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Triethylammonium-based protic ionic liquids with sulfonic acids: phase behavior and electrochemistry

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Abstract

Six triethylammonium-based protic ionic liquids (PILs) and two molten salts were synthesized via a proton transfer reaction from sulfonic acid to triethylamine (TEA). The PILs were characterized by ¹H NMR, ¹³C NMR, ¹H/¹⁵N NMR and FT-IR spectroscopic methods. The phase behavior of the PILs was studied using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The temperature dependences of the PILs electrical conductivity, viscosity, and electrochemical stability window (ECW) were studied. The highest electrical conductivity and ECW values are registered in triethylammonium triflate. The thermal and electrochemical characteristics of the salts obtained in this work have been analyzed in comparison with the literature data by the properties of triethylammonium-based salts with sulfonic acids.

Keywords: Triethylammonium salts, Ionic liquid, Synthesis, Thermal properties, Electrochemistry

1. Introduction

Protic ionic liquids (PILs) are one of the most important subclasses of ionic liquids. PILs are obtained via a neutralization reaction between Brønsted acids and Brønsted bases. These substances are salts containing a large organic cation and an organic or inorganic anion. The key feature of PILs is the presence of an exchangeable proton on the cation enabling the formation of hydrogen bonds with the anion. Ionic liquids are called "Designer solvents" [1] because variations of the cation and anion nature allow synthesizing salts with different physico-chemical properties. The persistently high interest in the PILs studies in the last few decades has been caused by a wide range of their possible applications. Thanks to the combination of some useful properties, such as low vapour pressure, high thermal stability, high electrical conductivity, large electrochemical window, PILs are used as the so-called "green solvents" [2–5], supercapacitors [6], and electrolytes for fuel cells [7–13].

In this work, we study PILs based on triethylamine with sulfonic acids. At present there are publications devoted to investigation of triethylamine-based PILs with trifluoroacetic [14–17], benzoic [14,16], formic [18,19], nitric [19], acetic [19–25], phosphoric [10,20,21,23,26,27], dibutylphosphoric [28,29], monofluorophosphoric [26], and phosphorous [10,15,17] acids. The most studied PILs among those with sulfonic acids are the salts with methanesulfonic [10,14,16,26,28,30–34], trifluoromethanesulfonic [10,14,16,26,30,31–33,35,36] and sulfuric [10,20–24,26] acids, and bis(tri(tetra)fluoromethylsulfonyl)imide [7,33,35,37–40]. There are also few works devoted to the synthesis and study of the properties of triethylamine-based PILs with p-toluenesulfonic [15,17], benzenesulfonic, as well as of fluorinated aromatic sulfonic acids (fluorobenzenesulfonic, trifluorobenzenesulfonic, perifluorobenzenesulfonic, perifluorobutanesulfonic, perfluoroctanesulfonic, and pentafluorobenzenesulfonic ones) [16,34,35]. It should be noted that the ionic liquids studied in most of the abovementioned works belong to the group of room temperature PILs.

The size of the electrochemical window (ECW) of ammonium PILs varies greatly (from 0.66 to 5.57 V) depending on the cation and anion nature and measurement conditions (temperature range, scanning speed) [5,18,41–43]. In PILs with di/triethylammonium cations, the ECW size ranges between 1.23–4.73 V [43,44]. Besides, work [44] shows that the ECW values for TEA/MsO obtained with glassy carbon, gold and platinum electrodes equaled 4.73, 2.83, and 2.47 V, respectively.

The experimental material accumulated so far allows us to find correlations between individual thermal and physico-chemical characteristics of PILs and to use them for predicting the properties of the PILs. It has been established that in many ionic liquids, the ratio of the glass transition temperature to the melting temperature $T_g/T_m = 2/3$ (the "2/3 law" for glass transition temperatures). In our earlier studies of triethanolamine-based protic ionic liquids with various sulfonic acids, we obtained that the T_g/T_m values of the PILs are located in the range of 0.64–0.69, which is in good agreement with the "2/3 law" [45]. At the same time, the authors of work [26] studied the properties of a lot of PILs based on aliphatic and aromatic amines with different acids (trifluoromethanesulfonic, difluorophosphoric, formic, phosphoric, sulfuric, nitric, methanesulfonic, tetrafluoroboric, hydrofluoric ones) and found that this rule could be easily applied only to a limited number of PILs in the ethylammonium family. However, when they tried to obtain a correlation between T_g and T_m for all the salts that were studied in the work and whose temperatures were determined, the deviation from the 2/3 ratio became quite significant. The authors concluded that this law was only true for the salts, whose melting points were less than 50% above their glass transition temperatures.

The authors of work [33] obtained a correlation of viscosities of triethylammonium methylsulfonate, trifluoromethyl sulfonate and imidazolium bis(trifluoromethylsulfonyl)imide with their vaporization enthalpies.

A correlation of different properties of PILs that is often tested by scientists is their dependence on ΔpK_a (the difference between the dissociation constant of the protonated base and acid in aqueous solution). Works [46–48] have determined a dependence of the thermal stability of PILs based on secondary and/or tertiary ammonium cations on the pK_a value of the original acid anion. According to work [46], the thermal stability of PILs with $\Delta pK_a > 15$ is similar to that of aprotic ionic liquids. Besides, a $\Delta p K_a$ threshold level has been found at which PILs have both good thermal stability and high ionicity. The authors of [49] who studied five protic ionic liquids with propylammonium, 3-hydroxy propylammonium as cations, and formate, acetate, trifluoroacetate as anions have established that PILs with high $\Delta p K_a$ values have a high density and low viscosity. At the same time, in work [47], the authors who studied the electrochemical properties of the PILs based on different amines and bis(trifluoromethanesulfonyl)amide acid have come to a conclusion that conductivity, density and viscosity by and large depend on the structure of amines rather than the $\Delta p K_a$. Electrochemical measurements for a series of protic ionic liquids based on 1,8-diazabicyclo[5.4.0]-7-undecene and tertiary amines (diethylmethyl amine and ethylmethylpropyl amine) with different Brønsted acids have revealed that the open circuit potential for H_2/O_2 cells grows with an increase in ΔpK_a of the constituent acid and base and passes through a maximum to gradually fall with a further increase in the $\Delta p K_a$ [50]. To sum up, it should be noted that the pK_a values determined for aqueous solutions may be incorrect for analysis of nonaqueous PILs [14]. The authors of work [51] used the Hammet acidity function values (H₀ values), calculated based on the H₀ of the pure forms of sulfuric and fluorosulfuric acids as the criterion of acidity evaluation of the original acids for PILs synthesis. They also emphasized that this analysis was correct for the members of the sulfuric acid family.

Thus, it remains urgent to determine physico-chemical and electrochemical properties of PILs and to find the correlation dependences between the different characteristics in order to select the optimal composition of new salts for their further effective applications.

2. Experimental part

2.1. Materials

Triethylamine was obtained from Acros organics, the sulfonic acids [sulfuric, methanesulfonic, trifluoromethanesulfonic (triflic), amidosulfonic (sulfamic), benzene sulfonic, 3-nitrobenzenesulfonic, 2-sulfobenzoic (*o*-sulfobenzoic), 5-sulfosalicylic] were of the highest purity available (Tokyo Chemical Industry, Acros organics and Sigma-Aldrich) and were used without further purification.

2.2. General procedure of PILs synthesis

The PILs were prepared via a triethylamine neutralization reaction directly with sulfonic acids in an argon atmosphere. A detailed description of the procedure of synthesizing ionic liquids is shown in work [15].

2.3. Methods

A detailed description of the experimental techniques is given in work [15]. The FT-IR spectra of the compounds were recorded on a Bruker Vertex 80V device in the region of 7500 - 370 cm⁻ ¹ from pellets with KBr. The NMR spectra were recorded on a Bruker Avance-500 spectrometer in DMSO-d₆ solution. All the ¹H, ¹³C NMR chemical shifts were referenced against TMS set as 0 ppm. The melting point, crystallization point and glass transition temperature were determined on a NETZCH DSC 401 F1-calorimeter at the rate of 10 °C min⁻¹. The TGA of the PILs was performed on a NETZCH TG 209 F1 analyzer in a flow of argon (20 ml/min) at a heating rate of 10 K/min. The PILs resistance was determined by the electrochemical impedance method with a Solartron 1260A complete with the electrochemical interface Solartron 1287 over the frequency range of 0.1 Hz - 1 MHz with the signal amplitude of 10 mV and with the accuracy higher than 0.2%. The viscosities (η) of the PILs were measured with a rotational programmable viscometer (Brookfield DV-II, spindle S18); the measurement accuracy was equal to ± 1 %. The electrochemical windows were obtained by using a PI 50-Pro-3 pulse potentiostat with automatic registration, and the data were processed using the PS Pack 2 software. The electrochemical investigations were carried out with a three-electrode cell with a platinum wire as the working electrode in the temperature range of 50-120° C. To maintain the temperature, we used a thermostat (TERMEX, Russia) in which the thermostating liquid was silicone oil PMS 20; the accuracy of maintaining the temperature was $\pm 0.1^{\circ}$ C. The density was measured with an Anton Paar DMA 5000M densimeter equipped with an Xsample 352 H automatic filling unit. The densimeter was calibrated with dry air and bidistilled water before every measurement.

The water contents of PILs at room temperature, determined by Karl–Fischer titration (V30, Mettler Toledo), were below 1 wt%.

3. Results and discussion

The structural formulas of the salts, aqueous dissociation constants of the original acids, and the abbreviations of the synthesized PILs are summarized in Table 1.

Table 1

Name, structural formulae and abbreviations of synthesized triethylammonium ILs.

Name	Structural formulas	pK _a starting acids	Salts abbreviation
hydrogen sulfate	NH+O ⁻ S-OH	1.99 [52]	TEA/HSO ₄



3.1. IR NMR spectroscopy characterization

Nitrogen atom protonation in tertiary amines, as a rule, is accompanied by a downfield ¹⁵N resonance shift [61]. The chemical shifts of the onium cation nitrogen in the ¹H/¹⁵N salts spectra are displaced 9 ppm downfield compared to the pure triethylamine signal (Table 2). The resonance signals of the protons of the NCH₂ and CH₃ groups in the ¹H NMR spectra of salt solutions are also shifted downfield relative to the original TEA. The frequency shift does not exceed 0.6 ppm. Besides, the ¹³C NMR chemical shifts of the cation are 2-3 ppm shifted upfield compared to the original TEA for the amine methyl fragment signal (Table 2).

Table 2

¹H, ¹³C and HMBC-¹H/¹⁵N chemical shifts of triethylamine and triethylammonium cation in DMSO- d_6 .

DIL	δ _H (ppm)		δ _C (ppm)		δ_N (ppm)	
FILS	NCH ₂	CH ₃	\mathbf{NH}^+	NCH ₂	CH_3	NH^+
TEA	2.43-2.39	0.93-0.9	-	45.73	11.77	-334.77
TEA/H ₂ SO ₄	3.08-3.03	1.18-1.15	4.31	45.84	8.64	-325.32
TEA/MsO	3.13-3.08	1.33 1.3	10.2	46.5	8.9	-326.5

TEA/TfO	3.12-3.07	1.19-1.16	8.82	45.8	8.6	-325.2
TEA/SAM	3.09-3.05	1.19-1.16	8.74	45.8	8.6	-325.6
TEA/BSu	3.09-3.05	1.19-1.16	9.15	45.8	8.76	-325.1
TEA/NBSu	3.12-3.08	1.18-1.15	8.83	45.9	8.8	-325.3
TEA/SBA	3.08-3.04	1.16-1.13	11.12	45.8	8.76	-325.3
TEA/SSA	3.13-3.06	1.18-1.15	9.02	45.7	8.5	-325.3

A detailed comparison of the bands in the IR- and NMR- spectra is presented in ESI.

The IR-spectra of the salts, in contrast to the spectra of the original compounds, contain a number of bands which we classify as the NH stretching vibrations in the region of 2533-2677 cm⁻¹ for aliphatic and 2257-2678 cm⁻¹ for aromatic acids [62–64]. Fig. 1 shows the IR-spectra of the synthesized salts in comparison with the pure TEA spectrum.





Thus, the NMR and IR spectroscopy studies have confirmed the presence of protonated amine.

3.2 Phase behavior of the synthesized compounds

The temperatures of phase transitions and thermal stability of materials are important physical properties of PILs determining their working temperature range.

The melting temperature, the cool crystallization temperature, the glass transition temperature and the decomposition temperature of the synthesized PILs in comparison with the literature data are given in Table 3.

Table 3

F==F===							
		T_{cr}	T_{m}	ΔH_{m}	$T_g / (\Delta c_p)$	T_{dec}	H_2O
PILs		$(^{\circ}C)$	(°C)	$(J \cdot g^{-1})$	$(^{\circ}C) / (J \cdot g)$	$(^{\circ}C)$	(wt%)
					${}^{1}K^{-1}$)		
	1:~	-22.9	33.1	20 67	_	203	0.81
	nq	-24 [14]	33 [14]	89.07	_	305 [14]	50 ppm
		-31 [30]	25 [30]		_	218 [30]	2 mol%
		-31.6 [28]	24.3 [28]		-78.9 [28]	—	100
IEA/MSU		_	21.6 [26]		-96.5 [26]	269.7	ppm
		_	33 [31]		-75 [31]	[26]	<1 ppm
		_	17.4 [10]		-62.1 [10]	290 [31]	_
						225 [10]	_
	liq	-29.3	33.2	35.55	_	315.4	0.50
	-	-20 [14]	32 [14]		-58 [14]	376 [14]	50 ppm
TEA/TfO		-13 [30]	26 [30]		_	322 [30]	2 mol%
		_	34.3 [10]	Q_{-}	_	358 [10]	_
		_	36 [35]	-	-58 [35]	380 [35]	_
	cr	26.8	66.8	13.95	-35.5	229	0.25
IEA/SAM			C		(0.162)		
		-14.6 (10K/min)	69.8 (10K/min)	37.87		310	0.77
TEA/BSu	cr	11 (5K/min)	76.3 (5K/min)			330 [16]	50 ppm
		106 [16]	119 [16]				
	cr	0.9	75.9	58.27	-42.7	298	0.57
TEA/NBSu					(0.140)		
TEA/SBA	cr	54.0	106.5	105.92		279	0.57
	solid	117.3	147.0	49.03	_	278	0.74
IEA/SSA		_	140 [65]		_	_	_
	cr	60.65	82.42	41.26	-60.7	259	0.72
TEA/HSO ₄			74.7 [10]		(0.046)	270 [10]	_
		4/7	84.2 [26]		_	262.8	<1 ppm
					-100.1 [26]	[26]	**

Key properties of the synthesized PILs

 T_{cr} is the crystallization temperature; T_m is the melting temperature; T_g is the glass transition temperature; T_{dec} is the decomposition temperature, which are stated as the temperatures corresponding to a 5% loss of the sample weight.

The measured temperatures of phase transitions for TEA/MsO(TfO) agree well with the literature data (Table 3). A certain deviation of the T_{cr} value obtained in this work for TEA/TfO from the literature data may be caused by the DSC experiment conditions, in particular, by the different scanning speed. The values of T_{cr} and T_m obtained in this work for TEA/BSu and the T_g value for TEA/HSO₄ differ a lot from the literature data (Table 3). The reason for such discrepancy cannot be easily identified.

As Table 3 shows, the TEA/SAM(NBSu, HSO₄) salts exhibit crystallization/melting and glass transition. The thermograms of the other salts show only the crystallization/melting transitions. It is possible that if the DSC thermograms of some PILs do not have glass transitions, the T_g value can be beyond the limits of the measured temperature range. As an example, Fig. 2 shows DSC thermograms of the TEA/NBSu and TEA/SBA. The exotherm (T_{cr}) observed on the heating cycle is associated with the crystallization of the supercooled liquid at 54°C for TEA/SBA and at 0.9°C for TEA/NBSu. Further heating of the salts results in the observation of the main endotherm associated with the melting point (T_m) at 106.5°C for TEA/SBA and at 75.9°C for TEA/NBSu. For TEA/SBA a small endothermic process (T_{cc}) is also observed at 83.9°C, associated with the crystal phase transition between two metastable phases [66]. The TEA/NBSu thermogram shows a glass transition.



Fig. 2. Differential scanning calorimeter (DSC) thermograms of the TEA/NBSu and TEA/SBA for the second heating steps.

The synthesized triethylammonium mesylate and triflate are in liquid state at ambient temperature and, thus, can be classified as room temperature ionic liquids. The melting point of the TEA/SBA(SSA) salts is above 100°C, which allows us to classify them as molten salts.

Substitution of the hydroxyl group in the hydrogen sulphate anion with different functional groups (CH₃, NH₂ CF₃) and benzene ring reduces the melting temperature of triethanolammonium mesylate, sulfamate, triflate and besylate, respectively. In [67], it has been found that the melting points vary depending on the nature of the anions. It has been determined that an increase in the anion radius in imidazole-based aprotic ionic liquids leads to a decrease in the salts melting points as the electrostatic force between the imidazolium cation and the anions becomes weaker. In some of the studied anions, such trend is observed for the salts with a sulfuric acid anion and its derivatives: MsO~TfO < SAM <BSu < HSO₄.

When studying the thermal characteristics of the PILs based on primary, secondary and tertiary ammonium cations with fluorinated (heptafluorobutyrate, pentadecafluorooctanoate) and non-fluorous (octanoate) anions, we found that the salts with fluorinated anions have higher melting points compared to those with hydrocarbons [68]. The TEA/TfO(MsO) synthesized in this work have similar T_m values. The reason why we did not observe any changes in the melting point under the transition from mesylate to triflate may be the small number of fluorine atoms in the TEA/TfO in comparison with the salts from reference [68].

Introduction of substituents in the BSu benzene ring and changes in their positions increase the melting points of TEA/NBSu(SBA, SSA). A comparison of the obtained characteristics for the TEA salts with the analogous properties for triethanolammonium-based (TEOA) salts [45] shows that almost all TEOA salts with sulfonic acids undergo glass transition, which is evidently associated with their viscosity. Besides, cooling causes only glass transition in triethanolammonium hydrogen sulphate, triflate, sulfobenzoate and sulfosalicylate, but does not lead to melt phase transition to crystalline state. The salts based on TEA with the same anions (except TEA/HSO₄) do not undergo glass transition, whereas the crystallization and melting phase transitions are observed. The DSC curve of the TEA/HSO₄ shows the temperatures of the three phase transitions. Among the studied PILs, only triethyl- and triethanolammonium sulfamates demonstrate similar thermal behavior. The decomposition temperatures of triethanolamine salts are about 100 °C lower than those of triethylamine salts [45]. In the functionalized four IL, the ILs containing TfO anion shows a higher stability than HSO₄ anion [69]. Thus, the thermal behavior of PILs depends both on the cation and anion nature.

The TG plots are shown in Fig. 3.



Fig. 3. TG analysis of the PILs.

The thermal stability of the studied triethylammonium-based ionic liquids lies within the temperature range of 200–320 °C. No correlation is observed between the T_{dec} and $\Delta p K_a$ values for the PILs synthesized in this work. For the TEA-based salts, we earlier found a correlation between the temperatures of crystallization and melting [15]. The values of T_c and T_m obtained in this work are also quite well described by the proposed correlation equation.

3.3. Electrical conductivity and electrochemical window

Electrical conductivity is a very important parameter for the assessment of the potential application of PILs in electrochemical devices [8,12,70–73]. The electrical conductivity of the synthesized PILs has been evaluated from their impedance spectra. As an example, the spectra of TEA/TfO at different temperatures are shown in Fig. 4. The spectra of the other PILs, except TEA/SAM, look similar. The spectra correspond to the equivalent circuit consisting of volume resistance of the electrolyte (R) connected in series with a constant phase element (CPE_{dl}). The impedance hodograph for TEA/SAM consists of two separated typical regions: an arc at high frequencies and a line in the low-frequency region. The electrode equivalent circuit consists of a constant phase element connected in series with a parallel combination of the bulk electrolyte resistance and a second CPE representing the cell geometric capacitance. The appearance of geometric capacitance is associated with the fact that the cell electrodes are separated by a low conductivity electrolyte. It should be noted that a temperature increase reduces the semicircle diameter and the arc gradually disappears [30].



Fig. 4. Impedance spectra for TEA/TfO at selected temperatures.

Fig. 5 presents temperature dependences of electrical conductivity of TEA salts studied in this work and TEOA salts obtained by us earlier in work [45].



Fig. 5. Arrhenius plot of electrical conductivity for TEA (a) and TEOA (b) based salts. The data on the electrical conductivity of TEA/PTSA and triethanolamine-based salts were taken from our previous works [15,45].

The obtained values of electrical conductivity of the TEA salts lie within the range of $10^{-4} \div 10^{-2}$ Ohm⁻¹·cm⁻¹. Triethylammonium triflate has the highest electrical conductivity value. The limited temperature range of electrical conductivity measurements for the salts with sulfuric, benzenesulfonic, 3-nitrobenzenesulfonic and amidosulfonic acids is associated with the melting temperature of these ionic liquids. It is possible to measure the electrical conductivity of the salts with TfO, MsO and PTSA [15] at the temperatures lower than their T_m as these salts are in metastable liquid state. The TEA/TfO(MsO) electrical conductivity values obtained in this work are in good agreement with the literature data presented in [28,30], the difference in the values at the same temperatures does not exceed 0.1 mS·cm⁻¹. These electrical conductivity values differ slightly more significantly from the data of work [10]. For example, for TEA/MsO and TEA/HSO₄, the difference in the electrical conductivity values at 120 °C was 5.3 and 2.8 mS·cm⁻¹, respectively.

The value of the PILs specific electrical conductivity depends on different factors: viscosity, ion size, ion aggregation and proton transfer mechanism (Grotthus proton-hopping and ion migration (vehicle)). It is known that if the proton transfer mechanism is ion migration, the electrical conductivity mainly depends on viscosity. For the PILs synthesized in this work, the electrical conductivity reduction correlates with the increase in the salts viscosity (see the Table S1 and Fig. S2 in the ESI). The electrical conductivity of the triethylammonium based salts with different sulfonic acids increases in the anion series in the following order: SAM < NBSu < BSu < HSO₄ < PTSA < MsO < TfO at 75 °C.

In work [28] devoted to studying the properties of PILs containing low-molecular-weight Bronsted acids and amine bases it was concluded that electrical conductivity of the salts did not solely depend on viscosity. It was found that the ethylenediammonium and di-n-butylammonium formate salts had similar viscosity values but different electrical conductivity. Besides, pyrrolidinium o-benzoic sulfimide and acetate had similar electrical conductivity values, whereas their viscosity differed by almost two orders of magnitude. Having studied the properties of PILs di(tri)ethylamine, diethanolamine, pyrrolidine, ethylenediamine, based on bis(2methoxyethyl)amine with formic, acetic, methylsulfonic acids and di-n-butylphosphate, the authors [44] came to a conclusion that salt electrical conductivity depended to a greater extent on the anion type rather than on the viscosity value. We did not observe such dependences in the salts that we studied.

A comparison of the electrical conductivity of TEA salts with the similar values for TEOA obtained by us earlier in [45] shows (Fig. 5) that the electrical conductivity of the TEA PILs is

mostly higher than that of the TEOA salts, which can be also associated with a higher viscosity of the latter. The electrical conductivity values of the TEOA salts lie within the range of $10^{-5} \div 10^{-3}$ Ohm⁻¹·cm⁻¹. The electrical conductivity of the TEOA-based salts also decreases with the increase in their viscosity.

The temperature dependent electrical conductivity values for TEA/(MsO, TfO) were fitted to the nonlinear Vogel–Tamman–Fulcher (VTF) equation [74,75]:

$$\kappa = \kappa_o \cdot \exp\left[\frac{-B}{T - T_o}\right],$$

where κ_0 is the electrical conductivity at infinitely high *T*; *B* is related to the activation energy E_a ; and T_0 is the ideal glass transition temperature. The VFT parameters calculated from the electrical conductivities of the salts are summarized in Table 4. **Table** 4

VFT parameters for electrical conductivity and ECW of the PILs.				
PILs	$\kappa_o (\mathrm{S} \cdot \mathrm{cm}^{-1})$	<i>B</i> (K)	$T_{o}\left(\mathrm{K} ight)$	R^2
TEA/MsO	0.35 ± 0.09	556 ± 81	191 ± 11.5	0.999
TEA/TfO	0.80 ± 0.04	925 ± 25	116 ± 3.2	0.999
TEA/PTSA [*]	0.06 ± 0.01	285 ± 37	246 ± 6.3	0.998

• the data of the work [15].

The Walden's rule is widely used for analyzing electroconductive properties of liquid systems. If a liquid consists of independent ions and their diffusion depends on the liquid viscosity, the Walden plot of such system shows an "ideal" line with the slope close to 1 (we used dilute aqueous solutions of KCl as the reference system). According to the positions of the dependences for this compound – above or below this "ideal" line – the ionic liquids are divided into "poor", "good" μ "superionic" types [76]. The Fig. 6 shows a Walden plot for TEA/TfO and TEA/MsO.



Fig. 6. Walden plot for TEA/TfO and TEA/MsO. The equivalent conductivity and viscosity values for 0.01M KCl were taken from [77,78] and [79], respectively.

As the Fig. 6 shows, the dependences for triethylammonium mesylate and triflate are close to the "ideal" KCl line but are still below it, which can, first and foremost, be explained by the ionic association of these salts.

Table 5 shows the ECW values for the studied PILs at the temperature of 120 °C.

Table 5

The ECW values for the PILs at 120 °C.

PILs	ECW (V) (120 °C)
TEA/TfO	2.80
TEA/MsO	2.50
TEA/SAM	2.0
TEA/BSu	1.95

TEA/NBSu	1.85
TEA/SBA	2.30
TEA/PTSA [*]	2.1
TEA/HSO ₄	2.5
TEA/SSA	No well-defined potential
	window can be obtained

the data of the work [15]

For the salts synthesized in this work and triethylammonium tosylate [15], the electrochemical window increases in the series of the salts as follows: NBSu < BSu < SAM < PTSA < SBA < HSO₄(MsO) < TfO (Table 5, Fig. 7). The ECW for TEA/MsO agrees well with the data of [44] obtained in similar conditions (2.47 V). In ESI section (see Fig. S3) the cyclic voltammograms of the TEA/MsO at a high number of cycles are shown. The little shifts of both cathodic and anodic potentials were observed when the number of cycles was increasing. The triflate PIL has a wider electrochemical window than the mesylate PIL, because the TfO anion is more stable against oxidation than the MsO anions. The improved stability is attributed to the greater delocalization of the negative charge in the triflate anion than in the mesylate anion [30].



Fig. 7. Cyclic voltammograms of the PILs at 120 $^{\circ}$ C (a) and of the TEA/TfO at different temperatures (b). The potential scan rate is 10 mV·sec⁻¹.

The reduction potential of the TEA cation depends on the anion, lies within the range of $(0.2\div1.1)$ V and grows in the following order: SAM < BSu(NbSu) < SBA(MsO) < PTSA < HSO₄ < TfO. The TEA/MsO salt has the biggest oxidation potential of the anion (1.9 V), which is 0.1–0.6 V higher than in the other PILs studied in this work. In all the PILs, a temperature increase reduces the ECW, both in the anode and the cathode regions. As an example, Fig. 7b

shows cyclic voltammograms of the TEA/TfO at different temperatures. The cathodic peak current at -0.6 V can be associated with the presence of dissolved oxygen in the PIL and, as a result, with the oxygen reduction reaction (ORR). The authors of [80], supposed that the possibility of an irreversible two-electron reaction leading to the formation of H_2O_2/H_2O on Pt. We did not control the water content in the sample after the CV experiment. The increase in the peak current and the shift of the ORR initial potential to the positive region caused by the temperature growth are attributed to enhanced kinetics for the ORR [81].

The ECW for triethylammonium salts is smaller than that for similar triethanolammonium PILs [45], in which the cation reduction potential also depends on the counterion nature. In reference [82] it is shown that every structure of the triethanolammonium-based PILs is stabilized through multiple H-bonds between the protons in the N-H and O-H groups of the cation and different oxygen atoms of the anion acid and the strong electrostatic interactions. It probably leads to higher TEOA cation decomposition overvoltage, making the ECW value for triethanolammonium PILs larger than for triethylammonium salts.

Thus, the electrochemical properties of the salts and their thermal behavior are determined by the nature of both the anion and the cation.

4. Conclusions

Six triethylammonium-based protic ionic liquids (triethylammonium mesylate, triflate, sulfamate, besylate, nitrobenzenesulfonate, hydrogen sulfate) and two molten salts (triethylammonium sulfobenzoate and sulfosalicylate) have been synthesized. The PILs have been characterized by ¹H NMR, ¹³C NMR, ¹H/¹⁵N NMR and FT-IR spectroscopic methods. The obtained spectral characteristics confirm salt formation.

In the TEA/SAM(NBSu, HSO₄) salts, we observed crystallization/melting processes and glass transition, while in the TEA/MsO(TfO, BSu, SBA, SSA) salts – only crystallization/melting transitions. It has been established that the TEA/MsO(TfO) salts have melting temperatures ~ 33°C and belong to room temperature PILs. The TEA/SBA(SSA) salts melt at the temperatures above 100 °C and belong to molten salts. The melting temperatures of the TEA/SAM(BSu, NBSu, HSO₄) are within the range of 66 - 83 °C.

The thermal stability T_d of the studied triethylammonium-based ionic liquids lies within the temperature range of 200–320 °C.

The obtained electrical conductivity values of TEA salts are within the range of $10^{-4} \div 10^{-2}$ Ohm⁻¹·cm⁻¹ depending on the temperature and the anion. In the PILs synthesized in this work, electrical conductivity decrease correlates with the increase in the salt viscosity.

The electrochemical window of the studied PILs at the temperature of 120 °C ranges from 1.85 to 2.8 V. A temperature increase narrows the ECW in all the studied PILs.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at

References

- [1] M. Freemantle, Chem. Eng. News 76 (1998) 32–37.
- [2] M.J. Earle, K. R. Seddon, Pure Appl. Chem. 72 (2000) 1391–1398.
- [3] D. Kogelnig, A. Stojanovic, M. Galanski, M. Groessl, F. Jirsa, R. Krachler, B.K. Keppler, Tetrahedron Lett. 49 (2008) 2782–2785.
- [4] R. Kordala-Markiewicz, H. Rodak, B. Markiewicz, F. Walkiewicz, A. Sznajdrowska, K. Materna, K. Marcinkowska, T. Praczyk, J. Pernak, Tetrahedron 70 (2014) 4784–4789.
- [5] Z. Chen, Sh. Liu, Z. Li, Q. Zhang, Y. Deng, New J. Chem. 35 (2011) 1596–1606.
- [6] L. Timperman, F. Beguin, E. Frackowiak, M. Anouti, J. Electrochem. Soc. 161 (2014) A228–A238.
- [7] Md.A.B.H. Susan, A. Noda, S. Mitsushima, M. Watanabe, Chem. Commun. 8 (2003) 938– 939.
- [8] A. Fernicola, B. Scrosati, H. Ohno, Ionics 12 (2006) 95–102.
- [9] K. Wippermann, J.Wackerl, W. Lehnert, B. Huber, C. Korte, J. Electrochem. Soc. 163 (2016) F25–F37.
- [10] H. Nakamoto, M. Watanabe, Chem. Commun. 43 (2007) 2539–2541.
- [11] S.S. Sekhon, P. Krishnan, B. Singh, K. Yamada, C.S. Kim, Electrochim. Acta 52 (2006) 1639–1644.
- [12] D.R. MacFarlane, N. Tachikawa, M. Forsyth, J.M. Pringle, P.C. Howlett, G.D. Elliott, J.H. Davis, M. Watanabe, P. Simon, C.A. Angell, Energy Environ. Sci. 7 (2014) 232–250.
- [13] J.-P. Belieres, D. Gervasio, C.A. Angell, Chem. Commun. 46 (2006) 4799–4801.
- [14] M. Martinez, Y. Molmeret, L. Cointeaux, C. Iojoiu, J.-C. Lepretre, N. El Kissi, P. Judeinstein, J.-Y. Sanchez, J. Power Sources 195 (2010) 5829–5839.
- [15] L.E. Shmukler, M.S. Gruzdev, N.O. Kudryakova, Yu.A. Fadeeva, A.M. Kolker, L.P. Safonova, RSC Adv. 6 (2016) 109664–109671.
- [16] M. Martinez, C. Iojoiu, P. Judeinstein, L. Cointeaux, J.-C. Lepretre, J.-Y. Sanchez, ECS Trans. 25 (2009) 1647–1657.
- [17] I.V. Fedorova, M.A. Krestyaninov, L.P. Safonova, J. Phys. Chem. A 121 (2017) 7675– 7683.
- [18] Ch. Zhao, G. Burrell, A.A.J. Torriero, F. Separovic, N.F. Dunlop, D.R. MacFarlane, A.M. Bond, J. Phys. Chem. B 112 (2008) 6923–6936.
- [19] T.L. Greaves, A. Weerawardena, I. Krodkiewska, C.J. Drummond, J. Phys. Chem. B 112 (2008) 896–905.
- [20] P. Attri, P.M. Reddy, P. Venkatesu., A. Kumar, T. Hofman, J. Phys. Chem. B 114 (2010) 6126–6133.
- [21] P. Attri, P.M. Reddy, P. Venkatesu, Indian J. Chem. 49A (2010) 736–742.
- [22] T. Kavitha, P. Attri, P. Venkatesu, R.S. Rama Devi, T. Hofman, J. Chem. Thermodyn. 54 (2012) 223–237.
- [23] V. Govinda, P.M. Reddy, I. Bahadur, P. Attri, P. Venkatesu, P. Venkateswarlu, Thermochim. Acta 556 (2013) 75–88.
- [24] R. Umapathi, P. Attri, P. Venkatesu, J. Phys. Chem. B 118 (2014) 5971-5982.
- [25] V. Govinda, P. Attri, P. Venkatesu, P. Venkateswarlu, J. Mol. Liq. 164 (2011) 218-225.
- [26] J.-Ph. Belieres, C.A. Angell, J. Phys. Chem. B. 111 (2007) 4926–4937.
- [27] T. Kavitha, P. Attri, P. Venkatesu, R.S. Rama Devi, T. Hofman, Thermochim. Acta 545 (2012) 131–140.
- [28] G.L. Burrell, I.M. Burgar, F. Separovic, N.F. Dunlop, Phys. Chem. Chem. Phys. 12 (2010) 1571–1577.
- [29] G.L. Burrell, I.M. Burgar, Q. Gong, N.F. Dunlop, F. Separovic, J. Phys. Chem. B 114 (2010) 11436–11443.
- [30] J.L. Lebga-Nebane, S.E. Rock, J. Franclemont, D. Roy, S. Krishnan, Ind. Eng. Chem. Res. 51 (2012) 14084–14098.
- [31] C. Iojoiu, M. Martinez, M. Hanna, Y. Molmeret, L. Cointeaux, J.-C. Lepretre, N. El Kissi, J. Guindet, P. Judeinstein, J.-Y. Sanchez, Polym. Adv. Technol. 19 (2008) 1406–1414.

- [32] K. Fumino, A.-M. Bonsa, B. Golub, D. Paschek, R. Ludwig, ChemPhysChem 16 (2015) 299–304.
- [33] A.-M. Bonsa, D. Paschek, D.H. Zaitsau, V.N. Emel'yanenko, S.P. Verevkin, R. Ludwig, ChemPhysChem 18 (2017) 1242–1246.
- [34] V. Di Noto, M. Piga, G.A. Giffin, S. Lavina, E.S. Smotkin, J.-Y. Sanchez, C. Iojoiu, J. Phys. Chem. C 116 (2012) 1361–1369.
- [35] C. Iojoiu, P. Judeinstein, J.-Y. Sanchez, Electrochim. Acta 53 (2007) 1395–1403.
- [36] C. Iojoiu, M. Hana, Y. Molmeret, M. Martinez, L. Cointeaux, N. El Kissi, J. Teles, J.-C. Lepretre, P. Judeinstein, J.-Y. Sanchez, Fuel Cells 10 (2010) 778–789.
- [37] H. Matsumoto, H. Sakaebe, K. Tatsumi, J. Power Sources 146 (2005) 45-50.
- [38] L. Timperman, P. Skowron, A. Boisset, H. Galiano, D. Lemordant, E. Frackowiak, F. Beguin, M. Anouti, Phys. Chem. Chem. Phys. 14 (2012) 8199–8207.
- [39] A. Brandt, J. Pires, M. Anouti, A. Balducci, Electrochim. Acta 108 (2013) 226–231.
- [40] Md.A.B.H. Susan, A. Noda, M. Watanabe, In Book Ionic Liquids IIIB: Fundamentals, Progress, Challenges, and Opportunities, ACS Symposium Series, American Chemical Society, Washington, DC, 2005.
- [41] M. Anouti, M. Caillon-Caravanier, C. Le Floch, D. Lemordant, J. Phys. Chem. B 112 (2008) 9406–9411.
- [42] B. Gorska, L. Timperman, M. Anouti, J. Pernak, F. Béguin, RSC Adv. 6 (2016) 55144– 55158.
- [43] T.L. Greaves, C.J. Drummond, Chem. Rev. 115 (2015) 11379–11448.
- [44] X. Lu, G. Burrell, F. Separovic, Ch. Zhao, J. Phys. Chem. B 116 (2012) 9160-9170.
- [45] M.S. Gruzdev, L.E. Shmukler, N.O. Kudryakova, A.M. Kolker, Yu.A. Sergeeva, L.P. Safonova, J. Mol. Liq. 242 (2017) 838–844.
- [46] M.Sh. Miran, H. Kinoshita, T. Yasuda, Md.A.B.H. Susan, M. Watanabe, Phys. Chem. Chem. Phys. 14 (2012) 5178–5186.
- [47] M.Sh. Miran, T. Yasuda, Md.A.B.H. Susan, K. Dokko, M. Watanabe, ECS Trans. 50 (2012) 285-291.
- [48] T.A. Siddique, S. Balamurugan, S.M. Said, N.A. Sairi, W.M.D.W. Normazlan, RSC Adv. 6 (2016) 18266–18278.
- [49] P.K. Chhotaray, R.L. Gardas, J. Chem. Thermodyn. 72 (2014) 117–124.
- [50] M.Sh. Miran, T. Yasuda, Md.A.B.H. Susan, K. Dokko, M. Watanabe, RSC Adv. 3 (2013) 4141–4144.
- [51] M. Hasani, J.L. Yarger, C.A. Angell, Chem. Eur. J. 22 (2016) 13312–13319.
- [52] CRC Handbook of Chemistry and Physics, 95th Edition, Editor W. M. Haynes, CRC Press, 2014.
- [53] A.K. Covington, R. Thompson, J. Solution Chem. 3 (1974) 603-617.
- [54] K.E. Gutowski, D.A. Dixon, J. Phys. Chem. A 110 (2006) 12044–12054.
- [55] E. Raamat, K. Kaupmees, G. Ovsjannikov, A. Trummal, A. Kütt, J. Saame, I. Koppel, I. Kaljurand, L. Lipping, T. Rodima, V. Pihl, I.A. Koppel, I. Leito, J. Phys. Org. Chem. 26 (2013) 162–170.
- [56] J.P. Guthrie, Can. J. Chem. 56 (1978) 2342-2354.
- [57] E.J. King, G.W. King, J. Am. Chem. Soc. 74 (1952) 1212–1215.
- [58] D.C. French, D.S. Crumrine, J. Org. Chem. 55 (1990) 5494–5496.
- [59] Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2017 ACD/Labs) (predict).
- [60] A. Agren, Acta Chem. Scand. 8 (1954) 266–279.
- [61] M. Witanowski, L. Stefaniak, G. Webb, In: Annual reports on NMR spectroscopy, Editor G.A. Webb, Academic Press, London, 1981.
- [62] K. Mori, S. Hashimoto, T. Yuzuri, K. Sakakibara, Bull. Chem. Soc. Jpn. 83 (2010) 328– 334.
- [63] R.R. Pinto, S. Mattedi, M. Aznar, Chem. Eng. Trans. 43 (2015) 1165–1170.

- [64] V.H. Paschoal, L.F.O. Faria, M.C.C. Ribeiro, Chem. Rev. 117 (2017) 7053-7112.
- [65] G. Smith, U.D. Wermuth, D.S. Sagatys, J. Chem. Crystallogr. 41 (2011) 17–25.
- [66] A.R. Neale, S. Murphy, P. Goodrich, C. Hardacre, J. Jacquemin, ChemPhysChem 18 (2017) 2040–2057.
- [67] S. Zhang, N. Sun, X. He, X. Lu, X. Zhang, J. Phys. Chem. Ref. Data 35 (2006) 1475–1517.
- [68] Y. Shen, D.F. Kennedy, T.L. Greaves, A. Weerawardena, R.J. Mulder, N. Kirby, G. Song, C.J. Drummond, Phys. Chem. Chem. Phys. 14 (2012) 7981–7992.
- [69] Z. Ullah, M.A. Bustam, Z. Man, N. Muhammad, A.S. Khan, RSC Adv. 5 (2015) 71449– 71461.
- [70] T. Yasuda, M. Watanabe, MRS Bull. 38 (2013) 560–566.
- [71] M. Galinski, A. Lewandowski, I. Stepniak, Electrochim. Acta 51 (2006) 5567–5580.
- [72] M. Armand, F. Endres, D.R. MacFarlane, H. Ohno, B. Scrosati, Nat. Mater. 8 (2009) 621– 629.
- [73] K. Mishra, S.A. Hashmi, D.K. Rai, J. Solid State Electrochem. 18 (2014) 2255–2266.
- [74] H. Vogel, Phys. Z. 22 (1921) 645-646.
- [75] G. Tammann, W. Hesse, Z. Anorg. Allg. Chem. 156 (1926) 245-257.
- [76] M. Yoshizawa, W. Xu, C.A. Angell, J. Am. Chem. Soc. 125 (2003) 15411–15491.
- [77] B.B. Owen, H. Zeldes, J. Chem. Phys. 18 (1950) 1083–1085.
- [78] H.E. Gunning, A.R. Gordon, J. Chem. Phys. 10 (1942) 126–131.
- [79] M. Kaminsky, Z. Phys. Chem. 12 (1957) 206-231.
- [80] A. Khan, X. Lu, L. Aldous, Ch. Zhao, J. Phys. Chem. C 117 (2013) 18334–18342.
- [81] L. Johnson, A. Ejigu, P. Licence, D.A. Walsh, J. Phys. Chem. C 116 (2012) 18048-18056.
- [82] I.V. Fedorova, L.P. Safonova, J. Phys. Chem. A 112 (2018) 4562–4570.

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Highlights

- Protic ionic liquids based on triethylamine with sulfonic acids were synthesized.
- The PILs were characterized by NMR and FT-IR spectroscopic methods.
- The phase behavior of the PILs using DSC and TGA was studied.
- The conductivity of salts are within the range of $10^{-4} \div 10^{-2}$ Ohm⁻¹·cm⁻¹.
- The electrochemical window of PILs at 120 °C lies within the range of 1.85–2.8 V.

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