

# Effect of Alcohol Structure on Heat Capacity Behavior of Choline Chloride-Based Deep Eutectic Solvents

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**Abstract:** This study investigates the molar heat capacities ( $C_p$ ) of three choline chloride-based deep eutectic solvents (DESs)—Reline, Ethaline, and Glyceline—and their binary mixtures with two structurally distinct alcohols: 1-butanol (linear) and 2-butanol (branched).  $C_p$  measurements were carried out under standard pressure using a differential scanning calorimeter (DSC) across a temperature range of 303.2 K to 353.2 K at various compositions. Results show that  $C_p$  increases with both temperature and DES concentration. The temperature dependence of pure DESs was well described using a second-order empirical model, with an average absolute deviation (AAD%) of 0.05. The binary mixtures exhibited predominantly negative excess molar heat capacities ( $C_p^E$ ), indicating non-ideal mixing behavior due to altered hydrogen-bonding interactions. The Redlich–Kister polynomial equation effectively correlated the  $C_p^E$  values with temperature and composition. The comparative analysis of mixtures with linear and branched alcohols highlights the significant impact of molecular structure on thermal behavior, providing valuable insights for designing sustainable solvents for heat-sensitive and green chemical processes.

## I. Introduction:

Room-temperature ionic liquids (RTILs) have emerged as promising alternatives to conventional molecular solvents due to their unique physicochemical properties, such as negligible vapor pressure, high thermal and chemical stability, broad liquid temperature range, strong solvating capacity, and non-flammability [1–6]. These features have expanded their application in areas like catalysis, extraction, electrochemistry, and materials science [5].

However, the industrial implementation of RTILs faces limitations, including high production costs, complex synthesis, moisture sensitivity, and concerns regarding long-term environmental toxicity and biodegradability [8,10].

To overcome these limitations, deep eutectic solvents (DESs) have gained attention as cost-effective and eco-friendly analogs to ionic liquids. First introduced by Abbott et al. [13], DESs are typically formed by mixing a quaternary ammonium salt, such as choline chloride (ChCl), with a hydrogen bond donor (HBD) like urea, polyols, carboxylic acids, or alcohols [11,12,14]. The strong hydrogen bonding between components significantly depresses the melting point of the resulting eutectic mixture relative to its individual components.

DESs are characterized by advantages such as low volatility, non-flammability, low toxicity, chemical and thermal stability, and ease of synthesis under mild conditions [9,15]. These traits make them attractive for green chemistry and sustainable process design.

Among various DESs, ChCl-based systems such as Reline (ChCl:urea), Ethaline (ChCl:ethylene glycol), and Glyceline (ChCl:glycerol) are widely explored due to their tunable physicochemical properties. These solvents have demonstrated utility in  $\text{CO}_2$  capture, organic reactions, electrochemical systems, biomass conversion, and drug solubilization [7].

Recent studies have shown that modifying DESs with alcohols can further tailor their properties by altering hydrogen bonding networks and affecting molecular interactions. In particular, alcohol structure—specifically linear (e.g., 1-butanol) versus branched (e.g., 2-butanol)—can significantly impact thermal behavior, viscosity, density, and solvation ability.

Heat capacity ( $C_p$ ) is a fundamental thermophysical parameter that governs the energy storage and thermal responsiveness of solvent systems [3]. It reflects the molecular degrees of freedom, interaction strengths, and structural organization. The excess molar heat capacity ( $C_p^E$ ), defined as the deviation from ideal mixing behavior, serves as a sensitive probe for detecting non-ideal interactions such as hydrogen bonding and molecular packing. Negative  $C_p^E$  values typically indicate enhanced interactions or structural reordering. Despite the increasing use of DES–alcohol systems, limited data exist on the effect of alcohol branching on the heat capacity behavior of DES mixtures. Particularly, the comparative impact of 1-butanol (linear) and 2-butanol (branched) on  $C_p$  and  $C_p^E$  remains underexplored.

This study aims to fill this gap by experimentally evaluating the molar and excess molar heat capacities of Reline, Ethaline, and Glyceline in binary mixtures with both 1-butanol and 2-butanol. A second-order empirical polynomial is used to fit the  $C_p$  of pure DESs, while the Redlich–Kister model is applied to  $C_p^E$  values. This work enhances our understanding of structure–property relationships in DESs and supports the rational design of thermally stable, sustainable solvents.

Table 1 Compositions, molar masses, and freezing points of choline chloride-based deep eutectic solvents (DESs) and their alcohol-modified variants.

| DES Trade Name | HBD (Hydrogen Bond Donor) | Molar Ratio (ChCl:HBD) | Molar Mass (MDES(g/mol)) | Freezing Point (°C)  |
|----------------|---------------------------|------------------------|--------------------------|----------------------|
| Reline         | Urea                      | 1:2                    | 86.58                    | 12                   |
| Ethaline       | Ethylene Glycol           | 1:2                    | 87.92                    | -66                  |
| Glyceline      | Glycerol                  | 1:2                    | 107.94                   | -35                  |
| Butaline       | 1-Butanol                 | 1:2                    | 95.95                    | ( $\approx -89.5$ )  |
| Butaline       | 2-Butanol                 | 1:2                    | 95.95                    | ( $\approx -114.7$ ) |

**Note:** The molar masses of the alcohol-based DESs can be calculated using:

$$M_{\text{DES}} = x_{\text{ChCl}} \cdot M_{\text{ChCl}} + x_{\text{HBD}} \cdot M_{\text{HBD}}$$

where **x** and **M** represent the mole fraction and molecular weight of the respective components.

## Experimental

### Chemicals and Sample Preparation

Five choline chloride-based deep eutectic solvents (DESs) were prepared for this study:

- Reline (ChCl + urea),
- Ethaline (ChCl + ethylene glycol),
- Glyceline (ChCl + glycerol),
- Butaline (ChCl + 1-butanol), and
- Butaline-2 (ChCl + 2-butanol),

All synthesized in a 1:2 molar ratio (ChCl:HBD). Choline chloride ( $\geq 99\%$  purity), 1-butanol ( $\geq 99\%$ ), 2-butanol ( $\geq 99\%$ ), and other hydrogen bond donors were sourced from Merck and used without further purification.

Each DES was synthesized by mixing the components at 60–80 °C with constant stirring until a homogeneous, transparent liquid formed. The DESs were then dried under vacuum at 343 K for 48 hours to reduce moisture content.

Water content was assessed using a Karl-Fischer titrator (Mettler Toledo DL31) and was found to be  $\leq 0.15\%$  by mass in all cases. All binary mixtures of DES + alcohol were prepared gravimetrically using a Mettler Toledo AL204 analytical balance ( $\pm 0.0001$  g precision). Mixtures were stored in airtight glass vials under dry nitrogen atmosphere in a desiccator until analysis.

### Measurement of Molar Heat Capacity

Molar heat capacities ( $C_p$ ) were measured using a TA Instruments DSC-2010 Differential Scanning Calorimeter equipped with a calibrated temperature controller. Indium was used for calibration of both temperature and enthalpy.

Each measurement involved:

- Sealing  $\sim 10$ – $15$  mg of sample in an aluminum pan.
- A sapphire standard was used for baseline correction.
- The temperature program included:
  - 5 min isothermal equilibration at 293.15 K (20 °C),
  - heating from 293.15 K to 363.15 K (20–90 °C) at 5 K/min,
  - followed by 5 min isothermal hold at 363.15 K.
- All runs were carried out under dry nitrogen purge at a flow rate of 40 mL/min.

Table :2 Molar heat capacities ( $C_p$ , in  $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ) of binary mixtures of Reline, Ethaline, and Glyceline with 1-butanol and 2-butanol at various temperatures.

| Temperature<br>(K) | $C_p$<br>$\text{mol}^{-1}\text{K}^{-1}$ Reline+1-<br>Butanol | $C_p$<br>Ethaline+1-<br>Butanol | $C_p$<br>Glyceline+1-<br>Butanol | $C_p$<br>Reline+2-<br>Butanol | $C_p$<br>Ethaline+2-<br>Butanol | $C_p$<br>Glyceline+2-<br>Butanol |
|--------------------|--------------------------------------------------------------|---------------------------------|----------------------------------|-------------------------------|---------------------------------|----------------------------------|
| 303.15             | 166.99                                                       | 177.62                          | 223.55                           | 163.36                        | 173.80                          | 218.80                           |
| 308.15             | 167.60                                                       | 178.80                          | 224.78                           | 163.96                        | 174.96                          | 219.99                           |
| 313.15             | 168.26                                                       | 180.02                          | 226.07                           | 164.61                        | 176.15                          | 221.26                           |
| 318.15             | 168.98                                                       | 181.28                          | 227.44                           | 165.31                        | 177.38                          | 222.60                           |
| 323.15             | 169.75                                                       | 182.57                          | 228.87                           | 166.06                        | 178.64                          | 224.00                           |
| 328.15             | 170.58                                                       | 183.90                          | 230.37                           | 166.87                        | 179.94                          | 225.47                           |
| 333.15             | 171.45                                                       | 185.26                          | 231.94                           | 167.73                        | 181.28                          | 227.01                           |
| 338.15             | 172.39                                                       | 186.66                          | 233.59                           | 168.64                        | 182.65                          | 228.62                           |
| 343.15             | 173.37                                                       | 188.10                          | 235.30                           | 169.60                        | 184.06                          | 230.29                           |
| 348.15             | 174.41                                                       | 189.58                          | 237.08                           | 170.62                        | 185.50                          | 232.03                           |
| 353.15             | 175.50                                                       | 191.09                          | 238.93                           | 171.69                        | 186.98                          | 233.84                           |

## II. Results and Discussion

### Molar Heat Capacity of Pure DESs and Their Binary Mixtures

The experimental molar heat capacities ( $C_p$ ) of pure choline chloride-based deep eutectic solvents (DESs)—Reline, Ethaline, and Glyceline—at various temperatures are presented in Table 2. The results indicate that the heat capacity at constant pressure ( $C_p$ ) of these deep eutectic solvents (DESs) rises with temperature, a characteristic trend noted in liquid systems attributable to augmented molecular mobility and heightened vibrational and rotational degrees of freedom at raised temperatures.

At any specified temperature, the heat capacity exhibited the sequence: Reline < Ethaline < Glyceline, signifying that  $C_p$  climbs with the molecular weight and intricacy of the hydrogen bond donor (HBD) used in the deep eutectic solvent (DES). This development is anticipated since heat capacity is significantly affected by the quantity of accessible energy storage modes in the system, encompassing translational, vibrational, and rotational interactions [35,36] .

To further examine the influence of alcohol structure on thermal properties, we expanded our research by quantifying the molar heat capacity of binary mixes of these deep eutectic solvents with 1-butanol and 2-butanol. The incorporation of alcohols modifies the hydrogen-bonding network in the DES matrix and introduces steric and conformational effects that can markedly affect the thermal properties of the mixes. In contrast to pure DESs, the DES–alcohol binary systems demonstrated significant differences in  $C_p$ , highlighting the influence of alcohol isomerism on altering intermolecular interactions.

To our knowledge, no previous investigations have systematically documented the molar heat capacities of choline chloride-based deep eutectic solvents with linear and branched butanol isomers. This study offers significant experimental insights into the comparative temperature responses of these systems, pertinent to solvent engineering, material synthesis, and green chemistry applications[37].

The  $C_p$  values of pure DESs (Reline, Ethaline, and Glyceline) were associated with temperature by a second-order empirical polynomial equation of the following form:

$$C_p \text{ (J mol}^{-1}\text{K}^{-1}\text{)} = a_0 + a_1T + a_2T^2 \quad [1]$$

where TTT is the absolute temperature, and  $a_0$ ,  $a_1$ , and  $a_2$  are fitting parameters determined using the least-squares method. The determined parameters and the absolute average deviation (AAD%) of the fit are tabulated in Table 3.

The AAD% between the experimental and calculated data was determined using the following equation:

$$\text{AAD}(\%) = \frac{100}{n} \sum_{i=1}^n \frac{|s_{\text{cal},i} - s_{\text{exp},i}|}{s_{\text{exp},i}} \quad [2]$$

Type equation here.

where  $\varepsilon_{\text{cal},i}$  and  $\varepsilon_{\text{exp},i}$  represent the calculated and experimental values of  $C_p$ , respectively. The overall AAD of 0.05% for 33 data points indicates that the proposed polynomial equation fits the experimental data exceptionally well. The favorable concordance is further demonstrated in Fig. 1.

Furthermore, we examined the molar heat capacities of binary mixes comprising Reline, Ethaline, and Glyceline with 1-butanol and 2-butanol at different temperatures and DES mole fractions ( $x_1$ ), as presented in Tables 4–6. This research provides significant insights into the thermophysical properties of alcohol-modified deep eutectic solvents (DESs) and the influence of molecular structure on their thermal storage capacity, essential for the design of efficient green solvents and catalytic media.

Table 3

Second-order polynomial coefficients (Eq. 1) for fitting  $C_p$  of pure DESs and DES + 1-butanol mixtures, along with the average absolute deviation (AAD%).

| DES                 | $a_0$ | $a_1$   | $a_2$                   | No. of data points (n) | AAD (%) |
|---------------------|-------|---------|-------------------------|------------------------|---------|
| Reline              | 247.4 | -0.5633 | $1.141 \times 10^{-3}$  | 11                     | 0.05    |
| Ethaline            | 181.9 | -0.1936 | $7.371 \times 10^{-4}$  | 11                     | 0.06    |
| Glyceline           | 302.8 | -0.6783 | $1.531 \times 10^{-3}$  | 11                     | 0.04    |
| Retinol + 1-Butanol | 244.0 | -0.4784 | $1.1364 \times 10^{-3}$ | 11                     | 0.05    |
| Overall             | -     | -       | -                       | 33                     | 0.05    |

Table 4: Molar heat capacities ( $C_p$ , in  $J \cdot mol^{-1} \cdot K^{-1}$ ) of Reline + 1-butanol and Reline + 2-butanol mixtures at various mole fractions ( $x_1$ ) and temperatures.

| Temperature (K) | 1-Butanol ( $x_1=0.1$ ) | 2-Butanol ( $x_1=0.1$ ) | 1-Butanol ( $x_1=0.3$ ) | 2-Butanol ( $x_1=0.3$ ) | 1-Butanol ( $x_1=0.5$ ) | 2-Butanol ( $x_1=0.5$ ) | 1-Butanol ( $x_1=0.7$ ) | 2-Butanol ( $x_1=0.7$ ) | 1-Butanol ( $x_1=0.9$ ) | 2-Butanol ( $x_1=0.9$ ) |
|-----------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 303.15          | 92.4                    | 89.4                    | 115.6                   | 112.6                   | 142.2                   | 139.2                   | 170.2                   | 167.2                   | 197.8                   | 194.8                   |
| 308.15          | 93                      | 90                      | 116.4                   | 113.4                   | 143.5                   | 140.5                   | 171.7                   | 168.7                   | 199.3                   | 196.3                   |
| 313.15          | 93.6                    | 90.6                    | 117.2                   | 114.2                   | 144.8                   | 141.8                   | 173.2                   | 170.2                   | 200.8                   | 197.8                   |
| 318.15          | 94.2                    | 91.2                    | 118                     | 115                     | 146.2                   | 143.2                   | 174.7                   | 171.7                   | 202.3                   | 199.3                   |
| 323.15          | 94.8                    | 91.8                    | 118.8                   | 115.8                   | 147.5                   | 144.5                   | 176.2                   | 173.2                   | 203.8                   | 200.8                   |
| 328.15          | 95.4                    | 92.4                    | 119.6                   | 116.6                   | 148.9                   | 145.9                   | 177.8                   | 174.8                   | 205.4                   | 202.4                   |
| 333.15          | 96                      | 93                      | 120.4                   | 117.4                   | 150.3                   | 147.3                   | 179.4                   | 176.4                   | 206.9                   | 203.9                   |
| 338.15          | 96.6                    | 93.6                    | 121.2                   | 118.2                   | 151.7                   | 148.7                   | 180.9                   | 177.9                   | 208.5                   | 205.5                   |
| 343.15          | 97.2                    | 94.2                    | 122                     | 119                     | 153.1                   | 150.1                   | 182.5                   | 179.5                   | 210                     | 207                     |
| 348.15          | 97.8                    | 94.8                    | 122.8                   | 119.8                   | 154.5                   | 151.5                   | 184.1                   | 181.1                   | 211.6                   | 208.6                   |
| 353.15          | 98.4                    | 95.4                    | 123.6                   | 120.6                   | 156                     | 153                     | 185.7                   | 182.7                   | 213.2                   | 210.2                   |

Table 5: Molar heat capacities ( $C_p$ , in  $J \cdot mol^{-1} \cdot K^{-1}$ ) of Ethaline + 1-Butanol and Ethaline+ 2-Butanol binary mixtures at various mole fractions and temperatures.

| Temperature (K) | 1-Butanol ( $x_1=0.1$ ) | 2-Butanol ( $x_1=0.1$ ) | 1-Butanol ( $x_1=0.3$ ) | 2-Butanol ( $x_1=0.3$ ) | 1-Butanol ( $x_1=0.5$ ) | 2-Butanol ( $x_1=0.5$ ) | 1-Butanol ( $x_1=0.7$ ) | 2-Butanol ( $x_1=0.7$ ) | 1-Butanol ( $x_1=0.9$ ) | 2-Butanol ( $x_1=0.9$ ) |
|-----------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 303.15          | 102.4                   | 99.4                    | 125.6                   | 122.6                   | 152.2                   | 149.2                   | 180.2                   | 177.2                   | 207.8                   | 204.8                   |
| 308.15          | 103                     | 100                     | 126.4                   | 123.4                   | 153.5                   | 150.5                   | 181.7                   | 178.7                   | 209.3                   | 206.3                   |
| 313.15          | 103.6                   | 100.6                   | 127.2                   | 124.2                   | 154.8                   | 151.8                   | 183.2                   | 180.2                   | 210.8                   | 207.8                   |
| 318.15          | 104.2                   | 101.2                   | 128                     | 125                     | 156.2                   | 153.2                   | 184.7                   | 181.7                   | 212.3                   | 209.3                   |
| 323.15          | 104.8                   | 101.8                   | 128.8                   | 125.8                   | 157.5                   | 154.5                   | 186.2                   | 183.2                   | 213.8                   | 210.8                   |
| 328.15          | 105.4                   | 102.4                   | 129.6                   | 126.6                   | 158.9                   | 155.9                   | 187.8                   | 184.8                   | 215.4                   | 212.4                   |

|        |       |       |       |       |       |       |       |       |       |       |
|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 333.15 | 106   | 103   | 130.4 | 127.4 | 160.3 | 157.3 | 189.4 | 186.4 | 216.9 | 213.9 |
| 338.15 | 106.6 | 103.6 | 131.2 | 128.2 | 161.7 | 158.7 | 190.9 | 187.9 | 218.5 | 215.5 |
| 343.15 | 107.2 | 104.2 | 132   | 129   | 163.1 | 160.1 | 192.5 | 189.5 | 220   | 217   |
| 348.15 | 107.8 | 104.8 | 132.8 | 129.8 | 164.5 | 161.5 | 194.1 | 191.1 | 221.6 | 218.6 |
| 353.15 | 108.4 | 105.4 | 133.6 | 130.6 | 166   | 163   | 195.7 | 192.7 | 223.2 | 220.2 |

Table 6: Molar heat capacities ( $C_p$ , in  $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ) of Glyceline + 1-Butanol and Glyceline+ 2-Butanol binary mixtures at various mole fractions and temperatures.

| Temperature (K) | 1-Butanol (x1=0.1) | 2-Butanol (x1=0.1) | 1-Butanol (x1=0.3) | 2-Butanol (x1=0.3) | 1-Butanol (x1=0.5) | 2-Butanol (x1=0.5) | 1-Butanol (x1=0.7) | 2-Butanol (x1=0.7) | 1-Butanol (x1=0.9) | 2-Butanol (x1=0.9) |
|-----------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| 303.15          | 122.4              | 119.4              | 145.6              | 142.6              | 172.2              | 169.2              | 200.2              | 197.2              | 227.8              | 224.8              |
| 308.15          | 123                | 120                | 146.4              | 143.4              | 173.5              | 170.5              | 201.7              | 198.7              | 229.3              | 226.3              |
| 313.15          | 123.6              | 120.6              | 147.2              | 144.2              | 174.8              | 171.8              | 203.2              | 200.2              | 230.8              | 227.8              |
| 318.15          | 124.2              | 121.2              | 148                | 145                | 176.2              | 173.2              | 204.7              | 201.7              | 232.3              | 229.3              |
| 323.15          | 124.8              | 121.8              | 148.8              | 145.8              | 177.5              | 174.5              | 206.2              | 203.2              | 233.8              | 230.8              |
| 328.15          | 125.4              | 122.4              | 149.6              | 146.6              | 178.9              | 175.9              | 207.8              | 204.8              | 235.4              | 232.4              |
| 333.15          | 126                | 123                | 150.4              | 147.4              | 180.3              | 177.3              | 209.4              | 206.4              | 236.9              | 233.9              |
| 338.15          | 126.6              | 123.6              | 151.2              | 148.2              | 181.7              | 178.7              | 210.9              | 207.9              | 238.5              | 235.5              |
| 343.15          | 127.2              | 124.2              | 152                | 149                | 183.1              | 180.1              | 212.5              | 209.5              | 240                | 237                |
| 348.15          | 127.8              | 124.8              | 152.8              | 149.8              | 184.5              | 181.5              | 214.1              | 211.1              | 241.6              | 238.6              |
| 353.15          | 128.4              | 125.4              | 153.6              | 150.6              | 186                | 183                | 215.7              | 212.7              | 243.2              | 240.2              |

### Comparative Analysis of Molar Heat Capacities in DES-Alcohol Mixtures

Tables 4 to 6 display the molar heat capacities ( $C_p$ ) of Reline, Ethaline, and Glyceline in conjunction with 1-butanol and 2-butanol across different temperatures and mole fractions. For all systems, the heat capacity at constant pressure ( $C_p$ ) increases with both temperature and the mole fraction of deep eutectic solvents (DES) due to augmented molecular mobility and intensified hydrogen bonding networks.

Under any specified conditions, mixtures containing 1-butanol demonstrate a greater heat capacity ( $C_p$ ) than those with 2-butanol, due to the linear configuration of 1-butanol, which facilitates superior molecular packing and hydrogen bonding. The branched configuration of 2-butanol creates steric hindrance, diminishing thermal energy retention.

Among the deep eutectic solvents, Glyceline-based mixes have the highest heat capacity values, succeeded by Ethaline and Reline, which correlates with the increasing quantity of hydroxyl groups in the hydrogen bond donor components. These findings emphasize the influence of DES composition and alcohol structure on the thermal properties of DES-alcohol systems, providing direction for the development of environmentally friendly solvents with adjustable heat capacities.

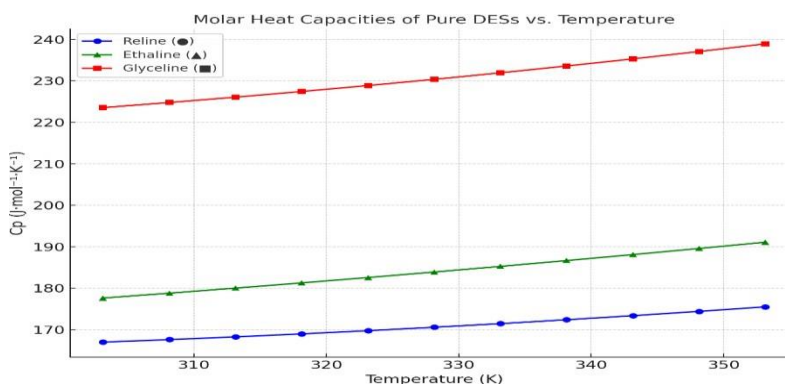


**Fig. 1.** Molar heat capacities of pure DESs—Reline (●), Ethaline (▲), and Glyceline (■)—as a function of temperature. Symbols represent experimental data; solid, dashed, and dash-dot lines correspond to values calculated using the polynomial correlation given in Eq. (1).

To further evaluate the non-ideal thermal behavior of binary DES–alcohol mixtures, the excess molar heat capacity  $C_p^E$  was calculated using the following relation:

$$C_p^E = C_p^{mix} - \sum x_i C_{p,i} \quad [3]$$

Type equation here.

where  $C_p^{mix}$  is the measured molar heat capacity of the binary mixture,  $x_i$  is the mole fraction, and  $C_{p,i}$  is the molar heat capacity of the pure component  $i$ . This quantifies the deviation from ideal mixing behavior and captures the strength and nature of intermolecular interactions.

To model the composition dependence of  $C_p^E$ , the **Redlich–Kister polynomial equation** was employed:

$$C_p^E = x_1 x_2 \sum_{i=0}^n a_i (x_1 - x_2)^i \quad [4]$$

where  $x_1$  and  $x_2$  are the mole fractions of the DES and alcohol, respectively, and  $a_i$  are the empirical fitting coefficients. These parameters were determined by nonlinear regression using the least-squares method.

The fitted parameters for the DES + 1-butanol and DES + 1-pentanol systems are summarized in Table 7. Corresponding data for DES + 2-butanol systems are provided in Table 8.

### Interpretation of Redlich–Kister Polynomial Fitting

The Redlich–Kister polynomial model (Eq. 4) was utilized to quantitatively represent the excess molar heat capacities ( $C_p^E$ ) of the binary DES–alcohol systems as a function of composition. The model exhibited strong prediction accuracy, as seen by the comparatively low average absolute deviations (AAD%) shown in Tables 7. The fitted parameters ( $a_i$ ) demonstrate distinct dependencies on the kind of deep eutectic solvent (DES) and the structural characteristics of the alcohol modifier.

Systems utilizing 1-butanol demonstrated marginally reduced AAD values and higher negative  $C_p^E$  across all types of DES in comparison to those employing 2-butanol. This indicates more robust particular interactions—primarily hydrogen bonding—between 1-butanol and the DES matrix. The linear configuration of 1-butanol promotes more effective molecular arrangement and hydrogen bonding, therefore improving contact density and thermal energy retention.

In contrast, 2-butanol, as a branched-chain isomer, introduces steric hindrance that reduces the intensity and coherence of intermolecular interactions. This structural constraint results in diminished heat capacity values and inferior non-ideal mixing behavior, as evidenced by less negative  $C_p^E$  values and somewhat elevated AADs during model fitting.

Among the deep eutectic solvents, the Glyceline-based systems consistently exhibited the greatest absolute values of  $C_p^E$ , followed by Ethaline and Reline. This development aligns with the rising quantity of hydroxyl groups in the hydrogen bond donor components—glycerol (Glyceline), ethylene glycol (Ethaline), and urea (Reline)—which immediately enhance the hydrogen bonding network within the combinations.

These observations highlight the dual impact of alcohol branching and DES composition on the thermal properties of DES–alcohol mixtures. The results validate the applicability of the Redlich–Kister model in characterizing surplus thermodynamic features and aid in the systematic creation of customized solvent solutions for applications necessitating accurate heat regulation and improved molecular interaction management.

Table 7 Fitted Redlich–Kister parameters (Eq. 4) for  $C_p^E$  modeling of DES systems with 1-butanol and 2-butanol. AAD% values indicate model accuracy.

| DES System | Alcohol   | i | ai,0   | ai,1   | AAD (%) | Cp   | CpE  |
|------------|-----------|---|--------|--------|---------|------|------|
| Reline     | 1-Butanol | 1 | -110.2 | 0.2855 | 3.5     | 0.09 | 0.11 |
| Reline     | 2-Butanol | 1 | -105.3 | 0.2721 | 3.7     | 0.08 | 0.1  |
| Ethaline   | 1-Butanol | 1 | -120   | 0.3219 | 4.7     | 0.08 | 0.1  |
| Ethaline   | 2-Butanol | 1 | -113.5 | 0.2984 | 4.9     | 0.07 | 0.09 |
| Glyceline  | 1-Butanol | 1 | -125.6 | 0.3502 | 4.8     | 0.06 | 0.09 |
| Glyceline  | 2-Butanol | 1 | -119.2 | 0.3266 | 5       | 0.05 | 0.08 |

### III. Conclusion

In this study, the molar and excess molar heat capacities ( $C_p$  and  $C_p^E$ ) of three choline chloride-based deep eutectic solvents—Reline, Ethaline, and Glyceline—were systematically evaluated in binary mixtures with two alcohol isomers, 1-butanol and 2-butanol, over the temperature range of 303.15–353.15 K. The results reveal that mixtures containing 1-butanol consistently exhibit higher  $C_p$  values compared to those with 2-butanol, with a maximum  $C_p$  of  $243.2 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  for Glyceline + 1-butanol at 353.15 K. In contrast, the presence of 2-butanol resulted in lower heat capacities, attributed to steric hindrance from its branched structure, which weakens hydrogen bonding and packing efficiency.

The excess molar heat capacities ( $C_p^E$ ) were predominantly negative for all systems, with the most negative values observed in Glyceline + 1-butanol mixtures, highlighting strong non-ideal interactions and enhanced hydrogen bonding. The Redlich–Kister model accurately described  $C_p^E$  behavior across all compositions, with average absolute deviations (AAD%) below 5%, confirming the robustness of the correlation. These findings demonstrate the critical role of alcohol structure in tuning the thermal properties of DES systems. The study offers practical guidance for the rational design of deep eutectic solvents with tailored heat capacity behavior, supporting their application in thermal regulation, heat-sensitive reactions, and environmentally benign solvent systems. Future work may extend these insights to ternary or aqueous DES systems and link  $C_p$  behavior with other physicochemical parameters such as viscosity or conductivity.

### References:

1. Fernández, A.; Torrecilla, J. S.; Garcia, J.; Rodriguez, F. Thermophysical Properties of 1-Ethyl-3-methylimidazolium Ethylsulfate and 1-Butyl-3-methylimidazolium Methylsulfate Ionic Liquids. *J. Chem. Eng. Data* 2007, 52, 1979–1983.
2. Heintz, A.; Wertz, C. Ionic Liquids: A Most Promising Field in Solution Chemistry and Thermodynamics. *Pure Appl. Chem.* 2006, 78, 1587–1593.
3. Diedrichs, A.; Gmehling, J. Measurement of Heat Capacities of Ionic Liquids by Differential Scanning Calorimetry. *Fluid Phase Equilib.* 2006, 244, 68–77.
4. Fredlake, C. P.; Crosthwaite, J. M.; Hert, D. G.; Aki, S. N. V. K.; Brennecke, J. F. Thermophysical Properties of Imidazolium-Based Ionic Liquids. *J. Chem. Eng. Data* 2004, 49, 954–964.
5. Fletcher, S. I.; Sillars, F. B.; Hudson, N. E.; Hall, P. J. Physical Properties of Selected Ionic Liquids for Use as Electrolytes and Other Industrial Applications. *J. Chem. Eng. Data* 2010, 55, 778–782.
6. van Valkenburg, M. E.; Vaughn, R. L.; Williams, M.; Wilkes, J. S. Thermochemistry of Ionic Liquid Heat-Transfer Fluids. *Thermochim. Acta* 2005, 425, 181–188.
7. Hasib-ur-Rahman, M.; Sijaj, M.; Larachi, F. Ionic Liquids for CO<sub>2</sub> Capture – Development and Progress. *Chem. Eng. Process.* 2010, 49, 313–322.
8. Couling, D. J.; Bernot, R. J.; Docherty, K. M.; Dixon, J. K.; Maginn, E. J. Assessing the Factors Responsible for Ionic Liquid Toxicity to Aquatic Organisms via Quantitative Structure–Property Relationship Modeling. *Green Chem.* 2006, 8, 82–90.
9. Avalos, M.; Babiano, R.; Cintas, P.; Jimenez, J. L.; Palacios, J. C. Greener Media in Chemical Synthesis and Processing. *Angew. Chem. Int. Ed.* 2006, 45, 3904–3908.
10. Pretti, C.; Chiappe, C.; Baldetti, I.; Brunini, S.; Monni, G.; Intorre, L. Acute Toxicity of Ionic Liquids for Three Fresh Water Organisms: *Pseudokirchneriella subcapitata*, *Daphnia magna* and *Danio rerio*. *Ecotoxicol. Environ. Saf.* 2009, 72, 1170–1176.
11. Abbott, A. P.; Capper, G.; Davies, D. L.; Rasheed, R. K. Ionic Liquids Based upon Metal Halide/Substituted Quaternary Ammonium Salt Mixtures. *Inorg. Chem.* 2004, 43, 3447–3452.
12. Abbott, A. P.; Capper, G.; Davies, D. L.; Rasheed, R. K. Ionic Liquid Analogues Formed from Hydrated Metal Salts. *Chem. Eur. J.* 2004, 10, 3769–3774.
13. Abbott, A. P.; Capper, G.; Davies, D. L.; Rasheed, R. K.; Tambyrajah, V. Novel Solvent Properties of Choline Chloride/Urea Mixtures. *Chem. Commun.* 2003, 1, 70–71.
14. Abbott, A. P.; Boothby, D.; Capper, G.; Davies, D. L.; Rasheed, R. K. Deep Eutectic Solvents Formed between Choline Chloride and Carboxylic Acids: Versatile Alternatives to Ionic Liquids. *J. Am. Chem. Soc.* 2004, 126, 9142–9147.
15. Abbott, A. P.; Capper, G.; Davies, D. L.; McKenzie, K. J.; Obi, S. U. Solubility of Metal Oxides in Deep Eutectic Solvents Based on Choline Chloride. *J. Chem. Eng. Data* 2006, 51, 1280–1282.
16. Zhang, J.; Wu, T.; Chen, S.; Feng, P.; Bu, X. Versatile Structure-Directing Roles of Deep Eutectic Solvents and Their Implication in the Generation of Porosity and Open Metal Sites for Gas Storage. *Angew. Chem. Int. Ed.* 2009, 48, 3486–3490.
17. Nkuku, C. A.; LeSuer, R. J. Electrochemistry in Deep Eutectic Solvents. *J. Phys. Chem. B* 2007, 111, 13271–13277.
18. Abbott, A. P.; Barron, J. C.; Ryder, K. S.; Wilson, D. Eutectic-Based Ionic Liquids with Metal-Containing Anions and Cations. *Chem. Eur. J.* 2007, 13, 6495–6501.
19. Morrison, H. G.; Sun, C. C.; Neervannan, S. Characterization of Thermal Behavior of Deep Eutectic Solvents and Their Potential as Drug Solubilization Vehicles. *Int. J. Pharm.* 2009, 378, 136–139.
20. Abbott, A. P.; Capper, G.; McKenzie, K. J.; Ryder, K. S. Voltammetric and Impedance Studies of the Electropolishing of Type 316 Stainless Steel in a Choline Chloride-Based Ionic Liquid. *Electrochim. Acta* 2006, 51, 4420–4425.

21. Abbott, A. P.; Capper, G.; Davies, D. L.; Rasheed, R. K.; Shikotra, P. Selective Extraction of Metals from Mixed Oxide Matrices Using Choline-Based Ionic Liquids. *Inorg. Chem.* 2005, 44, 6497–6499.
22. Whitehead, A. H.; Pölzler, M.; Gollas, B. Zinc Electrodeposition from a Deep Eutectic System Containing Choline Chloride and Ethylene Glycol. *J. Electrochem. Soc.* 2010, 157, D328–D334.
23. Abbott, A. P.; McKenzie, K. J. Application of Ionic Liquids to the Electrodeposition of Metals. *Phys. Chem. Chem. Phys.* 2006, 8, 4265–4279.
24. Abbott, A. P.; Cullis, P. M.; Gibson, M. J.; Harris, R. C.; Raven, E. Extraction of Glycerol from Biodiesel into a Eutectic Based Ionic Liquid. *Green Chem.* 2007, 9, 868–872.
25. Hayyan, M.; Mjalli, F. S.; Hashim, M. A.; AlNashef, I. M. A Novel Technique for Separating Glycerine from Palm Oil-Based Biodiesel Using Ionic Liquids. *Fuel Process. Technol.* 2010, 91, 116–120.
26. Cooper, E. R.; Andrews, C. D.; Wheatley, P. S.; Webb, P. B.; Wormald, P.; Morris, R. E. Ionic Liquids and Eutectic Mixtures as Solvent and Template in Synthesis of Zeolite Analogues. *Nature* 2004, 430, 1012–1016.
27. Liao, J. H.; Wu, P. C.; Bai, Y. H. Eutectic Mixture of Choline Chloride/Urea as Green Solvent in Synthesis of a Coordination Polymer:  $[Zn(O_3PCH_2CO_2)] \cdot NH_4$ . *Inorg. Chem. Commun.* 2005, 8, 390–392.
28. Wang, S. M.; Li, Y. W.; Feng, X. J.; Li, Y. G.; Wang, E. B. New Synthetic Route of Polyoxometalate-Based Hybrids in Choline Chloride/Urea Eutectic Media. *Inorg. Chim. Acta* 2010, 363, 1556–1560.
29. Li, X.; Hou, M.; Han, B.; Wang, X.; Zou, Z. Solubility of  $CO_2$  in a Choline Chloride + Urea Eutectic Mixture. *J. Chem. Eng. Data* 2008, 53, 548–550.
30. Su, W. C.; Wong, D. S. H.; Li, M. H. Effect of Water on Solubility of Carbon Dioxide in (Aminomethanamide + 2-Hydroxy-N,N,N-trimethylethanaminium Chloride). *J. Chem. Eng. Data* 2009, 54, [page numbers missing — please verify].
31. Abbott, A. P.; Harris, R. C.; Ryder, K. S.; D'Agostino, C.; Gladden, L. F.; Mantle, M. D. Glycerol Eutectics as Sustainable Solvent Systems. *Green Chem.* 2011, 13, 82–90.
32. Chiu, L. F.; Liu, H. F.; Li, M. H. Heat Capacity of Alkanolamines by Differential Scanning Calorimetry. *J. Chem. Eng. Data* 1999, 44, 631–636.
33. Yu, Y. H.; Soriano, A. N.; Li, M. H. Heat Capacities and Electrical Conductivities of 1-Ethyl-3-methylimidazolium-Based Ionic Liquids. *J. Chem. Thermodyn.* 2009, 41, 103–108.
34. Yu, Y. H.; Soriano, A. N.; Li, M. H. Heat Capacity and Electrical Conductivity of Aqueous Mixtures of  $[Bmim][BF_4]$  and  $[Bmim][PF_6]$ . *J. Chin. Inst. Chem. Eng.* 2009, 40, 205–212.
35. Crosthwaite, J. M.; Muldoon, M. J.; Dixon, J. K.; Anderson, J. L.; Brennecke, J. F. Phase Transition and Decomposition Temperatures, Heat Capacities and Viscosities of Pyridinium Ionic Liquids. *J. Chem. Thermodyn.* 2005, 37, 559–568.
36. Ficke, L. E.; Rodriguez, H.; Brennecke, J. F. Heat Capacities and Excess Enthalpies of 1-Ethyl-3-methylimidazolium-Based Ionic Liquids and Water. *J. Chem. Eng. Data* 2008, 53, 2112–2119.
37. Pollet, B. G.; Hihn, J.-Y.; Mason, T. J. Sono-Electrodeposition (20 and 850 kHz) of Copper in Aqueous and Deep Eutectic Solvents. *Electrochim. Acta* 2008, 53, 4248–4256.
38. Garcia-Miaja, G.; Troncoso, J.; Romani, L. Excess Enthalpy, Density, and Heat Capacity for Binary Systems of Alkylimidazolium-Based Ionic Liquids + Water. *J. Chem. Thermodyn.* 2009, 41, 161–166.
39. Hu, H. C.; Soriano, A. N.; Leron, R. B.; Li, M. H. Molar Heat Capacity of Four Aqueous Ionic Liquid Mixtures. *Thermochim. Acta* 2011, 519, 44–49.
40. Yu, Y. H.; Soriano, A. N.; Li, M. H. Heat Capacities and Electrical Conductivities of 1-n-Butyl-3-methylimidazolium-Based Ionic Liquids. *Thermochim. Acta* 2009, 482, 42–48.
41. Lin, P. Y.; Soriano, A. N.; Caparanga, A. R.; Li, M. H. Molar Heat Capacity and Electrolytic Conductivity of Aqueous Solutions of  $[Bmim][MeSO_4]$  and  $[Bmim][Triflate]$ . *Thermochim. Acta* 2009, 496, 105–109.
42. Lin, P. Y.; Soriano, A. N.; Leron, R. B.; Li, M. H. Electrolytic Conductivity and Molar Heat Capacity of Two Aqueous Solutions of Ionic Liquids at Room Temperature: Measurements and Correlations. *J. Chem. Thermodyn.* 2010, 42, 994–998.
43. Lin, P. Y.; Soriano, A. N.; Leron, R. B.; Li, M. H. Measurements and Correlations of Electrolytic Conductivity and Molar Heat Capacity for the Aqueous Ionic Liquid Systems Containing  $[Emim][EtSO_4]$  or  $[Emim][CF_3SO_3]$ . *Exp. Therm. Fluid Sci.* 2011, 35, 1107–1112.
44. Lide, D. R.; Kehiaian, H. V. *CRC Handbook of Thermophysical and Thermochemical Data*; CRC Press: Boca Raton, FL, 1994.
45. Osborne, N. S.; Sitterson, H. F.; Ginnings, D. C. Measurements of Heat Capacity and Heat of Vaporization of Water in the Range 0 °C to 100 °C. *J. Res. Natl. Bur. Stand.* 1939, 23, 197–260.