

Acidic Ionic Liquids as Composite Forming Additives for Ion-conducting Materials

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Abstract. This paper represents the material conductivity investigation of several AILs (Acidic Ionic Liquids) containing an alkane sulfonic acid group covalently bonded to pyridine and N-alkylimidazole cations. Three different anions (HSO_4^- , H_2PO_4^- and TsO^-) have been introduced in the structure of ionic liquids to evaluate the impact of this factor on material conductivity. Ion conductivity values in all studied ionic liquids obtained from impedance measurements in temperature range from 20 to 120 °C. Values of electroconductivity depending on ionic liquid's structure vary in range from $1.34 \cdot 10^{-5}$ to $1.05 \cdot 10^{-2}$ S/cm at 25 °C.

1. Introduction

Rising interest in the field of ionic liquids during the last decades has resulted in a great deal of scientific information concerning characteristics of these compounds - covering research about their physical, as well as chemical properties. Ongoing physicochemical studies of ionic liquids keep providing more and more comprehensive and detailed information that leads to a deeper insight into properties and application possibilities of these compounds not only for laboratory purposes, but also for potential industrial use [1,2].

Former evaluation of thermophysical properties of ionic liquids as crucial factor for industrial purposes, has shown application of ionic liquids, although with certain drawbacks, as possible alternative to currently used fluids [3]. One of the perspective fields of research using ionic liquids is proton conducting polymer electrolytes such as fuel cells [4-6] due to high temperature stability and low partial vapor pressure.

Because of the considerable number of possible cation and anion combinations, and structure modifications in ionic liquids as “designer compounds” [7] the aim of this study is to give an insight in ionic conductivity of alkane sulfonic acid group containing acidic ionic liquids (AILs) (Figure 1) to describe this class of ionic liquids. Acidic ionic liquids synthesized and examined in this paper include 3-(1-pyridinio)-1-propanesulfonate [PyPS] hydrogen sulfate (**1a**), dihydrogen phosphate (**1b**) and *p*-toluenesulfonate (**1c**), 3-(1-methyl-3-imidazolio)-1-propanesulfonate [MeImPS] hydrogen sulfate (**2a**), dihydrogen phosphate (**2b**) and *p*-toluenesulfonate (**2c**) as well as 3-(1-butyl-3-imidazolio)-1-propanesulfonate [BuImPS] hydrogen sulfate (**3a**), dihydrogen phosphate (**3b**) and *p*-toluenesulfonate (**3c**).



2. Experimental

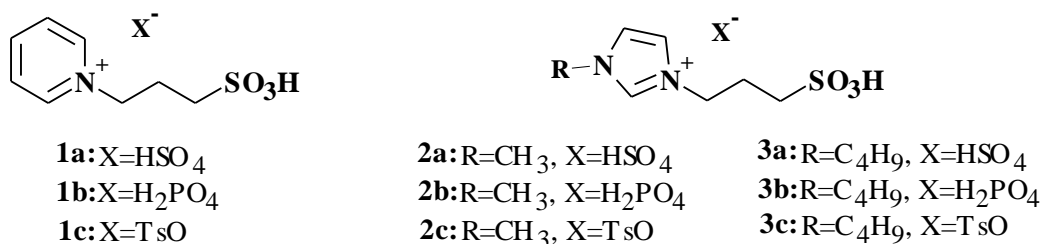


Figure 1. Structures of AILs investigated in this study.

2.1. Chemicals and instruments

Reagents for synthesis of ionic liquids were used as received without further purification: 3-(1-pyridinio)-1-propanesulfonate (98% purity), 1,3-propanesultone (98% purity), 1-methylimidazole (99% purity), 1-butylimidazole (98% purity) purchased from Sigma Aldrich, *p*-toluenesulfonic acid monohydrate (98% purity) was supplied from Fluka, sulfuric acid (95%) and phosphoric acid (85%) were purchased from Stanlab.

Toluene and diethyl ether were dried over P₂O₅ and redistilled before use.

¹H NMR spectra of ionic liquids were recorded on Varian 200 MR in D₂O. TG/DTA was done on DTG-60/60H Shimadzu. Impedance measurements were performed on Autolab PGSTA-30.

2.2. General procedure for synthesis of AILs

The acidic ionic liquids (AILs) used in this paper (Figure 1) except **1a-c**, were synthesized in two step synthesis similar to the methods described in literature [8, 9].

Ionic liquid **2a** was prepared as follows: 1-methylimidazole (0.05 mol) was dissolved in 30 mL of dry toluene, 1,3-propanesultone (0.05 mol) was added gradually. The mixture was stirred at 60 °C for 24 h. The resulting white zwitterion salt was filtered, washed repeatedly with hot ethanol and diethyl ether to remove non-ionic residues and dried in vacuum (2 Torr, 100 °C, 2h). Then, a stoichiometric amount of sulfuric acid was added and the mixture stirred for 12 h at 80 °C. The resulting viscous ionic liquid was repeatedly washed with dry toluene and after removal of the solvent dried in vacuum (2 Torr, 100 °C, 2h).

¹H NMR of **2a** (200 MHz, D₂O, TMS): δ 2.01-2.16 (m, 2H), 2.69 (t, 2H), 3.66 (s, 3H), 4.13 (t, 2H); 7.22 (s, 1H), 7.29 (s, 1H), 8.53 (s, 1H).

Ionic liquids **2b-c** and **3a-c** were prepared using the method described above. In case of ionic liquids **1a-c** the commercially purchased zwitterion salt PyPS was used. All ionic liquids were analyzed by ¹H spectroscopy, and the spectral data agreed with their structures and data given in literature [8, 9].

2.3. Electrochemical measurements

Autolab PGSTA-30 was used to do the impedance and cyclic voltammetry measurements. The measuring cell consisted of two stainless steel electrodes and platinum wire as a reference electrode. It was heated up to 120 °C and kept for 30 min under argon flow prior the measurements. The impedance spectra were measured in a two-electrode mode in a frequency range from 0.1 Hz to 1000 Hz with AC potential amplitude of 0.01 V in a temperature range from 120 °C to 20 °C (during the cooling process). The cell resistance was obtained by extrapolating to higher frequencies. Additional cyclic voltammetry measurements (including reference electrode, 10 mV s⁻¹, in potential range +/-2V) were also carried out and no water electrolysis was observed showing no influence of possible presence of free acid or water in the studied compounds.

3. Results and discussion

To examine ionic conductivity of propane sulfonic acid group containing acidic ionic liquids, in total nine compositionally different ionic liquids were examined.

As it can be seen from the data given in Table 1 change of anion gives considerable impact on the melting point of ionic liquid. $[\text{H}_2\text{PO}_4^-]$ anion containing [PyPS] and [MeImPS] show higher melting point temperatures, whereas $[\text{HSO}_4^-]$ anion in the structure produces liquid state ionic liquids in the room temperature.

Since ionic liquids are likely to absorb water from the environment, the conductivity values were obtained during cooling cycle after electrochemical cell was pre-dried at 120°C. The temperature dependence of conductivity in a studied temperature range is close to linear in Arrhenius coordinates and it was used to obtain activation energies (E_A).

Table 1. Physical properties of AILs depending on their structure.

	Melting point (°C) ^a	Melting point energy (J/g) ^a	Maximum stability point (°C) ^a	E_A (eV)	σ (S/cm), at 25 °C
1a	105	688	240	0.86	$6.57 \cdot 10^{-4}$
1b	123	291	262	1.03	$1.34 \cdot 10^{-5}$
1c	106	394	270	1.04	$1.35 \cdot 10^{-4}$
2a^b	-	-	250	0.70	$1.05 \cdot 10^{-2}$
2b	123	547	279	0.92	$1.14 \cdot 10^{-4}$
2c	80	408	276	1.21	$2.80 \cdot 10^{-5}$
3a^b	-	-	223	0.78	$1.57 \cdot 10^{-3}$
3b^b	-	-	232	1.02	$2.04 \cdot 10^{-5}$
3c	68	355	238	1.05	$2.72 \cdot 10^{-5}$

^a Determined by TG/DTA analysis;

^b AILs are in liquid state at room temperature;

Data given in Figure 2a, b, c, which represent conductivity measurements depending on the anion, show no significant drop of conductivity in higher temperature regions in case of all examined ionic liquids.

If [MeImPS] and [BuImPS] cations are compared then a decrease of conductivity can be observed in case of the ionic liquid with longer alkyl chain in the cation structure. The impact of the anion on conductivity as represented in Figure 2d, show that ionic liquids with $[\text{HSO}_4^-]$ anion, in case of [MeImPS] as cation, give noticeably higher values comparing to $[\text{H}_2\text{PO}_4^-]$ and $[\text{TsO}^-]$ anions.

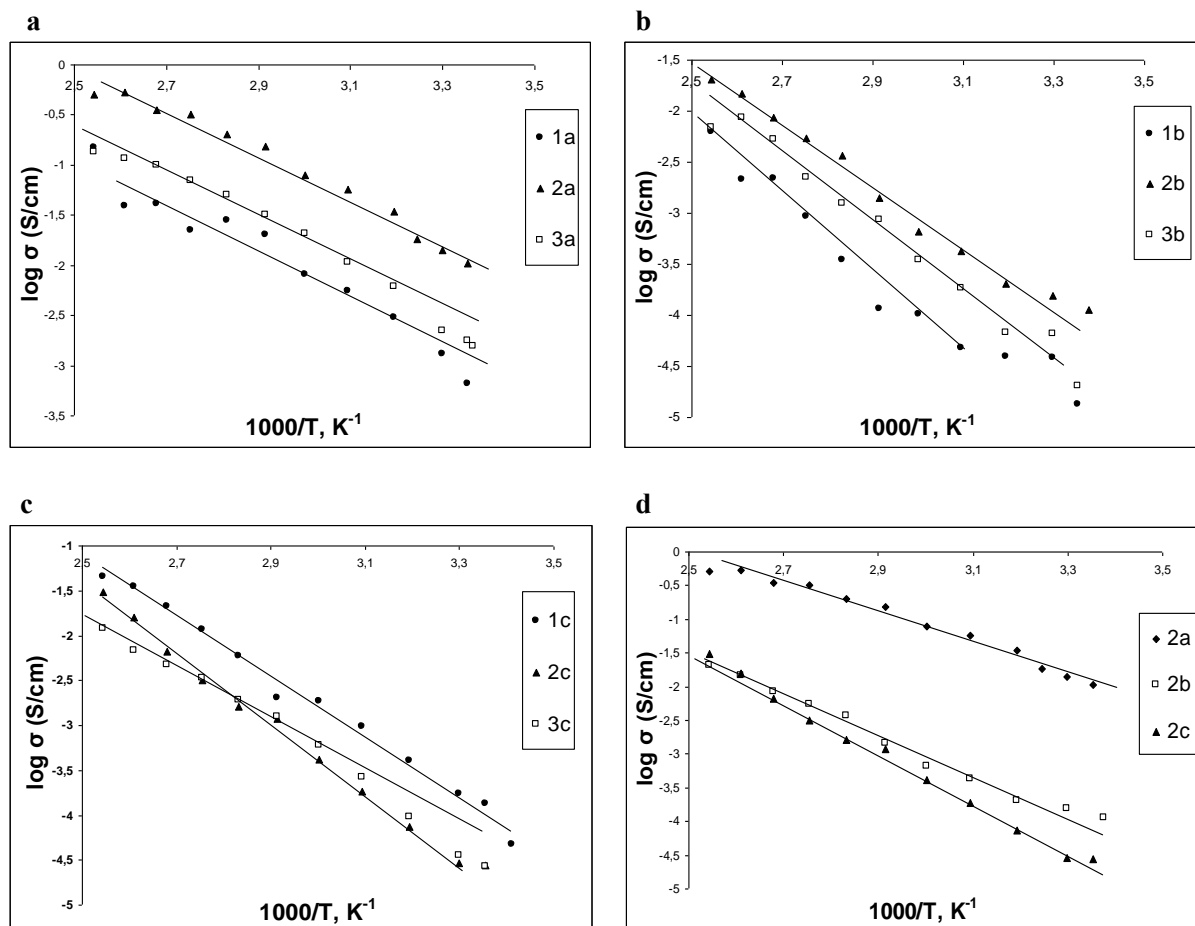


Figure 2 a, b, c. Electroconductivity change in various temperatures depending on the cation in ionic liquid's structure, **d** Electroconductivity change in various temperatures depending on the anion in [MeImPS] cation containing ionic liquids.

4. Conclusion

The hydrogen sulfate anion increased conductivity by one order to much higher values as compared to phosphate or tosylate anion. Prolonging of alkyl chain decreased electroconductivity.

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