Aqueous Mixture Viscosities of Phenolic Deep Eutectic Solvents

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Abstract

In this study, the aqueous mixture viscosities of two phenolic DESs, consisting of (1 ChCl: 3 phenol) and (1 ChCl: 4 phenol), were measured at atmospheric pressure over the temperature range of 293.15 - 333.15 K. According to the measured data, the values of viscosity deviations for the investigated aqueous systems were calculated to indicate deviating viscosity behavior with respect to ideality. Both aqueous systems showed negative viscosity deviations over the entire composition range and at all of the investigated temperatures. The Redlich-Kister model was applied to estimate the viscosity deviations of both aqueous systems at different compositions and temperatures, while the viscosity behavior, itself, was modeled by different literature models, consisting of the Grunberg-Nissan, Jouyban-Acree, McAllister, Preferential Solvation, and an Arrhenius-like viscosity model. All of the models presented satisfactory agreement, however the Preferential Solvation and the Jouyban-Acree models succeeded to achieve more reliable results as compared to the others. In addition to the mixture viscosity estimation models, the Jones-Dole viscosity model was applied to both of the aqueous systems to suggest the interactions in the mixture. By calculating and analyzing the values of the *B*-coefficients of this model, possibly stronger interactions among the DESs and water molecules in the mixture were suggested, as compared to the self-species interactions.

Keywords: DES; choline chloride; water; eutectic mixture; physical property; transport property; Excess viscosity, viscosity deviation; thermodynamic modeling.

1. Introduction

The Deep Eutectic Solvent (DES) is a recently-introduced type of green solvent, proposed by Abbott et al. at 2003 [1]. Because of some favorable environmental properties, such as biodegradability, sustainability, negligible toxicity, and very low vapor pressure, DESs are highly interesting for utilization in various industrial fields. However, in addition to the above-mentioned properties, which may be in common to those of most other green solvents, DESs have other very unique properties such as being "task-designable", and being cheap [2]. Low cost is quite an advantage for DESs, making them preferable for use in the industries over other green solvents, such as Ionic Liquids (ILs). Additionally, being a designer solvent is a most important feature of a DES, whereby researchers have the freedom to choose the most suitable hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD), and even their molar ratios, to achieve the physical properties or solvation power of their will, and in this manner, "design" the most convenient DES according to their aims. While this feature is extremely attractive for researchers, it also entails the necessity of extensive investigations on the molecular interactions and the mechanisms of hydrogen bond establishment in various DESs. The all-encompassing knowledge of molecular interactions in DES systems can then allow the prediction of the behavior of the fluid and facilitate suggestions on the best hydrogen bond acceptor - hydrogen bond donor couple for achieving a DES with the desired properties.

Various routes can be taken to obtain information on the molecular interactions within DES systems. Experimental characterization procedures, such as NMR, FTIR, and spectroscopy [3], molecular simulations [4], and solution property investigations [5] are the most common methods utilized for DESs. Amongst these methods, solution property investigation is perhaps the easiest, least expensive, and least time-consuming method which can provide initial clues

on molecular interactions within DES systems. This approach actually involves the experimental measurement of important physical properties such as density and viscosity of DES mixtures with other solvents, such as water or alcohols. Then, by comparing the measured mixture properties with the corresponding neat state properties, and also using thermodynamic relations and models, some important information about the molecular interactions between the DES and the investigated solvents can be obtained [6-9].

Water is most obviously the first candidate to be considered with DESs, making the aqueous mixtures to be studied for physical property measurements. Most of the published studies in literature have studied only densities and the volumetric behavior of aqueous DES mixtures [10-16]. Only a few limited studies have investigated viscosities of aqueous DES mixtures, consisting of Reline (1 ChCl: 2 urea) [17, 18], Glyceline (1 ChCl: 2 glycerol) [19, 20], Glucoline (2 ChCl: 1 glucose) [21] and the DESs composed of sodium halides: ethylene glycols [22]. It is obvious that the number of such studies, in comparison to numerous DESs established so far, is quite small. This shows the necessity to expand the knowledge of molecular interactions to a greater number of DESs by viscosity investigations on their aqueous solutions.

Phenolic DESs are a category of DESs which are prepared by using phenol as the hydrogen bond donor (HBD). They were introduced by Guo et al. in 2013 [23] by proposing choline chloride + phenol mixtures at five different molar compositions (1:2 - 1:6). After their introduction, this category of phenolic DESs, at different molar ratios, was considered for the various applications of CO_2 capture [24,25], liquid- liquid extraction, [26,27] and utilization in solar cells [28]. Up to now, only two studies have been devoted to investigating the physical properties of this family of DESs in mixtures with other components. In 2019, Gajardo-Parra et al. [29] measured the densities and viscosities of mixtures of the ChCl : phenol (1:2) DES

with 1-butanol over a temperature range of 293.15 to 333.15 K. They reported negative excess volume and viscosity deviation for the investigated mixtures. In 2021, Haghbakhsh et al. [5], carried out an investigation on the volumetric properties of aqueous mixtures of ChCl + phenol (1:4) over the temperature range of 293.15 - 333.15 K. They also reported negative excess volumes for the investigated mixtures.

Therefore, in this study, in order to expand the viscosity databank, as well as our knowledge on the molecular interactions of phenolic DESs, experimental viscosity measurements were carried out on aqueous mixtures of two phenolic DESs, namely ChCl + phenol (1:3) and ChCl + phenol (1:4) over the temperature range of 293.15-333.15 K. The achieved results were analyzed regarding the molecular interactions between the DES and water molecules. Also, according to the measured experimental data, the four different models of Grunberg-Nissan [30], Jouyban-Acree [31], McAllister [32] and Preferential Solvation [33,34] were developed to have estimation tools for calculating the viscosity at any desired composition.

2. Investigated compounds

Choline chloride and phenol were used for the preparation of the desired DESs. Also, water with high purity was purchased to minimize the effects of contaminants on the experimental results. Among the used chemicals, we have dried choline chloride to minimize any adsorbed moisture from air. For this purpose, choline chloride was kept in a vacuum oven for 24 hours at 60 ^{o}C. Table 1 reports the information on the chemicals used in this study.

Table 1. Initial mass purity, vendor, and purification method of the chemicals used in this study.

Chemical name	CAS number	IUPAC name	Source	Initial mass fraction purity	Purification method
Choline chloride	67-48-1	2-hydroxyethyl (trimethyl) azanium chloride	Acros Organics	99%	Dried 24 hours in oven vacuum
Phenol	108-95-2	benzenol	Merck	99%	No further purification
Water	7732-18-5	water	Merck	99.9%	No further purification

3. Experimental

a. DES preparation

The two molar ratios of 1:3 and 1:4 were considered for the DESs in this study. Here forth, 1 choline chloride + 3 phenol will be termed as DES1, while 1 choline chloride + 4 phenol will be called DES2. The required amounts of choline chloride and phenol were weighed by a Shimadzu UW1020H digital balance, with 0.001 g uncertainty, and poured into closed-cap vials. For better stirring, the sealed vials were placed in a shaker-incubator for 24 hours at the temperature of 30 ^{o}C. Then, to remove the absorbed moisture during DESs preparation, the vials were placed in a vacuum oven at the temperature of 50 ^{o}C for 24 hours. In this way, two homogenous transparent liquid phases of DESs were prepared. The water contents of these samples were measured by a Metrohm 787 KF Titrino Karl-Fischer titrator, resulting in 0.00655 and 0.00610 in mass fraction of water for DES1 and DES2, respectively.

b. Sample preparation

In this study two aqueous systems of DES1 and DES2 were considered. Nine different mixture samples for each of the systems of DES1 + water and DES2 + water were considered to cover the entire mixture concentration ranges.

c. *Viscosity measurement*

The viscosities of the nine samples, prepared as mentioned above for each the aqueous DES1 and DES2 systems, were measured with an Anton Paar SVM^{TM} 3000 viscometer. The viscometer was calibrated using the Anton Paar viscosity set of standard oils. The device had an accuracy of ±0.001 g/cm for density. The relative reproducibility uncertainty of viscosity was 0.35% according to the viscometer manufacturer, while the standard uncertainties of temperature and pressure measurements were 0.02 K and 5 kPa, respectively. The viscosities were measured at atmospheric pressure within the temperature range of 293.15 - 333.15 K, with temperature intervals of 10 K. Additionally, the viscosities of DES1, DES2, and water were measured within the same temperate range.

4. Correlations

a. *Arrhenius model*

The Arrhenius viscosity model is the best-known model to estimate the viscosities of fluids. This model is presented as Equation 1 [35].

$$\eta = \eta_0 \exp(\frac{-E_a}{RT}) \quad (1)$$

According to its mathematical expression, the Arrhenius model considers only the effects of temperature and does not involve the effect of concentration for mixtures. Therefore, this model should be optimized at each individual composition based on the adjustable parameters of η_0 and E_a, which denote the reference viscosity and activation energy parameter, respectively,

while *R* is the universal gas. For this purpose, Equation 2 is used as the objective function for optimization,

$$Ob.Fun = \sum_{i}^{n} \frac{\left| \eta_{mix,i}^{exp.} - \eta_{mix,i}^{cal.} \right|}{\eta_{mix,i}^{exp.}} \quad (2)$$

where $\eta_{mix,i}^{cal.}$ and $\eta_{mix,i}^{exp.}$ are the calculated mixture viscosity by the model and experimental mixture viscosity, respectively and *n* is the number of investigated data.

b. Grunberg-Nissan model

Grunberg and Nissan proposed a well-known viscosity model for binary mixtures [30],

$$\ln(\eta_{mix}) = x_i \ln(\eta_i) + x_j \ln(\eta_j) + x_i x_j G_{ij} \quad (3)$$

where η_i and η_j are the dynamic viscosities of pure components *i* and *j*, respectively, and η_{mix} is the mixture dynamic viscosity. x_i and x_j are mole fractions of components *i* and *j* in the mixture, respectively, and G_{ij} is the binary interaction parameter of the model which is temperature dependent and is adjusted at each temperature based on the experimental data according to Equation 2 as the objective function. However, in order to increase the predictive ability of the model, it is recommended to define a temperature-dependent relation for G_{ij}, as in Equation 4. In this way, instead of optimizing G_{ij} at each temperature, the parameters of G_1 and G_2 are optimized for the entire temperature range.

$$G_{ij} = G_1 + G_2 T \quad (4)$$

c. Jouyban-Acree model

The Jouyban-Acree viscosity model is another simple and well-known viscosity model used for mixtures. The mathematical expression of this model for binary liquid mixtures is given by Equation 5 [31],

$$\ln(\eta_{mix}) = x_i \ln(\eta_i) + x_j \ln(\eta_j) + A_0\left(\frac{x_i x_j}{T}\right) + A_1\left(\frac{x_i x_j (x_i - x_j)}{T}\right) + A_2\left(\frac{x_i x_j (x_i - x_j)^2}{T}\right) \quad (5)$$

where η_i and η_j are the dynamic viscosities of the pure molecular solvent and DES, respectively. The interactions of the molecular solvent and DES are considered by the adjustable parameters of A_0, A_1 and A_2, which are optimized according to experimental data and Equation 2 as the objective function.

d. McAllister model

The McAllister viscosity model is a reliable model which considers the activation energy of molecular motion in the mixture. The four-body form of this model for a binary mixture is presented as Equation 6 [32, 34],

$$\ln(\eta_{mix}) = x_i^4 \ln(\eta_i) + 4x_i^3 x_j \ln(\eta_{iiij}) + 6x_1^2 x_2^2 \ln(\eta_{1122}) + 4x_i x_j^3 \ln(\eta_{jjji}) + \mathrm{x}_j^4 \ln(\eta_j) - \ln(\mathrm{x}_i + \mathrm{x}_j \frac{Mw_j}{Mw_i})$$
$$+4x_i^3 x_j \ln(\frac{(3+\frac{Mw_j}{Mw_i})}{4}) + 6x_i^2 x_j^2 \ln(\frac{(1+\frac{Mw_j}{Mw_i})}{2}) + 4x_i x_j^3 \ln(\frac{(1+\frac{3Mw_j}{Mw_i})}{4}) + x_j^4 \ln(\frac{Mw_j}{Mw_i}) \quad (6)$$

where η_i and η_j are the dynamic viscosities of the pure molecular solvent and DES, respectively, and Mw_i and Mw_j are the molecular weights of the molecular solvent and DES, respectively. The interaction effects between the molecular solvent and DES are considered by

the three temperature-dependent parameters of η_{iiij}, η_{iijj} and η_{jjji}, which are optimized according to the experimental data for each temperature set. Thus, in order to avoid the optimization process for each temperature separately, and since these three parameters are temperature-dependent, one can define temperature-dependent relations for each, in the form of Equations 7-9.

$$\eta_{iiij} = K_1 + K_2 T \tag{7}$$

$$\eta_{iijj} = K_3 + K_4 T \tag{8}$$

$$\eta_{jjji} = K_5 + K_6 T \tag{9}$$

According to these equations, instead of optimization at each temperature, it is required to optimize parameters K_1, K_2, …, K_6 based on experimental data and Equation 2 as the objective function.

e. Preferential Solvation (PS) model

The preferential solvation model introduces a definition for mutual complex molecules or associated molecules which are created by the interactions of molecules *i* and *j* in the mixture. These mutual complex molecules (*ij* or *ii* or *jj*) are formed from interactions of the HBA (S_i) and HBD (S_j) molecules because of the strong hydrogen bonds established in the mixture. Equations 10-12 present the solvation equations for possible interactions between the HBA (S_i) and HBD (S_j) molecules in the mixture [34],

$$(S_i^L)_m + mS_j \xleftrightarrow{g_{j/i}} (S_j^L)_m + mS_i \tag{10}$$

$$(S_i^L)_m + m/2\, S_j \xleftrightarrow{g_{ij/i}} (S_{ij}^L)_m + m/2\, S_i \quad (11)$$

$$(S_i^L)_m + m/2\, S_{jj} \xleftrightarrow{g_{jj/i}} (S_{jj}^L)_m + m/2\, S_i \quad (12)$$

where superscript L refers to local molecules, m is the average number of molecules in a mutual complex molecule, and $g_{j/i}$, $g_{ij/i}$ and $g_{jj/i}$ are the preferential solvation adjustable parameters. The general form of the Preferential Solvation theory is shown by Equation 13.

$$\eta_{mix} = \sum_{i=1}^{N} x_i^L \eta_i^0 + \sum_{i=1}^{N}\sum_{j=1}^{N} x_{ij}^L \eta_{ij} \quad (13)$$

η_{mix}, η_i^0 and η_{ij} are the mixture, pure compound, and mutual complex dynamic viscosities, respectively. By expanding Equation 13, various interactions in the mixture are considered. However, according to the nature and type of the investigated molecules, some of the interactions are dominant and some have minor effects. Therefore, the less important interactions are neglected from the general form. For a binary liquid mixture of a molecular solvent (*i=1*) and a DES or an ionic liquid (*j=2*), the self-association interactions of the DES or ionic liquid (*22*) have the dominant effects in this theory, thus Equation 13 is simplified to Equation 14 [34].

$$\eta_{mix} = x_1^L \eta_1^0 + x_2^L \eta_2^0 + x_{22}^L \eta_{22} \quad (14)$$

x_1^L, x_2^L and x_{22}^L are the local compositions, which are calculated based on Equations 15-17 [34].

$$x_1^L = \frac{(1-x_2)^m}{(1-x_2)^m + g_{2/1}(x_2)^m + g_{ij/1}[(1-x_2)x_2]^{m/2}} \quad (15)$$

$$x_2^L = \frac{g_{2/1}(x_2)^m}{(1-x_2)^m + g_{2/1}(x_2)^m + g_{ij/1}[(1-x_2)x_2]^{m/2}} \quad (16)$$

$$x_{ij}^L = \frac{g_{ij/1}[(1-x_2)x_2]^{m/2}}{(1-x_2)^m + g_{2/1}(x_2)^m + g_{ij/1}[(1-x_2)x_2]^{m/2}} \quad (17)$$

By inserting Equations 15-17 into Equation 14, the finalized viscosity model of preferential solvation for the binary mixture of a molecular solvent and a DES is derived as Equation 18.

$$\eta_{mix} = \eta_1 + \frac{g_{2/1}(\eta_2-\eta_1)(x_2)^m + g_{ij/1}(\eta_{ij}-\eta_1)[(1-x_2)x_2]^{m/2}}{(1-x_2)^m + g_{2/1}(x_2)^m + g_{ij/1}[(1-x_2)x_2]^{m/2}} \quad (18)$$

The parameter *m* is taken as 2.5 [34], and the three temperature-dependent parameters of $g_{2/1}$, $g_{ij/1}$ and η_{ij} are fitted to the experimental data at each temperature. In order to minimize the fitting process of the model, it is recommended to define simple temperature-dependent relations for the three preferential solvation parameters in the form of Equations 19-21.

$$g_{2/1} = g_{2/1}^p + g_{2/1}^q T \quad (19)$$

$$g_{ij/1} = g_{ij/1}^p + g_{ij/1}^q T \quad (20)$$

$$\eta_{ij} = \eta_{ij}^p + \eta_{ij}^q T \quad (21)$$

In this way, the six parameters of $g_{2/1}^p$, $g_{2/1}^q$, $g_{ij/1}^p$, $g_{ij/1}^q$, η_{ij}^p and η_{ij}^q are optimized to the experimental data, with Equation 2 as the objective function.

f. Jones-Dole model

The Jones-Dole viscosity model presents the relative viscosity of a binary mixture (molecular solvent + DES) with respect to the DES molar concentration, as given by Equation 22. [36, 10]

$$\frac{\eta_{mix}}{\eta_0} = 1 + A\sqrt{C} + B \times C \quad (22)$$

where η_0 and η_{mix} are the pure molecular solvent and the mixture dynamic viscosities, respectively. C is the molar concentration of the DES in the mixture, and A and B are the Falkenhagen coefficient and viscosity B-coefficient, respectively [37].

The Falkenhagen coefficient shows the solute-solute interactions, and is calculated theoretically. However, it is usually considered negligible for nonelectrolyte solutions [37, 10]. Hence, Equation 22 reduces to Equation 23 for binary mixtures of a DES + a molecular solvent [10].

$$\frac{\eta}{\eta_0} = 1 + B \times C \quad (23)$$

Based on this equation, the viscosity B-coefficient is calculated as the slope of the diagram of relative viscosity ($\frac{\eta}{\eta_0}$) with respect to the DES molar concentration, C. By analyzing the values of the viscosity B-coefficient at different temperatures, some clues on the interactions between the DES and the molecular solvent come to light [38].

g. *Viscosity deviation model*

The viscosity deviation for a binary mixture is defined by Equation 24,

$$\Delta\eta_{mix} = (\eta_{mix}) - [x_1(\eta_1) + x_2(\eta_2)] \quad (24)$$

where $\Delta\eta_{mix}$ is the mixture viscosity deviation, η_1 and η_2 are the pure viscosities of the molecular solvent and the DES, respectively, and x_1 and x_2 are the molar compositions of the molecular solvent and the DES in the mixture, respectively. By definition, viscosity deviation is the difference between the measured viscosity of the mixture and the molar-averaged summation of the viscosities of the constituent pure components. To model the viscosity deviation, the Redlich-Kister model, one of the most common models for excess properties, is used. Equation 25 presents the general form of the Redlich-Kister model for a binary mixture [39],

$$\ln(\Delta\eta_{mix}) = x_1 x_2 \sum_{j=0}^{k} D_i (x_1 - x_2)^j \quad (25)$$

where the D_i 's are the Redlich-Kister coefficients which are optimized to the calculated values of viscosity deviations at each temperature based on Equation 26 as the objective function. The Redlich-Kister expansion can be expanded to any desired number of terms by considering a value for the parameter *k*. In this study, the value of *k* is considered as three, resulting in the expansion of the Redlich-Kister to four sentences.

$$Ob.Fun^{\Delta} = \sum_{i}^{n} \frac{\left|\Delta\eta_i^{exp.} - \Delta\eta_i^{cal.}\right|}{\Delta\eta_i^{exp.}} \quad (26)$$

In this relation, $\Delta\eta_i^{cal.}$ and $\Delta\eta_i^{exp.}$ are the calculated viscosity deviation by the Redlich-Kister model and the experimental viscosity deviation, respectively, and *n* is the number of investigated data.

5. Results and discussion

a. Viscosity measurements

The viscosities of pure water, DES1, and DES2, were measured and compared with the reported literature values at the corresponding temperatures and pressures. This comparison is actually one further validation step, in addition to the utilized standard oils. Table 2 presents the measured and literature values of viscosities of pure water, DES1, and DES2.

Table 2. Comparison of the measured viscosity values of the investigated DESs and water with the corresponding literature values at atmospheric pressure [a,b,c].

Reference	***T* (K)**					
	283.15	**293.15**	**303.15**	**313.15**	**323.15**	**333.15**
DES1 (1 ChCl : 3 Phenol)			***η* (mPa.s)**			
This study	-	72.041	43.095	27.842	19.109	13.769
Guo et al. [23]	-	57.84	35.17	23.08	-	-
Ji et al. [25]	-	-	41.2	26.84	18.62	-
DES2 (1 ChCl : 4 Phenol)			***η* (mPa.s)**			
This study	-	61.783	37.731	24.634	17.073	12.394
Guo et al. [23]	-	40.23	25.2	16.71	-	-
Ji et al. [25]	-	-	36.55	23.57	16.21	-
Water			***η* (mPa.s)**			
This study	-	0.997	0.799	0.646	0.550	0.480
Shekaari et al. [40]	-	0.994	0.799	0.662	0.549	-
Yadav et al. [19]	-	0.9836	0.7914	0.6492	0.5487	0.477
Yadav and Pandey [17]	-	0.9968	0.8012	0.665	0.5518	0.4791
Mjalli and Mousa [41]	-	1.002	0.798	0.653	0.547	0.466
Wang et al. [42]	-	1.00	0.80	0.65	0.55	-
Zhang et al. [43]	-	0.991	0.796	0.662	0.566	-

[a] Standard uncertainties u are $u(T)$=0.02 K, $u(p)$=5 kPa, and for viscosity the relative combined expanded uncertainty $U_r(\eta)$ = 2% (0.95 level of confidence).
[b] The molar composition of the prepared DES1 and DES2 and their standard uncertainties are (0.250±0.001 Choline chloride + 0.750±0.003 phenol) and (0.200±0.001 Choline chloride + 0.800±0.004 phenol) in mole fraction, respectively.
[c] Molecular weights of DES1 and DES2 are 105.49 and 103.21 g.mol^{-1}, respectively.

Although this table shows the good agreement among the measured and literature viscosity values, in order to compare also the trends with respect to temperature, Figure 1 is presented. According to this figure, the measured water viscosities are in excellent agreement to the literature values. Regarding DES1 and DES2, there are only a few published studies available

in open literature. In each study, the prepared DESs had different water contents affecting the results. However, there is still good agreement between our measured viscosities with the reported values of Ji et al.'s group [25]. In general, the comparisons in Table 2 and Figure 1 indicate the reliable measurements of the viscometer.

In the next step, the viscosities of the prepared aqueous mixtures of DES1 and DES2 were measured within the temperature range of 293.15-333.15 K and atmospheric pressure. Table 3 presents the measured values for the two mixtures. In this table, mixture viscosities at different temperatures and molar compositions have been reported. Regarding entities in this table, for instance for an aqueous mixture of DES1, a mixture at water molar compositions of 0.2, means the molar compositions of ChCl and phenol are 0.2 and 0.6, respectively. Also, water molar compositions of 0.2 for an aqueous mixture of DES2, means the molar compositions of ChCl and phenol are 0.16 and 0.64, respectively.

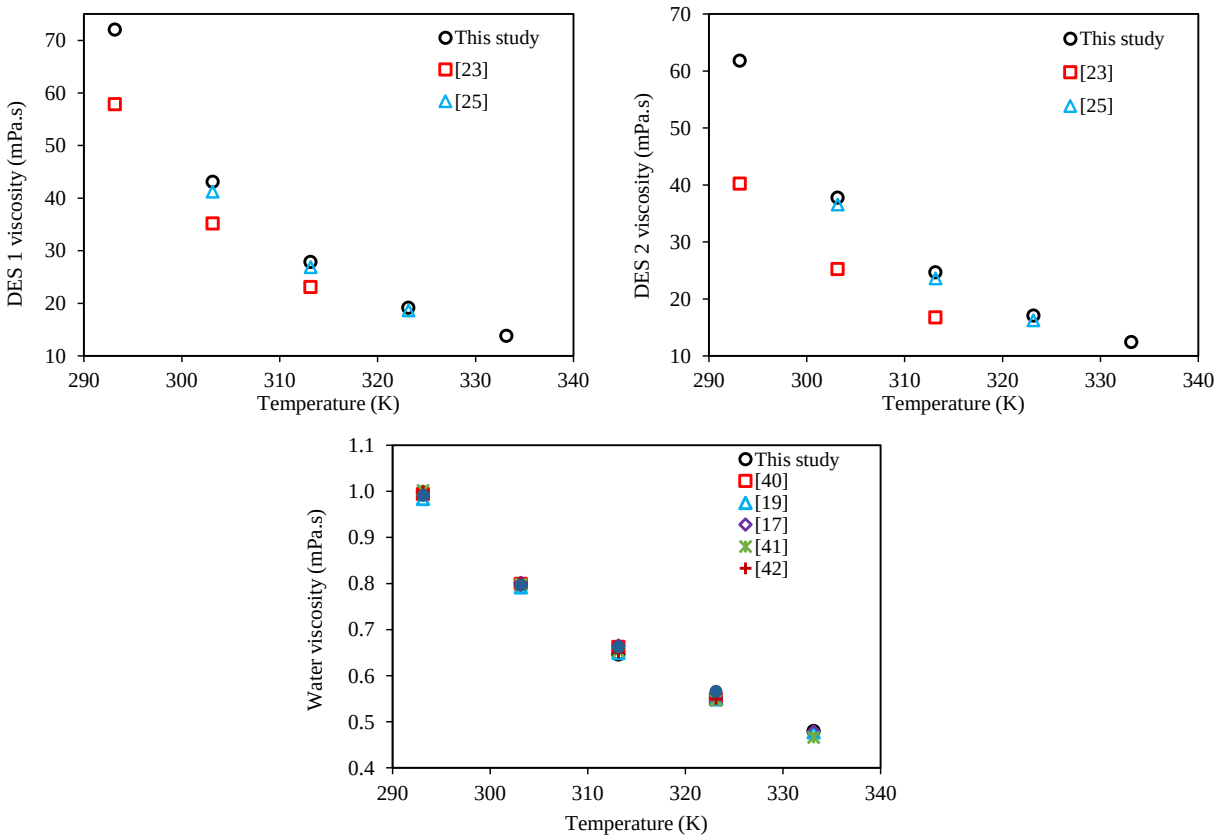

Figure 1. Comparison of the viscosity-temperature behavior of the investigated DESs and water in this study and the corresponding literature values (DES1: 1 ChCl : 3 phenol, DES2: 1 ChCl : 4 phenol).

In order to have a better overview of the measured values, Figure 2 is presented, showing the viscosity behavior with respect to mixture concentration for both aqueous systems of DES1 and DES2 at all of the investigated temperatures. As expected, viscosity decreases with increasing temperature at each fixed composition. Also, by increasing the water composition in both systems, the viscosities are decreased in an exponential manner. Viscosity depression by increasing water concentration is significantly higher at DES-rich concentrations. Figure 2 shows the significant effect of water on viscosity depression in both systems, where by adding only 10% (molar basis) of water to the investigated DESs, the viscosity can decrease by almost 25%.

The experimental density values of neat DES1 and DES2 at the investigated temperatures, as well as DES2+ water systems at the investigated temperatures and compositions, are available in earlier studies by our group [5,26].

Table 3. Measured viscosities of the aqueous mixtures of DES1 and DES2 at various temperatures and a pressure of 100 kPa [a,b,c].

Temperature (K)	**Viscosity (mPa.s)**										
	***x*₁ DES1 (1 ChCl : 3 phenol) + *x*₂ water**										
x_2 (water mole fraction)	0.000	0.100	0.200	0.300	0.401	0.499	0.601	0.700	0.800	0.900	1.000
293.15	72.041	56.094	40.935	29.561	21.484	15.369	10.567	7.478	4.918	2.774	0.997
303.15	43.095	34.531	26.614	19.262	14.376	10.554	7.469	5.415	3.639	2.094	0.799
313.15	27.842	22.761	17.593	13.304	10.142	7.612	5.522	4.077	2.792	1.639	0.646
323.15	19.109	15.893	12.403	9.647	7.480	5.716	4.232	3.175	2.209	1.320	0.550
333.15	13.769	11.618	9.216	7.279	5.722	4.437	3.340	2.542	1.794	1.089	0.480
	***x*₁ DES2 (1 ChCl : 4 phenol) + *x*₂ water**										
x_2 (water mole fraction)	0.000	0.100	0.200	0.300	0.400	0.500	0.600	0.701	0.800	0.900	1.000
293.15	61.783	43.900	34.948	27.379	20.064	14.906	11.076	7.315	4.816	2.827	0.997
303.15	37.731	27.667	22.499	17.929	13.501	10.306	7.782	5.290	3.576	2.128	0.799
313.15	24.634	18.552	15.237	12.394	9.539	7.438	5.722	3.983	2.739	1.660	0.646
323.15	17.073	13.260	11.035	9.002	7.046	5.586	4.364	3.101	2.163	1.334	0.550
333.15	12.394	9.923	8.309	6.800	5.391	4.334	3.433	2.485	1.753	1.099	0.480

[a] Standard uncertainties u are $u(T)$=0.02 K, $u(p)$=5 kPa, and for viscosity the relative combined expanded uncertainty $U_r(\eta)$ = 2% (0.95 level of confidence).

[b] The molar composition of the prepared DES1 and DES2 and their standard uncertainties are (0.250±0.001 Choline chloride + 0.750±0.003 phenol) and (0.200±0.001 Choline chloride + 0.800±0.004 phenol) in mole fraction, respectively.

[c] Molecular weights of DES1 and DES2 are 105.49 and 103.21 g.mol^{-1}, respectively.

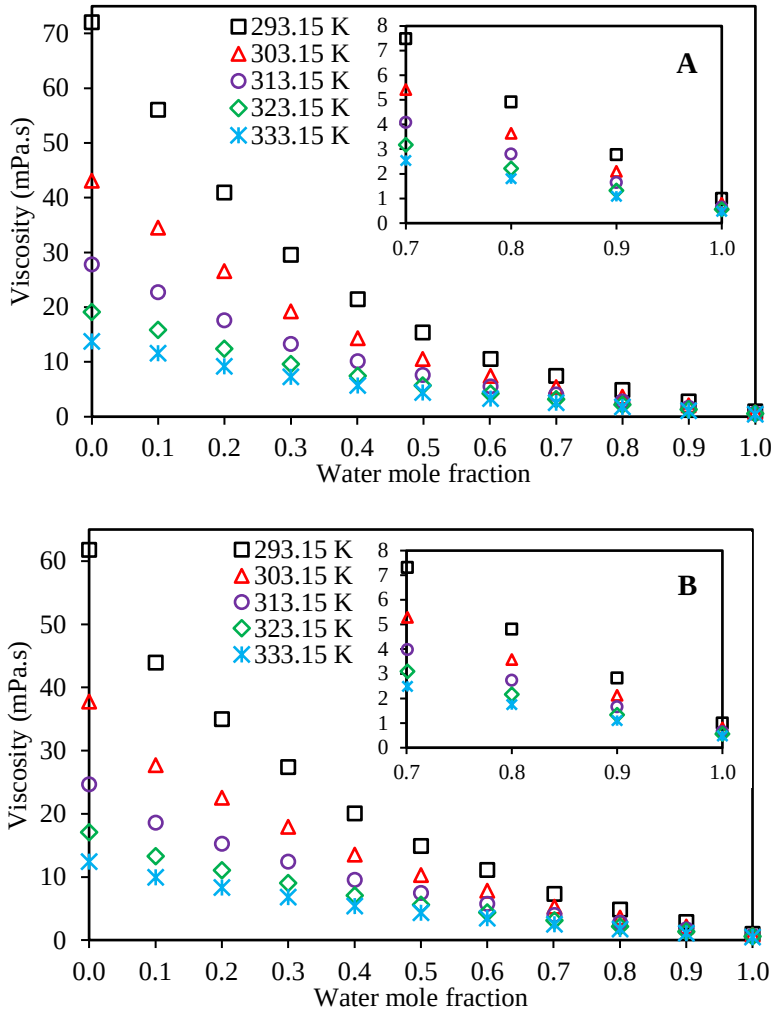

Figure 2. Behavior of viscosity-composition for both aqueous systems of DES1 and DES2 at a pressure of 100 kPa (A: DES1 (1 ChCl : 3 phenol) + water, B: DES2 (1 ChCl : 4 phenol) + water).

b. Viscosity deviation behavior

Following the measured viscosities, the values of viscosity deviations for both aqueous systems of DES1 and DES2 were calculated based on Equation 24 and presented in Table 4. Also, to have a more comprehensive investigation on this important property, the behavior of viscosity deviation with concentration is presented in Figure 3. It is observed that the viscosity deviations are negative for both aqueous systems, regardless of temperature and compositions. According

to Equation 24, these negative values show that the mixture viscosity is less than the molar arithmetic average viscosities of the pure DES and water. Such negative values indicate that both of the investigated systems are strongly non-ideal with negative deviations from the ideal state. Liquid viscosity is among the most challenging physical properties, with quite a complex functionality of many different properties and conditions, including for example, the molecular interactions in the liquid phase, the interstitial accommodations of the smaller molecules, and the shapes of the molecules (branched and linear structures) [44, 45]. These factors may act in competing directions to increase or decrease the liquid viscosity. Consider only one of these factors as responsible for viscosity increase or decrease in a liquid mixture, may lead to unfair justification with opposing unreliable discussions. For example, in the related literature, a number of studies claim that stronger interactions in a liquid mixture with respect to the individual neat components leads to negative values of viscosity deviation [46, 47, 42, 44], however, there are other studies which claim that stronger interactions lead to positive viscosity deviations [17,19,48,45]. The reason for such opposite discussions could possibly be blamed on only partially taking into consideration some factors among many (such as molecular interactions), and ignoring other contributing factors (such as interstitial accommodations or the molecule shapes).

According to the results presented in Table 4 and Figure 3, the negative values of viscosity deviations decrease by increasing temperatures for both aqueous systems. By elevating the temperature, both systems tend to a more ideal state with the association interactions in the mixture getting weaker. This behavior was also seen by other researchers for different types of DES mixtures [46, 42]. For the two systems of this study, the values of viscosity deviations are more negative for DES1 + water with respect to DES2 + water, which indicates more non-ideal

behavior, and possibly, stronger interactions for the unlike molecules in the DES1 + water system. At similar water concentrations, the greater number of phenol rings in the DES2 + water mixture compared to the DES1 + water mixture, surely has effects on the interstitial accommodations in the mixture, and this factor, together with the possibly stronger interactions of DES1 + water, results in greater viscosity reductions for the DES1 + water system. With respect to composition, both aqueous systems show almost the same trend for viscosity deviations, and the minimum viscosity deviations occur at water molar compositions of approximately 0.4.

Table 4. The calculated values of viscosity deviations for both aqueous DES systems at various temperatures at a pressure of 100 kPa.

Temperature (K)	**Viscosity deviation (mPa.s)**										
	***x*₁ DES1 (1 ChCl : 3 phenol) + *x*₂ water**										
x_2	0.000	0.100	0.200	0.300	0.401	0.499	0.601	0.700	0.800	0.900	1.000
293.15	0.000	-8.843	-16.897	-21.167	-22.068	-21.221	-18.777	-14.832	-10.288	-5.328	0.000
303.15	0.000	-4.334	-8.022	-11.144	-11.758	-11.435	-10.206	-8.073	-5.619	-2.935	0.000
313.15	0.000	-2.361	-4.810	-6.379	-6.794	-6.659	-5.976	-4.727	-3.293	-1.727	0.000
323.15	0.000	-1.360	-2.994	-3.894	-4.187	-4.132	-3.724	-2.943	-2.053	-1.086	0.000
333.15	0.000	-0.822	-1.895	-2.503	-2.718	-2.700	-2.442	-1.924	-1.344	-0.720	0.000
	***x*₁ DES2 (1 ChCl : 4 phenol) + *x*₂ water**										
x_2	0.000	0.100	0.200	0.300	0.400	0.500	0.600	0.701	0.800	0.900	1.000
293.15	0.000	-11.804	-14.678	-16.168	-17.405	-16.484	-14.236	-11.858	-8.339	-4.249	0.000
303.15	0.000	-6.371	-7.846	-8.722	-9.457	-8.959	-7.790	-6.552	-4.609	-2.364	0.000
313.15	0.000	-3.683	-4.599	-5.044	-5.499	-5.202	-4.519	-3.835	-2.705	-1.385	0.000
323.15	0.000	-2.161	-2.733	-3.114	-3.418	-3.226	-2.795	-2.389	-1.692	-0.869	0.000
333.15	0.000	-1.279	-1.702	-2.019	-2.237	-2.103	-1.813	-1.558	-1.110	-0.572	0.000

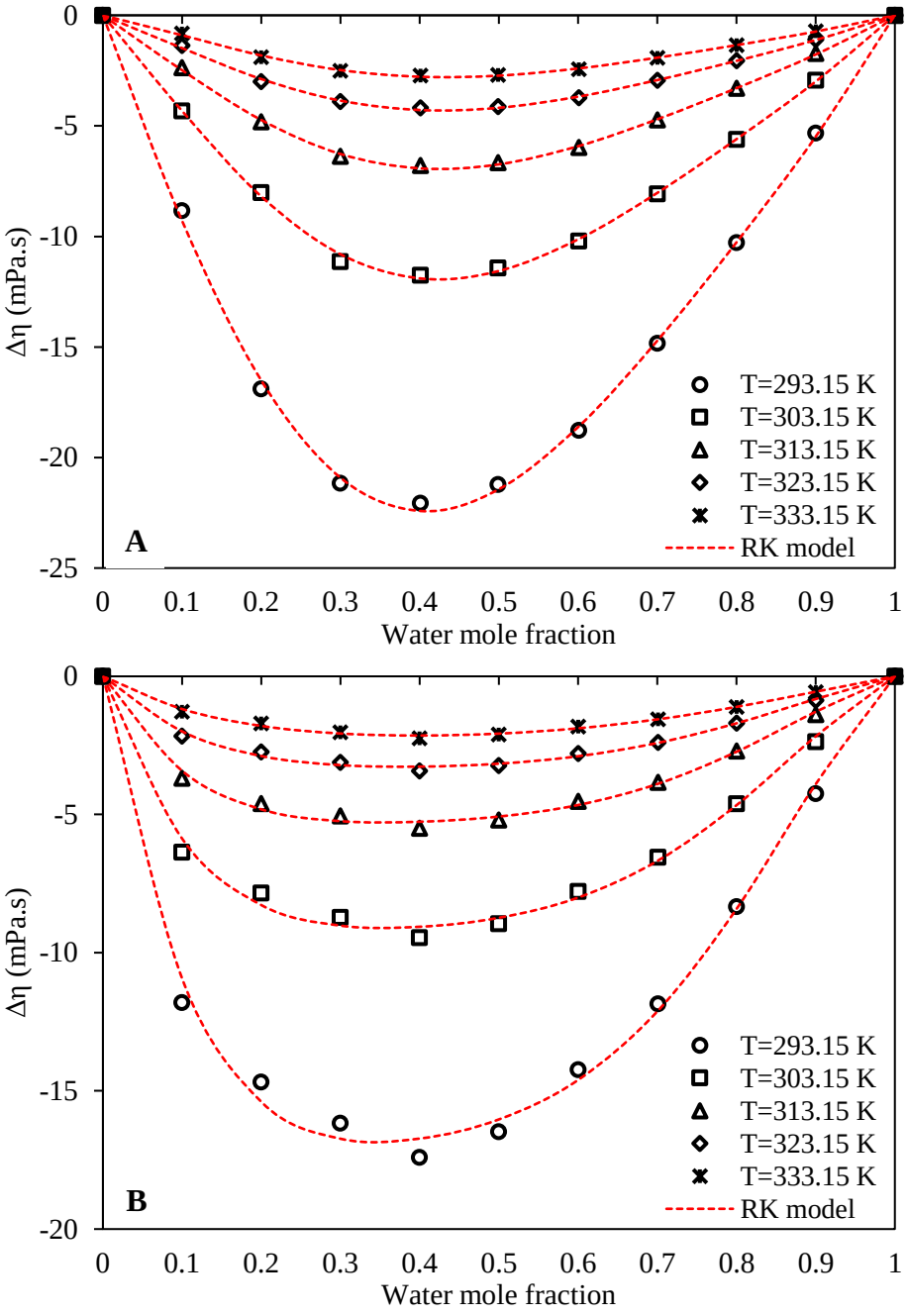

Figure 3. Behavior of viscosity deviation with respect to composition for the investigated systems at a pressure of 100 kPa (A: DES1 (1 ChCl : 3 phenol) + water, B: DES2 (1 ChCl : 4 phenol) + water).

To estimate the values of viscosity deviations at different concentrations and temperatures, the Redlich-Kister model (Eq. 25) was applied to both aqueous systems. Table 5 presents the optimized values of the Redlich-Kister coefficients for both investigated systems.

Table 5. The adjusted values of the Redlich-Kister coefficients for both aqueous systems at various temperatures and at a pressure of 100 kPa.

T (K)	RK coefficients				AARD%
	D_0	D_1	D_2	D_3	
	DES1 (1 ChCl : 3 phenol) + water				
293.15	-85.69	40.350	5.601	-21.740	1.80
303.15	-46.26	18.960	8.725	-15.170	1.27
313.15	-26.92	10.780	5.163	-9.134	1.77
323.15	-16.70	6.516	3.566	-6.221	2.45
333.15	-10.91	4.069	2.837	-4.550	2.56
	DES2 (1 ChCl : 4 phenol) + water				
293.15	-64.13	20.290	-28.590	44.560	4.01
303.15	-34.94	10.010	-15.250	24.450	4.11
313.15	-20.29	5.727	-9.107	14.200	3.90
323.15	-12.64	3.636	-4.677	7.028	3.66
333.15	-8.29	2.605	-2.145	2.729	3.12

In this table, the values of AARD% for the fitted Redlich-Kister models at each temperature are also presented. Figure 4 compares the behavior of the applied Redlich-Kister models with respect to the corresponding experimental values for both aqueous systems. According to the presented AARD% values of Table 5 and the trends of Figure 3, it is concluded that the applied Redlich-Kister model at each temperature is in good agreement with the experimental values, and also has reliable trends.

c. Mixture viscosity modellings

In order to estimate the mixture viscosities of both investigated aqueous systems at various temperatures, an Arrhenius-like viscosity model (Eq. 1) was applied at each specific composition. The parameters of this model were optimized for both aqueous systems and the values are reported in Table 6. Also, the corresponding values of AARD% for each

composition, which show the reliability of the applied models with respect to experimental values, were calculated according to Equation 27 and presented in Table 6.

$$AARD\% = \frac{100}{N}\sum_{i}^{n}\frac{\left|\eta_{mix,i}^{exp.} - \eta_{mix,i}^{cal.}\right|}{\eta_{mix,i}^{exp.}} \quad (27)$$

Table 6. The adjusted values of the parameters of Eq. 1, and the corresponding AARD% at each concentration for both aqueous systems.

Parameters	**Viscosity (mPa.s)**										
	***x*₁ DES1 (1 ChCl : 3 phenol) + *x*₂ water**										
x_2	0.000	0.100	0.200	0.300	0.401	0.499	0.601	0.700	0.800	0.900	1.000
η_0 *(mPa.s)*	3.843×10^{-5}	6.158×10^{-5}	1.101×10^{-4}	1.613×10^{-4}	2.426×10^{-4}	3.592×10^{-4}	5.917×10^{-4}	7.567×10^{-4}	9.222×10^{-4}	9.761×10^{-4}	1.821×10^{-3}
E_a *(j.mol^{-1})*	-3.518×10^{4}	-3.342×10^{4}	-3.125×10^{4}	-2.952×10^{4}	-2.774×10^{4}	-2.597×10^{4}	-2.384×10^{4}	-2.240×10^{4}	-2.090×10^{4}	-1.936×10^{4}	-1.535×10^{4}
AARD%	3.27	3.00	1.62	2.32	2.07	1.82	1.45	1.36	1.19	1.21	1.45
	***x*₁ DES2 (1 ChCl : 4 phenol) + *x*₂ water**										
x_2	0.000	0.100	0.200	0.300	0.400	0.500	0.600	0.701	0.800	0.900	1.000
η_0 *(mPa.s)*	5.152×10^{-5}	9.741×10^{-5}	1.297×10^{-4}	1.625×10^{-4}	2.428×10^{-4}	3.807×10^{-4}	4.927×10^{-4}	7.303×10^{-4}	9.030×10^{-4}	9.092×10^{-4}	1.821×10^{-3}
E_a *(j.mol^{-1})*	-3.410×10^{4}	-3.171×10^{4}	-3.046×10^{4}	-2.931×10^{4}	-2.758×10^{4}	-2.576×10^{4}	-2.440×10^{4}	-2.243×10^{4}	-2.090×10^{4}	-1.958×10^{4}	-1.535×10^{4}
AARD%	2.94	3.07	2.72	2.27	1.94	1.59	1.62	1.41	1.04	1.21	1.45

In the next step, the other models introduced in the Theory section (Preferential Solvation (Eq. 11), Grunberg-Nissan (Eq. 15), Jouyban-Acree (Eq. 17), and McAllister (Eq. 21) viscosity models), which in contrast to the Arrhenius-like model, not only consider the temperature, but also the concentration of the mixture in their formulation, are each optimized. Table 7 presents the fitted values of the adjustable parameters of the Preferential Solvation, Grunberg-Nissan, Jouyban-Acree, and McAllister models for both of the investigated aqueous systems. Also, in order to compare the accuracies of the models, the values of AARD% for each aqueous system were calculated according to Equation 27 and presented in this table. In addition, to have a

graphical comparison of the different models, Figures 4 and 5 are presented for both aqueous DES1 and DES2 systems, respectively. The Preferential Solvation model, thanks to its powerful theoretical background, is expected to have better results and trends for the aqueous systems considered, which is indeed confirmed by Table 7. Although the Jouyban-Acree model is a very simple model, it still succeeded to estimate the results significantly more accurately than the Grunberg-Nissan and McAllister models.

Table 7. The values of optimized coefficients for the Grunberg-Nissan [30], Jouyban-Acree [31], McAllister [32], and Preferential Solvation [33,34] models for viscosity modeling the investigated aqueous systems at a pressure of 100 kPa.

System	**Viscosity models**						**AARD%**
	Grunberg-Nissan parameters						
	G_1		G_2				
DES1 (1 ChCl : 3 phenol) + water	3.7763		-0.0048				12.47
DES2 (1 ChCl : 4 phenol) + water	4.5065		-0.0066				15.33
	Jouyban−Acree parameters						
	A_0	A_1		A_2			
DES1 (1 ChCl : 3 phenol) + water	708.1	644.5		703.8			2.14
DES2 (1 ChCl : 4 phenol) + water	775.4	722.5		455.7			2.86
	McAllister parameters						
	K_1	K_2	K_3	K_4	K_5	K_6	
DES1 (1 ChCl : 3 phenol) + water	124.01	-0.3491	27.44	-0.0764	260.27	-0.7479	6.54
DES2 (1 ChCl : 4 phenol) + water	117.36	-0.3318	45.69	-0.1299	159.02	-0.4535	7.17
	Preferential Solvation parameters						
	$g_{2/1}^{p}$	$g_{2/1}^{q}$	$g_{ij/1}^{p}$	$g_{ij/1}^{q}$	η_{ij}^{p}	η_{ij}^{q}	
DES1 (1 ChCl : 3 phenol) + water	5.1482	-0.0105	37.4125	-0.0956	19.3594	-0.0511	1.21
DES2 (1 ChCl : 4 phenol) + water	2.9393	-0.0063	13.8919	-0.0311	33.0546	-0.0891	3.19

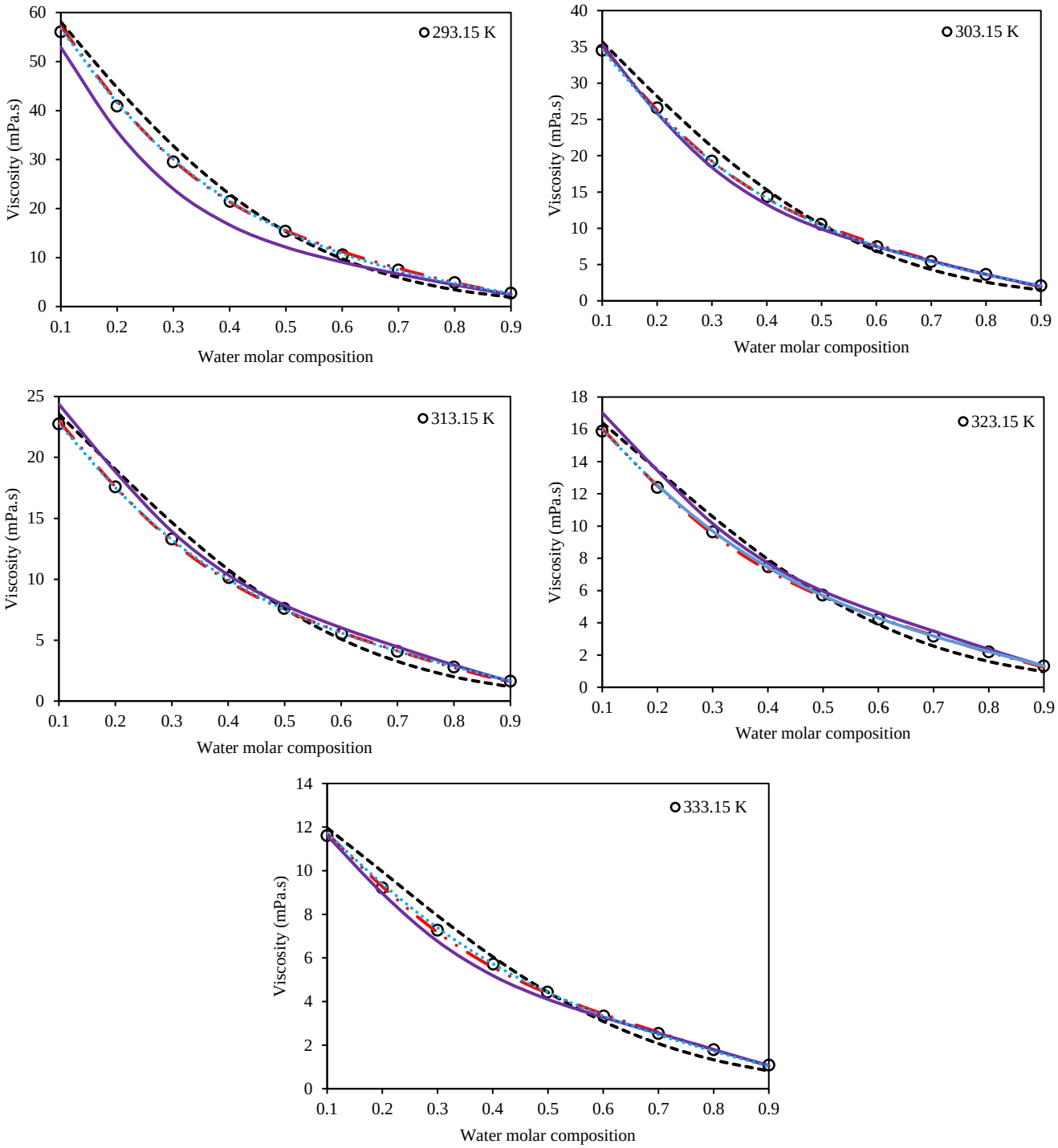

Figure 4. Comparison of the behavior of the Grunberg-Nissan [30], Jouyban-Acree [31], McAllister [32], and Preferential Solvation [33,34] models with respect to the experimental trends for the system of DES1 (1 ChCl : 3 phenol) + water at various temperatures and at a pressure of 100 kPa.

[Grunberg-Nissan (---), Jouyban-Acree (—••), McAllister (—), Preferential Solvation (•••), Experimental data (**o**)].

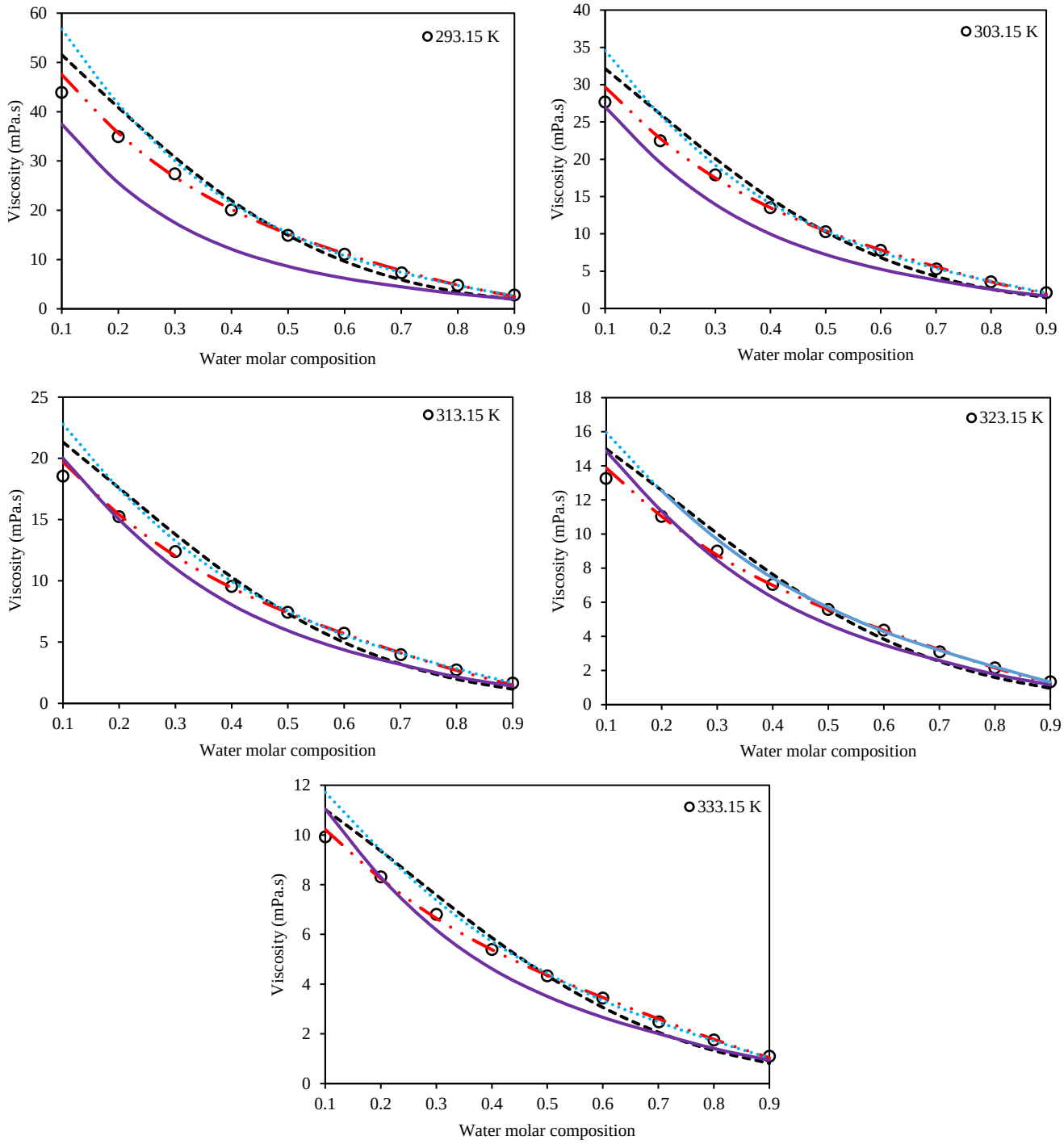

Figure 5. Comparison of the behavior of the Grunberg-Nissan [30], Jouyban-Acree [31], McAllister [32], and Preferential Solvation [33,34] models with respect to the experimental trends for the system of DES2 (1 ChCl : 4 phenol) + water at various temperatures and at a pressure of 100 kPa.

[Grunberg-Nissan (---), Jouyban-Acree (—••), McAllister (—), Preferential Solvation (•••), Experimental data (**o**)].

According to the presented curves in Figures 4 and 5, the more reliable trends of the Preferential Solvation and Jouyban-Acree models with respect to the other models is obvious. The differences among the model trends are more significant and better distinguishable for the aqueous DES2 system.

In the Theory section, it was explained that the relative viscosity of the mixture (mixture viscosity divided by pure water viscosity) can be represented by the well-established Jones-Dole model. According to this model, the values of the viscosity *B*-coefficients of DES1 and DES2 were calculated by the least-squares method at various temperatures and compositions, and the results are presented in Table 8. According to this table, the calculated values of viscosity *B*-coefficients are positive for both systems at all of the investigated temperatures, which suggest the occurrence of strong interactions among DES and water molecules in the mixture. Also clear from the table, is that upon increasing temperatures, the viscosity *B*-coefficient values decrease for both aqueous systems. This is because at higher temperatures, the interactions among the DES and water molecules weaken, resulting in decreased viscosity *B*-coefficients. The viscosity *B*-coefficient is actually an index for the interaction strength among molecules in the mixture. If the values of the viscosity *B*-coefficients of aqueous DES1 is compared to aqueous DES2 at the same temperature, the value is higher for the aqueous DES1 system than the aqueous DES2 system. This behavior suggests the stronger hydrogen bond interactions among DES1 and water molecules than DES2 and water molecules. This claim is also consistent with the discussions explained regarding the more negative values of viscosity deviations for aqueous DES1 than aqueous DES2.

Table 8. The values of the viscosity *B*-coefficients of the investigated DESs at infinite dilution at various temperatures and at a pressure of 100 kPa.

Temperature (K)	***B* (cm^3/mol)**										
	***x*$_1$ DES1 (1 ChCl : 3 phenol) + *x*$_2$ water**										
x_2	0.000	0.100	0.200	0.300	0.401	0.499	0.601	0.700	0.800	0.900	1.000
293.15	6.848	5.417	4.024	2.969	2.218	1.640	1.180	0.895	0.659	0.459	-
303.15	5.116	4.162	3.264	2.408	1.844	1.397	1.032	0.800	0.599	0.420	-
313.15	4.094	3.396	2.667	2.055	1.606	1.242	0.939	0.741	0.564	0.400	-
323.15	3.298	2.782	2.203	1.744	1.383	1.087	0.837	0.669	0.514	0.366	-
333.15	2.725	2.330	1.873	1.504	1.208	0.961	0.750	0.606	0.470	0.334	-
	***x*$_1$ DES2 (1 ChCl : 4 phenol) + *x*$_2$ water**										
x_2	0.000	0.100	0.200	0.300	0.400	0.500	0.600	0.701	0.800	0.900	1.000
293.15	5.751	4.135	3.354	2.690	2.025	1.560	1.221	0.861	0.635	0.469	-
303.15	4.385	3.251	2.691	2.192	1.693	1.338	1.062	0.769	0.579	0.428	-
313.15	3.544	2.697	2.253	1.872	1.476	1.190	0.961	0.711	0.543	0.406	-
323.15	2.882	2.260	1.911	1.590	1.273	1.042	0.852	0.642	0.494	0.370	-
333.15	2.397	1.938	1.647	1.372	1.110	0.920	0.762	0.582	0.450	0.337	-

6. Conclusions

This study is one further step to enrich the currently insignificant literature on the viscosities of aqueous DES systems by presenting novel experimental data and modeling for two aqueous DES systems, consisting of (1 ChCl: 3 phenol) and (1 ChCl: 4 phenol). For each aqueous system, nine different concentrations were prepared over the whole miscible composition range. The viscosities of the neat DESs and water, and the prepared aqueous mixtures were measured over the temperature range of 293.15 - 333.15 K and atmospheric pressure. The values of viscosity deviations were calculated at each temperature to clarify the viscosity deviations of the mixtures with respect to the ideal state. The Redlich-Kister model was also applied at all of the investigated temperatures to estimate the viscosity deviations of both aqueous mixtures with success. Negative viscosity deviations were obtained for both aqueous systems at all the investigated temperatures. The reason for negative viscosity deviations could be a combination of the two important and possibly dominant mechanisms of association

interactions and interstitial accommodations in the mixture. Most probably, the stronger interactions between the DES and water molecules in the mixture with respect to the self-interactions of DES and water in their pure states have significant effects on the negative values of viscosity deviations. The negative values, however, tend to zero by rising temperatures for both of the aqueous systems studied, which results from the weakening of the association interactions at higher temperatures, approaching closer to more ideal behavior.

As correlative tools, the behavior of mixture viscosity as a function of temperature was modeled by an Arrhenius-like model at each investigated composition. Also, the behavior of viscosity with respect to both mixture composition and temperature was modeled by the viscosity models of Grunberg-Nissan [30], Jouyban-Acree [31], McAllister [32], and Preferential Solvation [33,34]. Among the investigated models, the Preferential Solvation and the Jouyban-Acree models showed more reliable results with AARD% values of 1.21 and 2.14% for the aqueous DES1 system and 3.19 and 2.86% for the aqueous DES2 system, respectively. As a final conclusion, the viscosity *B*-coefficients of the Jones-Dole viscosity model were calculated for both aqueous systems. The positive values of the viscosity *B*-coefficients suggested strong interactions between the DES and water molecules in both systems. Also, by comparing the viscosity *B*-coefficients of the investigated aqueous systems, it is suggested that the aqueous DES1 system probably contains stronger hydrogen bond interactions with respect to the aqueous DES2 system.

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