid.

The accuracy of this method was checked by comparing the predicted densities with that of the measured densities. In Table 3, the third row shows the ARPE of the predicted densities using the Modified Lydersen–Joback–Reid method (method 3). The average of absolute relative percentage error for all tested DESs using method 3 was found to be 16.05%. Compare to method 2 this average of ARPE is eight folds higher. On the other hand, method 3 is independent of any experimental data and as can be seen from Table 3, the APRE values for DES8 and DES9 using this method attained acceptable accuracy for predicting the DES density with high molecular mass.

4. Conclusions

The current study introduced an empirical method to predict deep eutectic solvents densities as function of temperature. The critical properties of salt and Hydrogen bond donors were estimated using the Modified Lydersen–Joback–Reid method. The results of these were utilized to calculate the critical properties of the mixture using the Lee–Kesler equation. The Rackett equation modified by Spencer and Danner was employed to predict the DES density. The value of the average ARPE (1.9%) for all tested DESs showed that the applied method is of high prediction quality. An investigation for the effect of salt to HBD molar ratio on the predicted DESs densities revealed that the density of the DESs lies between the densities of the corresponding salt and HBD used in their synthesis. Moreover, the relative difference of densities between the DES and the HBD directly affects the quality of density prediction.

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