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*Research Article*

# Temperature Effects on Physiochemical Characteristics of Sugar-Based Natural Deep Eutectic Solvents

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Phase behavior, density, viscosity, conductivity, pH, and surface tension were measured, and FTIR was performed for a series of mixtures of sugar (glucose, fructose, xylose, and sucrose), water, and choline chloride (ChCl) at specific molar ratios. These mixtures, called sugar-based natural deep eutectic solvents (NADESs), were investigated as a function of temperature. Contact angle measurements indicated that NADES exhibited slightly lower wettability but higher surface tension than water. Temperature was found to greatly impact density, viscosity, and conductivity. The optimum water molar ratio for lower viscosity was found at ratios higher than those reported in the literature, indicating that the NADES investigated may have industrial process applications.

## 1. Introduction

Biofriendly solvents are essential to protect the environment when manufacturing products. Many industrial processes use volatile organic compounds that cause pollution. One type of nonvolatile solvent that has been recently developed is ionic liquids [1, 2]. However, ionic liquids are difficult to synthesize and have components that are not biodegradable [3]. Deep eutectic solvents (DESs), which are hydrogen bonded, are easily prepared from readily available, low-cost materials with little waste and a high yield [4–7]. Some DESs do not inactivate enzymes, so that they can be useful for the processing of biofuels [7–9]. Compared to ionic liquids, DESs also tend to be effective if water exists in the solvent, allowing for their use in wet biomass [6, 10]. Predrying of biomass prior to pretreatment can be expensive [11].

Not all DESs are environmentally friendly [6, 12]. DESs containing metal salts such as Zn are toxic [13]. Organic acid containing DES has been found to be toxic [14]. To keep the environment safe, it is essential to find nontoxic DES components, preferably including ones that can be sourced from waste biomass. Waste biomass from food production can be reduced to lighter components (such as sugar) with DES [15, 16]. Most of this sugar yield can be fermented into biofuels, while a portion could be used to prepare natural DES (NADES) to continue the degradation of waste biomass or use in other processes that require solvents. This means that a more circular economy could be achieved.

Sugars that can be obtained from the deconstruction of biomass include glucose, fructose, xylose, and sucrose [15, 17, 18]. NADES can be prepared using these sugars as hydrogen bond donors combined with one of the safest hydrogen bond acceptors, choline chloride [19, 20]. Various investigations have been carried out on these types of NADES. Liu et al. [21] made NADES with the hydrogen bond acceptor choline chloride and hydrogen bond donors glucose, fructose, xylose, and sucrose in a 1 : 1 molar ratio for use with n-propanol in a biphasic system [21]. The physical properties of NADES with a hydrogen bond acceptor of choline chloride and a hydrogen bond donor of fructose have been investigated [22, 23]. They found an increase in viscosity, density, and surface tension; so, it is probably necessary to heat the NADES before processing. Silva et al. [24] also found high viscosities and densities for NADES of choline chloride with glucose, fructose, or xylose at equimolar ratios, meaning that higher than ambient processing temperatures would be required [24]. Jurić et al. [25] confirmed the same behavior with the viscosity and density using choline chloride: fructose in a 1 : 1 molar ratio of NADES [25]. Mero et al. [26] found that when molar ratios of a choline chloride hydrogen bond acceptor and a betaine hydrogen bond donor were varied, physicochemical and thermal properties were tunable [26].

Zurob et al. [27] explored NADES with a hydrogen bond acceptor of choline chloride and a hydrogen bond donor of either fructose or glucose but added water as a component [27]. Zhao et al. [14] used a 5 : 5 : 2 molar ratio of choline chloride : water : sugar (glucose, fructose, or xylose), and they found a significantly lower viscosity for these NADESs in their study of rutin extraction from Japanese pagoda tree biomass [14]. Gabriele et al. [28] found for DES of choline chloride with either diethylene glycol, triethylene glycol, or polyethylene glycol 200, that dilution with water caused the interactions to weaken gradually up to a 1 : 3 : 8 choline chloride : glycol : water molar ratio, but the supramolecular structures remained to some extent [28]. Sugar-based NADESs are known as designer solvents because they can be easily tuned either by adding water or by varying the temperature or by varying the molar composition of the HBD and HBA [29]. Tuning physiochemical characteristics like viscosity by adding water is simple and less expensive, whereas tuning by varying temperatures is complex, energy-intensive, and expensive. Adding certain water molar ratios does not change the supramolecular structure of the solvent but significantly changes the viscosity, easing the flow in piping and making it more industry-friendly. However, adding water above a specific molar ratio has been found to affect DES nanostructure [30].

Analysis of the fundamental physicochemical properties or characteristics of one or several compounds is imperative for all research fields, and determining the physical characteristics of the newly developed NADES is essential. The physical properties of these solvents change with the molar ratio; therefore, NADES are a type of solvent with physical properties difficult for scientific communities to easily characterize. Typically, they are characterized as needed for a specific application. As there is a knowledge gap in the physical properties of sugar-based NADES of different molar ratios, we have investigated the physical properties of these sugar-based NADES, which have a high potential for pretreating biomass [31].

Thise work investigates the viscosity, density, pH, conductivity, surface tension, and Fourier transform infrared (FTIR) spectra of NADES comprised of choline chloride with either glucose,fructose, xylose, or sucrose using higher water molar ratios than have been investigated in the literature. This study may indicate processing possibilities that can be implemented at lower temperatures than those needed for viscous NADES without water.

## 2. Materials and Methods

*2.1. Raw Materials and Chemicals.* The chemicals used in Table 1 for the preparation of sugar-based NADES were purchased from Sigma-Aldrich.

Table 1: Sugar-based NADES compounds.

| Compound | Atomic structure | Purity | Cas No |
|---|---|---|---|
| Choline chloride | $C_5H_{14}ClNO$ | ≥98% | 67-48-1 |
| Glucose | $C_6H_{12}O_6$ | ≥99.5 | 50-99-7 |
| Fructose | $C_6H_{12}O_6$ | USP standard | 57-48-7 |
| Xylose | $C_5H_{10}O_5$ | 99% | 58-86-6 |
| Sucrose | $C_{12}H_{22}O_{11}$ | ≥99.5% | 57-50-1 |

*2.2. Methods*

*2.2.1. Preparation of NADES.* Sugar-based NADES were prepared by adding ChCl, to act as a hydrogen bond acceptor, to different sugars (glucose, fructose, sucrose, and xylose) that act as hydrogen bond donors in a 5 : 2 mole ratio in beakers. Deionized water was added to achieve a mole ratio of 7, 11, and 14 in the mixture solution. The mixtures were placed in an orbital shaker at 80°C and 400 RPM for 2 hours. After 1 hour, the cloudy sugar-based NADES became a clear solution and were fully transparent after 2 hours. The homogeneous solutions were sealed and stored at room temperature before physical characterization, and they remained clear with no solid particles for several months.

*2.2.2. Physiochemical Properties.* In this study, the characteristics, density, viscosity, ionic conductivity, and pH have been determined at the same condition for five different temperatures (22°C, 27°C, 40°C, 60°C, and 80°C); FTIR spectra and contact angles have been analyzed at 25°C. The five different temperatures were maintained with an oil bath system, and 25°C was maintained in a temperature-controlled room.

The melting points of the individual components, choline chloride, glucose, fructose, xylose, and sucrose, are 302°C, 146°C, 103°C, 90.5°C, and 186°C, respectively. However, the physical state of the mixtures of ChCl with different sugars and different mole ratios of water was liquid at ambient temperature (22°C).

DESs typically exhibit higher densities than water. Therefore, the density of sugar-based NADES was measured by using a 2 ml pycnometer for three different molar concentrations (5 : 2 : 7, 5 : 2 : 11, and 5 : 2 : 14 of ChCl, sugar, and water).

The viscosities of sugar-based NADES at five different temperatures were measured with the USS-DVT4 digital viscometer (US Solid, OH, USA). The instrument works on the shear force principle.

The ionic conductivity of sugar-based NADES was measured using a Starter 300C conductivity meter (OHAUS, NJ, USA) at five different temperatures and three different molar concentrations (5 : 2 : 7, 5 : 2 : 11, and 5 : 2 : 14 with ChCl, sugar, and water).

The pH values of the sugar-based NADES were measured by using an Orion Star A111 pH meter (Thermo Fisher Scientific, MA, USA). The temperatures that pH was measured at were 22°C, 27°C, 40°C, 60°C, and 80°C.

The contact angle of a solvent shows its wetting ability and adhesion property to any solid surface. The contact angles were measured on a VWR microcover glass (Radnor, PA, USA) substrate using OCA 25 contact angle systems (DataPhysics Instrument GmbH, Filderstadt, Germany, and Future Digital Scientific Corp., NY, USA).

Finally, the FTIR method was used to confirm the bonds of different molecules by obtaining a sample's infrared spectrum of absorption over a wide range of wavelengths. We used FTIR in our study to identify molecular structure shifts in sugar-based NADES. We analyzed FTIR spectra in sugar-based NADES using a Nicolet 6700 FTIR-ATR with a Smart iTR diamond ATR using 32 scans for each sample at $2\,cm^{-1}$ from 4000 to $600\,cm^{-1}$, measuring the vibration intensities from the plateaus at lower wavenumber.

## 3. Results and Discussion

*3.1. Phase Behavior.* In sugar-based NADES, the deep eutectic point is a principal characteristic as it denotes the lowest melting point of a mixture of ChCl and sugar compared to the individual melting points. In physical observation, the eutectic point of a mixture can be determined by observing its turbidity, which is the relative clarity and cloudiness of liquid, and it is measured by scattered light passing through it. The higher the scattering of light, the higher the cloudiness and turbidity. The turbidity of deep eutectic solvent varies with molar ratio, temperature, and mixing speed [32]. The eutectic point of a solution changes with the molar ratio of the composition of the solutions. To date, specifics about individual sugar-based NADES' eutectic compositions and accompanying binary phase diagrams have yet to be present in the literature. This lack of knowledge generates an interest in investigating the physical properties of sugar-based NADES at room temperature. Sugar-based NADESs have been observed in this work to be a one-phase liquid at a 5 : 2 : x molar ratio of ChCl (HBA): sugar (HBD): varying molar ratio of water at room temperature. The relatively low melting points of sugar-based NADES depend on the molar ratio of HBA and HBD, which make hydrogen bonds between the anion in HBA and the OH functional group in HBD. The number of anions in the HBA and OH groups in HBD changes with the molar ratio and water content; hence, the eutectic position changes. In addition, the number of OH groups in different sugars varies, which changes the eutectic point. Sugar-based NADES are colorless liquids at ambient temperature with specific molar ratios, as shown in Table 2.

In Table 2, the choline chloride, xylose, and water mixture with a 5 : 2 : 7 molar ratio is not an entirely colorless, easily flowing liquid. However, it is in a jelly-type and slow-flowing fluid as shown in Figure 1. This xylose-based NADES with a 5 : 2 : 7 molar ratio (shown second from the left in Figure 1) is cloudy, and its turbidity is high. Turbidity does decrease with increasing temperature, and it becomes fully transparent at a 40°C or higher temperature. However, all the other sugar-based NADES listed above are fully transparent at ambient temperature and their turbidity is close to the turbidity of DI water.

*3.2. Density.* Sugar-based NADES comprises only ChCl, sugar, and water with different molar ratios where ChCl acts as a hydrogen bond acceptor (HBA). In contrast, sugar and water act as hydrogen bond donors (HBD) compared to chloride [33]. The OH functional groups in the sugars and the water interact with the Cl anion in the ChCl. The interactions between the functional OH groups and the Cl anion in the ChCl depend on the number and orientation of the OH groups that significantly impact the densities [34]. For this reason, the densities of sugar-based NADES change with the molar ratio of HBA and HBD, which defines the number of anions and functional OH groups, respectively. In addition, temperature and excess water existing in the solvent also affect the density variation. So, measuring the density of sugar-based NADES is imperative to see the changing trend in solvent composition, molar ratio, and temperature.

Figure 2(a) shows that the density of glucose-based NADES decreases with increasing temperature, which is expected as a natural phenomenon for any liquid since more significant vibration means the molecules take up more space. The density of glucose-based NADES at 22°C with the addition of water for a molar ratio of 7, 11, and 14 (or 10%, 15%, and 20% (w/w) water addition) is $1.2070 \pm 0.0003$ g/ml, $1.2044 \pm 0.0001$ g/ml, and $1.2025 \pm 0.0003$ g/ml (reported in Supplementary Materials SI Table 1), respectively, which implies that the density of glucose-based NADES decreases with the addition of water. The effect of water addition in the other three sugar-based NADES follows the same trend, as shown in Figures 2(b)–2(d). This effect may indicate a loosening of the NADES supramolecular structure with water addition, as reported by Gabriele et al. [28]. Figures 2(b)–2(d) show that the densities of the other three sugar-based NADES follow a similar trend as the glucose-based NADES with temperature. Among the four sugar-based NADES, xylose-based NADES had the lowest density and sucrose-based NADES had the highest density, as shown in Figures 2(e) and 2(f). The lower density of xylose-based NADES is likely due to the lower number of OH functional groups that exist in the xylose compared to others and its lower molecular mass, and sucrose-based NADES' higher density is likely because sucrose is a disaccharide rather than a monosaccharide, as the other NADESs contain. Figures 2(b)–2(d) show that the density of sugar-based NADES decreases linearly with temperature.

*3.3. Viscosity.* The viscosities of sugar-based NADES depend on the tendency toward van der Waals interaction and hydrogen bond strength between HBA and HBD. A higher viscosity means stronger hydrogen bonding between HBA and HBD. As the number and orientation of HBD functional OH groups in different sugars differ, viscosities of different sugar-based NADES change with varying sugar types and molar ratios; moreover, the activation energy for formation changes with temperature, affecting the viscosity value. Water in the sugar-based NADES also affects the viscosity. Therefore, measuring

Table 2: Physical state/appearance of sugar-based NADES with glucose (Gl), xylose (Xy), fructose (Fr), sucrose (Su), and water (W) (molar ratios are numerically indicated).

| Compound | Molar ratio | Physical state |
|---|---|---|
| ChCl : Gl : W | 5 : 2 : 7 | Colorless liquid |
| ChCl : Gl : W | 5 : 2 : 11 | Colorless liquid |
| ChCl : Gl : W | 5 : 2 : 14 | Colorless liquid |
| ChCl : Fr : W | 5 : 2 : 7 | Colorless liquid |
| ChCl : Fr : W | 5 : 2 : 11 | Colorless liquid |
| ChCl : Fr : W | 5 : 2 : 14 | Colorless liquid |
| ChCl : Xy : W | 5 : 2 : 7 | Semisolid |
| ChCl : Xy : W | 5 : 2 : 11 | Colorless liquid |
| ChCl : Xy : W | 5 : 2 : 14 | Colorless liquid |
| ChCl : Su : W | 5 : 2 : 7 | Colorless liquid |
| ChCl : Su : W | 5 : 2 : 11 | Colorless liquid |
| ChCl : Su : W | 5 : 2 : 14 | Colorless liquid |

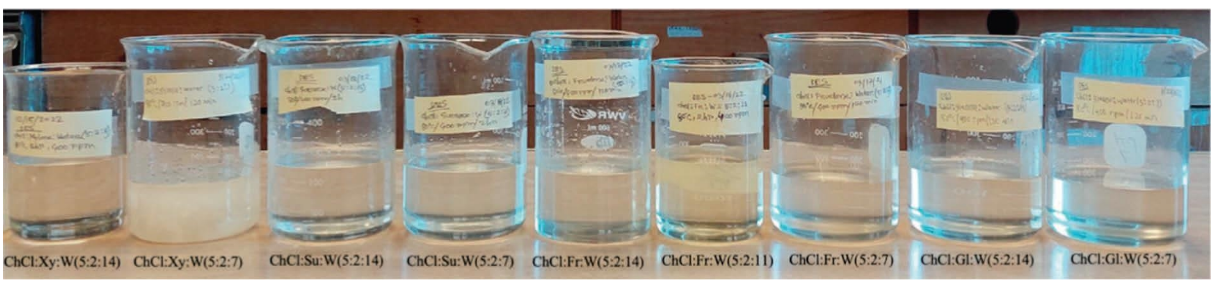


Figure 1: Turbidity of sugar-based NADES. From left to right, ChCl : Xy : W (5 : 2 : 14), ChCl : Xy : W (5 : 2 : 7), ChCl : Su : W (5 : 2:14), ChCl : Su : W (5 : 2 : 7), ChCl : Fr : W (5 : 2 : 14), ChCl : Fr : W (5 : 2 : 11), ChCl : Fr : W (5 : 2 : 7), ChCl : Gl : W (5 : 2 : 14), and ChCl : Gl : W (5 : 2 : 7).

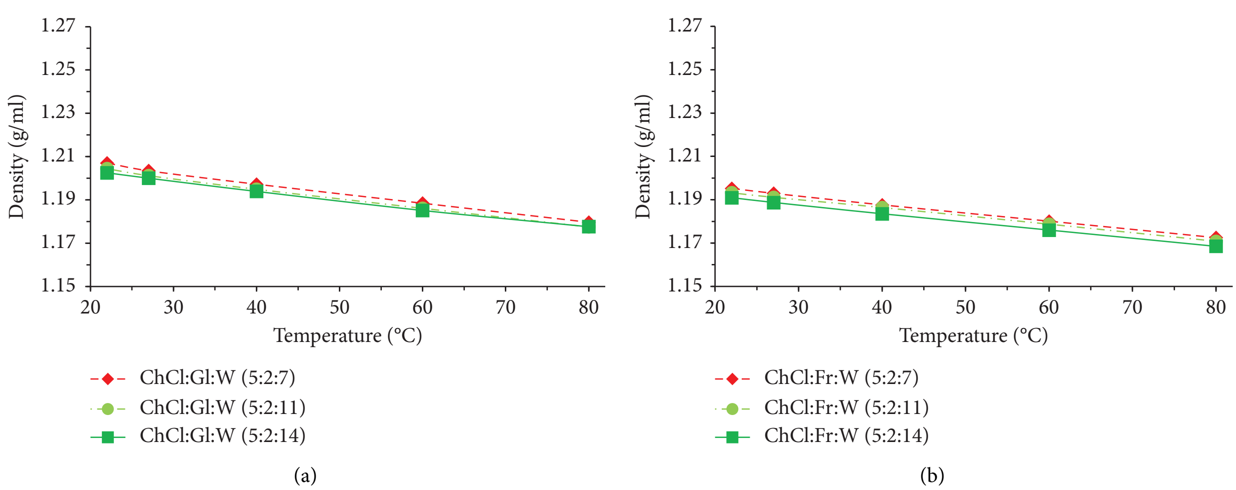


Figure 2: Continued.

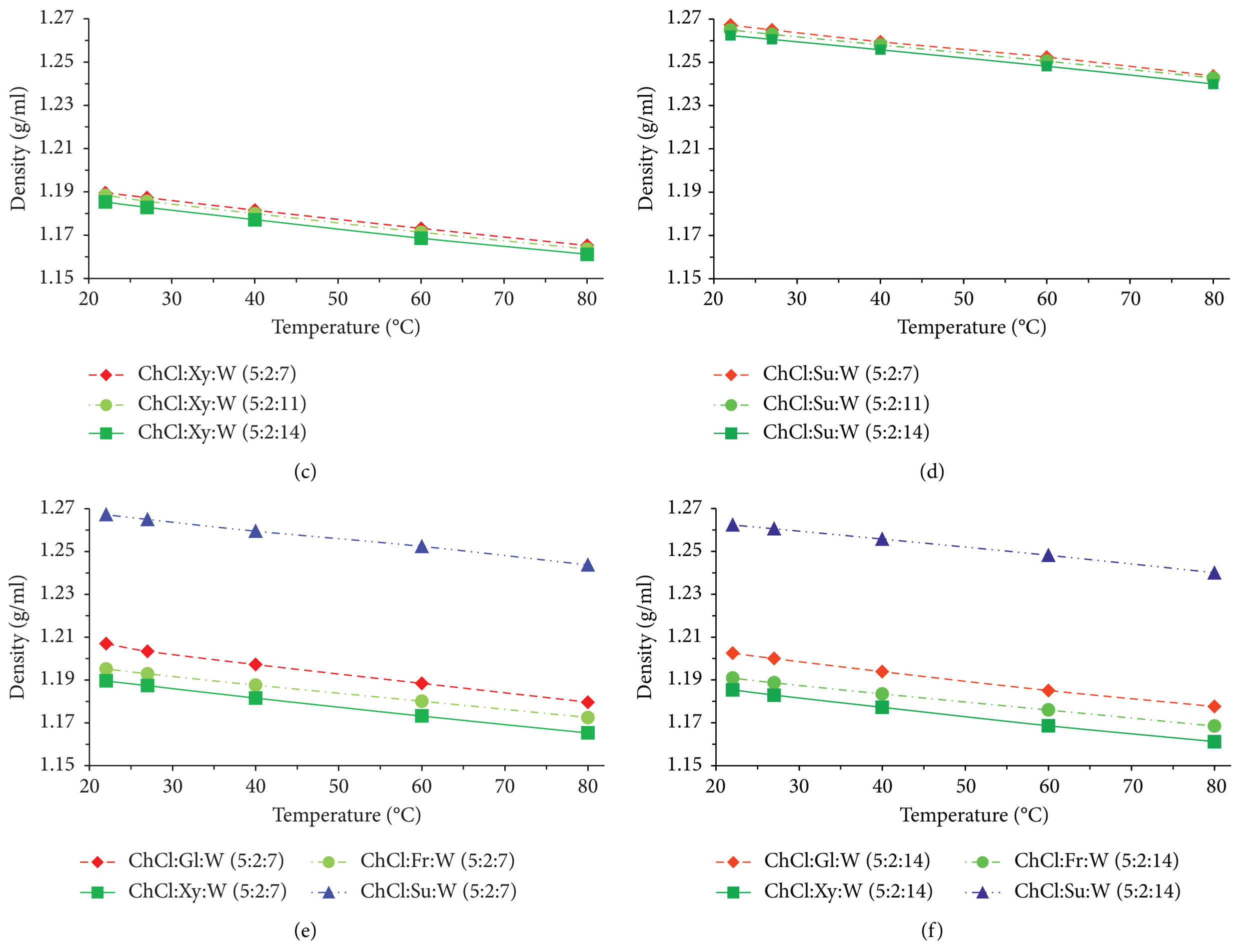


Figure 2: Density profiles of sugar-based NADES: (a) glucose-based NADES, (b) fructose-based NADES, (c) xylose-based NADES, (d) sucrose-based NADES, (e) sugar-based NADES with low water concentrations, and (f) sugar-based NADES with higher water concentrations.

the viscosity of sugar-based NADES is crucial to observe the trends for sugar variation, molar ratio changes, and temperature changes.

Figure 3 shows the viscosity of sugar-based NADES as a function of temperature. Glucose-based NADES has a viscosity of $569.33 \pm 0.33$, $551.33 \pm 1.86$, and $468.33 \pm 2.19$ MPa·s (reported in Supplementary Materials SI Table 2) for ChCl : Gl : W (5 : 2 : 7), ChCl : Gl : W (5 : 2 : 11), and ChCl : Gl : W (5 : 2 : 14), respectively, at 22°C as shown in Figure 3(a). Viscosities decrease exponentially with increasing temperature, eventually reaching $34.83 \pm 0.33$, $33.83 \pm 0.73$, and $33.17 \pm 0.6$ MPa·s, respectively, for the three NADESs at 80°C. The rapid decrease in viscosity with the increasing temperature is due to the induced thermal energy in the systems. Fructose, xylose, and sucrose-based NADES are shown in Figures 3(b)–3(d), respectively. These NADESs follow the same trend of rapidly decreasing viscosity with increasing temperature. In fructose-based NADES, the viscosity is almost the same for the three NADES with different water ratios as shown in Figure 3(b). Sucrose has 8 OH groups, compared to 5 OH groups for glucose and fructose and 4 OH groups for xylose. Among the four sugar-based NADES with the same molar ratio as shown in Figure 3(e), the sucrose-based NADES has the highest viscosity ($2553 \pm 6.01$ MPa·s), while the fructose-based NADES has the lowest viscosity ($386 \pm 1.32$ MPa·s) at 22°C. The reason for highly viscous sugar-based NADES is the stronger hydrogen bonding due to the higher number of OH functional groups and higher molecular weight for sucrose than the other sugars. However, the viscosity at 80°C for three of the sugar-based NADES (glucose, fructose, and xylose) is relatively similar, varying within a narrow range of $34.83 \pm 33$ MPa·s to $29.33 \pm 0.17$ MPa·s. In contrast, sucrose-based NADES varies from $96.33 \pm 0.17$ to $73 \pm 0.29$ MPa·s. The viscosity when the water-mole ratio has been increased from 7 to 14 for the same four sugar-based NADES is shown in Figure 3(f). The viscosity of sugar-based NADES is high at ambient temperature. Except for sucrose-based NADES, they still could be potential candidates for various processes to replace more hazardous solvents, particularly at higher processing temperatures. However, the thermal stability of these NADESs and the potential for higher water content to act as an antisolvent to fractionate biomass must be considered, depending on the application.

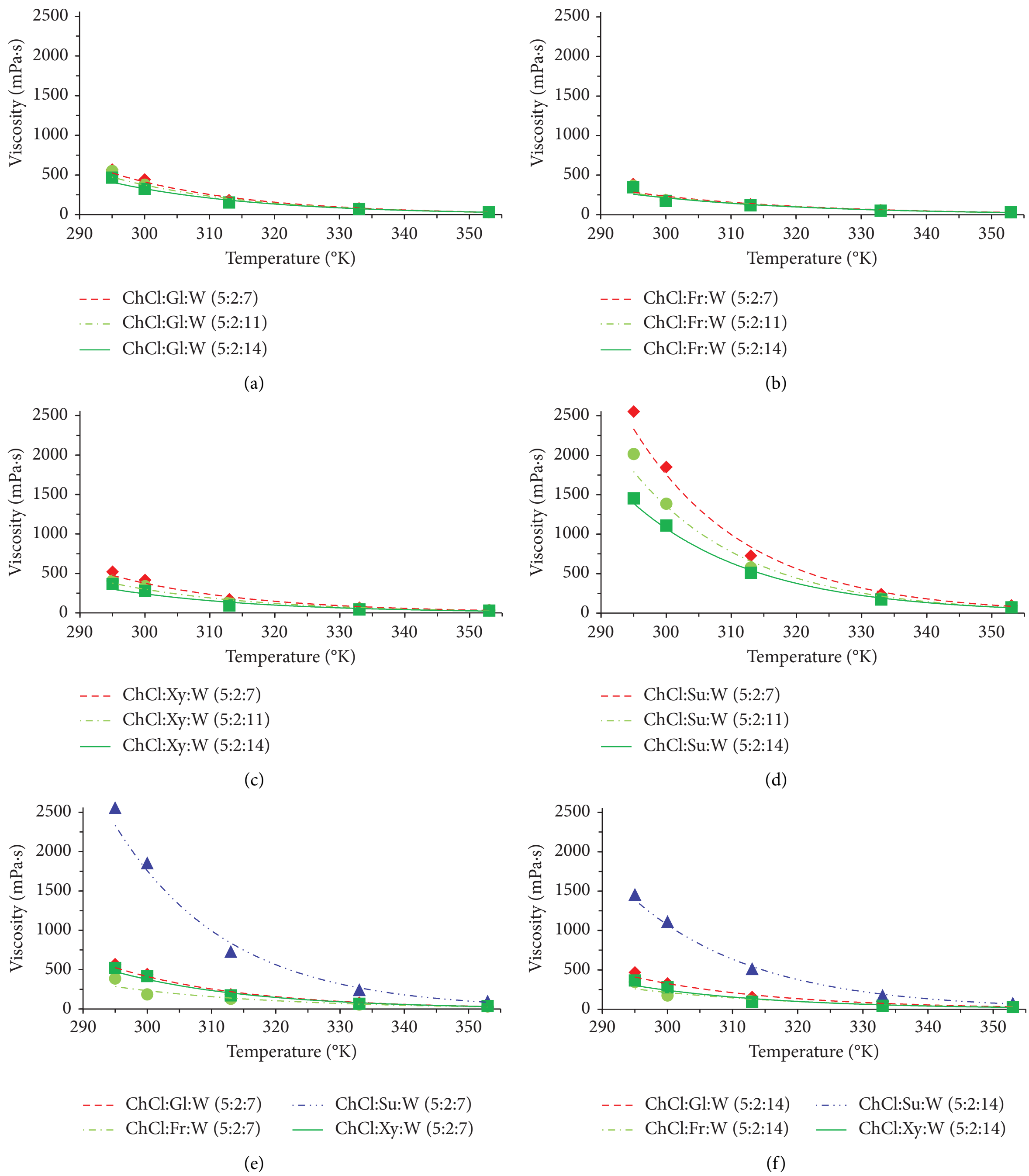


Figure 3: Viscosity profile of sugar-based NADES: (a) glucose-based NADES, (b) fructose-based NADES, (c) xylose-based NADES, (d) sucrose-based NADES, (e) sugar-based NADES with low water concentrations, and (f) sugar-based NADES with high water concentrations.

The strong temperature-dependence viscosity of sugar-based NADES can be best fitted with the Arrhenius model [35, 36] and the Vogel–Fulcher–Tammann (VFT) model [37]. However, this study has used the Arrhenius model, which is described as follows:

$$\mu = \mu o e^{[-E\mu/\mathrm{RT}]}, \qquad (1)$$

where $\mu$ is the viscosity, $\mu_o$ is a pre-exponential constant, $E_\mu$ is the activation energy, $R$ is the gas constant, and $T$ is the temperature in Kelvin. The values of $\mu_o$ and $E_\mu$ are given in Table 3.

For the 5 OH group glucose-based NADES, $E_\mu$, the activation energy for movement, appeared to show a maximum viscosity at the water-mole ratio of 5 : 2 : 11. This

Table 3: Viscosity-temperature model parameter.

| NADES | $\mu_o$ (mPa·s) | $E_\mu/R$ ($K^{-1}$) |
|---|---|---|
| ChCl : Gl : W (5 : 2 : 7) | $7.07\times10^{-6}$ | 5374.17 |
| ChCl : Gl : W (5 : 2 : 11) | $1.32\times10^{-6}$ | 5851.92 |
| ChCl : Gl : W (5 : 2 : 14) | $6.02\times10^{-6}$ | 5353.79 |
| ChCl : Fr : W (5 : 2 : 7) | $3.91\times10^{-6}$ | 6081.52 |
| ChCl : Fr : W (5 : 2 : 11) | $4.85\times10^{-6}$ | 6003.12 |
| ChCl : Fr : W (5 : 2 : 14) | $9.09\times10^{-6}$ | 5801.77 |
| ChCl : Xy : W (5 : 2 : 7) | $7.69\times10^{-6}$ | 5325.64 |
| ChCl : Xy : W (5 : 2 : 11) | $1.20\times10^{-6}$ | 5125.74 |
| ChCl : Xy : W (5 : 2 : 14) | $5.37\times10^{-6}$ | 6004.16 |
| ChCl : Su : W (5 : 2 : 7) | $1.78\times10^{-6}$ | 6222.19 |
| ChCl : Su : W (5 : 2 : 11) | $8.71\times10^{-6}$ | 6359.58 |
| ChCl : Su : W (5 : 2 : 14) | $1.97\times10^{-6}$ | 5346.87 |

suggests that a stable supramolecular structure can remain for these NADESs and that more hydrogen bonding can occur with this water-mole ratio. A similar trend is found for the disaccharide containing NADES, ChCl : Su : W. For these NADESs, higher than 11 water-mole ratios appear to reduce the hydrogen bonding. For the 5 OH group fructose-based NADES, a 5 : 2 : 11 mole ratio appeared to have a similar $E_\mu$ to the 5 : 2 : 7 mole ratio suggesting that similar numbers/strengths of hydrogen bonds with water are possible in this arrangement. Once the 5 : 2 : 14 mole ratio is reached for the fructose-based NADES, $E_\mu$ decreases, suggesting that the superlattices are partially disrupted. These findings suggest that higher than 5 : 2 : 14 mole ratios may not be useful if the essential nature of these NADESs is to be attained. The 4 OH xylose-based NADES showed a minimum in $E_\mu$ at a 5 : 2 : 11 mole ratio. This suggests that the arrangement of water molecules is less optimal for hydrogen bonding for the 5 : 2 : 11 mole ratio. The highest xylose-based NADES $E_\mu$ is found for the 5 : 2 : 14 mole ratio, suggesting that more hydrogen bonds can form in this ratio. For practical industrial use, different water ratios may thus be optimal for different NADES. Future density functional theory (DFT) molecular studies may be able to clarify these observations.

*3.4. Ionic Conductivity.* The ionic conductivity of sugar-based NADES depends on the number of ions, the interaction and bonding strength between cation and anion, and the mobility of ions in the solvents. The main ions expected for the NADES investigated would be chloride ions from the ChCl. Generally, highly viscous solvents, even with a high concentration of ions, show low ionic conductivity because of their resistance to flow. Moreover, ionic conductivity changes with temperature because gaining extra energy allows the solvent to improve the flow of ions. The ionic conductivity of sugar-based NADES at low temperatures (22°C to 80°C) was lower than that of high-temperature (577°C to 927°C) molten salts, such as LiCl, NaCl, KCl, and their mixtures [38].

The ionic conductivity of sugar-based NADES increases with increasing temperature as shown in Figure 4(a). Increasing conductivity with temperature does not mean that the number of ions increases but the mobility of ions increases with additional thermal energy. The ionic conductivity of sugar-based NADESs is in the order of 0.6 mS/cm–8 mS/cm, which is similar to the ionic conductivity of some imidazolium-based ionic liquids [39–41].

Figure 4(a) shows the conductivity of the glucose-based NADES that increased with increasing temperature, which varied from 1293 ± 4.62 $\mu$S/cm at 22°C to 3573.33 ± 56.08 $\mu$S/cm at 80°C for ChCl : Gl : W (5 : 2 : 7) (reported in Supplementary Materials SI Table 3). This conductivity trend was similar for higher water-mole ratios but with increased conductivity. Fructose-based NADES and xylose-based NADES gave a higher ionic conductivity that varied from 2280.67 ± 1.20 and 2392.22 ± 6.39 $\mu$S/cm at 22°C to 6010 ± 20.82 and 6230 ± 40.41 $\mu$S/cm at 80°C as shown in Figures 4(b) and 4(c), respectively. The ionic conductivity of sugar-based NADES increased with higher water-mole ratios. This increase in ionic conductivity relates to the finding for lower viscosity with higher water-mole ratios, which allow the ions to slip past each other more easily [41]. The sucrose-based NADES has the lowest ionic conductivity because of its high viscosity, as shown in Figure 4(c). Among four different sugar-based NADESs with the same water molar ratio of 7, the xylose-based NADES shows the highest conductivity at ambient temperature, as shown in Figure 4(e). This finding may relate to its lower molecular mass. The four NADESs with a water molar ratio of 14 follow the same trend but with an increased ionic conductivity value, as shown in Figures 4(f) and 4(e). Ionic conductivity is vital for electrochemical applications, and the values found for these NADESs suggest they could be investigated for such applications [42]. The conductivity of the glucose-based NADES, as shown in Figure 4(a), increased with increasing temperature, which varied from 1293 ± 4.62 $\mu$S/cm at 22°C to 3573.33 ± 56.08 $\mu$S/cm at 80°C for a water-mole ratio of 7 (in Supplementary Materials SI Table 3). This conductivity trend was similar for higher water-mole ratios. Fructose-based NADES, as shown in Figure 4(b), and xylose-based NADES, as shown in Figure 4(c), gave a higher ionic conductivity that varied from 2280.67 ± 1.20 and 2392.22 ± 6.39 $\mu$S/cm at 22°C to 6010 ± 20.82 and 6230 ± 40.41 $\mu$S/cm at 80°C, respectively. The ionic conductivity of sugar-based NADES increased with higher water-mole ratios. This relates to the finding for lower viscosity with higher water-mole ratios, which allow

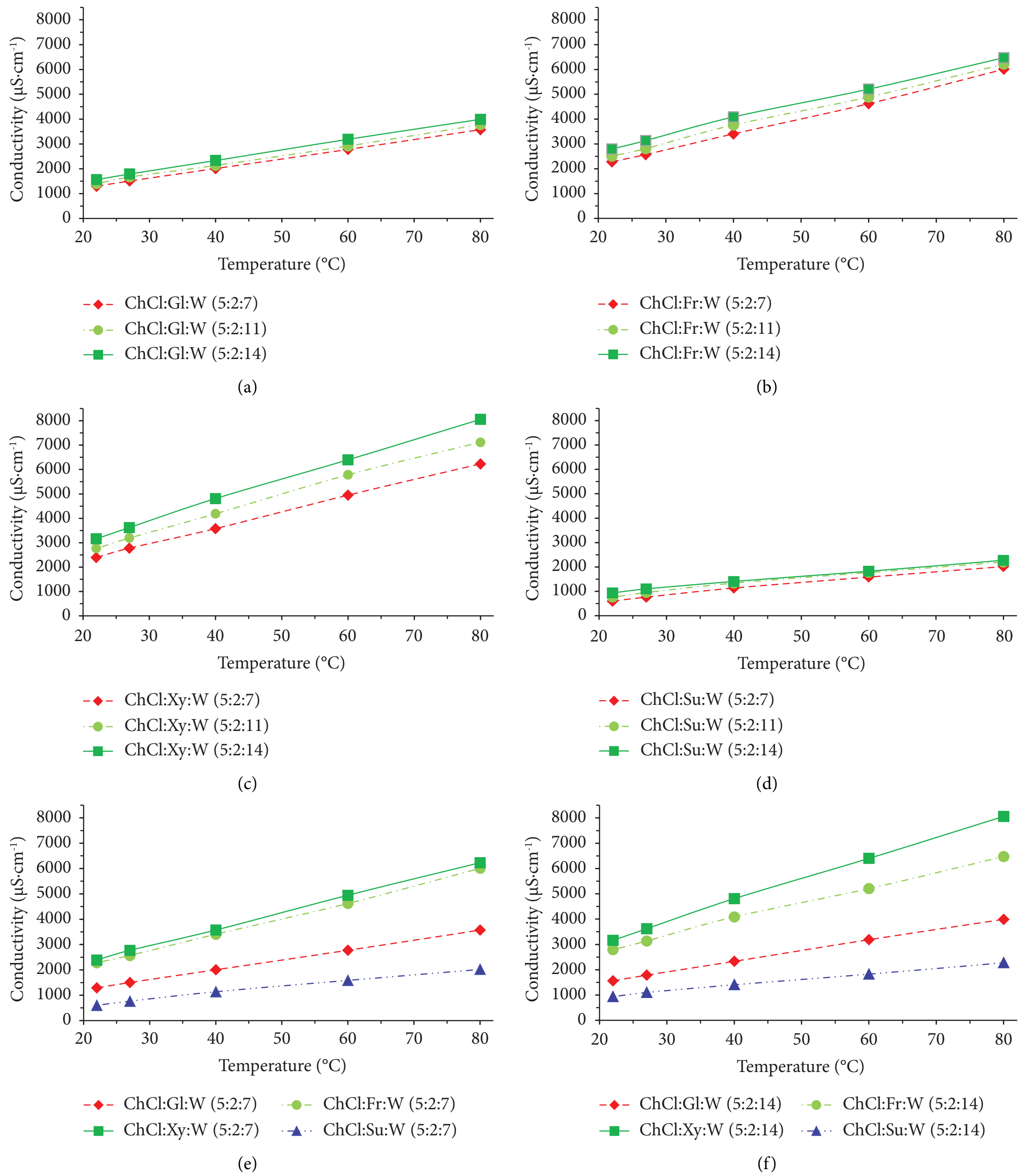


FIGURE 4: Conductivity profile of sugar-based NADES: (a) glucose-based NADES, (b) fructose-based NADES, (c) xylose-based NADES, (d) sucrose-based NADES, (e) sugar-based NADES with low water concentrations, and (f) sugar-based NADES with high water concentrations.

the ions to slip past each other more easily [41]. The sucrose-based NADES, as shown in Figure 4(c), has the lowest ionic conductivity because of its high viscosity. Among the four different sugar-based NADES with the same water-molar ratio of 7, as shown in Figure 4(e), the xylose-based NADES shows the highest conductivity at ambient temperature. This finding may relate to its lower molecular mass. The four NADES with a water-molar ratio of 14, as shown in Figure 4(f), follow the same trend as Figure 4(e) but with an increased ionic conductivity value. Ionic conductivity is important for electrochemical applications, and the values found for these NADESs suggest that they could be investigated for such applications [42].

*3.5. pH.* The pH of sugar-based NADES is slightly acidic, varying from 3 to 5, and is almost independent of temperature, as shown in Figure 5. The slight acidity in sugar-based NADES is likely due to the presence of choline chloride, which is a weak acid, and OH groups in the sugar

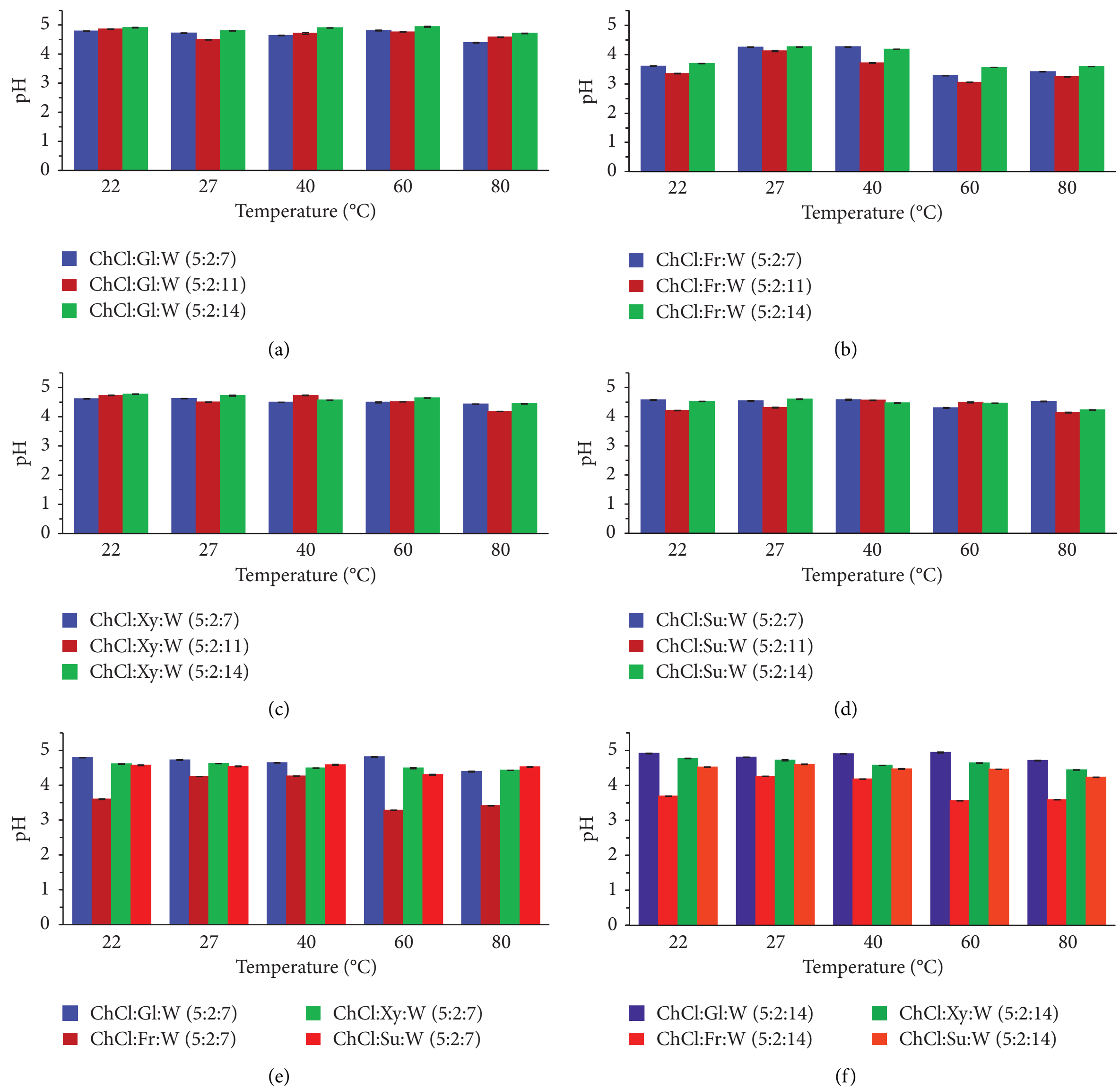


Figure 5: pH profile of sugar-based NADES: (a) glucose-based NADES, (b) fructose-based NADES, (c) xylose-based NADES, (d) sucrose-based NADES, (e) sugar-based NADES with low water concentrations, and (f) sugar-based NADES with high water concentrations.

and the water [43]. In glucose-based NADES, the pH of glucose-based NADES with changing water-mole ratios of 7, 11, and 14 varied from 4.39 to 4.94 (reported in Supplementary Materials SI Table 4), and the temperature effect on pH value is negligible, as shown in Figure 5(a). Among the four sugar-based NADES, fructose-based NADES is more acidic than others and slightly temperature dependent, that is, higher at 22 and 40°C, as shown in Figure 5(b).

Xylose-based NADES and sucrose-based NADES follow the same trend as glucose-based NADES, as shown in Figures 5(c) and 5(d), respectively. The comparison of different sugar-based NADESs with the same molar ratio indicates that glucose-based NADESs are slightly acidic and fructose-based NADES are more acidic than the other two, as shown in Figure 5(c). This agrees with the finding that a higher fructose content in NADES led to a higher acidity [44]. Choline chloride has also been reported to be slightly acidic [43]. The pH of these NADESs is not likely to adversely affect processes that are conducted at neutral pH.

*3.6. Contact Angle.* The contact angle, the angle between the measuring substrate under the droplet and the tangent of the liquid surface, increases with higher surface tension. The higher the contact angle, the higher the surface tension. Surface tension is a measure of the energy required to increase the surface area of a material. It is related to the tendency of a material to keep the smallest surface area possible. Its effects are most prevalent in liquids due to intermolecular interactions among molecules. If the glass is

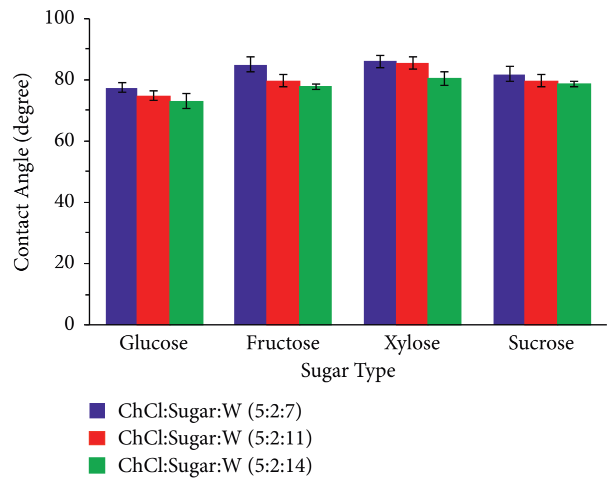


FIGURE 6: Contact angle profile of sugar-based NADES.

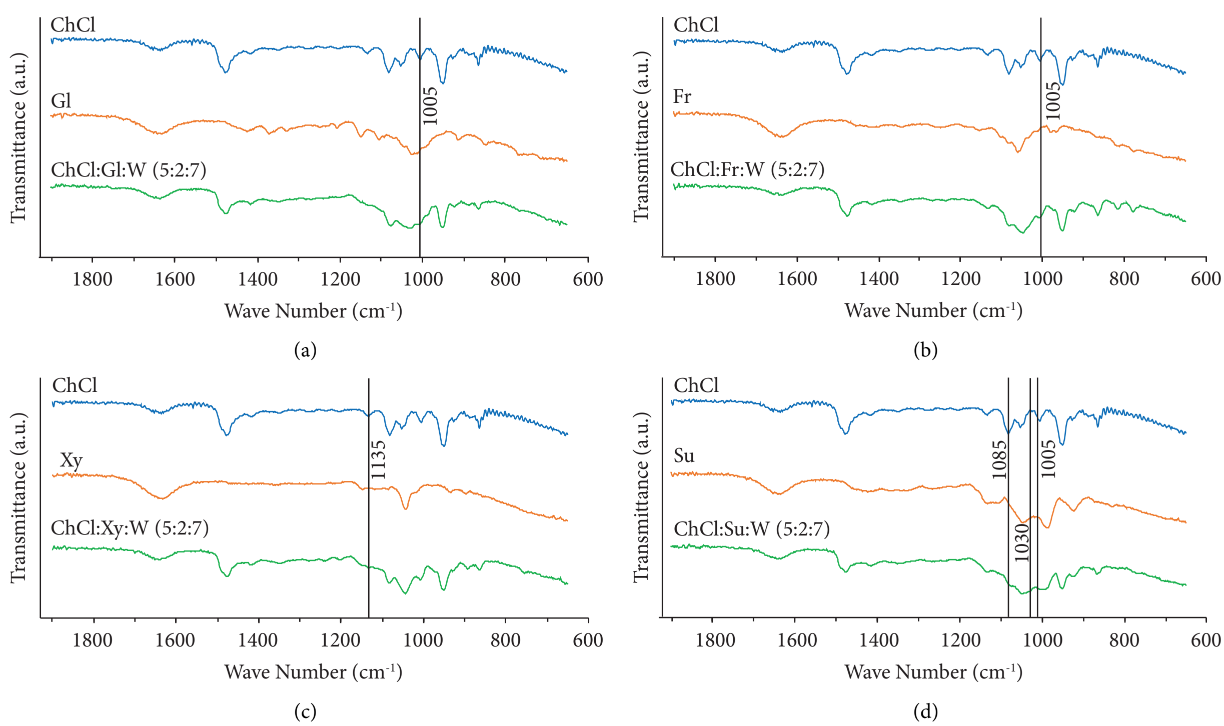


FIGURE 7: FTIR profile of sugar-based NADES: (a) glucose-based NADES, (b) fructose-based NADES, (c) xylose-based NADES, and (d) sucrose-based NADES.

the solid substrate, as in this work, hydroxyl groups will be the outer molecular layer [45]. These groups will interact with the NADES components to allow a slightly lower energy state, thus allowing for some wettability.

Figure 6 shows that the contact angles for sugar-based NADES were high but still less than 90 degrees, varying from 73° to 86°. These high contact angles mean that sugar-based NADESs have a high surface tension but are wettable on a solid surface. The xylose-based NADES had the highest contact angle at a molar ratio of 5 : 2 : 7 (ChCl : Xy : W) in ambient temperature, with the contact angle decreasing with added water. Choline chloride, a quaternary ammonium salt, can increase surface tension.

Compared to the other NADES, glucose-based NADES had a lower contact angle that decreased with a higher water molar ratio, suggesting that the surface tension of glucose-based NADES could be slightly lower than the others. Sucrose-based NADES followed the same trend as glucose and fructose-based NADES. The contact angle of DI water on the same substrate was measured to be 49.76°, which is lower than the sugar-based NADES; therefore, sugar-based NADES have a slightly lower wettability and higher surface tension than water. This property of the NADES investigated will allow for less "stickiness" to high-energy surfaces, such as the glass or metal used in industrial processes.

*3.7. Fourier Transform Infrared Spectroscopy (FTIR).* FTIR is a valuable tool to obtain accurate information about the structure and hydrogen bonding of sugar-based NADES to elicit the mystery of the unique properties of these solvents. NADES are known to form by hydrogen bonding [32]. Figure 7 shows the FTIR fingerprint region for ChCl, sugars, and the 5 : 2 : 7 (ChCl : sugar : water) molar ratio NADES. For the glucose-, fructose-, and sucrose-based NADES, the ChCl C-O vibration near 1005 $cm^{-1}$ disappears in the NADES or has moved to a slightly higher wavenumber. For the xylose-based NADES, the C-C vibration at 1135 $cm^{-1}$ for both ChCl and xylose appears to be shifted to a slightly higher wavenumber [46, 47].

For sucrose-based NADES, the C-O ChCl vibration expected near 1005 $cm^{-1}$ appears to have shifted to a higher wavenumber. A C-O ChCl vibration expected near 1085 $cm^{-1}$ appears to be shifted to a slightly lower wavenumber. Except for the vibrations discussed above, the NADES investigated appeared to have a combination of the components' spectra.

## 4. Conclusions

Physiochemical properties of sugar-based NADES, density, viscosity, ionic conductivity, pH, contact angle, and FTIR, were performed and reported in this study. These properties of sugar-based NADES depend on the interaction of hydrogen bonds between the Cl anion in ChCl and the OH groups in sugar. The number of OH functional groups in the given sugar greatly influences the properties measured, particularly viscosity and ionic conductivity. The pH of sugar-based NADES is slightly acidic to almost neutral, which makes them a potential alternative for many industrial processes. Nevertheless, depending on the application, other factors must be considered, such as the thermal stability of these NADESs and the higher water content acting to reduce process efficiency. The higher ionic conductivity of sugar-based NADES, like that of ionic liquids, makes them a potential candidate for electrochemical applications. With the addition of water or heating, the viscosity of sugar-based NADES could be tuned. The shifts in FTIR spectra for these NADESs compared to their components indicate that it is possible that a supermolecular structure may have been formed.

## Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

## Conflicts of Interest

The authors declare that they have no conflicts of interest regarding the publication of this article.

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## Supplementary Materials

The supplementary materials include tables of the data found. Supplementary Materials SI Table 1 has the densities in g/ml of the sugar-based NADES investigated at five different temperatures. Supplementary Materials SI Table 2 has the viscosities in mPa·s of the sugar-based NADES investigated at five different temperatures. Supplementary Materials SI Table 3 has the conductivities in $\mu$S/cm of the sugar-based NADES investigated at five different temperatures. Supplementary Materials SI Table 4 has the pH of sugar-based NADES investigated at five different temperatures. (*Supplementary Materials*)

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