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New electrolytes for solar battery based on imidazolium and piperidinium cations

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Abstract

For electrochemical applications at high temperatures, a series of imidazolium and piperidinium -based cations with different anions were synthesized and studied as electrolytes for solar battery. The syntheses are based on a dialkylation reaction of methylimidazole and N-alkylpiperidine followed by anion exchange. The structures of ILs, were identified by using ¹H, ¹³C, ¹⁹F, ³¹P NMR and FT-IR spectroscopy. Their physicochemical and dielectric properties, including melting point, thermal stability, conductivity, and activation energies are determined. The thermal investigations have revealed that the melting points were slightly higher than 100°C, which may be interest for solid electrolyte applications. The obtained results encourage us to use the imidazolium with other anions in view to synthesis ILs with better dielectric properties for electrochemical application.

Keywords: electrochemical applications; electrolytes; solar battery; dielectric properties.

1. Introduction

During the last decade, ILs have been considered as a promising green reaction media and as a novel solvent [1-3]. Initially, ILs were developed by electrochemists [4-6], who were looking for ideal electrolytes suitable for batteries [6-10]. Owing to the ionic environment effect on the chemical reactions [11-15], the main focus of electrochemists was shifted to general ionic liquid characterization in view to better applications. Ionic liquids currently have a large variety application field, which continues to expand because of their use as electrolytes for devices and processes. In addition, other applications in enzyme catalysis and multiphase bio-process operations were reported [16].

This work is a continuation of our previous study [17,18], which focused on understanding the dielectric proprieties behavior of imidazolium and piperidinium

cations with different anions such as, $[\text{PF}_6^-]$, $[\text{BF}_4^-]$, Using differential scanning calorimetry (DSC), their thermal property as; Glass transition temperature (T_g), Melting point (T_m) and decomposition temperature (T_d) were measured and investigated in detail.

The dielectric properties of obtained products were measured by impedance spectroscopy in the frequency range from (10^{-2} to 10^6 Hz) and over the temperature range near glass transition (T_g). Dielectric data were analyzed using complex permittivity (ϵ^*) and complex electrical modulus (M^*) for the ILs samples at various temperatures. The evolution of the complex permittivity (ϵ' , ϵ'') as a function of frequency and temperature was investigated.

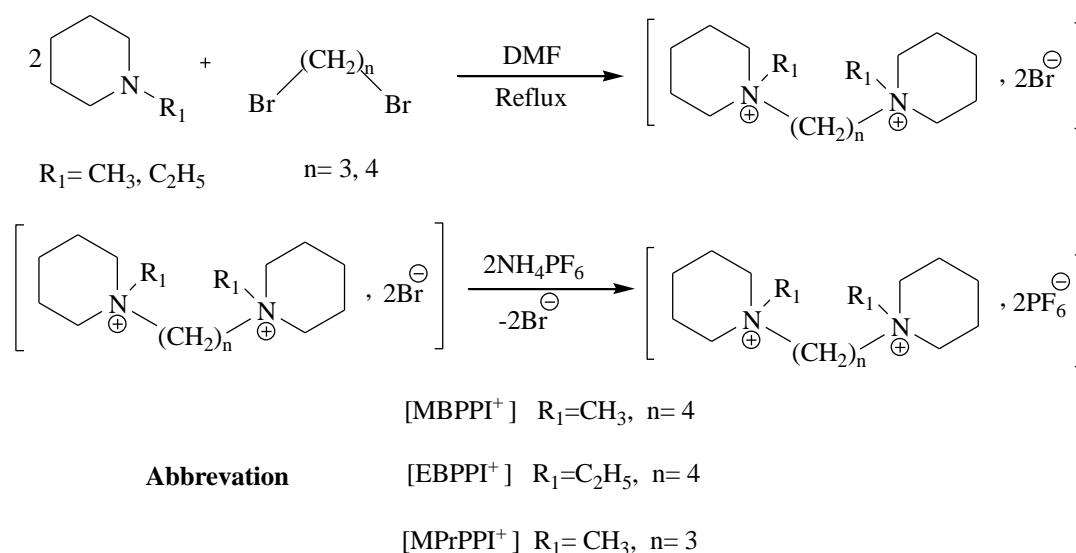
2. Experimental

2.1. Reagents and materials

The reagents used in this study are: 1,3-dibromopropane (98 wt.%), 1,4-dibromobutane (99.5 wt.%), N-methyl piperidine (95 wt.%), N-ethyl piperidine (97 wt.%), ammonium tetrafluoroborate and hexafluorophosphate ammonium (99.5 wt.%), diethyl ether and N,N-dimethylformamide. They were purchased from Fluka and used as received. Deionized H_2O was obtained by using a Millipore ion-exchange resin deionizer.

2.2. Synthesis and characterization

The synthesis of bis- piperidinium tetrafluoroborate $[\text{MBPPI}^+][\text{BF}_4^-]$ is taken as an example of the synthesis of these ionic liquids and is illustrated in Scheme 1.



Scheme 1 General synthesis of piperidinium ionic liquids $[\text{R}_1\text{R}_n\text{BPPI}^+][\text{BF}_4^-]$.

2.2.1. NMR and infrared spectroscopy measurements

^1H NMR (400 MHz), ^{13}C NMR, ^{19}F (100.6 MHz) spectra were recorded on DRX 400 MHz spectrometer. The chemical shifts (δ) are given in ppm and referenced to the internal solvent signal namely TMS and CFCl_3 , respectively. IR spectra were recorded on FT-IR Perkin-Elmer Spectrum BX spectrophotometer with a resolution of 4 cm^{-1} in the range $4000\text{-}650\text{ cm}^{-1}$.

2.2.2. Synthesis of bis-methyl piperidinium butylidene bromide $[\text{MBPPI}^+][2\text{Br}^-]$

The synthesis procedure was carried out as reported elsewhere [17,18]. Briefly, N-methyl piperidine (12.15 mL, 100 mmol) and 1,4-dibromobutane (5.21 mL, 50 mmol) were dissolved in DMF (20 mL) before being stirred at 70°C for 7 hours. The obtained mixture was evaporated under vacuum and washed then with diethyl ether (100 mL) to give the bis-methyl piperidinium butylidene bromide as a yellowish solid (13.20 g, 31.86 mmol).

2.2.3. Synthesis of 1-Butyl-3-methylimidazolium tetrafluoroborate $[\text{BMIM}^+][\text{BF}_4^-]$

A metathesis reaction of $[\text{MBPPI}^+][2\text{Br}^-]$ (2.30 g, 10.08 mmol) with ammonium tetrafluoroborate (1.04 g, 9.91 mmol) gives the desired compound using domestic microwave. The spectra details are given below:

^1H -RMN (CDCl_3) δ_{H} (ppm) : ^1H -RMN (D_2O) δ_{H} (ppm): 1.63 (m, 4H, $\text{CH}_2\text{CH}_{2\text{d}}\text{CH}_2$), 1.85 (m, 8H, $\text{CH}_2\text{CH}_{2\text{c}}\text{CH}_2$), 2.29 (m, 2H, $\text{CH}_2\text{CH}_{2\text{e}}\text{CH}_2$), 3.05 (s, 6H, $\text{NCH}_{3\text{a}}$), 3.34-3.36 (t, 12H, $\text{NCH}_{2\text{b}}\text{CH}_{2\text{c}}$).

^{13}C -RMN (CDCl_3) δ_{C} (ppm) : ^{13}C -RMN (D_2O) δ_{C} (ppm) : 15.13 ($\text{CH}_2\text{C}_{\text{f}}\text{H}_2\text{CH}_2$), 19.51 ($\text{CH}_2\text{C}_{\text{e}}\text{H}_2\text{CH}_2$), 20.40 ($\text{CH}_2\text{C}_{\text{d}}\text{H}_2\text{CH}_2$), 47.70 ($\text{NC}_{\text{a}}\text{H}_3$), 59.63 ($\text{NC}_{\text{b}}\text{H}_2\text{CH}_2$), 61.63 ($\text{NC}_{\text{c}}\text{H}_2\text{CH}_2$).

^{19}F -RMN (CDCl_3) δ_{F} (ppm) : -151.32 (s, BF_4^-). IR: 2946, 2876 [$\nu(\text{C-H})$], 1467 [$\delta(\text{C-H})$], 1279 [$\nu(\text{C-N})$], 1230 [$\nu(\text{B-F})$].

2.3. Thermal analysis

Differential scanning calorimetry (DSC) thermogram was recorded by using a NETZSCH DSC 204 F1 instrument. The sample (9 mg) was placed in an aluminum pan and cooled from room temperature to -150°C for 3 min. Subsequently, a heating scan was performed from -150°C to 200°C at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$. For this salt, a melting transition (onset temperature of the endothermic peak, T_m) and glass transition (T_g) were observed on heating and the crystallization temperature (T_{cry}) was detected in the onset of an exothermic peak on cooling within the temperature range studied.

2.4. Measurement of dielectric properties

The dielectric measurements in the frequency range (10^{-2} to 10^6 Hz) and temperature interval (-57 to -7°C) were carried out by means of a Novocontrol high resolution

alpha dielectric analyzer. The analyzer was supported by Quatro temperature controller using pure nitrogen as heating agent and providing temperature stability better than 0.2 K. Electric field in the range between 3 and 6 Vcm^{-1} was applied. The measurements were conducted using platinum electrodes in parallel plate capacitor configuration.

3. Results and discussion

3.1. Thermal analysis

Using differential scanning calorimetry (DSC), their thermal property as; Glass transition temperature (T_g), Melting point (T_m) and decomposition temperature (T_d) were measured and investigated in detail.

ILs	^a MW (g mol^{-1})	^b T_g ($^{\circ}\text{C}$)	^c T_{s-s} ($^{\circ}\text{C}$)	^d T_m ($^{\circ}\text{C}$)	^e ΔH_m ($\text{J}\cdot\text{g}^{-1}$)	^f T_d ($^{\circ}\text{C}$)
[MBPPI ⁺][PF ₆ ⁻]	399.24	-	-	103.36	15.29	336.00
[MPrPPI ⁺][PF ₆ ⁻]	385.39	21.42	-	137.00	22.27	303.73
[EBPPI ⁺][PF ₆ ⁻]	427.47	-1.80	74.30	123.15	14.26	283.00

^a Molecular weight.

^b Glass transition temperature (T_g).

^c Solid- solid transition temperature (onset of solid-solid peak) (T_{s-s}).

^d Melting point (onset of the endothermic peak) (T_m).

^e Enthalpy of melting temperature.

^f Decomposition temperature (position of decomposition peak) (T_d).

- Not detected.

Table 1 Thermal properties of dicationic piperidinium ionic liquids.

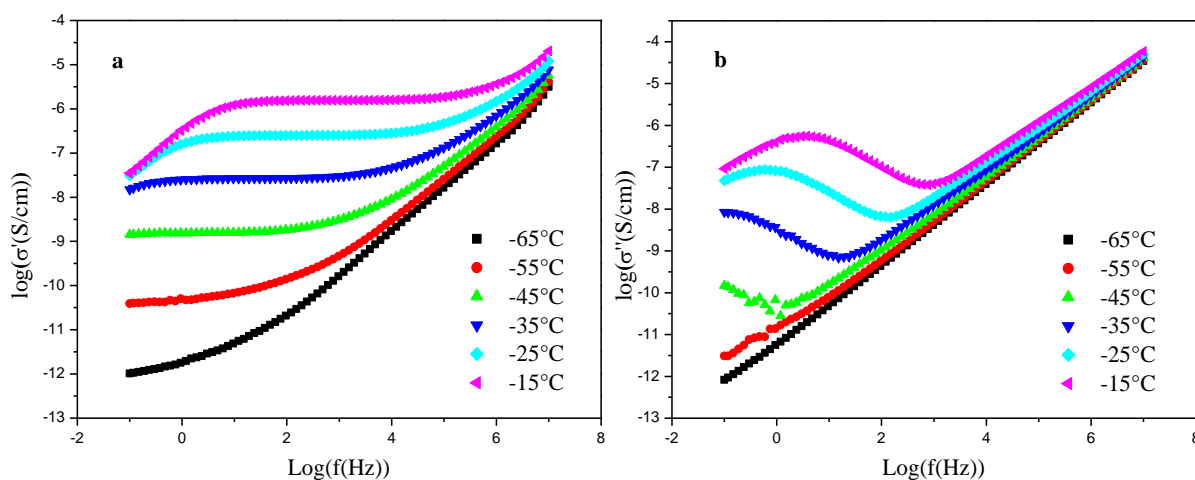


Figure 1. Frequency dependence of the conductivity (real part) of [MBPPI⁺][BF₄⁻] at various temperatures.

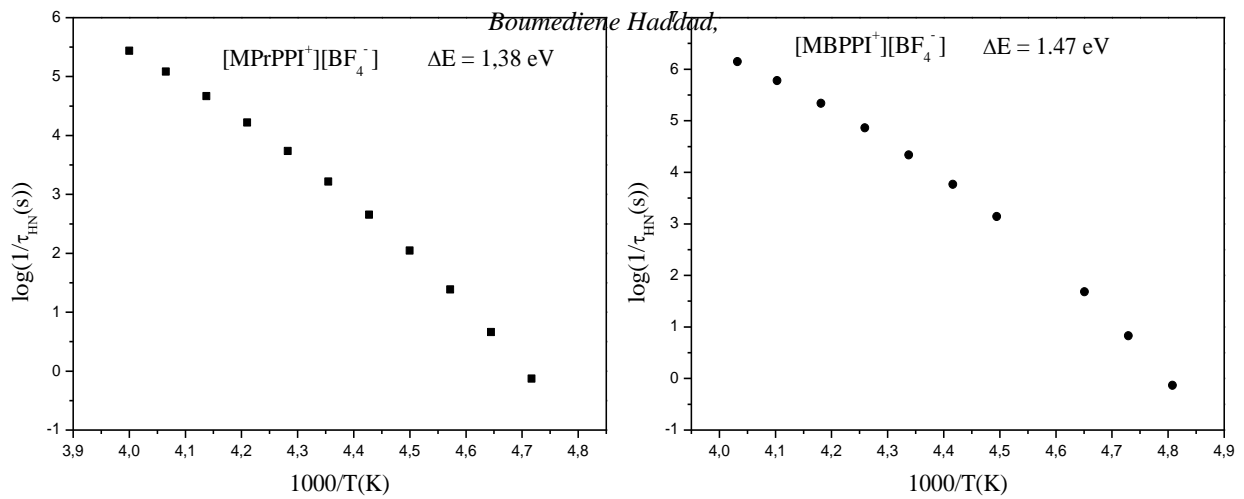


Figure 2. Temperature dependence of the relaxation times

3.2. Frequency dependent conductivity studies

In order to understand the ion dynamics in IL, the conductivity of our sample was determined at different temperatures. For the data analysis, we observe that the conductivity increases as the temperature is elevated whatever applied frequency.

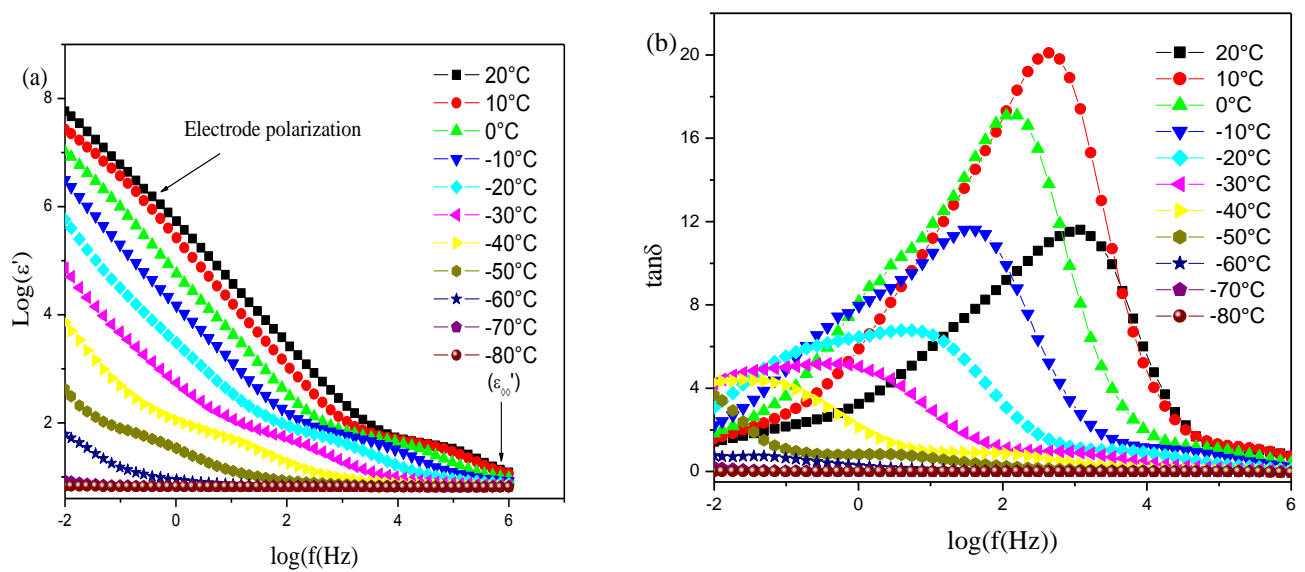


Figure 3. Frequency dependence of (a) ϵ' and (b) $\tan\delta$ at the different temperatures for [EBPPI⁺][PF₆⁻].

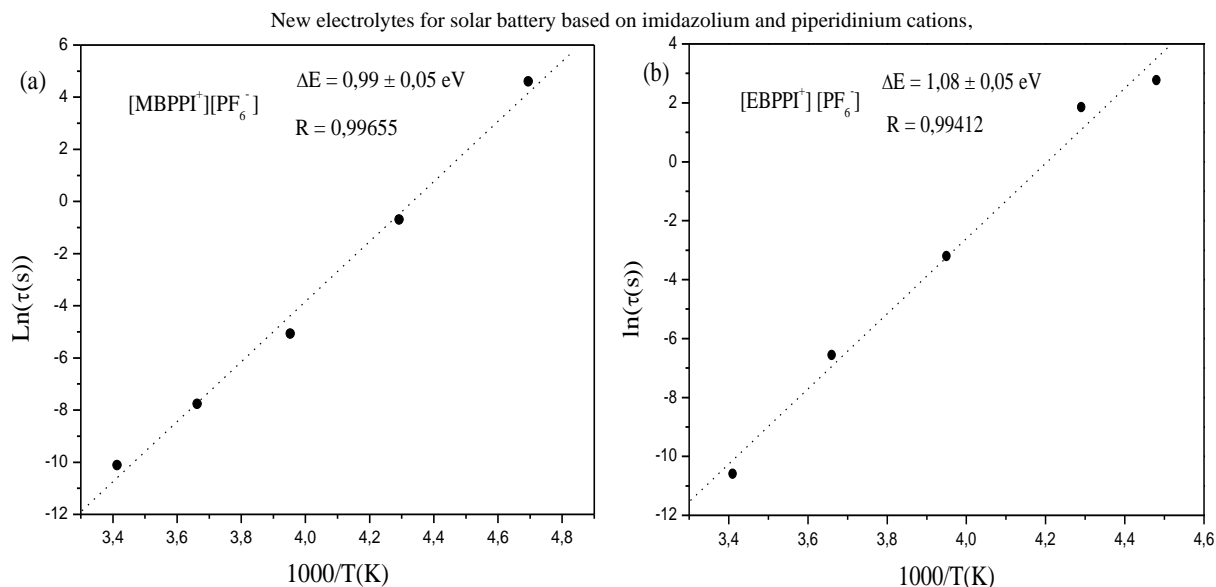


Figure 4. Temperature dependence of the relaxation times

4. Conclusion

Novel ionic liquids (ILs) based on the piperidinium tetrafluoroborate and hexafluorophosphate as bis-methyl piperidinium butylidene $[\text{MBPPI}^+]$, bis-methyl piperidinium propylidene $[\text{MPPrPPI}^+]$ and bis-ethyl piperidinium butylidene $[\text{EBPPI}^+]$ cations were successfully synthesized.

The thermal investigations have revealed that the melting points were slightly higher than 100°C , which may be interest for solid electrolyte applications. The obtained results encourage us to use the imidazolium with other anions in view to synthesis ILs with better dielectric properties for electrochemical application.

The results of dielectric properties indicate that

- The real part of the dielectric function ϵ' at $f_c = (\omega_c/2\pi)$ turns from the high frequency limit to the static value ϵ_s .
- The dielectric loss ϵ'' decrease on increasing the frequency, this can be explained by means of the dielectric polarization mechanism of Ionic liquid.
- At lower frequencies, it is observed that σ' decreases from σ_0 and this is due to electrode polarization that results from blocking of charge carriers at the electrodes.

The relaxation data were characterized by the empirical Havriliak–Negami (H–N) equation The temperature dependence of the relaxation times was shown to be governed by the VFT equation.

The obtained results encourage us to use the imidazolium with other anions in view to synthesis ILs with better dielectric properties for electrochemical application.

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