



Synthesis and physicochemical properties of the mixtures based on choline acetate or choline chloride

Damian Połomski^{a,b}, Piotr Garbacz^a, Kenneth Czerwinski^c, Maciej Chotkowski^{a,b,*}

^a Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

^b Biological and Chemical Research Centre, University of Warsaw, Żwirki i Wigury 101, 02-089 Warsaw, Poland

^c Radiochemistry Group, University of Nevada, Las Vegas, NV 89154, USA

ARTICLE INFO

Article history:

Received 25 June 2020

Received in revised form 2 November 2020

Accepted 17 November 2020

Available online 20 November 2020

Keywords:

Choline acetate

Choline chloride

Carboxylic acids

Urea

Deep eutectic solvents

ABSTRACT

In this work the physicochemical properties of newly obtained mixtures (ChM) based on choline acetate (ChAc)/chloride (ChCl) as a hydrogen bond acceptor (HBA) and carboxylic acids (oxalic (OxA), malonic (MA), citric (CA), acetic (AA), formic (FA))/ urea (U) as a hydrogen bond donors (HBD) are discussed. NMR study showed slow reaction between choline and carboxylic acid, leading to obtain ester and water. After 3 weeks of synthesis, water content (w_{H_2O}) increased ca. 1.4 and 1.9 times for ChAc+FA and ChAc+OxA respectively. This factor is acid strength (as HBD) depends. Moreover, the results clearly shown that w_{H_2O} can be rapidly determined based on the measurements of the refractive index. The densities of the examined systems are in the range 1.084–1.296 g·cm⁻³ at 298.15 K, while kinematic viscosity at the same temperature varies from ca. 19 cSt to 2190 cSt for ChAc+FA and ChAc+CA respectively. The highest conductivity was measured in ChCl+FA system and equaled 14.60 mS·cm⁻¹.

© 2020 Elsevier B.V. All rights reserved.

1. Introduction

The increasing importance of ‘green chemistry’ has led to a great interest in development a new class of environmentally friendly compounds such an ionic liquids (IL). However, it has been confirmed that some of these solvents have disadvantages such as toxicity, poor biodegradable [1,2] and high cost of synthesis [3]. This leads to evaluating a related class of liquid mixtures named deep-eutectic solvents (DES). Such types of systems can be obtained by mixing a quaternary ammonium salts (e.g. choline chloride, ethylammonium chloride) with a) metal salts (e.g. ZnCl₂, SnCl₂) or b) a hydrogen-bond donors (e.g. urea, malonic acid, glycerol) [4–6]. The DES are mixtures whose melting points are lower than either of the individual components. For example, the freezing point of the mixture choline chloride + urea (in molar ratio 1:2) is 285.15 K while the individual component freezing points are 575.15 K for ChCl and 406.15 K for U [7].

Eutectic mixtures are attractive solvents for industrial usage such as liquid for extraction [8], in separation processes of oil [9],

metal electrodeposition [10–12], metal electropolishing [13], synthesis of metal nanoparticles [14–15], gas adsorption [16–18], and a biotransformation [19].

Despite many applications of DES, no stricter definition of these mixtures has been developed to date [20]. The very popular term “hydrogen bond complexes” often used to describe such types of systems is unclear and in our opinion cannot be applied to describe the interaction of the components in all types of DES. Moreover, formally for eutectics solvents the chemical reaction between their components should not be observed.

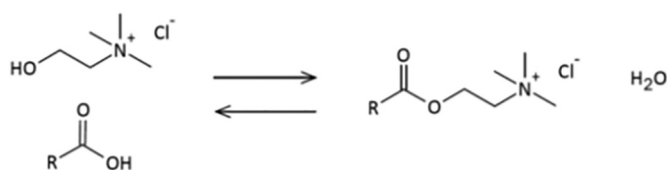
Regardless of the definition problems, the properties of these mixtures are very interesting in context of their availability and safety. From this point of view the subgroup of DES called Natural Deep Eutectic Solvents (NADES) are especially attractive [21–22]. They are formed by naturally occurring compounds, such as sugars, sugar alcohols, amino acids, organic acids (as a hydrogen bond donor (HBD)) and e.g. choline derivatives (as a hydrogen bond acceptor (HBA)).

A recent paper by Rodriguez et al. [23] showed that mixing choline chloride with carboxylic acid and heating for 2 h at 60 °C, 80 °C or 100 °C leads to DES that contains several percent of appropriate ester and water (Eq. (1), where *R* is the alkyl group or hydrogen). This observation clearly showed that their physicochemical properties must be carefully

* Corresponding author at: Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland.

E-mail address: mchotk@chem.uw.edu.pl (M. Chotkowski).

examined and H₂O content is an important consideration that cannot be completely eliminated.



Rodriguez et al. [23] stated that elevated temperature accelerates this process. Moreover, after a long period of time a significant increase of water content in the ChCl+carboxylic acid mixtures was observed.

This manuscript presents the results of the preliminary studies on the physicochemical properties of the systems based primarily on choline acetate and urea or carboxylic acids. These mixtures provide suitable properties e.g. biodegradability, relatively high conductivity, satisfactory viscosity and the possibility of water content control by applying right organic acid (e.g. formic). Combination of above mentioned factors enables testing of NADES in context of their application as a medium for various reaction e.g. electrogeneration of reduced forms of technetium-99 m – one of the most important radionuclide applied in nuclear medicine. The results obtained in this work delivered additional information on the esterification process in examined systems and the correlation of the water content with the strength of carboxylic acid. This result provides a means to correlate some physicochemical properties with the chemical behaviour of the constituent compounds.

2. Experimental

2.1. Materials

All experiments described in this paper were prepared using analytical grade chemicals: choline acetate (ChAc), choline chloride (ChCl), urea (U), oxalic acid anhydrous (OxA), malonic acid (MA), citric acid monohydrate (CA), formic acid (FA), acetic acid (AA). Chemicals are listed in Table 1.

2.2. Preparation of mixtures

To prepare the mixtures selected HBAs were mixed with HBDs at appropriate molar ratios in closed vials. To obtain homogeneous liquid phase each sample was slightly heated in a metallic heating block. All procedures for the examined mixtures are given in Table 2. To maintain the molar proportions of the reagents such as DES based on ChCl with urea (1:2), the investigated systems were prepared in the same molar ratio. Only one of the systems (choline acetate + citric acid) was formulated in a molar ratio of 2:1, as a 1:2 ratio did not result in a homogeneous liquid phase. Based on the results obtained by Rodriguez et al. [23] and in order to minimize the acceleration of the esterification reaction at elevated temperatures, heating time was minimized.

Table 1
Chemical used in the study.

Chemical materials	Molar mass (g·mol ⁻¹)	Source	Mass fraction purity
Choline acetate (ChAc)	163.21	IoLiTec	0.98
Choline chloride (ChCl)	139.62	Sigma-Aldrich	≥0.98
Urea (U)	60.06	Merck	≥0.99
Oxalic acid anhydrous (OxA)	90.03	Sigma-Aldrich	≥0.99
Malonic acid (MA)	104.06	Sigma-Aldrich	≥0.99
Citric acid monohydrate (CA)	210.14	Chempur	≥0.99
Formic acid (FA)	46.03	POCH	≥0.98
Acetic acid (AA)	60.05	POCH	≥0.99

2.3. Measurements

The water content (w_{H2O}) of the mixtures and their components were measured using Schott Instruments TitrLine KF - Coulomat AG (Honeywell, Fluka). Measurements included an assessment of weak organic acids on determination of H₂O content in the samples, see SI 1. The densities (ρ) of all samples were measured using Gay-Lussac pycnometers (Carl Roth GmbH, volume 1.029 ml) and precise balance (RADWAG PS 210/C/2) from 298.15 K to 323.15 K temperature range. The accuracy of obtained density results was verified by comparison with densities obtained from measurements collected on the Anton Paar DMS 4500 apparatus. (SI 2). The kinematic viscosities (ν) were measured using Ubbelohde viscometer (Carl Roth GmbH). Measurements were performed from 293.15 to 333.15 K. The kinematic viscosities (ν) were measured using Ubbelohde viscometer (Carl Roth GmbH). The uncertainties of the w_{H2O}, ρ, ν were determined based on three repeated measurements. The electrical conductivity (κ) was registered by conductivity cell (ECF-1 t 0429/19) coupled with conductivity meters (Elmetron CX-401) from 293.15 to 333.15 K. The refractive index (n_D) measurements were made using Abbe refractometer at a temperature of 298.15 K. The uncertainties of the κ and n_D were determined based on the devices resolutions. The ¹H and ¹³C NMR spectra of samples were acquired on the Bruker AVANCE III 500 MHz spectrometer with the 5 mm CPPBBO BB probe at the temperature of 298 K. The samples were measured in the 3 mm NMR tube, which was placed in the 5 mm NMR tube filled with methanol-*d*₄ (≥99.8 atom % D, Sigma Aldrich). The magnetic field was stabilized using the ²H signal of methanol. The signals of the methyl group of methanol were used as references of the chemical shifts of the proton (3.31 ppm) and carbon-13 (49.0 ppm) [24]. Thermogravimetric analysis in nitrogen atmosphere were done using TGA Q50 (TA Instruments Inc.) The N₂ flow rate was 40 mL·min⁻¹ from 298.15–673.15 K, and heating rate was 10 K·min⁻¹. The uncertainty of the determine decomposition temperature is 0.05 K. The electrochemical measurements were performed using CHI700C (CH Instruments, Inc.) electrochemical analyser. All electrochemical measurements were carried out in a three electrode system with Au, Pt and Ag/Ag⁺ {(10 mmol dm⁻³) in 1-ethylpyridinium bis (trifluoromethylsulfonyl)imide [C₂py][Tf₂N]} as a working, a counter and a reference electrode respectively. All the potential are given vs. ferrocene (Fc/Fc⁺) system.

3. Results and discussion

After synthesis, the mixtures were divided into small parts (0.5 ml) and stored in Eppendorf closed vials at room temperature for a total of 1.5 month. An aliquot ca. 100 μl of ChAc+OxA, ChAc+FA mixtures was regularly taken from new (not opened since the beginning of the experiments) vial to determine the water content changes over time. The moisture of the pure components before obtaining the mixtures was 0.47 ± 0.04 wt%, 0.66 ± 0.03 wt% and 0.74 ± 0.04 wt% respectively for ChAc, FA, OxA.

The changes in water content due to component acid strength was examined for systems with oxalic and formic acid, the strongest and weakest carboxylic acids evaluated. Within the first few days after mixing of the compounds rapid increase in water content (Fig. 1). After ca. 3 weeks apparent water saturation is reached.

The water content measured in ChAc+FA and ChAc+OxA equaled 1.9 wt% and 3.8 wt% respectively and is strictly depends on the acid strength (pK_a) of the hydrogen bond donors. The highest value of this parameter was observed for the mixture based on the strongest organic acid – OxA. This relationship is presented in Fig. 2.

Rodriguez N.R. et al. [23] also noticed increase of the water content of choline chloride with carboxylic acids and discussed that this is due to the esterification reaction. The work from [23] examined water content immediately after synthesis or months after preparation, formation kinetics were not addressed. It was also noted elevated temperature

Table 2
Composition and conditions of preparing mixtures based on choline acetate and choline chloride.

Abbrev	Hydrogen bond acceptor (HBA)	Hydrogen bond donors (HBD)	Molar ratio (HBA/HBD)	Conditions	
				Temperature (K) ^a	Heating Time (min.) ^b
ChAc + U	choline acetate	urea	1:2	338.15	25
ChAc + OxA		oxalic acid	1:2	333.15	60
ChAc + MA		malonic acid	1:2	338.15	40
ChAc + CA		citric acid	2:1	343.15	120
ChAc + FA		formic acid	1:2	RT	5
ChAc + AA	choline chloride	acetic acid	1:2	RT	5
ChCl + MA		malonic acid	1:2	353.15	150
ChCl + FA		formic acid	1:2	333.15	7
ChCl + AA		acetic acid	1:2	RT	5

^a u(T) = ±0.05 K.

^b u(t) = ±0.1 min

accelerates this process. The results from in Fig. 1 in the current study clearly show that the highest increases in water content is observed within a few days after synthesise of the examined mixtures. It is the fact that according to the reaction (1), drying of the mixtures based on choline acetate/chloride and carboxylic acids will promote esterification process, therefore water will always be present in the sample.

The NMR measurements for mixture ChAc+AA were performed in order to confirm the esterification reaction. The ¹H and ¹³C spectra showed the presence of the acetylcholine in the samples (See Fig. 3). The ¹H and ¹³C chemical shifts of choline acetate and acetylcholine are in agreement with literature data [25] but due to high concentration of acetic acid they are systematically shifted by approximately -0.4 ppm (¹H) and -1.0 ppm (¹³C). For the sample soon after synthesis, the molar ratio of the acetylcholine to choline acetate determined from the integrals of ¹H NMR peaks is 0.030(3). The equilibrium is not achieved for 7 days since the amount of acetylcholine is approximately threefold smaller after few days in comparison the case of 3 months.

The nature of the components of the mixtures, their molar ratios, and the temperature are the main factors that determine the densities and kinematic viscosities of the examined systems. Experimental values of kinematic viscosities (ν), densities (ρ), conductivities (\mathbf{k}) of mixtures based choline acetate/chloride are listed in Table 3.

Kalhor P. et al. [26] reported from the literature [27–30] that densities of DES are from 0.785 to 1.63 g·cm⁻³, with the majority falling

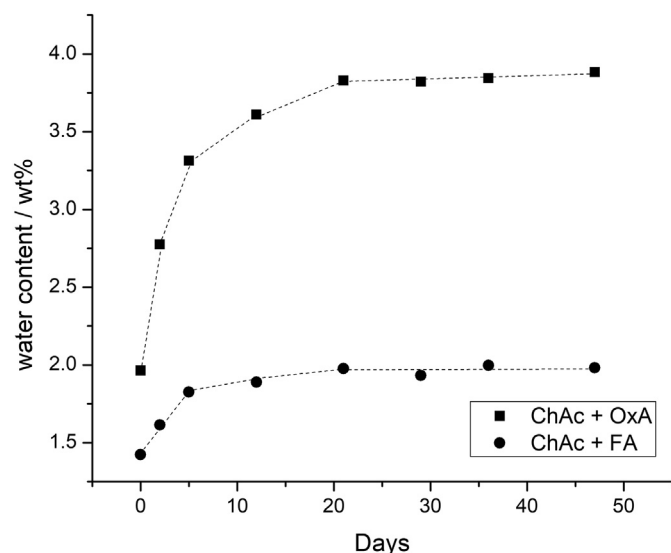


Fig. 1. Changes in water content of ChAc + OxA, ChAc + FA.

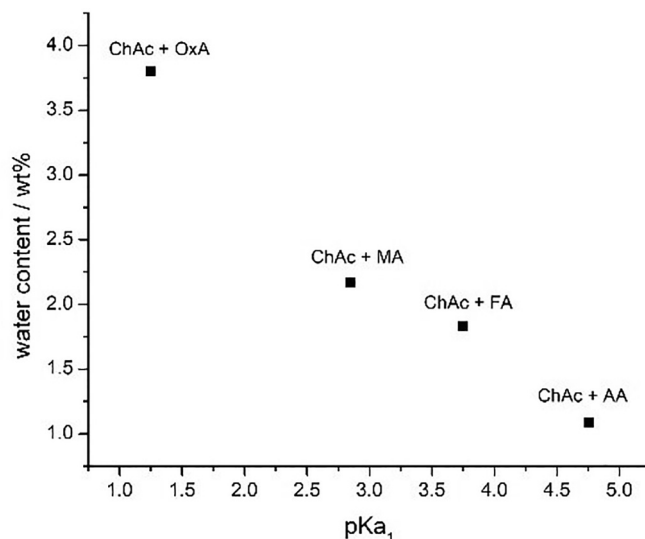


Fig. 2. Water content of the mixtures based on choline acetate as a function of pK_{a1} (after 3 weeks of synthesis).

from 1.0 to 1.35 g·cm⁻³ at 298.15 K. The densities of examined systems based on choline are in the range of 1.084 to 1.296 g·cm⁻³ at 298.15 K. The lowest density value is observed for ChAc+AA and equals 1.084 g·cm⁻³. For the ChCl + MA in molar ratio 1:2, the density is 1.257 g·cm⁻³ and is close to evaluated by Abbott et al. [31] value of 1.25 g·cm⁻³.

The kinematic viscosities of the examined mixtures are in the range ca. from 19.18 cSt to ca. 2192.13 cSt at 298.15 K. The analyses of the viscosities of selected mixtures presented in Table 3 shows strong influence of the nature of ChM components (type of anion, HBD, temperature, etc.). It is worth noting that viscosity values for ChAc + MA - 375.23 cSt (437.15 cP) is lower than for ChCl+MA - 711.43 cSt (894.26 cP), while the water content is higher for the latter.

Taking into account the data presented in Table 3 and using the Eqs. (2–3) dynamic viscosity (η) and activation energy of lamination flow (E_{η}) in the examined systems [5] were calculated.

$$\eta = \nu \cdot \rho \quad (2)$$

where η – dynamic viscosity, ν – kinematic viscosity, ρ – density.

$$\ln \eta = \ln \eta_0 + \frac{E_{\eta}}{RT} \quad (3)$$

where η_0 – constant, E_{η} – activation energy viscosity, T – temperature (K), R – universal gas constant (8.314 J·K⁻¹·mol⁻¹).

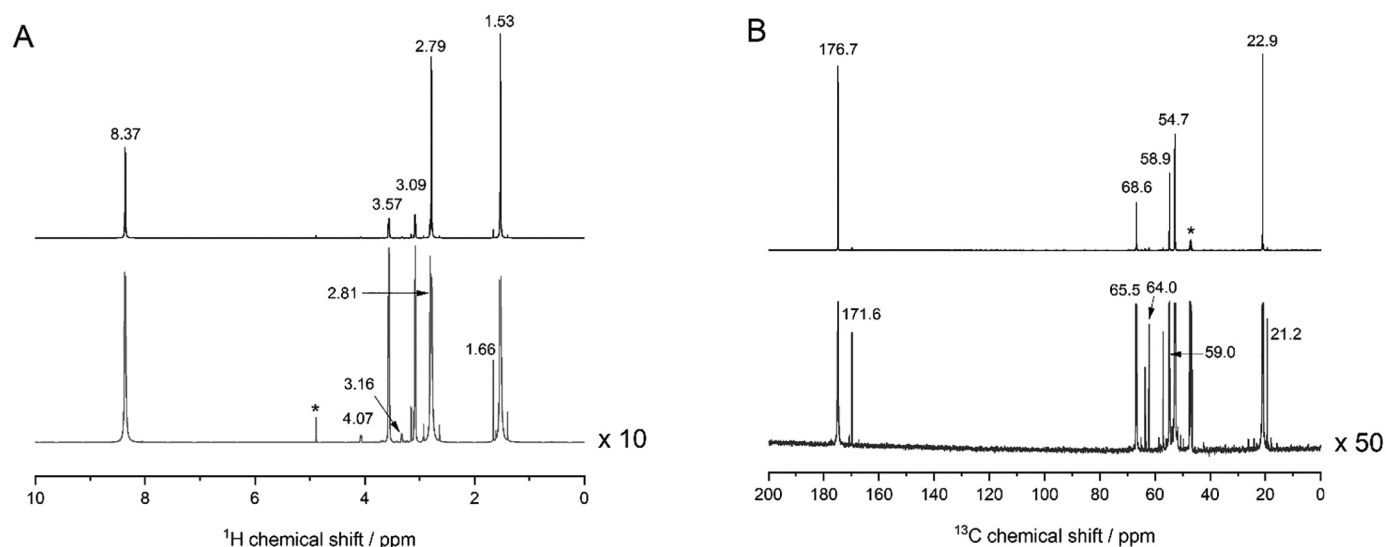


Fig. 3. (A) ^1H and (B) ^{13}C NMR spectra of the sample measured 3 months after the reaction. The chemical shifts of signals are shown for choline acetate in the upper trace and for acetylcholine in the bottom magnified trace. The signals of the acetate and acetic acid are not resolved due to fast exchange of the acetic group.

The natural logarithm of the dynamic viscosity reciprocal of the temperature for selected ChM are presented in Fig. 4, and Table 4 (with correlation coefficient $R^2 > 0.99$).

The activation energy of laminar flow values are in the range 22.37–60.69 $\text{kJ}\cdot\text{mol}^{-1}$. The E_{η} parameters for examined ChM are significantly larger than those for high temperature molten salts based on chlorides and conventional liquids, e.g. water or ethanol [32].

The electrolytic conductivity (κ) is found to be strongly correlated with viscosity. An increase in viscosity causes a decrease in electrolytic conductivity [33]. This feature is observed for the examined mixtures (Table 3). In the literature [31,34–35], the κ parameter for ionic liquids and DES is in the range 0.1–14 $\text{mS}\cdot\text{cm}^{-1}$. The synthesized mixtures based on choline acetate/chloride and selected carboxylic acid suitable electrolytic conductivity from 0.19 to 14.60 $\text{mS}\cdot\text{cm}^{-1}$ for ChAc+CA and ChCl+FA respectively.

For the examined mixtures, the temperature-conductivity dependence is described by an analogous expression to Eq. (3), namely:

$$\ln \kappa = \ln \kappa_0 + \frac{E_{\kappa}}{RT} \quad (4)$$

where κ_0 – constant, E_{κ} – activation energy for electrical conductivity, T – temperature (K), R – universal gas constant ($8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$).

Fig. 5 presents the natural logarithm of conductivity reciprocal of temperature for the studied ChM based on choline acetate. The E values

listed in Table 4 correlate with those obtained by Abbott A.P. et al. [4] for eutectic mixtures of zinc chloride and donor molecules such as acetamide ($E = -28 \text{ kJ}\cdot\text{mol}^{-1}$) and urea ($E = -77 \text{ kJ}\cdot\text{mol}^{-1}$).

Fig. 6 presents the influence of water content on refractive index for the examined mixtures.

All of obtained ChM have large values of n_D , which are comparable with mixtures (e.g. ChCl + OxA - 1.480, ChCl+MA - 1.478) studied by Abbott et al. [31]. As the water concentration increases in the given mixtures (ChAc+OxA, ChAc+FA, ChAc+AA), the refractive index decreases reaching the values characteristic for pure water (n_D for H_2O equals 1.333) [36]. The refractive index is linearly correlated with water content in the mixture (Table 5, correlation coefficient $R^2 > 0.999$). This observation clearly shows that this simple, easy and quickly method can be applied for direct determination of H_2O in such types of mixtures.

The initial decomposition temperature (T_d) is very important factor indicating the maximum temperature at which the mixtures remain without high mass loss. Delgado-Mellado et al. have reported the thermal properties for the eutectic mixtures based on choline chloride [38]. The TGA measurements were made to study the thermal stability of the obtained systems. Fig. 7 presents the dynamic TGA curves for five mixtures based on choline acetate and selected hydrogen bond acceptor. The highest T_d value (approx. 410 K) among the studied mixtures was recorded for ChAc+U. In general, the values of the initial decomposition temperature for the studied ChM are between those of their pure components. The highest values of mass loss is observed for mixtures based

Table 3

Kinematic viscosity (ν), density (ρ), conductivity (κ), water content ($w_{\text{H}_2\text{O}}$) at 298.15 K and 323.15 K of mixtures (after 3 weeks of synthesis).

Mixtures	ν (cSt) ^a		ρ ($\text{g}\cdot\text{cm}^{-3}$) ^b		κ ($\text{mS}\cdot\text{cm}^{-1}$) ^c		$w_{\text{H}_2\text{O}}$ /wt% ^d
	298.15 K ^e	323.15 K ^e	298.15 K ^e	323.15 K ^e	298.15 K ^e	323.15 K ^e	298.15 K ^e
ChAc+U	1228.50	177.13	1.176	1.164	0.24	1.36	0.98
ChAc+OxA	1130.03	212.23	1.296	1.286	0.48	1.30	3.83
ChAc+MA	375.23	93.18	1.165	1.155	0.79	2.23	2.17
ChAc+CA	2192.13	525.20	1.211	1.198	0.19	0.50	4.43
ChAc+FA	19.18	9.43	1.119	1.105	9.93	15.82	1.98
ChAc+AA	51.03	20.12	1.084	1.074	3.28	4.96	1.09
ChCl+MA	711.43	168.68	1.257	1.223	0.43	1.03	2.32
ChCl+FA	21.13	10.40	1.155	1.138	14.60	19.05	3.40
ChCl+AA	44.53	18.20	1.104	1.089	4.55	6.55	1.55

Uncertainties: ^a ν = 5%; ^b ρ = $\pm 0.8\%$; ^c κ = $\pm 0.05 \text{ mS}\cdot\text{cm}^{-1}$; ^d $w_{\text{H}_2\text{O}}$ = $\pm 6\%$; ^e $u(T)$ = $\pm 0.05 \text{ K}$

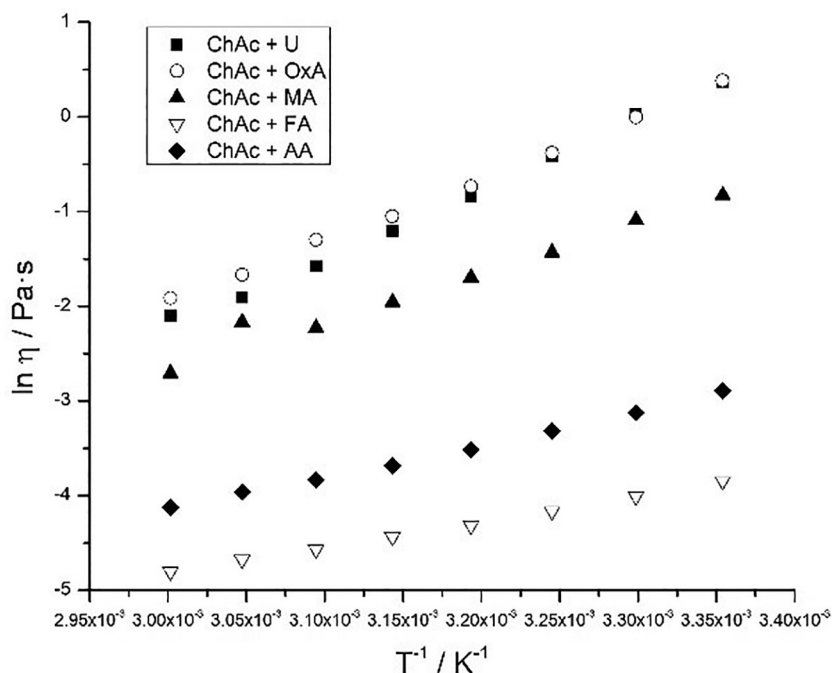


Fig. 4. Natural logarithm of dynamic viscosity vs. reciprocal of temperature for selected mixtures based on choline acetate.

Table 4

E_{η} and E_{λ} for the mixtures based on choline acetate.

Mixtures	E_{η}^a ($\text{kJ}\cdot\text{mol}^{-1}$)	E_{λ}^b ($\text{kJ}\cdot\text{mol}^{-1}$)
ChAc + U	60.69	-55.52
ChAc + OxA	53.94	-32.51
ChAc + MA	41.80	-35.83
ChAc + FA	22.37	-12.06
ChAc + AA	28.57	-13.61

Uncertainties: $^a u(E_{\eta}) = \pm 5\%$; $^b u(E_{\lambda}) = \pm 5\%$

on formic and acetic acids. It should be noted that such types of systems undergo relatively fast evaporation of one of the component (FA or AA) rather than initial decomposition.

The electrochemical characterization of the mixtures containing choline halides as hydrogen bond acceptor in the presence of appropriate hydrogen bond donor is known. The electrochemical window potentials for ChCl + U, ChBr + U and ChI + U are 4.29 V, 3.32 V, 1.25 V respectively [37]. The examined mixtures show that the widest potential window (1.65 V) were observed for ChAc+MA and for ChAc+U

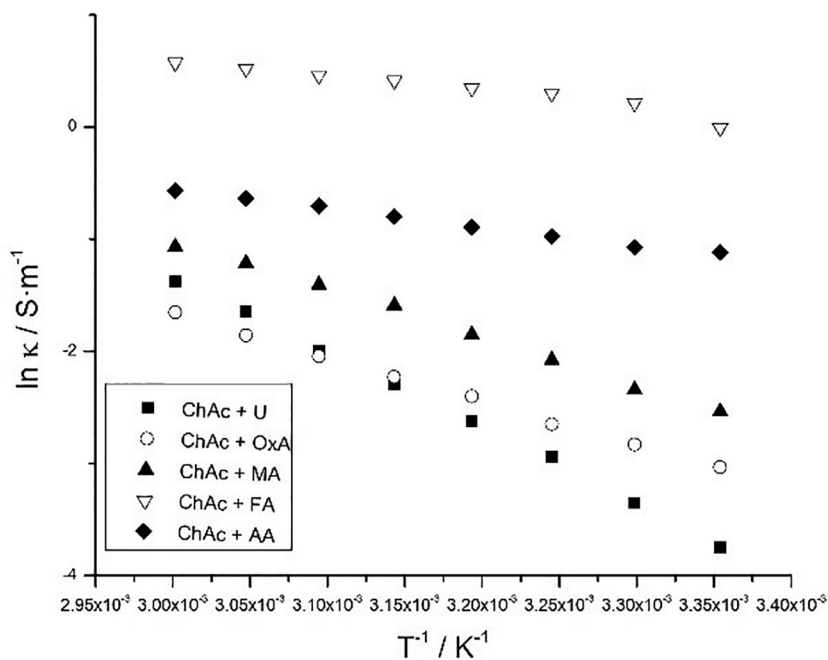


Fig. 5. Natural logarithm of conductivity reciprocal of temperature for selected mixtures based on ChAc.

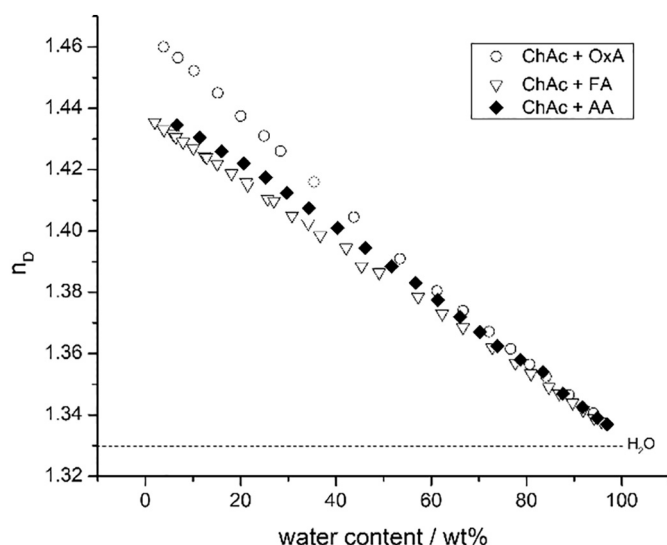


Fig. 6. Refractive index of mixtures as a function of H₂O concentration.

Table 5

Dependence of the refractive index on H₂O concentration in mixtures at temperature 298.15 K.

Abbrrev	Equation	Adj. R ²
ChAc + OxA	$n_D = -13.42 \cdot 10^{-4} * (\text{wt}\% \text{H}_2\text{O}) + 1.464$	0.999
ChAc + FA	$n_D = -10.32 \cdot 10^{-2} * (\text{wt}\% \text{H}_2\text{O}) + 1.437$	0.999
ChAc + AA	$n_D = -10.99 \cdot 10^{-4} * (\text{wt}\% \text{H}_2\text{O}) + 1.444$	0.999

Uncertainties: $u(n_D) = \pm 0.001$

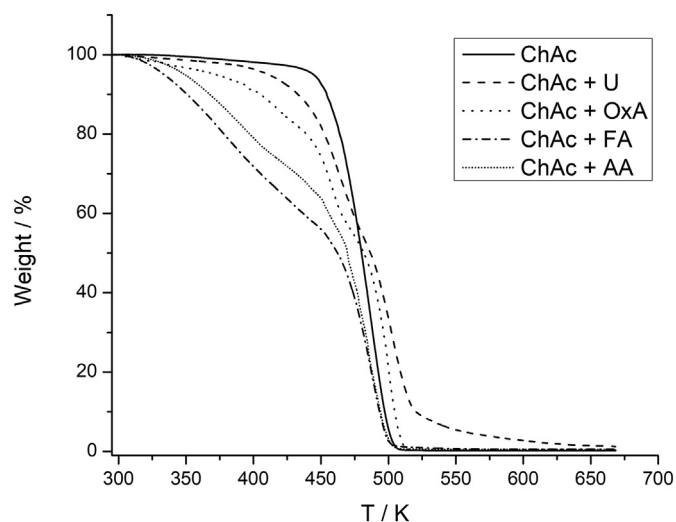


Fig. 7. TGA plots to illustrate thermal decomposition of choline acetate and mixtures based on ChAc.

(1.30 V). In comparison to chloride analogous this parameter is lower due to lower stability of acetate ions.

4. Conclusion

In this work, we described the physicochemical properties of newly formulated mixtures based on choline acetate/chloride as a hydrogen bond acceptor (HBA) and simple carboxylic acids (oxalic, malonic, citric, acetic, formic) or urea as hydrogen bond donors (HBD). The

measurement of physicochemical properties showed that density and viscosity of these mixtures decrease with increasing temperature and are in the range characteristic for similar mixtures. The NMR and Karl Fischer titration studies confirmed the esterification reactions taking place between choline cation and organic acid. An increase of the water content is correlated with the acid strength (pK_a) used as HBD. Additionally, determination of the refractive index may be applied as a simple method for water content determination. Due to relatively high vapor pressure of acetic acid these mixtures can be used under atmospheric pressure at room temperature.

Examined mixtures can be applied as a reaction medium in compound synthesis where slightly acidic conditions and small fraction of water are required. It is possible to control the latter factor in the sample choosing organic acid as HBD.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The contribution of Damian Połomski was realized within Project No POWR.03.02.00-00-1009/17-00 (Operational Project Knowledge Education Development 2014-2020 co-financed by European Social Fund).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2020.114820>.

References

- [1] M. Petkovic, K.R. Seddon, L.P.N. Rebelo and, C.S. Pereira, Ionic liquids: a pathway to environmental acceptability, *Chem. Soc. Rev.* 40 (2011) 1383–1403, <https://doi.org/10.1039/c004968a>.
- [2] M.C. Bubalo, K. Radošević, I. Radojčić Redovniković, I. Slivac, V. Gaurina Srček, Toxicity mechanisms of ionic liquids, *Arh. Hig. Rada Toksikol.* 68 (2017) 171–179, <https://doi.org/10.1515/aiht-2017-68-2979>.
- [3] Selection of ionic liquids suppliers: (a) Sigma-Aldrich (www.sigma-aldrich.com); (b) Iolitec (www.iolitec.de) 2020 (accessed 1 March 2020).
- [4] A.P. Abbott, J.C. Barron, K.S. Ryder, D. Wilson, Eutectic-based ionic liquids with metal-containing anions and cations, *Chem. Eur. J.* 13 (2007) 6495–6650, <https://doi.org/10.1002/chem.200601738>.
- [5] A.P. Abbott, G. Capper, S. Gray, Design of improved deep eutectic solvents using hole theory, *Chem. Phys. Chem.* 7 (2006) 803–806, <https://doi.org/10.1002/cphc.200500489>.
- [6] A.P. Abbott, R.C. Harris, K.S. Ryder, Application of hole theory to define ionic liquids by their transport properties, *J. Phys. Chem. B* 111 (2007) 4910–4913, <https://doi.org/10.1021/jp0671998>.
- [7] A.P. Abbott, G.C. Apper, D.L. Davies, R.K. Rasheed, V. Tambyrajah, Novel solvent properties of choline chloride/urea mixtures, *Chem. Commun.* (2003) 70–71 <https://doi.org/10.1039/B210714G>.
- [8] J. Li, Z. Han, Y.Z. Bo Yu, Efficient extraction of major catechins in *Camelliasinensis* leaves using green choline chloride-based deep eutectic solvents, *RSC Adv.* 5 (2015) 93937–93944, <https://doi.org/10.1039/c5ra15830c>.
- [9] A.S.B. Gonzalez, M. Francisca, G. Jimeno, S. Lago García de Dios, M.C. Kroona, Liquid–liquid equilibrium data for the systems {LTTM + benzene + hexane} and {LTTM + ethyl acetate + hexane} at different temperatures and atmospheric pressure, *Fluid Phase Equilib.* 360 (2013) 54–62, <https://doi.org/10.1016/j.fluid.2013.09.010>.
- [10] R. Bernasconi, A. Lucotti, L. Nobili, L. Magagnin, Ruthenium Electrodeposition from deep eutectic solvents, *J. Electrochem. Soc.* 165 (13) (2018) D620–D627, <https://doi.org/10.1149/2.0541813jes>.
- [11] M.A. Miller, J.S. Wainright, R.F. Savinel, Iron Electrodeposition in a deep eutectic solvent for flow Batterie, *J. Electrochem. Soc.* 164 (4) (2017) A796–A803, <https://doi.org/10.1149/2.1141704jes>.
- [12] M. Manolova, R. Böck, Electrodeposition of Pd from a deep eutectic solvent system: effect of additives and hydrodynamic conditions, *Trans. IMF* 97 (3) (2019) 161–168, <https://doi.org/10.1080/00202967.2019.1605755>.
- [13] A.P. Abbott, N. Dsouza, P. Withey, K.S. Ryder, Electrolytic processing of superalloy aerospace castings using choline chloride-based ionic liquids, *Trans. IMF* 90 (2012) 9–14, <https://doi.org/10.1179/174591912X13228247936644>.

- [14] H.G. Liao, Y.X. Jiang, Z.Y. Zhou, S.P. Chen, S.G. Sun, Shape-controlled synthesis of gold nanoparticles in deep eutectic solvents for studies of structure–functionality relationships in electrocatalysis, *Angew. Chem. Int. Ed.* 47 (2008) 9100–9103, <https://doi.org/10.1002/anie.200803202>.
- [15] B.L. Kuhn, G.C. Paveglio, S. Silvestri, E.I. Muller, M.S.P. Enders, M.A.P. Martins, N. Zanatta, H.G. Bonacorso, C. Radke, C.P. Frizzo, TiO₂ nanoparticles coated with deep eutectic solvents: characterization and effect on photodegradation of organic dyes, *New J. Chem.* 43 (2019) 1415–1423, <https://doi.org/10.1039/c8nj05957h>.
- [16] X. Li, M. Hou, Z. Zhang, B. Han, G. Yang, X. Wang, L. Zou, Absorption of CO₂ by ionic liquid/polyethylene glycol mixture and the thermodynamic parameters, *Green Chem.* 10 (2008) 879–884, <https://doi.org/10.1039/b801948g>.
- [17] G. Cui, M. Lv, D. Yang, Efficient CO₂ absorption by azolide-based deep eutectic solvents, *Chem. Commun.* 55 (2019) 1426–1429, <https://doi.org/10.1039/c8cc10085c>.
- [18] J. Patino, M.C. Gutierrez, D. Carriazo, C.O. Ania, J.B. Parra, M.L. Ferrera, F. del Monte, Deep eutectic assisted synthesis of carbon adsorbents highly suitable for low-pressure separation of CO₂–CH₄ gas mixtures, *Energy Environ. Sci.* 5 (2012) 8699–8707, <https://doi.org/10.1039/c2ee22029f>.
- [19] I. Juneidi, M. Hayyana, M.A. Hashima, Intensification of biotransformations using deep eutectic solvents: overview and outlook, *Process Biochem.* 66 (2018) 33–60, <https://doi.org/10.1016/j.procbio.2017.12.003>.
- [20] M.A.R. Martins, S.P. Pinho, J.A.P. Coutinho, Insights into the nature of eutectic and deep eutectic mixtures, *J. Solut. Chem.* 48 (2019) 962–982, <https://doi.org/10.1007/s10953-018-0793-1>.
- [21] A. Paiva, R. Craveiro, I. Aroso, M. Martins, R.L. Reis, A.R.C. Duarte, Natural deep eutectic solvents – solvents for the 21st century, *ACS Sustain. Chem. Eng.* 2 (2014) 1063–1071, <https://doi.org/10.1021/sc500096j>.
- [22] Y.H. Choi, J. van Spronsen, Y. Dai, M. Verberne, F. Hollmann, I.W.C.E. Arends, G.J. Witkamp, R. Verpoorte, Are natural deep eutectic solvents the missing link in understanding cellular metabolism and physiology? *Plant Physiol.* 156 (2011) 1701–1705, <https://doi.org/10.1104/pp.111.178426>.
- [23] N. Rodríguez Rodríguez, A. van den Bruinhorst, L.J.B.M. Kollau, M.C. Kroon, K. Binnemans, Degradation of deep-eutectic solvents based on choline chloride and carboxylic acids, *ACS Sustain. Chem. Eng.* 7 (2019) 11521–11528, <https://doi.org/10.1021/acssuschemeng.9b01378>.
- [24] H.E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Organomet. Chem.* 62 (1997) 7512–7515, <https://doi.org/10.1021/jo971176v>.
- [25] R. Santos, A. Rocha, A. Matias, C. Duarte, I. Sá-Nogueira, N. Lourenço, J.P. Borges, P. Vidinha, *RSC Adv.* 3 (2013) 24400–24405, <https://doi.org/10.1039/C3RA44258F>.
- [26] P. Kalhor, K. Ghandi, Deep eutectic solvents for pretreatment, extraction, and catalysis of biomass and food waste, *Molecules* 24 (2019) 4012, <https://doi.org/10.3390/molecules24224012>.
- [27] Q. Zhang, K.D.O. Vigier, S.R. Franc, O. Jerome, Deep eutectic solvents: syntheses, properties and applications, *Chem. Soc. Rev.* 41 (2012) 7108–7146, <https://doi.org/10.1039/C2CS35178A>.
- [28] E.L. Smith, A.P. Abbott, K.S. Ryder, Deep eutectic solvents (DESs) and their applications, *Chem. Rev.* 114 (2014) 11060–11082, <https://doi.org/10.1021/cr300162p>.
- [29] B. Tang, K.H. Row, Recent developments in deep eutectic solvents in chemical sciences, *Monatsh. Chem.* 144 (2013) 1427–1454, <https://doi.org/10.1007/s00706-013-1050-3>.
- [30] G. García, S. Aparicio, R. Ullah, M. Atilhan, Deep eutectic solvents: physicochemical properties and gas separation applications, *Energy Fuel* 29 (2015) 2616–2644, <https://doi.org/10.1021/ef5028873>.
- [31] A.P. Abbott, D. Boothby, G. Capper, D.L. Davies, R.K. Rasheed, Deep eutectic solvents formed between choline chloride and carboxylic acids: versatile alternatives to ionic liquids, *J. Am. Chem. Soc.* 126 (2004) 9142–9147, <https://doi.org/10.1021/ja048266j>.
- [32] A.M. Popescu, V. Constantin, Viscosity of alkali fluoride ionic melts at temperatures up to 373.15 K above melting points, *Chem. Eng. Commun.* 202 (2015) 1703–1710, <https://doi.org/10.1080/00986445.2014.970254>.
- [33] John O.M. Bockris, Amulya K.N. Reddy, *Modern Electrochemistry 1*, Springer, Ionics, 1998 461–463.
- [34] F. Endres, A.P. Abbott, D.R. Mac Farlane, *Electrodeposition from Ionic Liquids*, Wiley-VCH Verlag, Weinheim, 2008.
- [35] P. Wasserscheid, P. Welton, *Ionic Liquids in Synthesis*, Weinheim, Wiley-VCH Verlag, 2003.
- [36] RefractiveIndex.Info, <https://refractiveindex.info/?shelf=main&book=H2O&page=Hale2020> (accessed 1 March 2020).
- [37] Q. Li, J. Jiang, G. Li, W. Zhao, X. Zhao, T. Mu, The electrochemical stability of ionic liquids and deep eutectic solvents, *Sci. China Chem.* 59 (5) (2016) 571–577, <https://doi.org/10.1007/s11426-016-5566-3>.
- [38] N. Delgado-Mellado, M. Larriba, P. Navarro, V. Rigual, M. Ayuso, J. García, F. Rodríguez, Thermal stability of choline chloride deep eutectic solvents by TGA/FTIR-ATR analysis, *J. Mol. Liq.* 260 (2018) 37–43, <https://doi.org/10.1016/j.molliq.2018.03.076>.