Dual Modulation of the Anion-Driven Thermodynamic Properties of Aqueous Choline Halide-Based Deep Eutectic Solvents

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Abstract

Deep eutectic solvents (DESs) are considered tunable solvents since their specific properties can be achieved based on the choice of components and their relative concentrations in the mixture. In this work, we investigate the influence of the variation in halide ions (F^-, Cl^-, Br^-, I^-) of choline salts used on the thermodynamic and physicochemical properties of choline halide-based DESs. Our findings have shown that the density of choline halide-based DESs decreases nonlinearly with increasing mole fraction of water, following a trend based on the size of the halides, with choline iodide showing the highest density. Temperature-dependent density data reveal that the thermal expansion coefficient decreases slightly with increasing water content, indicating more stable volume behavior at higher mole fraction of water. The excess molar volume (V^E) of the DES mixtures exhibits complex behaviors depending on the choline halide used, with both negative and positive V^E observed across different water mole fractions. These variations are linked to the hydrogen bonding interactions between the DES components and water molecules. In addition, viscosities decrease with increasing water content, suggesting the disruption of hydrogen bonding networks and enhanced mobility of the ions, which contributes to the observed increase in conductivity. Excess molar Gibbs energies, enthalpies, and entropies of activation have been determined.

Keywords: deep eutectic solvent, excess molar volume, water, choline halide, thermodynamic

I. INTRODUCTION

Deep eutectic solvents (DESs) are a class of green solvents formed by combining hydrogen bond donors (HBDs), such as alcohols, and hydrogen bond acceptors (HBAs), such as quaternary ammonium halide salts. The hydrogen bonding interaction between the two components leads to an increase in boiling point and strongly influences all other solvent properties. [1–3] DESs are considered designer solvents since specific properties can be achieved based on the choice of components and their relative concentrations in the mixture. These solvents are also attracting considerable attention in a wide range of applications, which include but not limited to electrochemistry,[4–8] catalysis,[9–12] reaction media,[13–15] and gas absorption.[16–20]

Since the inception of DESs, many HBDs and HBAs have been explored to examine the influence of varying compositions and ratios on their physicochemical properties. Choline chloride has been the most studied HBA in various diol-based DESs.[21] However, only few studies have investigated the effect of different HBD salt anions on the properties of DESs. Martins et al. found that substituting the chloride anion with the larger and less electronegative bromide anion in the hydrogen bond donor (HBD) resulted in a lesser decrease in the eutectic temperature from the melting temperature of the pure DES components. Urea showed strong negative deviations with ChCl but small positive deviations with ChBr, highlighting the crucial role of anion interactions in mixtures, especially in ChCl/urea systems. [22] Shen et al. reported that the increase in size and decrease in electronegativity of halide anions ($Cl^- > Br^- > I^-$) causes the O-H bond length of ethylene glycol HBD to shorten and the $H\cdots X^-$ bond in the $O{-}H\cdots X^-$) structure to elongate, resulting in an increase of the solvated ion size, a decrease in the bulk ionic conductivity, and increase in double layer capacitance. [23] Alfurayj et al. outlined that using choline fluoride instead of choline chloride as HBA in DES ethaline hastens the relaxation dynamics and decreases the polarity of DES.[24] It is also important to note that fluoride anions exist in two distinct

environments: one where they are freely solvated with ethylene glycol, and the other where they are associated with choline.[25] Pandian et al.[26] examined the influence of halide identity and varying molar percentages of choline halide (ChX) salts in choline halide–based deep eutectic solvents (DESs) on their solvation dynamics, phase behavior, polarity, viscosity, and conductivity. They found that the slow dynamics of DESs formed with ChF or ChBr and ethylene glycol (EG) are due to strong hydrogen-bond networks and more rigid structures. In contrast, the slow dynamics of ChBr- and ChI-based DESs are also attributed to the heavier mass of the halide ions. The liquidus temperatures reached a minimum at 4 mol % for ChI, 10 mol % for ChBr, and 20 mol % for ChCl.[26] For ChF, no clear melting point was detected; instead, it transitioned into a supercooled "glassy" liquid state beyond 30 mol %. These findings underscore the halide- and composition-dependent nature of choline halide-based DESs. The underlying behaviors are still being actively investigated.[26]

The stoichiometric addition of water to DESs has also been reported to tune the physicochemical properties of DESs.[27,28] Previously, the effect of water on solvation dynamics in wet ethaline was explored, revealing an enhancement in both solvation dynamics and polarity as the weight percent of added water was increased from 1 wt. % to 28.5 wt. %.[29] We also found that the addition of water not only impacted the conductivity, fluidity, and ionicity,[30] but also enhanced the mass transport and electrokinetics while preserving the large electrochemical stability window offered by DESs. [31]

In this paper, we provide a comprehensive investigation of the influence of varying halide anions (X = F^-, Cl^-, Br^-, I^-) of ammonium salt and co-solvent water addition on the thermodynamic and physicochemical properties of DESs. We found that the density of choline halide-based DESs increases with the size of the halide anion in the choline halide HBA and

decreases nonlinearly with increasing mole fraction of water. The excess molar volume (V^E) of DES mixtures shows complex behavior, with both negative and positive V^E observed depending on the choline halide, linked to hydrogen bonding interactions between DES components and water. Additionally, conductivity increases with water addition until a maximum is reached, due to the increased fluidity and ionicity.

II. EXPERIMENTAL SECTION

Materials. Anhydrous ethylene glycol (EG, ≥ 99.8% purity) and choline chloride (ChCl, ≥ 99.0% purity) were purchased from Sigma – Aldrich. Choline bromide (ChBr, > 98.0% purity) and choline iodide (ChI, > 98.0 purity) were obtained from Tokyo Chemical Industry Co. Ltd. The silver oxide (Ag_2O, ≥ 99.0 purity) and hydrofluoric acid (HF, 49% purity) used for choline fluoride synthesis were obtained from Fisher Scientific. The ultrapure water used in this experiment was purified using a Millipore Milli-Q system to a resistivity of 18.2 MΩ cm.

Synthesis of choline fluoride. Choline fluoride (ChF) was synthesized according to the published procedure.[32] Briefly, the conversion of choline chloride salt to choline hydroxide was achieved by introducing silver oxide to an aqueous choline chloride solution. The resulting solution was neutralized to a pH of 7.0 by adding aqueous hydrofluoric acid solution to produce a choline fluoride solution. Subsequently, water was removed under vacuum at 50 °C for 72 hours.

Preparation of DESs. Ethylene glycol and choline chloride were dried separately using activated 4Å molecular sieves and under vacuum at a temperature of 120 ºC for 72 hours, respectively. To ensure a controlled and inert environment, the preparation of DES samples was performed inside the argon-filled glovebox. The DES samples were prepared by mixing the choline halide (ChX, X=F, Cl, Br, I) salts with ethylene glycol at 1:9 molar ratio in a sealed glass vial. Following the previously reported procedure,[33] the mixtures were heated at 80 ºC for 2 hours

using a sonicator to obtain clear liquid and the resulting mixtures were cooled to room temperature. Pre-determined stoichiometric amounts of water were then added quantitatively to the DES samples to produce a pseudo-binary mixture of DES and water. To ensure consistency, all batches were prepared in triplicate following the same protocol.

The experimental challenge encountered was the hygroscopic nature of the DES samples, meaning water was inherently present in unknown amounts. To address this, the individual components were dried prior to mixing as described in the previous paragraph.

Conductivity measurements. A Pine Research Instrumentation WaveDriver 200 bipotentiostat equipped with a frequency response analyzer and a two-electrode cell with 1.0 cm^{-1} cell constant was utilized to measure the conductivity of the samples through electrochemical impedance spectroscopy. The impedance measurements were performed at the frequency range of 100 kHz to 100 Hz and an amplitude of 10 mV around the open circuit potential to obtain the Nyquist plot. From this plot, the solution resistance was then determined by extrapolating the intersection of the complex impedance data at high frequency and the real component of the impedance. The ionic conductivity of the samples was then calculated by dividing the estimated solution resistance by the cell constant. The cell constant of the two-electrode cell was determined by measuring the resistances of standard solutions with known conductivities and was found to be equal to 1.0 cm^{-1}. Measurements were replicated three times at each temperature for every system, and the averages were reported. The standard deviations were used to represent the error bars. Sample masses were weighed using a Cole-Parmer LB-200-124e analytical balance with an accuracy of 0.1 mg.

Viscosity and density measurements. The viscosity of the samples at 298 K was measured using a Rheosense microviscometer with a microfluidic chip calibrated at 1-100 cP and

temperature controller with an equilibration time of 15 minutes before every measurement. Measurements were replicated three times at each temperature for every system, and the averages were reported. To measure the temperature-dependent density measurements of the DES samples, an Anton Paar DMA 500 density meter with oscillating U-tube and temperature control unit was utilized. The samples were made sure to be free of any bubbles and to be at least 1 mL before injecting into the U-tube to ensure measurement accuracy.

Thermal expansion coefficients. Thermal expansion coefficients of pseudo-binary mixtures at various mole fractions of water (x_w) and constant pressure are determined within the temperature range of 298–323 K using equation (1):

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

where α_P represents the thermal expansion coefficient, and ρ denotes the density of the mixture. The derivative $\left(\frac{\partial \rho}{\partial T}\right)_P$ in the thermal expansion equation can be computed from the slope of the density–temperature curves of the mixture at each x_w.[34]

Excess molar volumes. The excess molar volumes (V^E) of pseudo-binary mixtures of DES and water are calculated at atmospheric pressure from 298 to 323 K using equation (2):

$$V^E = \left(\frac{x_{DES} MW_{DES} + x_w MW_w}{\rho_{mix}}\right) - \left(\frac{x_{DES} MW_{DES}}{\rho_{DES}} + \frac{x_w MW_w}{\rho_w}\right) \quad (2)$$

Here, x_{DES} and x_w are the mole fractions of DES and water in the mixture, respectively, and MW_{DES} MW_w are the molecular weights of DES and water, respectively. ρ_{mix}, ρ_{DES}, and ρ_w are the densities of the pure mixture, DES, and water, respectively, at each mole fraction of water. We treat the mixtures between DESs and water in this study as a pseudo-binary system, where the molecular

weight of DES is the molar weight average of DES components, ethylene glycol (EG) and choline halide (ChX, X=F, Cl). The MW_{DES} is calculated by equation (3).[35]

$$MW_{\mathrm{DES}} = x_{\mathrm{ChX}} MW_{\mathrm{ChX}} + x_{\mathrm{EG}} MW_{\mathrm{EG}} \quad (3)$$

Excess molar volumes can be fitted using the well-established fitting equation of binary systems at constant temperature using the Redlich-Kister (R-K) model,[36] equation (4):

$$V^{\mathrm{E}} = x_{\mathrm{w}}(1 - x_{\mathrm{w}}) \sum_{i=0}^{i=n} a_i (1 - 2x_{\mathrm{w}})^i \quad (4)$$

Where x_w is the mole fraction of water in the mixture, a_i are the R-K polynomial coefficients, and n is the order of the polynomial fit. The order of the polynomial, n, can be optimized to give the best fit of the R-K model to the experimentally determined excess molar volumes, where higher n values result in a better fit. The reliability of the R-K model and its optimized coefficients (a_i) with respect to the experimental excess molar volumes are tested by calculating the standard deviation (σ_{V^E}) as shown in equation (5).

$$\sigma_{V^E} = \sqrt{\frac{\sum (V^{\mathrm{E}}_{\mathrm{exp}} - V^{\mathrm{E}}_{\mathrm{calc}})^2}{m - i}} \quad (5)$$

where $V^{\mathrm{E}}_{\mathrm{exp}}$ and $V^{\mathrm{E}}_{\mathrm{calc}}$ are the experimental and R-K calculated excess molar volumes, m is the number of samples, and i is the number of the R-K coefficients used to fit the experimental data and depends on the mixture.

Excess molar Gibbs energy of activation. The excess molar Gibbs energy of activation (G^{*E}) of pseudo-binary mixtures of DES and water are calculated in the temperature range of 298 to 323 K, in 5 K increments, using Eyring's absolute rate theory[37] as expressed in equation (6):

$$G^{*E} = RT[ln(\eta V) - x_{DES}\ln(\eta_{DES}V_{DES}) - x_w\ln(\eta_w V_w)] \quad (6)$$

where R is the gas constant, T is temperature, x_{DES} and x_w are the mole fractions of DES and water, η, η_{DES}, η_w are the viscosities of DES/water mixture, pure DES, and water, and V, V_{DES}, V_w are their corresponding molar volumes.

Enthalpy and entropy of activation. The enthalpy of activation ($H^{\ddagger}$) of the DES/water mixtures is directly related to the temperature dependence of the excess molar Gibbs energy of activation (G^{*E}) according to the Gibbs-Helmholtz equation in equation (7).

$$\left[\frac{\partial\left(\frac{G^{*E}}{RT}\right)}{\partial T}\right]_{x,p} = -\frac{H^{\ddagger}}{RT^2} \quad (7)$$

Then, the entropy of activation ($S^{\ddagger}$) of the DES/water mixtures was calculated using equation (8).

$$\Delta G^{*E} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \quad (8)$$

III. RESULTS AND DISCUSSION

The addition of a third component (e.g., water in this case) to the binary deep eutectic solvent will give rise to a ternary system. Here, the DES/water system is treated as a pseudo-binary mixture because of the constant ratio between the choline halides and ethylene glycol.

Figure 1 depicts the density of DES mixtures composed of various choline halides (ChX, X = F, Cl, Br, I) and ethylene glycol in 1:9 molar ratio with indicated mole fractions of water in temperature range of 298 – 323 K. The molar ratio of 1:9 was chosen because choline iodide is soluble in ethylene glycol at this ratio. For consistency, the same molar ratio is used for all other DES samples containing different choline halide salts. The density of choline halide-based DESs

decreases nonlinearly with increasing mole fractions of water, following the trend choline iodide > choline bromide > choline chloride > choline fluoride. This trend is attributed to the larger ionic radius of iodide compared to the other halides, and the longer hydrogen bond length and weaker hydrogen bond strength of –H···I-.[6,38,39] The decrease in density with higher water content is due to water having a lower density than choline halide-based DESs. When the x-axis represents water content in weight percent (wt.%), the decrease in density appears approximately linear, as shown in **Figure S1**. This behavior arises because weight percent and mole fraction are calculated differently. Mole fraction accounts for the number of particles, so even small additions of water can cause significant changes, especially in mixtures with components of different molecular weights. As a result, the relationship becomes nonlinear.

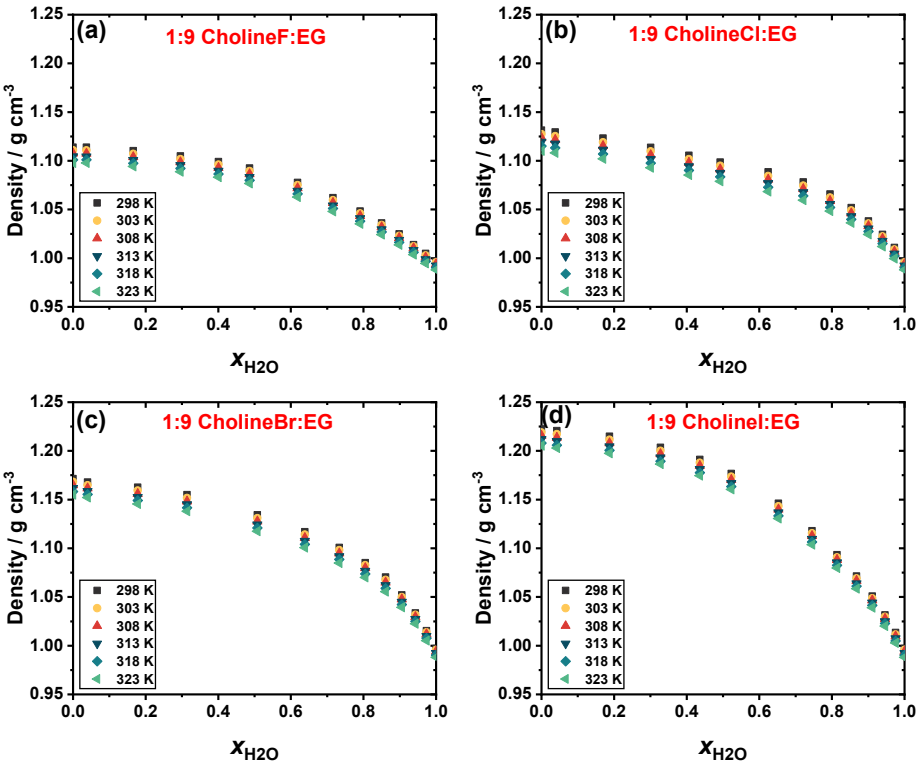

Figure 1. Density of several deep eutectic solvents composed of (a) choline fluoride, (b) choline chloride, (c) choline bromide, (d) choline iodide and ethylene glycol at a 1:9 molar ratio with indicated mole fractions of water in a temperature range of 298 – 323 K.

Figure S2 and **Tables S1-S4** present the numerical values of the densities of the DES mixtures composed of various choline halides (ChX, X = F, Cl, Br, I) with ethylene glycol in a 1:9 molar ratio as a function of temperature and water addition. The data indicates that the density of choline halide-based DESs marginally decreases with increasing temperature, which can be attributed to the thermal expansion that causes the liquid molecules to move further apart. From the temperature-dependent density data, the thermal coefficients of the DES mixtures at constant pressure were calculated using equation (1) and are reported in **Tables S5-S8**. The thermal expansion coefficient quantifies how much a volume of a material changes with temperature. The thermal expansion coefficient of choline halide-based DESs exhibits a slight decrease with increasing water content, indicating minimal isobaric expansion. This suggests that as water content increases, the tendency of DES mixtures to expand under constant pressure diminishes, reflecting a more stable volume behavior.

The temperature-dependent density of the DES mixtures was used to determine the excess molar volume (V^E) of choline halide-based DESs at a temperature range of 298-323 K, utilizing equation (2). Excess molar volume is used to analyze the interactions between DES and water. The observed V^E results from two types of interactions between the components: a positive contribution from physical interactions dominated by dispersion forces, and a negative contribution from chemical or specific interactions that cause a reduction in volume. This reduction is linked to the hydrogen bond strengths, and other complex interaction mechanisms.[40] The V^E values for the DES mixtures were reported in **Tables S9-S12**. The excess molar volume data were then fitted using the Redlich-Kister model, as described by equation (4), and the results are illustrated in **Figure 2**. The Redlich-Kister equation was employed to develop a mathematical model that describes the

behavior of excess molar volumes in relation to mixed compositions. This model is a polynomial, and the number of terms is determined as part of the fitting process. Nine terms were necessary for a reliable fit of the excess molar volumes of the choline halide-based DES mixtures. **Table S13-S16** present the Redlich-Kister polynomial coefficients (a_i) used to fit the experimental excess molar volumes of the studied DES mixtures. The standard deviations (σ_{VE}) were also calculated using equation 5 for each temperature to ensure that the model and its optimized coefficients are accurate compared to the experimental data. The very small σ_{VE} values for the choline halide-based DES mixtures at all temperatures confirm the reliability of the fitted Redlich-Kister models.

The V^E of DES mixture composed of choline fluoride and ethylene glycol (1:9 molar ratio) in **Figure 2a** is negative for $x_w \leq 0.62$ and becomes positive beyond this mole fraction of water. In contrast, **Figure 2b** shows the opposite trend for choline chloride and ethylene glycol (1:9), where V^E is positive at $x_w \leq 0.62$ and turns negative at higher water content. In Figure 2c, the V^E of the 1:9 choline bromide: ethylene glycol mixture exhibits a maximum at $x_w \leq 0.18$ and two minima at $x_w = 0.31$ and $x_w = 0.86$. Similarly, **Figure 2d** shows that for the 1:9 choline iodide: ethylene glycol mixture, V^E remains negative up to $x_w \leq 0.65$ with a minimum at $x_w = 0.33$, then becomes positive at $x_w \geq 0.65$, reaching a maximum at $x_w = 0.81$.

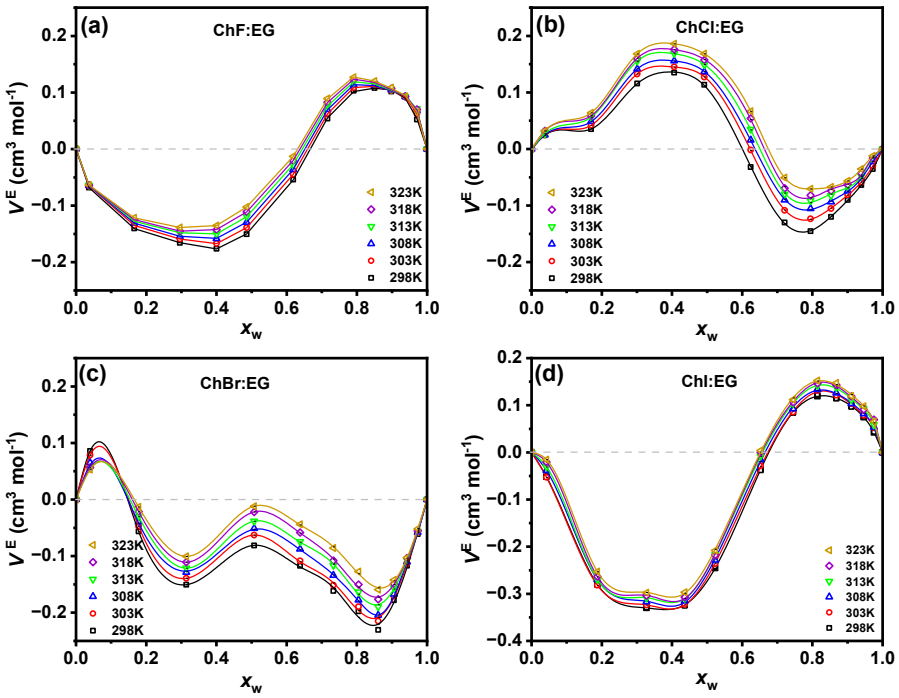

Figure 2. Excess molar volumes (V^E) of deep eutectic solvents composed of (a) choline fluoride, (b) choline chloride, (c) choline bromide, (d) choline iodide and ethylene glycol at a 1:9 molar ratio in a temperature range of 298 – 323 K. The symbols correspond to the experimental V^E values, while the solid lines represent the Redlich-Kister fits of the experimental values.

Figure 3 compares the V^E plots of different choline halides (ChX, X = F, Cl, Br, I) with ethylene glycol in a 1:9 molar ratio at 298 K. The 1:9 ChF:EG and 1:9 ChI:EG systems exhibit similar V^E trends, with 1:9 ChI:EG showing more negative V^E at $x_w \leq 0.65$. While the larger and more polarizable I^- seem to introduce more steric bulk, its weaker hydrogen bond strength and weaker hydration may allow greater molecular rearrangement compared to F^-, leading to denser packing and thus a more negative V^E. The F^-, being smaller, more charge-dense and highly hydrated, could introduce more structural rigidity, preventing efficient packing. Interestingly, at low water content, the V^E of 1:9 ChCl: EG is positive, suggesting that the interactions of Cl^- with EG and its hydration shell prevent efficient molecular packing. As x_w increases, the V^E increase

since extra water reinforces the hydration shell of Cl^-, but at higher x_w, it starts decreasing as excess water allows for restructuring and better molecular accommodation.

The observed trends are broadly consistent with the findings of Caleman et al.,[41] which show that halide ions exhibit distinct solvation behaviors in water depending on their size and polarizability. According to their atomistic simulations, the smaller, charge-dense fluoride ion (F^-) displays a markedly different solvation entropy due to its strong structuring effect, which leads to more ordered solvation shells at lower water content. In contrast, the intermediate-sized and more polarizable halides (Cl^-, Br^-, and I^-) tend to prefer the interface and interact more weakly with surrounding water molecules, resulting in more dynamic and less structured solvation shells. These results highlight that the interplay between ion size, hydration strength, and solvent structure is critical in determining the macroscopic properties of choline halide-based DESs.

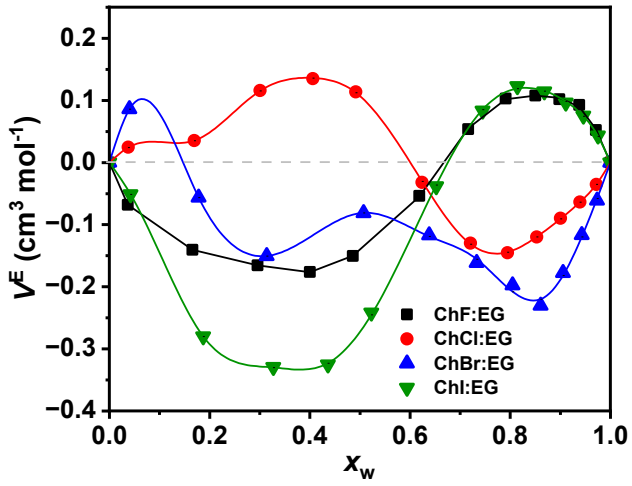

Figure 3. Excess molar volumes (V^E) of deep eutectic solvents composed of choline halides and ethylene glycol at a 1:9 molar ratio at 298 K. The symbols correspond to the experimental V^E values, while the solid lines represent the Redlich-Kister fits of the experimental values.

The effect of different molar ratios of choline halides (ChX; X = F, Cl) with ethylene glycol (EG) on the V^E was investigated and is shown in **Figure 4**. In **Figure 4a**, the distinction between the V^E values for the 1:2 and 1:9 molar ratios of choline fluoride and ethylene glycol is more pronounced at higher water content ($x_w \geq 0.62$), with the 1:9 ratio showing positive V^E and the 1:2 ratio displaying negative V^E. In the more dilute 1:9 ChF:EG mixture, the addition of large amounts of water may cause less disruption to the molecular interactions, resulting in positive V^E. Conversely, the 1:2 ChF:EG ratio could experience stronger hydrogen bonding with water molecules, leading to negative V^E. **Figure 4b** shows that the V^E for the 1:2 ChCl: EG mixture exhibits a minimum at x_w = 0.68, while the 1:9 ChCl: EG mixture initially shows a positive V^E between x_w = 0.49 and x_w = 0.62, transitioning to a negative V^E beyond this range. At low water content, water molecules disrupt the existing hydrogen bonding network in the 1:9 ChCl:EG mixture, causing an expansion in the molar volume. As more water is added, new interactions between the water molecules and the DES components form, resulting in a negative V^E.

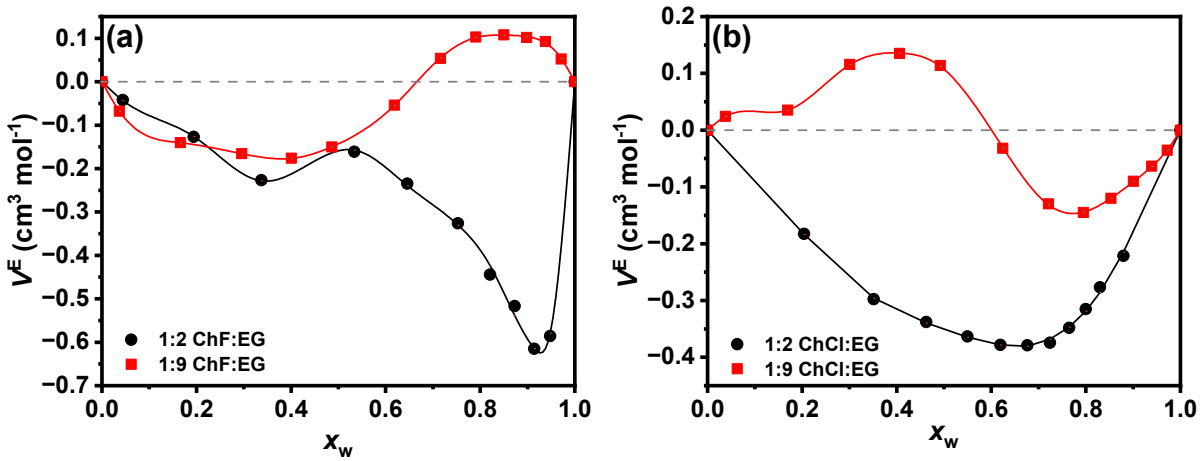

Figure 4. Excess molar volumes (V^E) of **(a)** choline fluoride and ethylene glycol, and **(b)** choline chloride and ethylene glycol at a 1:2 and 1:9 molar ratio and 298 K. The symbols correspond to the experimental V^E values, while the solid lines represent the Redlich-Kister fits of the experimental values. The experimental V^E data for 1:2 ChX (X=F, Cl) and ethylene glycol are adapted from ref [42] with permission from American Chemical Society, Copyright (2024).

The conductivities of choline halide-based DESs at 298 K were measured and plotted in **Figure 5a**. Among them, the DES with ChCl as the HBA exhibits the highest conductivity, followed by ChBr, ChI, and ChF. As water content increases, the conductivity of each DES mixture rises, reaching a maximum at x_w = 0.85, 0.79, 0.80, and 0.81 for ChF:EG, ChCl:EG, ChBr:EG, and ChI:EG, respectively, as listed in **Table S17**. The transition from increasing to decreasing conductivity observed at around 50 wt.% water can be attributed to a shift from the 'water-in-DES' to the 'DES-in-water' regime.[43] Since conductivity depends on both ion mobility and the concentration of charged species, the viscosity (inverse of fluidity) and ionicity (an estimate of the number of free ions) were measured. As shown in **Figures 5b** and **5c**, the sharp decrease in viscosity, indicating enhanced ion mobility, and the increase in ionicity explain the increase in conductivity of the DES mixtures at $x_w \leq 0.8$. The viscosity and conductivity of choline halide-based DESs with varying water content are reported in **Table S18**. The conductivity and viscosity of choline halide-based DESs as a function of water content expressed in weight percent (wt. %) are plotted in **Figure S3**. Beyond 50 wt. % water, conductivity starts to decline, which is consistent with the slower decrease in viscosity observed in **Figure 5b** and **Figure S3**.

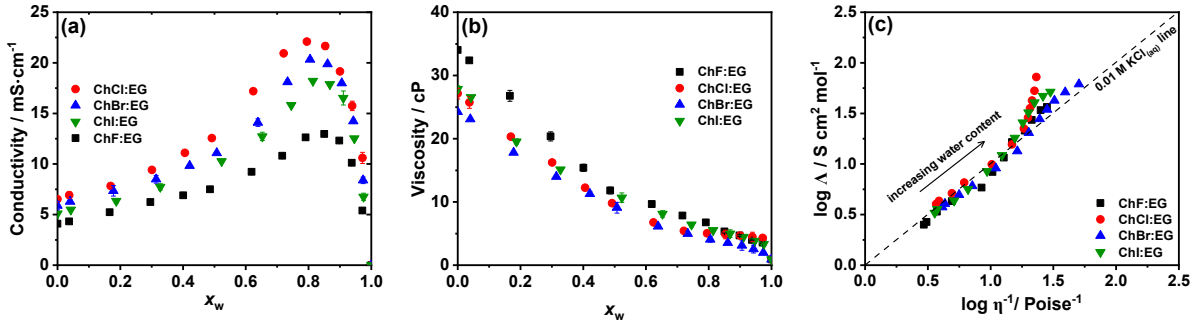

Figure 5. (a) Conductivity, **(b)** viscosity, and **(c)** ionicity of deep eutectic solvents composed of choline halides (ChX, X = F, Cl, Br, I) and ethylene glycol with various water content at a 1:9 molar ratio and at 298 K.

As the water content increases, the choline halide-based DESs become increasingly diluted. At water contents beyond approximately $x_w = 0.8$ (50 wt. % water), water molecules solvate the halide ions more effectively, resulting in a higher prevalence of these solvated halide ions. This behavior aligns with the observed decline in conductivity shown in **Figure 5a**. **Figure S4** and **Figure 2** summarize how halide variation affects the conductivity, viscosity, and excess molar volumes of choline halide-based DESs.

In addition, the excess molar Gibbs energy of activation (G^{*E}) was calculated using Eyring's absolute rate theory[37] (Equation 6) to understand how interactions in DES–water mixtures affect molecular mobility and viscous flow beyond ideal behavior. As shown in **Figure 6** and **Tables S19–S22**, all choline halide-based DESs exhibit positive G^{*E} values across all water contents, indicating strong interactions between DES components and water that increase the activation barrier to flow (i.e., hinder transport).[44] For most water contents, the G^{*E} follows the trend: ChF > ChI > ChCl > ChBr, which is consistent with the viscosity trends observed in **Figure 5b**.

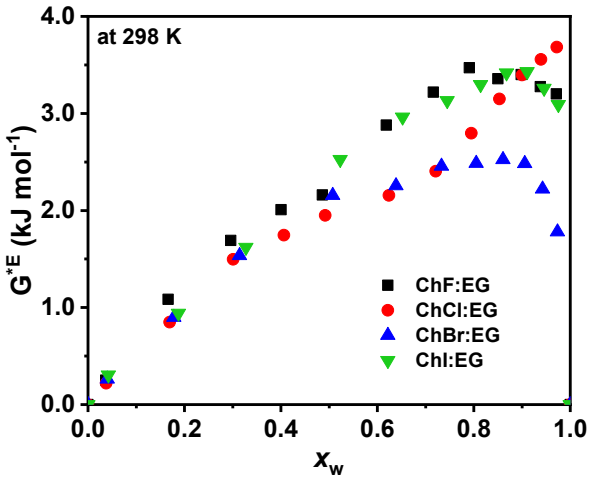

Figure 6. Excess molar Gibbs energy of activation, G^{*E}, of deep eutectic solvents composed of choline halides (ChX, X = F, Cl, Br, I) and ethylene glycol with varying water content at a 1:9 molar ratio and at 298 K.

The enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of activation for DES–water mixtures were also calculated using equations (7) and (8) and are summarized in Tables S23–S30. At most water contents, choline halide-based DESs exhibit positive $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values. A positive $\Delta H^{\ddagger}$ reflects strong intermolecular interactions resisting flow, while a positive $\Delta S^{\ddagger}$ implies increased molecular freedom during flow. This suggests that the system is structured at rest but becomes more disordered under shear, as water partially disrupts the DES network and enhances mobility without fully breaking the interactions.

IV. CONCLUSIONS

The presented work highlights how water–DES interactions are highly dependent on the involved ions and the compositional ratios. It examines the influence of halide ion variation and water addition in choline halide-based deep eutectic solvents (DESs) composed of choline halides (ChX, X = F, Cl, Br, I) and ethylene glycol at a 1:9 molar ratio. Water is added as a co-solvent to DESs to enhance their properties, such as reducing viscosity. As more water is added, it disrupts the hydrogen bonding between the hydrogen bond donor and acceptor, leading to the formation of hydrated halide ion clusters.[43] The density of these DESs increases with the size of the halide anion ($I^- > Br^- > Cl^- > F^-$) and decreases non-linearly with increasing water content. To quantify how much a volume of a DES mixture changes with temperature, the thermal expansion coefficients were determined, showing a slight decrease with water content. This indicates minimal isobaric expansion, suggesting that higher water content leads to a more stable volume response under constant pressure. To further understand the structural changes induced by water, excess molar volume was analyzed. Each choline halide-based DES exhibits distinct excess molar volume behavior, reflecting unique interactions with water molecules influenced by hydrogen bonding strength and polarizability. These variations highlight the role of the halide anion in modifying the solvation environment and molecular interactions within the DES mixtures. Conductivity

measurements at 298 K reveal that ChCl-based DES has the highest conductivity, followed by ChBr, ChI, and ChF. Conductivity increases with water content, reaching a maximum at specific x_w values before declining. The increase in conductivity is supported by the increase in fluidity (inverse of viscosity) and enhancement in ionicity.

SUPPLEMENTARY MATERIAL

The supplementary material provides the density, thermal expansion coefficients, excess molar volume, Redlich-Kister Model coefficients, conductivity, and viscosity of choline halide-based deep eutectic solvents with varying water contents.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

D.M. Prado: Conceptualization (lead); Methodology (lead); Validation (equal); Formal analysis (equal); Investigation (equal); Writing – original draft (lead); Writing – review & editing (equal). R.C. Prado: Formal analysis (equal); Data Curation (lead); Writing – review & editing (equal). K. Poling: Investigation (equal). P. Hood: Investigation (equal). A.C. Samia: Writing – review & editing (equal) C. Burda: Conceptualization (lead); Methodology (lead); Validation (equal);

Writing – review & editing (equal); Supervision (lead); Project administration (lead); Funding acquisition (lead)

DATA AVAILABILITY

The data that support the findings of this study is available in the supporting information.

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