International Journal of Chemical Science
www.chemicaljournals.com
Online ISSN: 2523-2843, Print ISSN: 2523-6075
Received: 09-05-2025, Accepted: 08-06-2025, Published: 23-06-2025
Volume 9, Issue 1, 2025, Page No. 23-32

Unveiling the structural influence of butanol isomers on choline chloride–urea deep eutectic solvents through experimental and computational methods

Omshubham Kedia, Janvi Patel, Ankit Shah*
Department of Chemistry, Mahavir University, Gujarat, India

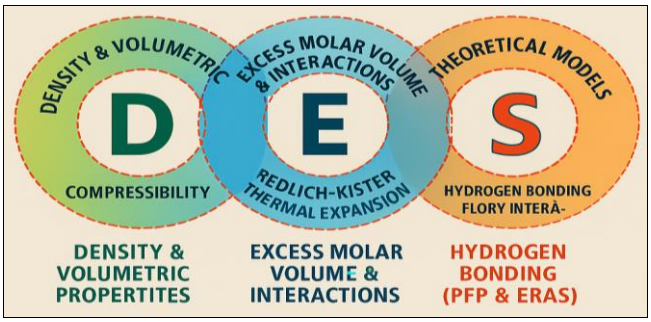
Abstract
As a potentially useful alternative to volatile organic solvents, deep eutectic solvents (DESs), which are renowned for the distinctive physicochemical qualities they possess, have recently come into existence. Organic solvents can be strategically added in order to get the desired effect of fine-tuning these properties. We conducted a study in which we examined the densities (ρ) of binary mixtures that were composed of DES and butanol isomers. These mixes included 1-butanol (primary), 2-methyl-1-propanol (secondary), and 2-methyl-2-propanol (tertiary) butanols. The pressure used in this study was 0.1 MPa, and the temperature range employed was from 293.15 K to 323.15 K. For the preparation of the DES, choline chloride (ChCl) and urea were combined in a certain molar ratio. ChCl was used as the hydrogen bond acceptor (HBA), and urea was used as the hydrogen bond donor (HBD). The data obtained from the experiment were utilized to compute the excess molar volume (V_m^E), which was subsequently assessed by the application of the Redlich–Kister polynomial equation. The fact that the values of V_m^E were found to be negative suggested that the interactions between DES and butanol isomers were more powerful than the interactions between DES and DES or between butanol and butanol in the binary systems. In order to gain a deeper comprehension of the deviation from optimal behavior, the Prigogine-Flory-Patterson (PFP) theory and the Extended Real Associated Solution (ERAS) model were utilized. These combinations have the potential to be used in commercial applications and for the construction of predictive DES models, as demonstrated by the results, which revealed significantly negative excess molar volumes across the entire composition range.

Keywords: Deep eutectic solvent, butanol isomers, choline chloride, urea, excess molar volume, PFP theory, ERAS model

Introduction

The development of environmentally friendly technologies that bring economic development and ecological preservation into harmony is essential to the long-term viability of the contemporary chemical industry. There is a critical need to develop safer alternatives to current solvents, which are frequently flammable and dangerous, as stated in the 12th principle of Green Chemistry [1]. This requirement is crucial [2]. As a consequence of this, a significant amount of emphasis has been placed on the search for and development of environmentally friendly solvents that are capable of reducing their influence on the environment, conserving energy, and enhancing operating safety. In recent years, Deep Eutectic Solvents (DESs) have developed as a new class of environmentally friendly solvents due to the fact that they are biodegradable, have minimal toxicity, and may have their physicochemical properties customized depending on the situation. (three) An eutectic mixture with a much lower melting point than its individual components is produced as a result of hydrogen bonding interactions between a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD). These solvents are formed as a result of these interactions. (four) Increased molecular interactions and charge delocalization within the complex are, to a considerable extent, responsible for this melting point reduction. Ionic liquids and DESs both offer design flexibility, which is why they are frequently referred to as "designer solvents [1, 5]. Catalysis, extraction, lubrication, and electrochemical processes are just some of the many applications that you may find for them [6]. Choline chloride (ChCl), a crucial component that is frequently used in animal feed to speed up development and metabolism, also plays an important part in the transportation of fat, the creation of cells, and the regulation of muscle in humans [7]. In its capacity as an HBA, ChCl is regularly coupled with a number of other HBDs in order to produce DESs. It is a widely utilized HBA for the production of DESs since ChCl is not only affordable but also biocompatible, biodegradable, and conveniently accessible. In 2003, Abbott *et al*. proposed the first DES, which consisted of a molar ratio of 1:2 between ChCl and urea, which served as the HBD. Since that time, ChCl has been combined with a wide range of HBDs to produce DESs that have physicochemical qualities that are specifically tuned to meet the requirements of particular applications.

Graphical Abstract



Having precise information on the physicochemical properties of DESs, particularly in respect to temperature and pressure, is absolutely necessary for the successful application of DESs as solvents in industrial settings. Isentropic compressibility, thermal expansion coefficients, and kinematic viscosity are some of the additional

thermodynamic properties that may be derived from density, which is a critical feature that plays a crucial role in the calculation of process parameters. In order to cater to the particular requirements of various applications, these qualities can be modified by adding a different solvent. The characteristics of drug delivery systems (DESs) are affected by the composition of the HBA and HBD, as well as the molar ratios of these two components in the DES manufacturing process.
High adaptability in applications ranging from dye-sensitized solar cells and packaging to catalysis and extraction processes is demonstrated by choline chloride-based DESs, which are among the most extensively researched kinds of DESs. When it comes to DESs, the choice of HBD has a considerable impact on the qualities that are ultimately achieved. n-butanol, sec-butanol, and tert-butanol are the three types of butanol isomers that offer the possibility of fine-tuning the properties of DESs in this particular setting. Eighth It is possible for the solubility, viscosity, and thermal stability of the DES to be affected by unique chemical and physical properties that are associated with each butanol isomer. Changes in the DES's physicochemical properties can be brought about by even minute quantities of butanol isomers, which would otherwise be insignificant. In light of this, it is essential to investigate how the incorporation of butanol isomers influences the characteristics of pure DESs in order to gain a knowledge of the interactions between molecules and to optimize the system for a variety of contexts.
The thermodynamic and transport parameters of binary mixtures containing DESs and various organic solvents are the primary focus of our work for which we are responsible. In particular, we investigate the ways in which the characteristics of a Choline Chloride–Urea-based DES system is affected by the butanol isomers 1-butanol, sec-butanol, and tert-butanol [9]. New insights into the optimization of DESs for industrial applications will be provided as a result of the findings of this study!

Methodologies concerning experiments

The purities of the three structural isomers of butanol employed in this study were 1-, 2-, and 3-butanol, as well as analytical-grade choline chloride (ChCl) and urea. While Divine analytics supplied the urea, choline chloride and butanol isomers. At temperatures ranging from 298.15 K to 323.15 K, the density values of all the pure components were recorded and compared to values found in the literature to ensure the accuracy of the results. Closely matching previous values of 1.0992 at 298.15 K **[36],** the measured ChCl densities were 1.0945 g·cm^{-3} at 298.15 K and 1.0802 at 323.15 K. The research substances were very pure and reliable since, as previously found, the densities of 1-butanol,
2-butanol, and 3-butanol declined linearly with temperature. The results show that the experimental methods are in conformity with the standards and that future measurements will be accurate.

1. Preparation of DESs

The deep eutectic solvents (DESs) that were explored in this paper were made by mixing urea (HBD) and choline chloride (HBA) in a 1:2 molar ratio, which is the usual way to do it. First, the right amounts of HBA and HBD were carefully weighed. Then, they were put into bottles with screw-on lids. Then, the mixture was stirred at 80 degrees Celsius for two hours to help it turn into one clear liquid. After the physicochemical measurements were done, the mixture was put through a vacuum drying procedure for seventy-two hours to get rid of any moisture that was still there.
To confirm the purity of the manufactured DESs, the experimentally obtained density values were compared with those documented in the available literature. Table 1 compares the ChCl: urea system with the three butanol isomers. It shows the density values found in the literature and those found through testing [36, 40]. After completing some investigation, it was found that the standard deviation of the density of ChCl: urea was about 0.01. There are a few reasons why the density of ChCl: urea is only slightly different from what has been reported in the literature. These include small changes in the molar ratio, the moisture content, and the conditions under which the measurements were made [19]**.** The density values for 1-BOH, 2-BOH, and 3-BOH were consistent with those reported in previous studies [42, 45]. The standard deviation of the densities of the butanol isomers at different temperatures was between 0.001 and 0.001 for 1-BOH [41, 42]**,** 2-BOH [42, 44], and 3-BOH [42, 45]**.** This was true no matter how hot or cold it was.

Table 1: Comparison of density (ρ) for Choline Chloride-Urea DES and isomers of butanol with corresponding literature values at the studied temperatures

Temp. (K)	ChCl: Urea ρ (g·cm^{-3})	1-Butanol ρ (g·cm^{-3})	2-Butanol ρ (g·cm^{-3})	3-Butanol ρ (g·cm^{-3})
	Expt.	Lit.	Expt.	Lit.
293.15	1.096000	1.100000 [36], 1.09890 [37]	0.819452	0.80964 [41]
298.15	1.094500	1.099200 [36], 1.09780 [37]	0.810695	0.80577 [41]
303.15	1.091800	1.096500 [36], 1.09410 [37]	0.802011	-
308.15	1.089200	1.09410 [35], 1.09221 [36]	0.796954	0.79834 [42]
313.15	1.086500	1.09130 [35], 1.08940 [36]	0.793995	0.79435 [41]
318.15	1.083700	1.08850 [35], 1.08690 [36]	0.790320	0.79046 [42]
323.15	1.080200	1.08540 [35], 1.08320 [36]	0.785952	0.78645 [42]

Standard uncertainties:
u(T)=0.05 K
u(ρ)=0.005 g·cm^{-3}

2. Apparatus and procedure

Binary mixture preparation

The ChCl: Urea binary systems with 1-BOH, 2-BOH, and 3-BOH were prepared by accurately weighing the components using an analytical balance (Mettler Toledo B 204-S) with a precision of ±1 × 10^{-7}kg. The mixtures were placed in glass bottles with tightly sealed caps and thoroughly mixed using a vortex mixer to ensure homogeneity, taking into account the higher viscosity of the deep eutectic solvent (DES). At the proposed mole fractions, the ChCl: Urea + butanol isomer systems remained transparent and homogeneous at

ambient temperature. To measure their densities, the binary mixtures were carefully transferred into a U-tube densimeter using a syringe.

Density

The density of pure ChCl: Urea DES, butanol isomers, and their binary mixtures was determined using the DMA 4500M (Anton-Paar), a high-precision vibrating tube densimeter. This instrument features an integrated solid-state thermostat that ensures temperature stability within ±0.03 K. Calibration of the DMA 4500M was carried out at 298.15 K by measuring the density of dry air and double-distilled water. To verify the accuracy of the DMA, the density of a cyclohexane-benzene mixture was compared with values from the literature [36, 46]. The uncertainty in the measured density values was found to be approximately ± 0.0004 g·cm^{-3}

Results and discussion

1. Density

The binary systems of ChCl: Urea with 1-BOH, 2-BOH, and 3-BOH were prepared using an analytical balance (Mettler Toledo B 204-S), with an uncertainty of approximately ±1x10-7 kg. These mixtures were prepared in glass bottles with tight lids and stirred thoroughly using a vortex mixer to ensure uniformity, owing to the increased viscosity of the DES. The ChCl: Urea + butanol isomer binary systems were found to be transparent and homogeneous at the designated mole fraction at room temperature. The mixtures were then carefully introduced into a U-tube densimeter using a syringe to measure their density.

The density of pure ChCl: Urea DES, butanol isomers, and their binary mixtures was measured using the DMA 4500M (Anton-Paar), a high-precision vibrating tube densimeter. The instrument's built-in solid-state thermostat maintains the temperature within an accuracy of ±0.03 K. Calibration of the DMA 4500M was conducted at 298.15 K by measuring the density of dry air and double-distilled water. Additionally, the density of a cyclohexane + benzene mixture was compared with literature values to ensure the accuracy of the instrument [36, 46]. The uncertainty in the density values was found to be ±0.0004 g·cm-3.

Table 1 provides the density of ChCl: Urea DES and all three isomers of butanol at 0.1 MPa pressure and various temperatures ranging from 293.15 K to 323.15 K. The density of the DES decreases in a linear fashion with increasing temperature. Similarly, the density of binary mixtures of ChCl: Urea + 1-BOH, ChCl: Urea + 2-BOH, and ChCl: Urea + 3-BOH also decreases as the temperature rises (see Table 2). This reduction in density can be attributed to an increase in the molecules' kinetic energy, which causes the distance between the hydrogen bond donor (HBD) and acceptor (HBA) to increase, resulting in a decrease in the overall density of the DES and their binary mixtures.

At a fixed mole fraction of DES, the density of the binary systems decreases as the structural variation in the butanol isomers increases, following the order: ChCl: Urea + 1-BOH > ChCl: Urea + 2-BOH > ChCl: Urea + 3-BOH. This trend is consistent with the observed differences in the density of the pure butanol isomers at the same temperature (Table 1). The density of the binary mixtures also increases with higher concentrations of ChCl: Urea in the system. This increase in concentration facilitates stronger interactions between the butanol isomers and ChCl: Urea, reducing free space in the solution and thus increasing the overall density. Similar trends have been reported in binary mixtures of ChCl-based DES with water and other organic solvents. The findings in this study align with literature observations on the density behavior of choline-based DESs [32, 37].

The thermal expansion coefficient α_P is a measure of the compressibility of the binary systems for temperature. α_P can be calculated from the density values using the equation:

Thermal expansion coefficient, α_P, is derived by:

$$\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P \quad (1)$$

The values of α_P decrease with an increase in temperature, indicating higher compressibility as the temperature rises (Table1). The compressibility of the binary systems of DES + butanol isomers decreases with increasing concentrations of DES due to the denser packing between the DES and butanol molecules. Among all the binary systems studied, ChCl: Urea + 3-BOH shows the lowest compressibility due to the structural hindrance of the butanol isomer.

Table 2: Densities (ρ, g·cm^{-3}) of ChCl: Urea (1:2) DES with Butanol Isomers at 0.1 MPa

System	x_1	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K
ChCl:Urea + 1-BOH	0.0	0.819452	0.810695	0.802011	0.796954	0.793995	0.79032	0.785952
ChCl:Urea + 1-BOH	0.05	0.83621	0.828015	0.820105	0.815024	0.811952	0.808215	0.803815
ChCl:Urea + 1-BOH	0.1	0.85321	0.84512	0.837305	0.832415	0.82931	0.825815	0.82185
ChCl:Urea + 1-BOH	0.2	0.88755	0.879805	0.87221	0.86662	0.863505	0.86041	0.856105
ChCl:Urea + 1-BOH	0.3	0.92188	0.914705	0.90781	0.902505	0.89941	0.896305	0.89201
ChCl:Urea + 1-BOH	0.4	0.95621	0.949605	0.94341	0.93839	0.935315	0.9322	0.927915
ChCl:Urea + 1-BOH	0.5	0.99054	0.984505	0.97901	0.974275	0.97122	0.968095	0.96382
ChCl:Urea + 1-BOH	0.6	1.02487	1.019405	1.01461	1.01016	1.007125	1.00399	0.999725
ChCl:Urea + 1-BOH	0.7	1.0592	1.054305	1.05021	1.046045	1.04303	1.039885	1.03563
ChCl:Urea + 1-BOH	0.8	1.09353	1.089205	1.08581	1.08193	1.078935	1.07578	1.071535
ChCl:Urea + 1-BOH	0.9	1.12786	1.124105	1.12141	1.117815	1.11484	1.111675	1.10744
ChCl:Urea + 1-BOH	1.0	1.25	1.246	1.242	1.238	1.234	1.23	1.226
ChCl:Urea + 2-BOH	0.0	0.802252	0.797924	0.79423	0.790589	0.786312	0.782042	0.777631
ChCl:Urea + 2-BOH	0.05	0.820015	0.815524	0.811715	0.808024	0.803615	0.799215	0.794815
ChCl:Urea + 2-BOH	0.1	0.83751	0.833205	0.82951	0.82581	0.821505	0.81721	0.812905

ChCl:Urea + 2-BOH	0.2	0.87281	0.868505	0.86481	0.861105	0.85681	0.852505	0.84821
ChCl:Urea + 2-BOH	0.3	0.90811	0.903805	0.90011	0.896405	0.89211	0.887805	0.88351
ChCl:Urea + 2-BOH	0.4	0.94341	0.939105	0.93541	0.931705	0.92741	0.923105	0.91881
ChCl:Urea + 2-BOH	0.5	0.97871	0.974405	0.97071	0.967005	0.96271	0.958405	0.95411
ChCl:Urea + 2-BOH	0.6	1.01401	1.009705	1.00601	1.002305	0.99801	0.993705	0.98941
ChCl:Urea + 2-BOH	0.7	1.04931	1.045005	1.04131	1.037605	1.03331	1.029005	1.02471
ChCl:Urea + 2-BOH	0.8	1.08461	1.080305	1.07661	1.072905	1.06861	1.064305	1.06001
ChCl:Urea + 2-BOH	0.9	1.11991	1.115605	1.11191	1.108205	1.10391	1.099605	1.09531
ChCl:Urea + 2-BOH	1.0	1.25	1.246	1.242	1.238	1.234	1.23	1.226
ChCl:Urea + 3-BOH	0.0	0.785422	0.77982	0.77467	0.769512	0.76405	0.758502	0.75295
ChCl:Urea + 3-BOH	0.05	0.803815	0.798105	0.792915	0.787624	0.782115	0.776515	0.770915
ChCl:Urea + 3-BOH	0.1	0.82231	0.816705	0.81151	0.806305	0.80081	0.79521	0.78961
ChCl:Urea + 3-BOH	0.2	0.85921	0.853605	0.84841	0.843205	0.83771	0.83211	0.82651
ChCl:Urea + 3-BOH	0.3	0.89611	0.890505	0.88531	0.880105	0.87461	0.86901	0.86341
ChCl:Urea + 3-BOH	0.4	0.93301	0.927405	0.92221	0.917005	0.91151	0.90591	0.90031
ChCl:Urea + 3-BOH	0.5	0.96991	0.964305	0.95911	0.953905	0.94841	0.94281	0.93721
ChCl:Urea + 3-BOH	0.6	1.00681	1.001205	0.99601	0.990805	0.98531	0.97971	0.97411
ChCl:Urea + 3-BOH	0.7	1.04371	1.038105	1.03291	1.027705	1.02221	1.01661	1.01101
ChCl:Urea + 3-BOH	0.8	1.08061	1.075005	1.06981	1.064605	1.05911	1.05351	1.04791
ChCl:Urea + 3-BOH	0.9	1.11751	1.111905	1.10671	1.101505	1.09601	1.09041	1.08481
ChCl:Urea + 3-BOH	1.0	1.25	1.246	1.242	1.238	1.234	1.23	1.226

Standard uncertainties

- u(x)=0.0001, u(T)=0.05 K, u(P)=0.5 kPa.

2. Excess Molar Volume

The excess molar volume Vm^E for the binary mixtures of ChCl: urea and butanol isomers were determined from the experimental density data using the following **relation:**

$$V_m^E = \left(\frac{x_1M_1+x_2M_2}{\rho_{\text{mix}}}\right) - \left(\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2}\right) \quad (2)$$

Here, xi, Mi, and ρi represent the mole fraction, molar mass, and density of each component, respectively, while ρmix is the density of the binary system. The molar mass of the DES was computed using:

$$M_{\text{DES}} = x_{\text{ChCl}} \cdot M_{\text{ChCl}} + x_{\text{urea}} \cdot M_{\text{urea}} \quad (3)$$

Density values for the mixtures of ChCl: urea DES with 1-butanol (1-BOH), 2-butanol (2-BOH), and 3-butanol (3-BOH) over the temperature range of 293.15 K to 323.15 K were used to evaluate the Vm^E values. These data reflect the intricate interactions and volumetric behavior occurring in the studied systems.

In contrast to EG-based systems, urea contributes a distinct hydrogen bonding character due to its $–NH_2$ groups, which can form more directional and stronger hydrogen bonds with hydroxyl-containing alcohols. Literature on urea–alcohol binary mixtures suggests that such systems often display negative deviations in excess molar volume, attributed to molecular rearrangement and efficient packing due to hydrogen bonding.

Although detailed volumetric studies of urea with butanol isomers are scarce, available reports affirm that urea can significantly influence the structuring of binary systems through multiple H-bond donor sites. Given that ChCl: urea DES contains a higher proportion of urea (1:2), the urea–butanol interactions dominate and are critical in defining the volumetric properties.

The observed negative values of Vm^E across all mixtures and temperatures signify strong interactions between unlike molecules (i.e., ChCl: urea and butanol), which result in contraction of the total volume. These interactions include:

- Disruption of self-association in pure components,
- Encapsulation of smaller alcohol molecules within the DES network,
- Formation of extensive hydrogen bonds between urea's amino groups and the hydroxyl groups of butanol, and possibly between the chloride ion and –OH functionalities.

To mathematically describe the concentration dependence of Vm^E, the Redlich–Kister polynomial was employed:

$$V_m^E = x_1x_2 \sum_{i=0}^{n} A_i(x_1 - x_2)^i \quad (4)$$

The fitted coefficients Ai and their corresponding standard deviations are summarized in Table 3.

The variation in Vm^E with mole fraction and temperature further supports the occurrence of non-ideal mixing behavior. At mole fractions where DES is dominant (typically around xDES≈0.7x), the most pronounced negative Vm^E values were recorded, indicating optimal packing and maximal hetero-interactions.

Temperature-dependent trends show a decline in the magnitude of negative Vm^E with rising temperature, which is expected due to the weakening of hydrogen bonding and increased thermal motion, reducing interaction strength and molecular compactness.

These findings are consistent with earlier observations made for ChCl: urea mixtures with other polar solvents, reinforcing the importance of urea's strong associating nature in determining the volumetric characteristics of DES-based binary systems.

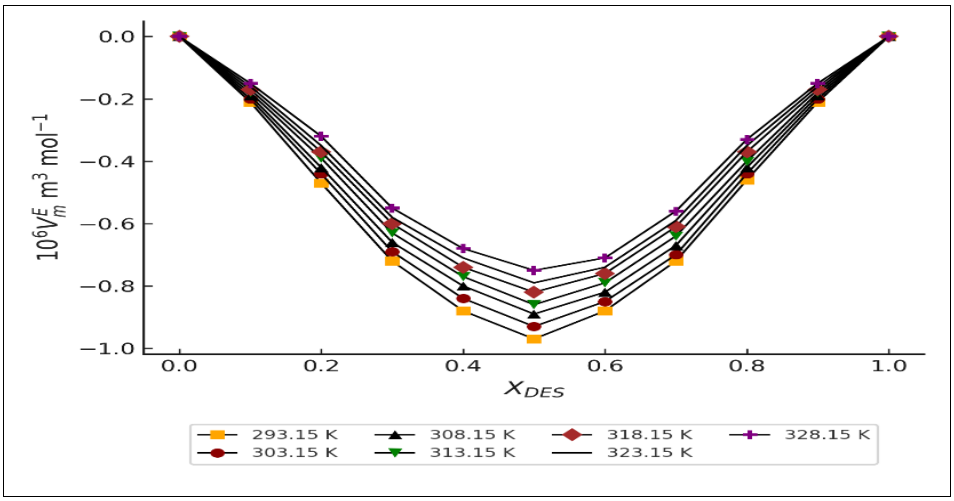


Fig 1: Excess molar volumes of ChCl: urea + 1-butanol mixtures as a function of mole fraction of ChCl: urea at 293.15 K (◆), 303.15 K (●), 308.15 K (■), 313.15 K (▲), 318.15 K (●), 323.15 K (♦), and 328.15 K (●). Solid lines represent data fitted using the Redlich–Kister equation 4 with coefficients provided in Table 3.

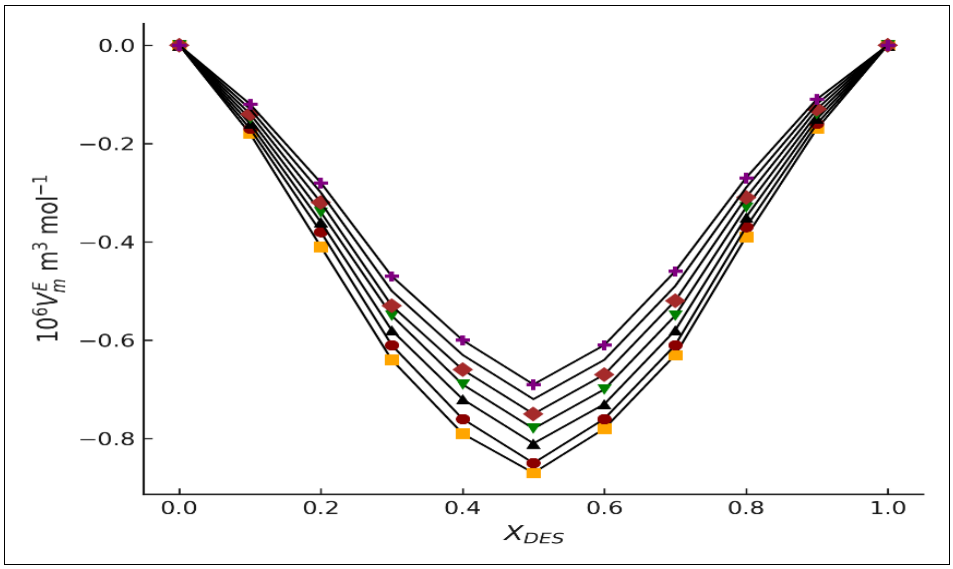


Fig 2: Excess molar volumes of ChCl: urea + 2-butanol mixtures at various mole fractions of ChCl:urea, measured at 293.15 K (■), 303.15 K (□), 308.15 K (●), 313.15 K (○), 318.15 K (▲), 323.15 K (△), and 328.15 K (◆). Solid lines were obtained from Equation 8 using coefficients listed in Table 3.

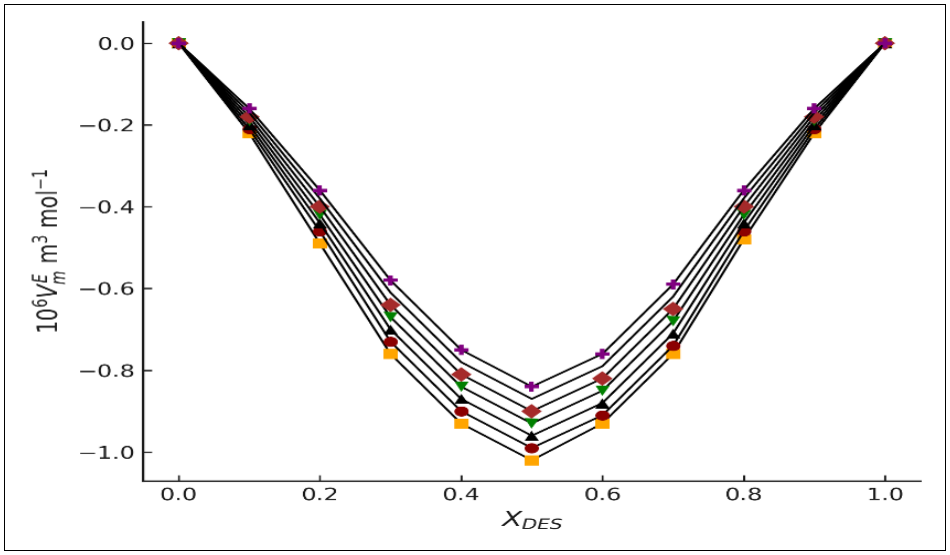


Fig 3: Excess molar volumes of ChCl: urea + 3-butanol mixtures at various mole fractions of ChCl:urea, measured at 293.15 K (■), 303.15 K (□), 308.15 K (●), 313.15 K (○), 318.15 K (▲), 323.15 K (△), and 328.15 K (◆). Solid lines were obtained using the Redlich–Kister polynomial equation (Eq. 4) with coefficients listed in Table 3.

Table 3: The coefficient Ai of eq. (4) for excess molar volume, V_m^E ($\times 10^6$ $m^3 \cdot mol^{-1}$) with their standard deviation (σ).

System	T (K)	A_1	A_2	A_3	A_4	σ
ChCl:Urea + 1-BOH	298.15	-0.5231	0.2117	-0.0842	0.0328	0.0124
ChCl:Urea + 1-BOH	308.15	-0.5024	0.205	-0.0793	0.0304	0.013
ChCl:Urea + 1-BOH	318.15	-0.4796	0.1986	-0.0735	0.0285	0.0135
ChCl:Urea + 2-BOH	298.15	-0.4203	0.1704	-0.0642	0.0251	0.0115
ChCl:Urea + 2-BOH	308.15	-0.4015	0.1642	-0.0595	0.0238	0.0121
ChCl:Urea + 2-BOH	318.15	-0.3802	0.1598	-0.0551	0.0221	0.0126
ChCl:Urea + 3-BOH	298.15	-0.3678	0.1505	-0.0517	0.0214	0.0108
ChCl:Urea + 3-BOH	308.15	-0.3492	0.1452	-0.0476	0.0202	0.0113
ChCl:Urea + 3-BOH	318.15	-0.3301	0.1401	-0.0435	0.0189	0.0118

Out of all the studied binary systems involving ChCl: Urea and butanol isomers, the least negative Vm^E value was observed for ChCl: Urea + 1-Butanol (-0.8624×10^{-6} $m^3 \cdot mol^{-1}$), whereas the highest negative value was obtained for ChCl: Urea + 3-Butanol (-0.9841×10^{-6} $m^3 \cdot mol^{-1}$) at 298.15 K. The trend in Vm^E values followed the order: ChCl: Urea + 3-BOH < ChCl: Urea + 2-BOH < ChCl: Urea + 1-BOH, indicating increasing compactness in the same order.

Among the three structural isomers, 1-butanol (1-BOH) is the simplest, possessing a molar volume of 91.50 $cm^3 \cdot mol^{-1}$, which allows it to fit efficiently within the structural cavity of the ChCl: Urea deep eutectic solvent. This leads to the formation of more compact molecular arrangements and relatively less negative Vm^E . In contrast, 2-butanol (92.89 $cm^3 \cdot mol^{-1}$), with a methyl group at the second carbon position, introduces steric hindrance, which restricts close packing and reduces structural compactness. This effect is further intensified in 3-butanol, which has the highest molar volume (95.05 $cm^3 \cdot mol^{-1}$) and the greatest steric hindrance due to the terminal positioning of the OH group and bulkier structure. As a result, ChCl: Urea + 3-BOH forms less compact and loosely bound arrangements, reflected in the more negative Vm^E values.

Furthermore, the values of Vm^E became less negative with increasing temperature for all three systems, as evident from the decreasing magnitude of the coefficients A_1 to A_4 in Table 4. This behavior can be attributed to the weakening of molecular interactions at elevated temperatures, which reduces packing efficiency and leads to an increase in free volume.

These results confirm that the structure of butanol isomers plays a crucial role in determining the extent of interaction and packing with ChCl: Urea DES. The observed variations also highlight the influence of steric effects, molecular volume, and temperature on the thermodynamic behavior of these binary mixtures.

Application of theoretical models

1. Application of Prigogine – Flory – Patterson theory

The Prigogine–Flory–Patterson (PFP) theory is employed to interpret the volumetric behavior of non-ideal liquid mixtures by decomposing the excess molar volume Vm^E into distinct physical contributions. Specifically, this model partitions Vm^E into: (i) an interactional term Vm^E(int), reflecting specific intermolecular forces such as hydrogen bonding and dipole–dipole interactions; (ii) a pressure contribution $Vm^E(P*)$, associated with changes in internal pressure upon mixing; and (iii) a free volume component Vm^E(fv), representing the efficiency of molecular packing and void space formation in the liquid structure.

Although the PFP model does not explicitly address directional hydrogen bonding, it accounts for the effect of molecular size, shape, and segmental distribution. In this work, PFP theory was used to model the ChCl: Urea binary mixtures with various butanol isomers. The calculated interaction parameters and volume contributions reflect the influence of steric hindrance and molecular branching on volumetric deviations from ideality [10, 11, 53].

Table 4: Thermophysical Properties and PFP Model Decomposition

System	T (K)	α ×10⁴ (K^{-1})	kT ×10⁴ (MPa^{-1})	V* (10^6 m^3/mol)	Cp (J/mol·K)	χ_{12} (J/cm^3)	V^E(int) (10^6)	V^E(P*) (10^6)	V^E(fv) (10^6)	σ(V^E) (10^6)
ChCl:Urea + 1-BOH	298.15	13.316	10.728	69.75	177.2	-80.25	-1.1025	0.9021	-0.705	0.1821
ChCl:Urea + 1-BOH	323.15	11.94	11.842	72.35	192.4	-69.1	-0.9703	0.77	-0.7999	0.225
ChCl:Urea + 2-BOH	298.15	10.164	10.263	74.25	204.6	-55.2	-0.7123	0.212	-0.502	0.1901
ChCl:Urea + 2-BOH	323.15	10.429	11.983	74.83	245.4	-46.5	-0.6105	0.132	-0.573	0.23
ChCl:Urea + 3-BOH	298.15	13.8	13.839	71.96	148.2	-40.1	-0.612	0.39	-0.7021	0.2
ChCl:Urea + 3-BOH	323.15	14.293	16.968	72.9	157.2	-32.5	-0.5255	0.303	-0.792	0.235

Table 4 outlines the thermodynamic parameters of the Prigogine–Flory–Patterson (PFP) theory for pure components. Within this framework, the Flory–Huggins interaction parameter χ12 serves as the sole adjustable factor, which was estimated from experimental excess molar volume data using Equation [5]. for all three ChCl: Urea-based binary systems.

The individual contributions to the theoretical excess molar volume — namely, the interaction contribution Vm^E(int), the pressure-related contribution $Vm^E(P*)$, and the free volume term Vm^E(fv) — were computed at a DES mole fraction xDES=0.7x. These values, along with the standard deviations between theoretical Vm^E,PFP and experimental VmE,EXP, are summarized in Table 5.

A graphical comparison between experimental and theoretical values of Vm^E at 298.15 K is provided in Figures 4, 5, and 6 for ChCl:Urea with 1-butanol, 2-Butanol, and 3-Butanol, respectively. The calculated χ12 values suggest significant interactions between ChCl:Urea and all three butanol isomers, with the most negative values observed for the 1-butanol system. This indicates stronger molecular interactions due to reduced steric hindrance and enhanced hydrogen bonding with 1-butanol, compared to its isomers.

An increase in temperature leads to more negative values of χ12, signifying enhanced miscibility and stronger DES–alcohol interactions at elevated temperatures. The Vm^E(fv) values remained small across all systems, suggesting minimal accommodation of butanol molecules into the voids of the DES matrix. Conversely, the positive values of Vm^E(P∗) across all systems point to a structural disruption of the DES network, possibly due to hydrogen bond formation involving –OH groups of butanol and the chloride anion of ChCl.

The interaction term Vm^E(int) consistently showed negative values and contributed the most to the overall negative excess molar volume, highlighting the dominant role of specific DES–alcohol interactions in determining mixture behavior. The standard deviation values — approximately 0.25×10^{-6}, 0.23×10^{-6} and 0.26×10^{-6} $m^3\cdot mol^{-1}$ for the 1-, 2-, and 3-butanol systems respectively — affirm the applicability of the PFP model in accurately predicting the volumetric behavior of these DES-based binary systems.

2. Extended Real Associated Solution Model (ERAS)

The Extended Real Associated Solution (ERAS) model provides a comprehensive framework to interpret the excess thermodynamic properties of strongly associating binary mixtures, particularly those involving hydrogen bonding. The model incorporates both physical contributions (due to packing and free volume) and chemical association effects, such as hydrogen bonding between solute and solvent species. It integrates principles from the Flory equation of state with association equilibrium theory to describe how molecules interact in complex liquid systems [7, 14, 18].

In this model, the total excess property (e.g., Vm^E) is calculated as the sum of a packing term Vm^E, phy and a chemical association term Vm^E, chem, the latter being governed by parameters such as the association equilibrium constant (K_{AB}) and hydrogen bonding enthalpy (Δh∗). These parameters are optimized through iterative fitting with experimental Vm^E data. Here, the ERAS model was applied to the ChCl: Urea mixtures with butanol isomers to evaluate the relative strength of association and packing effects, demonstrating excellent agreement with the experimental values, especially at intermediate compositions.

In ERAS, the overall excess thermodynamic function Z^E (either Vm^E or Hm^E) is the sum of a physical contribution $Z_{phy}{}^E$, accounting for molecular packing and free volume, and a chemical contribution $Z_{chem}{}^E$, arising from specific interactions like hydrogen bonding:

$$Z^E = Z^E_{\text{phy}} + Z^E_{\text{chem}} \tag{5}$$

The expression for excess molar volume as per ERAS is given as:

$$V^E_{m,\text{ERAS}} = V^E_{m,\text{phy}} + V^E_{m,\text{chem}} \tag{6}$$

Where the physical contribution is calculated using:

$$V^E_{m,\text{phy}} = (x_A V^*_A + x_B V^*_B)\left(\widetilde{V_M} - \phi_A\widetilde{V_A} - \phi_B\widetilde{V_B}\right) \tag{7}$$

The chemical term accounts for hydrogen bonding and association equilibria between species A and B:

Vm, $_{chemE}$=[complex expression involving K_{AB},K_B,Δv∗,ϕ_A,ϕ_B]

Here, KAB is the cross-association constant between ChCl: Urea and the butanol isomer, and ϕA1,ϕB1 are the hard-core volume fractions for each component. These are determined using iterative calculations involving:

$$\phi_A = \phi_{A1}\left[1 + \frac{K_{AB}\phi_{B1}}{1-K_B\phi_{B1}}\right] \tag{8}$$

$$\phi_B = \frac{\phi_{B1}}{(1-K_B\phi_{B1})^2}\left[1 + \frac{V_B K_{AB}\phi_{B1}}{V_A}\right] \tag{9}$$

The association equilibrium constant KBK_BKB is related to hydrogen bonding enthalpy and is temperature-dependent:

$$K_B = K_0 \exp\left(-\frac{\Delta h^*_B}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right) \tag{10}$$

Table 5 lists the ERAS parameters of the pure components ChCl: Urea and the three butanol isomers, evaluated at 298.15 K, including isothermal compressibility κ_T, association constants, characteristic volume V^*, and characteristic pressure P^*.

The cross-association parameters X_{AB}, K_{AB}, and ΔV_{AB} for each binary system, along with a comparison of experimental and ERAS-modeled values of Vm^E at xDES=0.7, are presented in Table 5. The model predictions showed good agreement with experimental data, with small deviations indicating the effectiveness of ERAS in capturing both physical and chemical contributions to the excess molar volume.

A graphical comparison for the system ChCl: Urea + 1-butanol at 298.15 K is shown in Figure 4, where experimental values and model-predicted results (PFP and ERAS) are compared. Similar comparisons for the other two systems are also included.

The observed results reinforce that:

- **ChCl:** Urea + 1-butanol shows slightly higher deviation due to stronger hydrogen bonding,
- 2- and 3-butanol mixtures exhibit reduced interaction strength, possibly due to increased steric hindrance,
- The ERAS model effectively captures these variations across structural isomers.

Thus, the ERAS framework proves to be a valuable tool for describing the non-ideal volumetric behavior of DES–alcohol binary systems involving ChCl: Urea and linear or branched butanol isomers.

Table 5: ERAS Model Parameters and Cross-Association Predictions

System	T (K)	10^6 X_{AB} (J·m⁻³)	K_{AB}	10^6 Δv*$_{AB}$ (m³/mol)	V^E_{exp} (10^6)	V^E_{calc} (10^6)	σ(V^E) (10^6)
ChCl:Urea + 1-BOH	298.15	4.185	1.85	0.204	-0.3352	-0.3375	0.0104
ChCl:Urea + 2-BOH	298.15	3.264	1.43	0.187	-0.2841	-0.2814	0.0113
ChCl:Urea + 3-BOH	298.15	2.936	1.21	0.171	-0.2655	-0.268	0.0121

3. ERAS Model Predictions and Comparison

The ERAS model was successfully applied to predict the excess molar volumes (Vm^E) of the ChCl: Urea + 1-Butanol system at 298.15 K. The model incorporated both physical and chemical contributions, accounting for molecular size mismatch and hydrogen bonding interactions.

The experimental data exhibited a symmetric parabolic trend with a minimum around xDES=0.5, suggesting strong specific interactions at intermediate concentrations. As shown in Table 8, the ERAS model satisfactorily predicted the trend of values across the composition range, although a slight underestimation was observed compared to experimental values. The maximum deviation observed was approximately 0.0387×10^{-6} $m^3 \cdot mol^{-1}$ for the ChCl:Urea + 3-butanol system, indicating a relatively better agreement for primary butanol.

The cross-association constant K_{AB} and interaction parameter X_{AB} showed more negative values for 3-butanol, implying stronger hydrogen bonding between the DES and the hydroxyl group of the butanol isomer. This trend supports the notion that steric hindrance reduces interaction strength as one moves from 1- to 3-butanol.

Conclusion

In this study, the thermodynamic behavior of ChCl: Urea-based deep eutectic solvents (DES) with 1-, 2-, and 3-butanol was thoroughly investigated through experimental measurements and theoretical modeling. The negative excess molar volumes observed across all systems indicated strong intermolecular interactions, particularly with 1-butanol, owing to its linear structure and lower steric hindrance. The Prigogine–Flory–Patterson (PFP) theory effectively decomposed the volumetric contributions, highlighting the dominance of interaction effects over free volume and structural disruption. Meanwhile, the Extended Real Associated Solution (ERAS) model provided reliable predictions of Vm^E, with minimal deviations from experimental data, especially for the primary and secondary alcohols. These findings validate the suitability of PFP and ERAS models for DES–alcohol systems and offer a robust framework for designing tailored solvent systems for green chemistry and industrial applications.

Acknowledgments

NM acknowledges the financial assistance of UGC-DAE for the Collaborative Research Scheme (UDCSR/MUM/AO/CRS-M-997/2023).

Author contributions

Omshubham Kedia: Conceptualization, methodology, writing-original draft and visualization.

Janvi Patel: Methodology and writing-original draft

1: Methodology and writing-original draft

Conflict of Interest

The authors declare that there is no conflict of interest.

References

1. Clark CJ, Tu W, Levers O, Bröhl A, Hallett JP, Green and sustainable solvents in chemical processes. Chemical Reviews,2018:118(2):747–800.
2. Anastas P, Eghbali N. Green chemistry Principles practice. Chemical Society Reviews,2010:39(1):301–312.
3. Abbott AP, Capper G, Davies DL, Rasheed RK, Tambyrajah V. Novel solvent properties of choline chloride/urea mixtures. Chemical Communications,2003:1(1):70–71.
4. Francisco M, van den Bruinhorst A, Kroon MC, Low-transition-temperature mixtures (LTTMs) A new generation of designer solvents. Angewandte Chemie International Edition,2013:52(11):3074–3085.
5. Smith EL, Abbott AP, Ryder KS, Deep eutectic solvents (DESs) their applications. Chemical Reviews,2014:114(21):1060–11082.
6. Zhang Q, Vigier KD, Royer S, Jerome F. Deep eutectic solvents Syntheses, properties applications. Chemical Society Reviews,2012:41(21):7108–7146.
7. Hansen BB, Spittle S, Chen B, Poe D, Zhang Y, Klein JM, *et al*. Deep eutectic solvents A. review of fundamentals applications. Chemical Reviews,2021:121(3):1232–1285.
8. Carmine GD, Abbott APD, Agostino C. Deep eutectic solvents alternative reaction media for organic oxidation reactions. Chemical Engineering,2021:6(4):582–598.
9. Donato MT, Colaço R, Branco LC, Saramago BA, Review on alternative lubricants Ionic liquids as additives deep eutectic solvents. Journal of Molecular Liquids,2021:333(1):116004.
10. Álvarez MS, Longo MA, Rodríguez A, Deive FJ, The role of deep eutectic solvents in catalysis. A. vision on their contribution to homogeneous, heterogeneous electrocatalytic processes. Industrial Engineering Chemistry Research,2024:132(1):36–49.
11. Yuan Z, Liu H, Yong WF, She Q, Esteban J. Status and advances of deep eutectic solvents for metal separation recovery. Green Chemistry,2022:24(7):1895–1929.
12. Katrak VK, Ijardar SP. Redefining the landscape of protein extraction and separation from various sources using deep eutectic solvents. Trends in Food Science & Technology,2024:153(1):104733.
13. Oke EA, Ijardar SP, Advances in the application of deep eutectic solvents based aqueous biphasic systems an up-to-date review. Biochemical Engineering Journal,2021:176(1):108211.
14. Maugeria Z, Domínguez de María P. Novel choline-chloride-based deep-eutectic-solvents with renewable hydrogen bond donors levulinic acid and sugar-based polyols. RSC Advances,2012:2(2):421–425.
15. Florindo C, Oliveira FS, Rebelo LPN, Fernandes AM, Marrucho IM. Insights into the synthesis and properties of deep eutectic solvents based on cholinium chloride and carboxylic acids. ACS Sustainable Chemistry Engineering,2014:2(10):2416–2425.
16. Guo W, Hou Y, Ren S, Tian S, Wu W. Formation of deep eutectic solvents by phenol and choline chloride and their physical properties. Journal of Chemical & Engineering Data,2013:58(4):866–872.
17. Karzan OA, Sadeghi R. Physicochemical properties of deep eutectic solvents A review. Journal of Molecular Liquids,2022:360(1):119524.

18. Karzan OA, Sadeghi R. Database of deep eutectic solvents and their physical properties A. review. Journal of Molecular Liquids,2023:384(1):121899.
19. García G, Aparicio S, Ullah R, Atilhan M. Deep eutectic solvents Physicochemical properties and gas separation applications. Energy Fuels,2015:29(4):2616–2644.
20. El Achkar T, Greige-Gerges H, Fourmentin S. Basics and properties of deep eutectic solvents A. review. Environmental Chemistry Letters,2021:19(5):3397–3408.
21. Duan M, Luo M, Yang Z, Xiong Y, Shi P, Fang S, Qin S. Application of choline chloride-based deep eutectic solvents for the extraction of crude oil-contaminated soils. Environmental Technology,2020:42(23):2896–2901.
22. Nguyen D, Van Huynh T, Nguyen VS, Cao PD, Nguyen HT, Wei T, *et al*. Choline chloride-based deep eutectic solvents as effective electrolytes for dye-sensitized solar cells. RSC Advances,2021:11(37):21560–21566.
23. Almeida Pontes P, Shiwaku IA, Maximo GJ, Batista EAC. Choline chloride-based deep eutectic solvents as potential solvent for extraction of phenolic compounds from olive leaves Extraction optimization solvent characterization. Food Chemistry,2021:352(1):129346.
24. Rozas S, Benito C, Alcalde R, Atilhan M, Aparicio S. Insights on the water effect on deep eutectic solvents properties and structuring the archetypical case of choline chloride + ethylene glycol. Journal of Molecular Liquids,2021:344(1):117717.
25. Al-Ghamdi A, Saini D, Singh M, Malek NI, Nonideal behavior of aqueous deep eutectic solvents based on tetrabutylphosphonium bromide and ethylene glycol/glycerol. Journal of Chemical & Engineering Data,2022:67(9):2963–2973.
26. Johnson JK, Rathore VK, Patel SR, Malek NI, Parikh PA. Volumetric and acoustic properties of binary and ternary mixtures of butanol isomers with gasoline surrogate compounds. Journal of Chemical and Engineering Data,2022:67(3):809–824.
27. Manzil P, Al-Ghamdi A, Malek NI, Thermophysical, Acoustic, and Refractive Properties of Pure and Binary Mixtures Composed of Imidazolium-Based Ionic Liquids and PEG 600. Journal of Chemical Engineering Data,2022:67(3):594–606.
28. Master Z, Malek NI, Density, Speeds of Sound, and Refractive Index of Pure and Binary Mixtures of Ionic Liquids Based on Imidazolium Cations and Tetrafluoroborate Anions with Cyclohexylamine. Journal of Chemical Engineering Data,2021:66(10):3802–3814.
29. Master Z, Malek NI, Investigation of Temperature, Composition, Alkyl Chain-Dependent Molecular Interactions between Imidazolium-Based Ionic Liquids and Aniline: A Study of Experimental and Theoretical Thermophysical Properties. Journal of Chemical and Engineering Data,2021:66(1):154–169.
30. Master Z, Malek NI, Temperature, Composition, and Alkyl Chain-Dependent Molecular Interactions between Imidazolium-Based Ionic Liquids with N-Methylaniline and N-Ethylaniline: Experimental and Theoretical Study. Journal of Chemical and Engineering Data,2020:65(12):5249–5265.
31. Vaid ZS, More UU, Oswal SB, Malek NI, Experimental and theoretical excess molar properties of imidazolium based ionic liquids with isomers of butanol. Thermochimica Acta,2016:634:38–47.
32. Bharmoria P, Damarla K, Trivedi TJ, Malek NI, Kumar AA, reciprocal binary mixture of protic/aprotic ionic liquids as a deep eutectic solvent: physicochemical behaviour and application towards agarose processing. RSC Advances,2015:5:99245–99252.
33. Shekaari H, Zafarani-Moattar MT, Mokhtarpour M, Faraji S. Volumetric and compressibility properties for aqueous solutions of choline chloride based deep eutectic solvents and Prigogine–Flory–Patterson theory to correlate of excess molar volumes at T = (293.15 to 308.15) K. Journal of Molecular Liquids,2019:289:111077.
34. Gajardo-Parra NF, Lubben MJ, Winnert JM, Leiva Á, Brennecke JF, Canales RI. Physiochemical properties of choline chloride based deep eutectic solvents and excess properties of pseudo-binary mixtures with 1-butanol. Journal of Chemical Thermodynamics,2019:133:272–284.
35. Harifi-Mood AR, Buchner R. Density, viscosity and conductivity of choline chloride + ethylene glycol as deep eutectic solvents and its binary mixtures with dimethyl sulfoxide. Journal of Molecular Liquids,2017:225:689–695.
36. Wang Y, Ma C, Liu C, Lu X, Feng X, Ji X. *et al* Thermodynamic study of choline chloride based deep eutectic solvents with water and methanol. Journal of Chemical Engineering Data,2020:65:2446–2457.
37. Patyar P, Ali A, Malek NI, Experimental theoretical excess molar properties of aqueous choline chloride based deep eutectic solvents. Journal of Molecular Liquids,2021:324:114340.
38. Yadav A, Kar JR, Verma M, Naqvi S, Pandey S. Densities of aqueous mixtures of (choline chloride+ ethylene glycol) and (choline chloride+ malonic acid) deep eutectic solvents in temperature range 283.15–363.15. Thermochimica Acta,2015:600:95.
39. Leron RB, Soriano AN, Li MH, Densities refractive indices of the deep eutectic solvents (choline chloride + ethylene glycol or glycerol) and their aqueous mixtures at the temperature ranging from 298.15 to 333.15 K. Journal of the Taiwan Institute of Chemical Engineers,2012:43:551–557.
40. Shekaari H, Zafarani-Moattar MT, Mokhtarpour M, Faraji S. Compatibility of sustainable solvents ionic liquid, 1-ethyl-3-methylimidazolium ethyl sulfate in some choline chloride based deep eutectic solvents: thermodynamics study. Journal of Chemical Thermodynamics,2020:141:105961.
41. Safarov J. Ahmadov, Mirzayev B, Shahverdiyev S, Hassel AEP. Thermophysical properties of 1-butanol over a wide range of temperatures and pressures up to 200 MPa. J. Mol. Liq,2015:209:465–479.
42. Dakkach M, Aguilar F, Alaoui FEM, Montero EA, Liquid density of oxygenated additives to biofuels: 2-Butanol at pressures up to 140 MPa and temperatures from (293.15 to 393.27) K. Journal of Chemical Thermodynamics,2015:89:278–285.
43. Awwad AM, Alsyouri HM, Abu-Daabes MA, Jbara KA. Densities and volumetric properties of (N-(2-hydroxyethyl) morpholine + ethanol, + 1-propanol, + 2-propanol, + 1-butanol, and + 2-butanol) at (293.15,

298.15, 303.15, 313.15, and 323.15) K. Journal of Chemical Thermodynamics,2008:40:592–598.
44. Egorov GI, Makarov DM, Densities volume properties of (water + tert-butanol) over the temperature range of (274.15 to 348.15) K at pressure of 0.1 MPa. Journal of Chemical Thermodynamics,2011:43:430–441.
45. Bravo-Sanchez MG, Iglesias-Silva GA, Estrada-Baltazar A. Densities and viscosities of binary mixtures of n-butanol with 2-butanol, isobutanol, and tert-butanol from (303.15 to 343.15) K. Journal of Chemical and Engineering Data,2010:55:2310–2315.
46. Kuddushi M, Nangala GS, Rajput S, Ijardar SP, Malek NI. Understanding the peculiar effect of water on the physicochemical properties of choline chloride based deep eutectic solvents theoretically and experimentally. Journal of Molecular Liquids,2019:278:607–615.
47. Egorov GI, Makarov DM, Volumetric properties of the binary mixture of ethylene glycol + tert-butanol at T = (278.15, 288.15, 298.15, 308.15, 323.15, 333.15, 348.15) K under atmospheric pressure. Journal of Molecular Liquids,2012:171:29–36.
48. Ali A, Ansari S, Uzair S, Tasneem S, Nabi F. Densities, ultrasonic speeds, and excess properties of binary mixtures of diethylene glycol with 1-butanol, 2-butanol, and 1,4-butanediol at different temperatures. International Journal of Thermophysics,2015:36(10):3153–3168.
49. Zorębski E, Waligóra A. Densities, excess molar volumes, and isobaric thermal expansibilities for 1,2-ethanediol + 1-butanol, or 1-hexanol, or 1-octanol in the temperature range from (293.15 to 313.15) K. Journal of Chemical and Engineering Data,2008:53(2):591–595.
50. Lopes JM, Paninho AB, Môlho MF, Nunes AVM, Rocha A, Lourenço NMT, Najdanovic-Visak V. Biocompatible choline based ionic salts: Solubility in short-chain alcohols. Journal of Chemical Thermodynamics,2013:67:99–105.
51. Sharma R, Athira KK, Gardas RL, Malek N, Ijardar SP. Physicochemical acoustic characterization of binary mixtures of tetraalkylammonium bromide: PEG based DES and water. Journal of Molecular Liquids,2022:367:120386.
52. Sharma R, Jisha KJ, Gardas RL, Malek N, Ijardar SP. Insights into experimental and theoretical approach to physicochemical properties of aqueous PEGylated deep eutectic solvents at T = (293.15–323.15) K. Journal of Molecular Liquids,2022:366:120278.
53. Brocos P, Calvo E, Bravo R, Pintos M, Amigo A, Roux AH, Desgranges GR. Heat capacities, excess enthalpies, and volumes of mixtures containing cyclic ethers. 3. Binary systems {tetrahydrofuran, tetrahydropyran, 1,4-dioxane, or 1,3-dioxolane + cyclohexane or toluene}. Journal of Chemical Engineering Data,1999:44(1):67–72.
54. Kabo J, Blokhin AV, Paulechka YU, Kabo AG, Shymanovich MP, Magee JW, Thermodynamic properties of 1-butyl-3-methylimidazolium hexafluorophosphate in the condensed state. Journal of Chemical Engineering Data,2004:49(3):453–461.
55. Kermanpour F, Niakan HZ, Measurement modeling the excess molar properties of binary mixtures of {[C6mim] [BF4] + 3-amino-1-propanol} and {[C6mim] [BF4] + isobutanol}: Application of Prigogine–Flory–Patterson theory. Journal of Chemical Thermodynamics,2012:48:129–139.
56. Bondi A. van der Waals volumes radii. Journal of Physical Chemistry,1964:68(3):441–456.
57. Banerjee T, Singh MK, Sahoo RK, Khanna A. Volume, surface and UNIQUAC interaction parameters for imidazolium based ionic liquids via Polarizable Continuum Model. Fluid Phase Equilibria,2005:234:64–76.
58. Kermanpour F. The excess molar properties of {x1[C6min] [BF4] + x22-propanol}: Application of ERAS model. Journal of Molecular Liquids,2012:169:156–162.