Refractive Index of 48 Neat Deep Eutectic Solvents and of Selected Mixtures: Effect of Temperature, Hydrogen-Bonding Donors, Hydrogen-Bonding Acceptors, Mole Ratio, and Water

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ABSTRACT: The refractive index (RI) is an important physiochemical property of deep eutectic solvents (DESs) for application in the optical identification of specific substances or measuring the concentration of solutes in solutions. However, the available data on the RI of DESs is limited. Here, a systematic investigation on the RI of 48 typical DESs and 30 mixtures with water was conducted under atmospheric pressure. The effect of temperature in the range 293.15−338.15 K, hydrogen-bonding donors (HBDs), and hydrogen-bonding acceptors (HBAs) on RI was investigated. Furthermore, the RI of DESs as a function of mass percentage in the range of 20−80% water was also studied. It was found that the RI of DESs and its aqueous binary mixtures decreases linearly with the increase of temperature. HBDs and HBAs had a significant influence on the RI of DESs. Among them, the RI of choline chloride (ChCl)/phenol and ChCl/o-cresol were obviously higher than those of other DESs. It was also found that the addition of water would decrease the RI of DESs, and the RI of DES content in percentage (wt %) of water binary mixtures increases linearly as a function of mass percentage of DESs for 20 DESs. However, for the other 10 DESs, there is no linear relationship between the RI and the DES content.
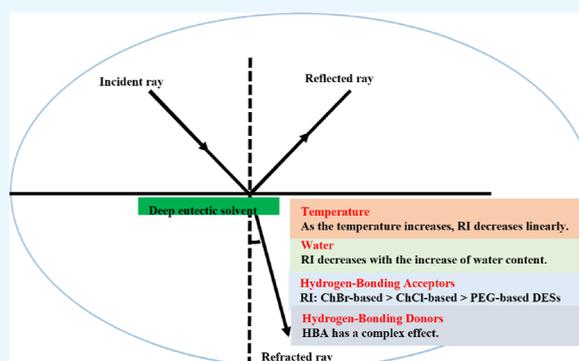
1. INTRODUCTION

Deep eutectic solvents (DESs) are deemed as a new class of green organic solvents introduced by Abbott et al. in 2003,[1] which are versatile alternatives to ionic liquids and traditional solvents. In general, a DES refers to a eutectic mixture of two or three components composed of a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD)[2] in a certain stoichiometric ratio, whose freezing point is significantly lower than the melting point of each of the neat components.[3,4] Over the last two decades, DESs have been widely studied and applied in academic community for their unique physical and chemical properties, such as less toxicity,[5] often good thermal stability, high biocompatibility,[6] and biodegradability.[7−11] Moreover, DESs possess attractive prices due to readily available raw materials with low costs and simple preparation procedures. Therefore, DESs as potential green solvents have been applied in liquid fuel purification;[12−15] absorption of SO_2 and CO_2;[16,17] extraction and separation of metal ions,[18,19] nanofibers,[20] and effective components from natural products[21−24] and biomacromolecules;[24−26] synthesis;[27] drug solubilization;[28,29] and even biological transformations.[30]

Refractive index (RI) is defined as the ratio of the velocity of light of a specified wavelength in air to its velocity in the examined substance. RI reported for some DESs include,[31−58] N,N-diethylethanol ammonium chloride/polyols,[34] tetrabuty-

lammonium chloride/amino acids,[37] ChCl/acids,[39] ChCl/polyols and one of its mixtures with water,[42,48] etc. Ma et al. have observed that the density and RI of the neat and aqueous mixtures decreased linearly with increasing temperature and increased with increasing DES mole fraction.[56] Meanwhile, a few groups utilized the limited experimental data on DESs and proposed models to predict the RI of DESs.[35,51−53] For example, novel quantitative structure−property relationship and group contribution models were developed for the prediction of RI of DESs based on molecular parameters of cations and HBDs, temperatures, and the mole ratio of HBA to HBD.[42,45,54] However, the prediction model for RI of DESs might not be applied to all systems and often requires sophisticated calculations, and the predicted data do not always match the experimental values as well.[55] Moreover, compared to a wide variety of DESs, the experimental data are relatively few and not systematic. Hence, a consistent and

systematic investigation on RI of DESs is an effective supplement to the RI database.

Here, the RI of 48 typical DESs was measured, and the effect of temperature, HBDs, HBAs, and water on the RI was investigated. Among all 48 DESs, the RI of ChCl:propionic acid (1:2),[39] ChCl:glutaric acid (1:1),[57] ChCl:ethylene glycol (1:2),[6,15,32,35,42,48,54−56] ChCl:glycerol (1:2),[6,15,31,32,35,48,50,54−56] ChCl:D-fructose (1:1),[33] ChCl:phenol (1:2),[49] ChCl:propanedioic acid (1:1),[2,15,56−58] and ChCl:lactic acid (1:1)[5] had been reported before. Apart from reporting ChCl-based DESs, our group measured the RI of another three new types of DESs, such as ChBr-based, betaine-based, and PEG-based DESs. Particularly, the effect of HBDs and ratios of HBA/HBDs on the RI of DESs was systematically discussed, to the best of our knowledge.

2. EXPERIMENTAL SECTION

2.1. Materials. A detailed sample description, including choline chloride (ChCl), betaine, acetic acid, propionic acid, phenol, o-cresol, choline bromide (ChBr), formic acid, glucose, triethanolamine, butyric acid, 2-phenylpropionic acid, L-glutamic acid, oxalic acid·2H$_2$O, propanedioic acid, glutaric acid, lactic acid, ethylene glycol, glycerol, xylitol, D-fructose, MgCl$_2$·6H$_2$O, Zn(Ac)$_2$·2H$_2$O, citric acid·H$_2$O, urea, polyethylene glycol 200 (PEG 200), and thiourea, is provided in Table S1, and all these chemicals were of analytical grade. All the solvents were used without any further purification except for phenol, which was redistilled. The ultrapure water was produced by a water purifier (Arium Advance EDI, Sartorius, Germany) in our laboratory.

All the DESs were prepared following earlier reported methods.[59] A brief preparation process is as follows: HBA and HBD were mixed and heated at 353.2 K under constant stirring until a homogeneous liquid appeared, and then continued stirring for 1 h. The water content of DESs was detected by a Karl Fischer coulometric titration (Mettler Toledo C20S) and has been specified for each DES. This information is provided in Table S2.

Among the 48 DESs, 6 DESs will precipitate after several days at room temperature, that is, the 6 mixtures that were unstable in the liquid form precipitated. We conducted X-ray powder diffraction (XRD) analysis, which was carried out using an X'pert3 Powder (PANalytical B.V., Netherlands) instrument. The Cu Kα radiation (λ = 1.5418 nm) was used in the experiment, and the tube voltage and current were set at 40 kV and 30 mA, respectively. The data were measured from 5.5 to 40° (2θ) at a scan speed of 10°/min at 298.15 K under atmospheric pressure. When the precipitate is observed, the composition of the liquid phase becomes unknown. RI is ill-defined in this case. Therefore, the n_D values for unstable liquids and their aqueous solutions must be immediately analyzed after preparation.

2.2. Measurement. RI and n_D of the investigated systems were measured using a WYA-2W Abbe refractometer (binocular, Shanghai INESA Physico-Optical Instrument Co., Ltd.) utilizing a yellow light beam of 589.3 nm sodium D line at atmospheric pressure. This instrument covers the refractive-index range of 1.3000−1.7200 with a manufacturer-stated uncertainty (±0.0003). The temperature was controlled by a thermostatic water-circulating bath (CF41, JULABO, Germany) with an uncertainty (±0.05 K) by circulating the water through the plastic pipe to maintain the temperature of the measuring prism (in which the DES was placed and sealed).

Prior to the analysis of the DES samples, the accuracy of the Abbe refractometer was first checked with ultrapure water over the temperature range of 293.15−338.15 K, and the measurement values were compared with the reference data.

For each measurement, about 2−3 drops of DES were loaded on the measuring prism and sealed, and the Abbe refractometer was stabilized for about 1 min to obtain the set temperature of 293.15 K. After each measurement, the prism was rinsed 3 times with ultrapure water and then wiped with lens paper. Reported values are the average of at least two measurements.

3. RESULTS AND DISCUSSION

In the preparation of DESs, HBA (ChCl-/ChBr-based, betaine-based, and PEG-based) and HBD [formic acid, acetic acid, propionic acid, succinic acid, butyric acid, oxalic acid· 2H$_2$O, propanedioic acid, glutaric acid, lactic acid, ethylene glycol, glycerol, xylitol, D-fructose, D-mannose, glucose, MgCl$_2$·6H$_2$O, Zn(Ac)$_2$·2H$_2$O, FeCl$_3$, ZnCl$_2$, triethanolamine, phenol, o-cresol, 2-phenylpropionicacid, L-glutamic acid, and citric acid·H$_2$O] were all prepared according to the mole ratio 2:1, 1:1, and 1:2; thus, 100 kinds of DESs were prepared. Different mole ratios have a great influence on the physical state of DESs, and some of the prepared ChCl-based DESs are solid at room temperature. Since the Abbe refractometer can only measure liquids, the DES in liquid form was selected to measure RI.

It is worth noting that among the 48 DES prepared, 42 DES are clear and homogeneous liquids that are stable even after 1 month. However, 5 DESs [ChCl:formic acid (1:1), ChCl:butyric acid (1:2), ChCl:Zn(Ac)$_2$·2H$_2$O (1:1), ChCl:triethanolamine (1:2), and ChBr:ethylene glycol (1:2) mixtures precipitated and ChCl:glucose (2:1)] will precipitate, and 1 DES [ChCl:glucose (2:1)] will become unhomogeneous. Thus, there were 6 mixtures that were unstable in liquid form and have been noted in this category. Therefore, RI was measured as early as possible after the preparation. Take ChCl:butyric acid (1:2) as an example, the XRD patterns of choline chloride and crystal precipitation of ChCl:butyric acid (1:2) are shown in Figure S1. The main characteristic diffraction peaks are at 2θ = 11.068, 15.810, 17.317, 18.690, 22.147, 28.441, 28.840, and 29.327°, respectively. It was found that all of the main peak positions and peak heights for the precipitation were basically identical with ChCl. Thus, it may be concluded that the precipitation may be the choline chlorides or the co-crystal of choline chlorides and butyric acid. All in all, 6 mixtures were unstable in liquid form and have been noted in this category. The precipitate could be either ChCl or a co-crystal of ChCl and the respective acid; thus, we will carry out PXRD, thermogravimetric analysis, differential scanning calorimetry, and infrared spectrometry analysis to clarify whether they are ChCl or the co-crystal according to the reviewer's suggestion to clarify whether they are ChCl or the co-crystal.

3.1. Literature Comparison. Up to date, 19 references relevant to this work have been investigated. The experimental data and reported values for ChCl:propionic acid (1:2),[39] ChCl:glutaric acid (1:1),[57] ChCl:ethylene glycol (1:2),[6,15,32,35,42,48,54−56] ChCl:glycerol (1:2),[6,15,31,32,35,48,50,54−56] ChCl:D-fructose (1:1),[33] and ChCl:phenol (1:2)[49] have been compared graphically illustrated in Figure S2. It can be seen that the deviations of our data from multiple results available in the literature are
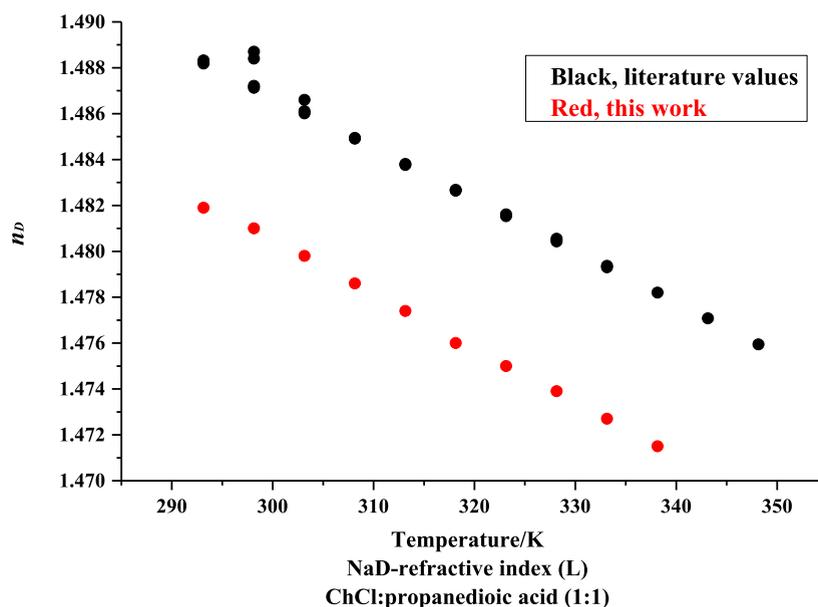
Figure 1. Deviations of the authors' data from multiple results available in the literature. The ChCl:propanedioic acid (1:1) data is taken from the literature.[2,15,56−58]

lower than 0.003. The standard uncertainty of $u(n_D)$ (±0.003) is consistent with these deviations.

However, deviations of our data from the results available in the literature reach 0.0066 and 0.0325 for ChCl:propanedioic acid (1:1)[2,15,56−58] and ChCl:lactic acid (1:1),[5] respectively. The experimental data has been compared graphically in Figure 1, and the existing significant deviations have been discussed. For ChCl:propanedioic acid, the mass fraction purity of propanedioic acid reported in the literature[57] is ≥99%, while our mass fraction purity is 98%. The water content in percentage (wt %) of dried DES is 0.47%, which is observed at 1.69% in our experiment. The large difference in water content of DESs was mainly responsible for the larger deviations in RI of ChCl:propanedioic acid. As for the large deviations of ChCl:lactic acid (1:1), it can be observed that HBD is D,L-lactic acid with 91.4% purity used by Rafael Alcalde's group,[5] while HBD in our experiment is L-lactic acid with 90% purity. Asymmetric carbon atoms in lactic acid molecules have different refractive abilities in the polarized light plane, so the RI deviation of ChCl:lactic acid (1:1) is significant.

In conclusion, ChCl-based DESs prepared with propionic acid, glutaric acid, ethylene glycol, glycerol, D-fructose, and phenol have similar RI values, but those prepared with propanedioic acid and lactic acid have much lower RI values than the corresponding literature data, meaning that the water content and purity of materials used in the preparation should be indicated.

3.2. Effect of Temperature on RI. The experimental RI as a function of temperature from 293.15 to 338.15 K and stability at room temperature for the studied DESs have been presented in Table S2 and plotted in Figure 2.

Since the RI values of some DESs are very close, the data is divided into 2 groups for clear display, as shown in Figure 2A,B. In order to analyze the effect of temperature, the relationship between the RI of DESs and temperature was fitted to a linear equation: $n_D = aT + b$, where n_D, a, T, and b are the RI, slope, temperature, and intercept, respectively. The fitted line uses the Kelvin temperature as the variable T and the

RI of DESs as n_D. The fitted equations have good linearity and adj. R-Square >0.99. The linear equation and correlation coefficient square are shown in Table S3. Leron's group also reported that the RI of chloride-based DESs decreased linearly with the temperature.[32]

It is well known that the RI of a compound in condensed phase depends on its molecular polarizability and its number density (namely, molar concentration). Therefore, it is not surprising that for a given substance (including mixtures of fixed composition), n_D decreases with rising temperature. From Figure 2, it is observed that RI values decrease with the increase in temperature, following the usual trend. The reason could be that the DESs molecules obtain more kinetic energy with an increase in temperature, which leads to more vibration of molecules, and then the distance between molecules and atoms increase. In other words, the increase in temperature of the DES medium will naturally lead to a decrease in the number of molecular groups, molecules, and atoms per unit length, and the number of polarizations will decrease; thus, RI will decrease with the increase in temperature. On the other hand, the temperature coefficient (slope absolute values) of most chloride-/bromide-based DESs are basically between −0.0002 and −0.0003 in the temperature range of 293.15 to 338.15 K. It implies that RI is sensitive to temperature. Take ChCl:butyric acid (1:2) as an example; the RI values decrease from 1.4512 to 1.4372 with the temperature from 293.15 to 338.15 K. Specifically, for every 1° decrease in temperature, the RI decreases by 0.000311. However, the temperature coefficient of seven PEG-based DESs is between 0.00031 and 0.00035, which indicates that the RI of seven PEG-based DESs is sensitively affected by temperature. However, the slope absolute values of ChCl:glycol (2:1), ChCl:MgCl$_2$·6H$_2$O (2:1), and ChCl:MgCl$_2$·6H$_2$O (1:1) are 0.000089333, 0.000136485, and 0.00012097, respectively. From Figure 2A, it can be seen that as the x-axis increases, the three lines do not change significantly. Especially, the linear fitting curve for ChCl:glycol (2:1) is almost parallel to the x-axis; in other words, temperature has no obvious effect on the RI. In short, DESs have different responses to temperature. In practical
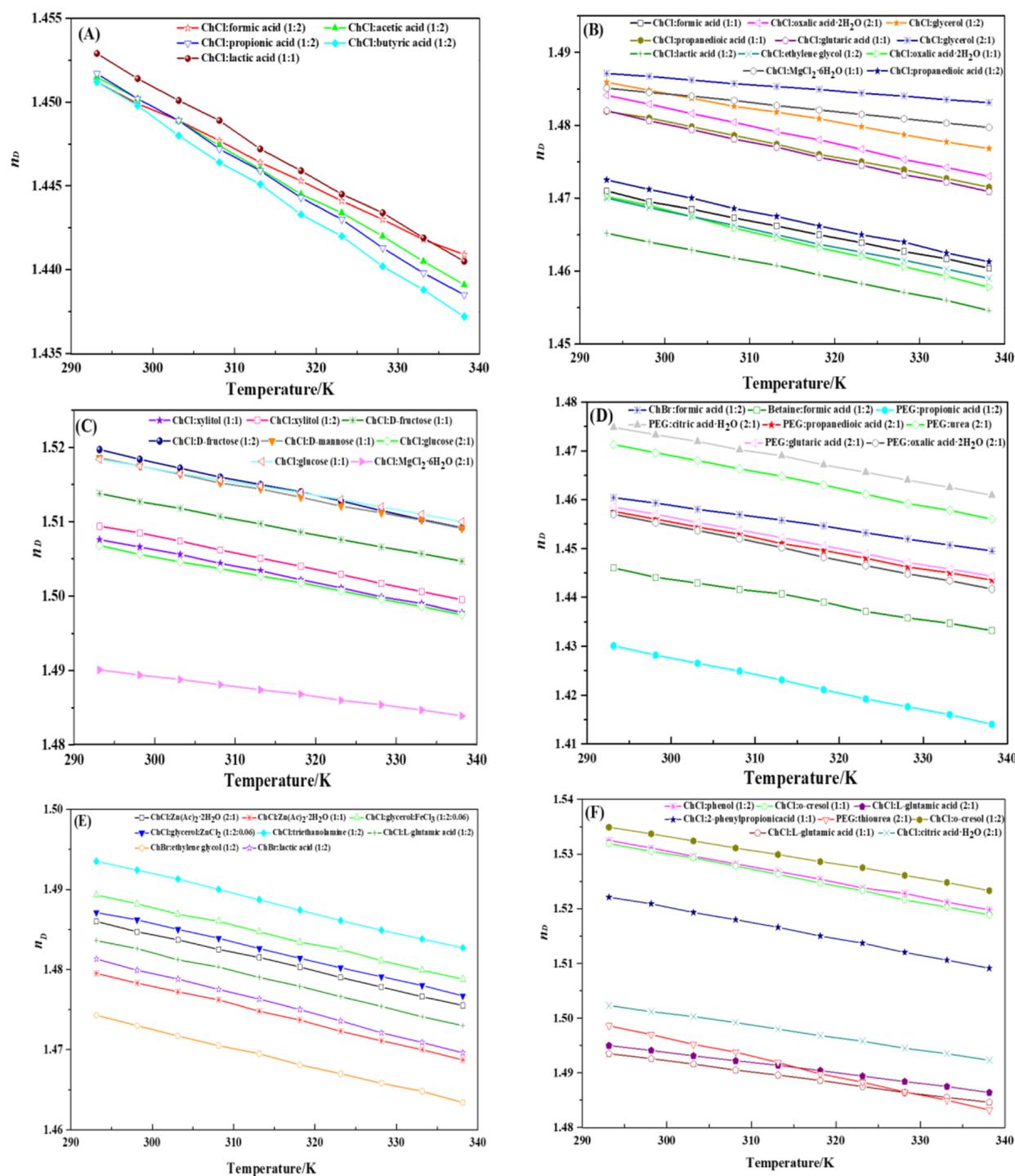
Figure 2. Effect of temperature on the RI of neat 48 DESs.

applications, according to the change of RI with temperature, we can select the appropriate DESs.

3.3. Effect of HBDs and Ratios of HBA:HBD on RI. The effect of HBDs and ratios of HBA:HBD on the RI of ChCl-/ChBr-based, betaine-based, and PEG-based DESs at 298.15 K is illustrated in Figure 3. Figure 3A,B present the RI of ChCl-based DESs with different mole ratios of HBA:HBD. Figure 3C only displays the RI of ChCl-based DESs (including acetic acid, propionic acid, butyric acid, glutaric acid, ethylene glycol, D-mannose, triethanolamine, phenol, 2-phenylpropionicacid, and citric acid·H$_2$O) because DESs composed of the other

ratios of HBA:HBD were often solid at room temperature. Figure 3D provides the effect of HBD on the RI of betaine-based, ChBr-based, and PEG-based DESs.

For all the DESs varying in HBD, the highest RI is ChCl:*o*-cresol (1:2), followed by ChCl:phenol (1:2) and ChCl:*o*-cresol (1:1). PEG:propionic acid (1:2) has the lowest RI of 1.4282, followed by ChCl:butyric acid (1:2) (1.4498) and ChCl:formic acid (1:2) (1.4499). HBDs can obviously affect the RI of ChCl-/ChBr-based and PEG-based DESs. The range of RI for all studied DESs is between 1.4498 and 1.5337 at 298.15 K. Second, the DESs formed from polyols (i.e., xylitol, D-fructose,
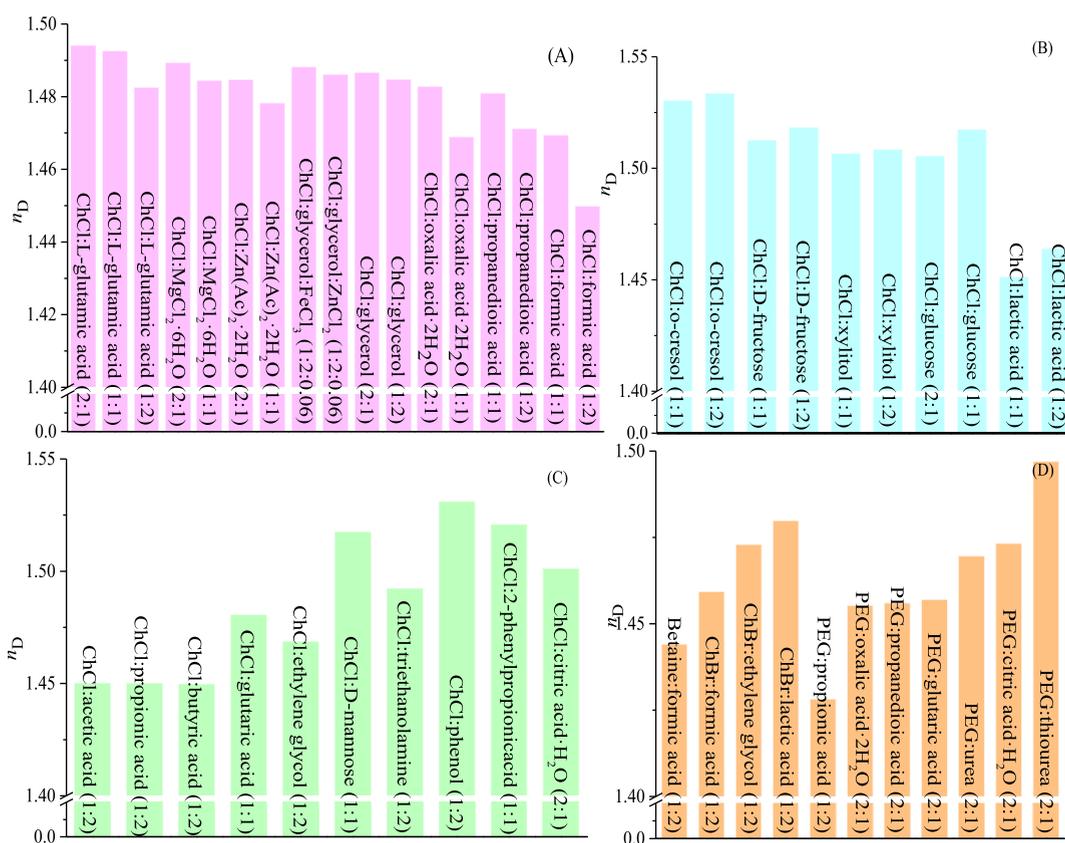
Figure 3. Effect of HBD at 298.15 K on RI of ChCl-based DESs (A, B, and C), betaine-based, ChBr-based, and PEG-based (D).

D-mannose, and glucose) have high RI values. Third, the range of RI in the whole studied temperature is very small, ca. 0.0111. Lastly, ChCl-based DESs composed of organic acids (formic acid, acetic acid, butyric acid, etc.) have the lowest RI.

3.4. Effect of HBAs on RI. We also selected six systems to investigate the effect of HBAs on RI and fix the HBD. Figure 4 shows the effect of HBAs on the RI of DESs at 298.15 K. For all the 13 DESs varying in HBA, the highest RI is ChCl:citric

Figure 4. Effect of HBAs at 298.15 K on the RI of ChCl-/ChBr-based, PEG-based, and betaine-based DESs.

acid·H_2O (2:1). PEG:propionic acid (1:2) has the lowest RI of 1.4282, followed by betaine:formic acid (1:2). Apart from the effect of HBD on the decreasing rate of ChCl-based DESs, the influence of HBA on the RI is also analyzed. When fixing the mole ratio of HBA:HBD at 1:2, the slope of ChCl:formic acid and betaine:formic acid is lower than that of ChBr:formic acid, implying a higher extent of the DES-dependent effect on the RI of DESs. A comparison between ChCl:oxalic acid·$2H_2O$ (2:1) and PEG:oxalic acid·$2H_2O$ (2:1) could conclude that HBA has an obvious effect on the slope.

RI of ChCl-based, ChBr-based, and PEG-based DESs could be listed as ChBr-based DESs (i.e., ChBr:formic acid, ChBr:ethylene glycol, and ChBr:lactic acid) > ChCl-based DESs (i.e., ChCl:formic acid, ChCl:ethylene glycol, and ChCl:lactic acid), ChCl-based DESs (i.e., ChCl:propionic acid, ChCl:citric acid·H_2O, and ChCl:oxalic acid·$2H_2O$) > PEG-based DESs (i.e., PEG:propionic acid, PEG:citric acid·H_2O, and PEG:oxalic acid·$2H_2O$). It may be that ChBr-based DESs have a higher density compared to ChCl-based DESs and PEG-based DESs.

3.5. RI of DESs + water. For some mixtures studied in Table S3, water is present both in DESs and as a solvent. Water from both sources is indistinguishable in the formed solutions. Therefore, in order to avoid misleading the water-containing DESs and facilitate the preparation of the mixtures of DESs and water, the compositions (wt %) in Table S3 were reported in mass fractions of $m_{DES}/(m_{DES} + m_{water}) \times 100\%$. For some DESs, they are unstable in water, such as the hydrolysis of $FeCl_3$ in water. The choline chloride + glycerol + $FeCl_3$+water mixtures are most probably heterogeneous. Thus, the representative 30 DESs were selected to investigate the RI of DESs + water due to water being an environmentally friendly
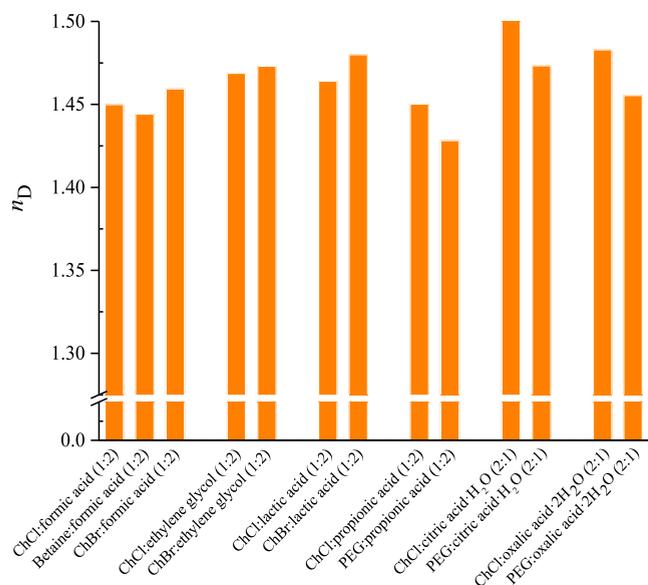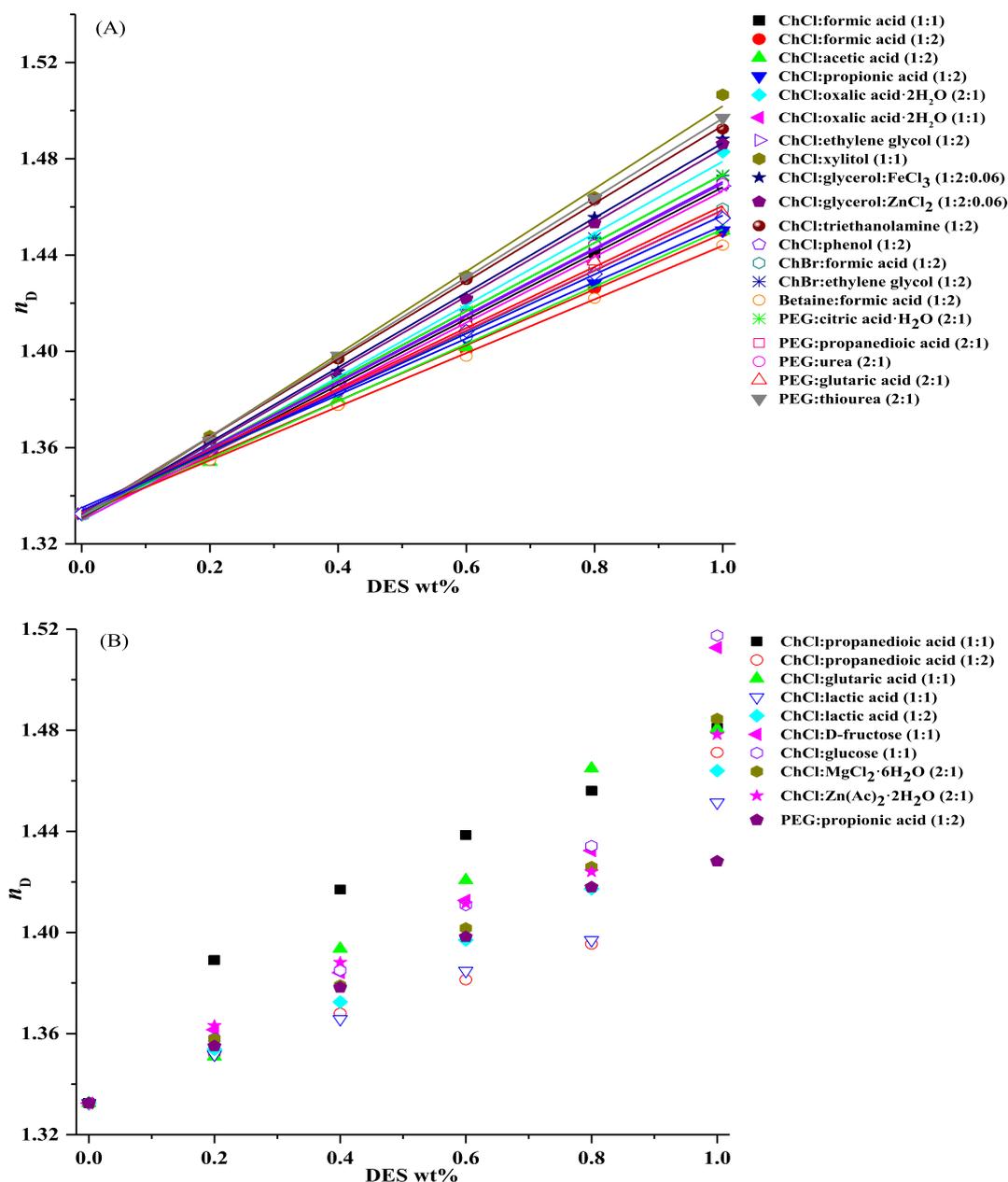
Figure 5. Effect of DES content in percentage (wt %) of water binary mixtures at 298.15 K. (A) Linear relationship with DES content in percentage (wt %) of water binary mixtures; (B) nonlinear relationship with the DES content in percentage (wt %) of water binary mixtures.

green solvent, and the values of the RI of DESs + water in the range of 293.15 to 338.15 K are listed in Table S3.

Figure 5A,B shows the effect of DES content in percentage (wt %) of water binary mixtures on the RI of 30 DESs in the DESs + water binary system at 298.15 K. The linear equation correlation coefficient square (r^2) of RI of DES content in percentage (wt %) of water binary mixtures at 298.15 K is shown in Table S5. RI of pure water is 1.3325 at 298.15 K; thus, we conceive that the addition of water to the DES would decrease the RI of ChCl-/ChBr-based, betaine-based, and PEG-based DESs. As expected, RI decreased as the mass fraction of DESs decreased. Take ChCl:formic acid (1:1) as an example, the RI at 298.15 K is ordered at 1.4695 (100% DES) > 1.4409 (80% DES) > 1.4120 (60% DES) > 1.3848 (40% DES) > 1.3587 (20% DES) > 1.3325 (pure water). That is to say, the presence of water in DESs + water would decrease RI.

More precisely, the increasing percentage of DES on RI in DESs + water systems could be divided into two categories at 298.15 K. The first is expressed by the slope a in the fitted equation, $y = ax + b$. The fitted line uses DES content in percentage (wt %) of water binary mixtures as the variable x and RI as the y axis. The fitted equation is shown in Figure 5A. The value of slope is always positive due to the fact that increasing the DES wt % increases the RI. A more positive value of the slope suggests that RI has a positive correlation in the aqueous solution. The RIs of ChCl:phenol (1:2) + water and ChCl:xylitol (1:1) + water are more sensitive than those of betaine:formic acid (1:2) + water and ChCl:formic acid (1:2) + water. Moreover, the slope of ChCl:formic acid (1:1) + water is higher than that of ChCl:formic acid (1:2) + water. Similarity, the slope of ChCl:oxalic acid·2H$_2$O (2:1) + water is higher than that of ChCl:oxalic acid·2H$_2$O (1:1) + water.
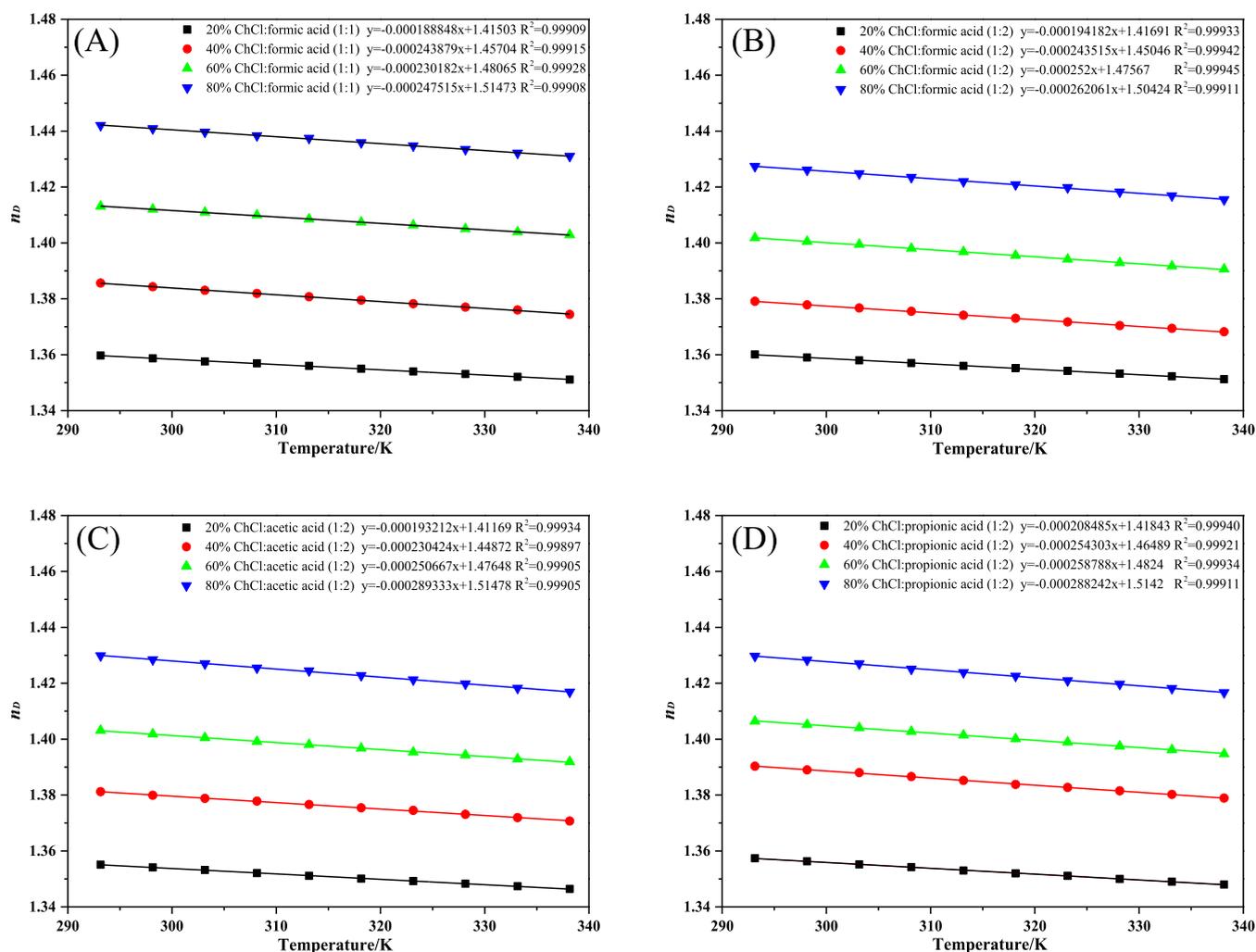
Figure 6. Effect of temperature on RI of DESs + water mixtures as a function of mass percentage in the range of 20−80% DES: (A) ChCl:formic acid (1:1) + water, (B) ChCl:formic acid (1:2) + water, (C) ChCl:acetic acid (1:2) + water, and (D) ChCl:propionic acid (1:2) + water.

According to our results, when the n_D of the above-studied DES is known, the RI of the DES aqueous solution may be calculated by comparing the RI of neat DES and water.

However, for the other ten ChCl-based and one PEG-based DESs, there is no linear relationship between the DES wt % and the RI, i.e., ChCl:propanedioic acid (1:1), ChCl:propanedioic acid (1:2), ChCl:glutaric acid (1:1), ChCl:lactic acid (1:1), ChCl:lactic acid (1:2), ChCl:D-fructose (1:1), ChCl:glucose (1:1), ChCl:MgCl$_2$·6H$_2$O (1:1), ChCl:Zn-(Ac)$_2$·2H$_2$O (1:1), and PEG:propionic acid (1:2). Leron et al. have obtained correlations for the density and RI of the binary mixtures as functions of temperature and composition and calculated the values using a RedlichKister type equation.[32] The RI of the binary mixtures was predicted using the following mixing rules such as the Arago−Biot (A−B), Gladstone−Dale (A−B), Lorentz−Lorenz (L−L), Eykman, Heller, Weiner, Newton, and Eyring−John. It is worth noting that these equations need to know the density to calculate the RI. The RI deviations for the binary systems were the deviation of n_D from ideality that is expected to correlate well with excess mole volumes V^E.

3.6. Effect of Temperature on RI of DESs + Water. The effect of temperature on the overall change in RI of four DESs has been plotted in Figure 6, i.e., ChCl:formic acid (1:1),

ChCl:formic acid (1:2), ChCl:acetic acid (1:2), and ChCl:propionic acid (1:2). RI of other 26 DESs are plotted in Figure S3.

It is interesting to note that the values of RI at the 20% DESs are close to water. It is understandable when the DESs + water system contains 20% DESs, the DES molecules are surrounded by water molecules, and the solution system is close to the water system. For example, the mole ratio of H$_2$O:DES is close to 41:1 in the 20% ChCl:formic acid (1:1) + water system, and the mole ratio of H$_2$O:DES is 108:1 in the 20% PEG:oxalic acid·2H$_2$O (2:1) + water system.

As can be seen from Figures 6A−D and S3, the results show that the relationship between the RI of DES + water and temperature could be linearly fitted with the equation $y = ax + b$, where y, a, x, and b are the RI, slope, temperature, and intercept, respectively. The decreasing rate of RI as a function of temperature could be expressed by the slope a in the fitted equation. The value of slope is always negative due to the fact that increasing the temperature decreases the RI. A more negative value of the slope suggests that the RI is more sensitive to temperature. A decreasing trend in n_D with temperature was also observed, which is similar to that of the corresponding neat DESs. This behavior is consistent with

those observed in other aqueous DES mixtures reported in the literature.

4. CONCLUSIONS

In this work, a variety of 48 neat eutectic mixtures were prepared by a heating process. The RI of DESs and of selected mixtures with water were studied in the range of temperatures from 293.15 to 338.15 K. As expected, RI would linearly decrease with increasing temperature. Both HBD and HBA have a profound effect on the RI of DESs. When fixing the HBD, the RI decreased in the order ChBr-based > ChCl-based > PEG-based DESs. However, HBAs did not have a uniform effect on the RI in our studies.

Water presents a strong influence on the RI of binary mixture DESs. The addition of water to DESs would decrease the RI of DESs extensively. RI of DES content in percentage (wt %) of water binary mixtures investigated in the range of 293.15 to 338.15 K increases as a function of DES wt %, and 21 DESs there are good linear relationship between the DES wt % and RI. However, for the other ten DESs, there is no good linear relationship between the DES wt % and RI. The results of this work are intended to enrich the RI database of DESs, which would be useful in the utilization and design of their probable applications.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c03502.

> Detailed Information of Materials Used; XRD patterns of choline chloride and precipitation of ChCl:butyric acid (1:2); RI of Neat DESs (wt %) Investigated in the Range of 293.15 to 338.15 K and Physical Appearance (Sodium D-line); The comparison of RI between measured DESs and reported values; Linear Equation, Correlation Coefficient Square (r^2) of RI of Neat DESs in the Range of 293.15 to 338.15 K; RI of DES Content in Percentage (wt %) of Water Binary Mixtures Investigated in the Range of 293.15 to 338.15 K (Sodium D-line); Linear Equation, Correlation Coefficient Square (r^2) of RI of DES Content in Percentage (wt %) of Water Binary Mixtures at 298.15 K (PDF)

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Notes

The authors declare no competing financial interest.

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