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Microwave Synthesis and Properties of a Series of N-alkyl-N-methylimidazolium Chloride Ionic Liquids

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Seven N-alkyl-N-methylimidazolium chloride ionic liquids were synthesized under the organic-solvent-free condition with microwave irradiation. The structures were characterized and confirmed by ^{1}H NMR and melting points were determined by differential scanning calorimetry (DSC). Their surface tensions and water adsorption properties were measured at room temperature. The results showed that there was a decrease in surface tension and water adsorption with an increasing substituting alkyl chain length in the 1-position of N of the cation. However the melting points increased with an increasing substituting alkyl chain length of the N of the cation.

Key Words: Ionic liquids, Microwave synthesis, Surface tension, Water adsorption properties.

INTRODUCTION

The room temperature ionic liquids (RTILs) attracted significant and growing interest in recent years especially those based upon the 1-*n*-alkyl-3-methylimidazolium cation[1-3]. They have intrinsically useful properties, such as thermal stability, high ionic conductivity, negligible vapour pressure and a large electrochemical window. So applications have also been found in different areas, such as an alternative recyclable and environmentally benign reaction media for chemical processes. Examples of their usefulness in biocatalysis[4] and catalysis have been reported, for example hydroformylation[5], hydrogenation[6], olefin oligomerization[7], Heck reactions[8], alkylation[9], Friedel-Crafts reactions[10], Diels-Alder reactions[11], Beckmann rearrangement reactions[12] and Baylis-Hillman reactions[13].

At present, the ionic liquids are mainly synthesized by heating reflux and microwave-assisted. The latter is superior to the former, because an efficient microwave-assisted preparation of 1,3-dialkylimidazolium chlorides has reduced the reaction time from several hours to a few minutes in a process that avoids the use of a large excess of organic solvents as the reaction medium. It is significant to note the yield is improved by microwave-assisted method[14]. In this paper, seven N-alkyl-N-methylimidazolium chloride ionic liquids are synthesized under the organic-solvent-free condition with microwave irradiation in an unmodified household microwave oven. We shorten the reaction time and improve the yield.

EXPERIMENTAL

1-Methylimidazole, 1-chloroalkanes (C_4, C_6, C_8, C_{10}, C_{12}, C_{14} and C_{16}), ethyl acetate and acetone were products of AR grade and purchased from Chinese Sinopharm Chemical Reagent Co., Ltd.

Melting points were determined by differential scanning calorimetry (DSC, Perkin-Elmer Pyris I apparatus); A Bruker Avance 400 spectrometer was used for ^{1}H NMR measurements; the surface tension were determined with a BZY-2 surface tensionmeter using du Nouy Ring method.

Ionic liquids preparation

Synthesis of 1-dodecyl-3-methylimidazolium chloride ([C_{12}MIM]Cl): In a representative reaction procedure, 1-chlorododecane (1.05 mmol) and 1-methyl-imidazole (1.0 mmol) were placed in a test tube, mixed thoroughly using a vortex mixer and the contents were heated intermittently in the microwave oven at power P3 corresponding to 350 W (30 s irradiation with 10 s mixing) until the solution into golden colour. The resulting ionic liquid [C_{12}MIM]Cl was then cooled to room temperature and recrystallize with acetone and dried at 35 ºC in vacuum.

A general schematic representation and the preparation of 1,3-dialkylimidazolium chlorides are given in Table-1.

TABLE-1
PREPARATION OF 1,3-DIALKYL IMIDAZOLIUM CHLORIDES USING MICROWAVES

Substrate (1 mmol)	MW-Power (W)	MW-Time (s)	Yield (%)
[BMIM]Cl	350	30 + 30 + 30 + 30 + 30	80
[HMIM]Cl	350	30 + 30 + 30 + 30 + 30	89
[OMIM]Cl	350	60 + 60 + 30 + 30 + 30	89
[C_{10}MIM]Cl	350	60 + 60 + 30 + 30 + 30 + 30	92
[C_{12}MIM]Cl	560	60 + 30 + 30 + 30 + 20 + 10	92
[C_{14}MIM]Cl	560	60 + 30 + 30 + 30 + 20 + 10	91
[C_{16}MIM]Cl	560	60 + 30 + 30 + 30 + 20 + 20	92

The structures of ionic liquids were characterized by a Bruker Avance 400 spectrometer and the ^{1}H NMR spectral data was listed in Table-2.

RESULTS AND DISCUSSION

Differential scanning calorimetry experiments performed in sealed Al pans were also carried out on a Perkin-Elmer Pyris I apparatus. Samples were heated from 0 to 100 ºC to remove their thermal history at 10 ºC/min, during which the T_m was determined. Melting point data of ionic liquids was listed in Table-3.

The results show that there is a increase in melting points with an increasing substituting alkyl chain length of the N of the cation, except that the which of former two is below freezing.

TABLE-2
^{1}H-NMR SPECTRAL DATA OF IONIC LIQUIDS (D_2O, δ, ppm)

Ionic liquid	^{1}H-NMR
[BMIM]Cl	10.22 (s, 1H), 7.81 (s, 1H), 7.67 (s, 1H), 4.13 (s, 3H), 4.34-4.38 (t, *J* = 7.32, 7.34 Hz, 2H), 1.87-1.94 (m, 2H), 1.35-1.40 (m, 2H), 0.85-0.88 (t, *J* = 7.36, 7.40 Hz, 3H)
[HMIM]Cl	10.23 (s, 1H), 7.81 (s, 1H), 7.61 (s, 1H), 4.13 (s, 3H), 4.34-4.36 (t, *J* = 7.38, 7.44 Hz, 2H), 1.88-1.92 (m, 2H), 1.34-1.40 (m, 6H), 0.84-0.89 (t, *J* = 6.51, 6.56 Hz, 3H)
[OMIM]Cl	10.25 (s, 1H), 7.80 (s, 1H), 7.59 (s, 1H), 4.13(s, 3H), 4.31-4.35 (t, *J* = 7.40, 7.46 Hz, 2H), 1.89-1.92 (m, 2H), 1.32-1.38 (m, 4H), 1.25-1.28 (m, 6H), 0.84-0.89 (t, *J* = 6.52, 6.58 Hz, 3H)
[C_{10}MIM]Cl	10.27 (s, 1H), 7.78 (s, 1H), 7.53 (s, 1H), 4.13 (s, 3H), 4.31-4.35 (t, *J* = 7.35, 7.40 Hz, 2H), 1.88-1.91 (m, 2H), 1.30-1.33 (m, 4H), 1.23-1.26 (m, 10H), 0.85-0.89 (t, *J* = 6.57, 6.59 Hz, 3H)
[C_{12}MIM]Cl	10.27 (s, 1H), 7.72 (s, 1H), 7.50 (s, 1H), 4.12 (s, 3H), 4.29-4.33 (t, *J* = 7.36, 7.40 Hz, 2H), 1.88-1.91 (m, 2H), 1.30-1.32 (m, 4H), 1.23-1.25 (m, 14H), 0.85-0.89 (t, *J* = 6.56, 6.59 Hz, 3H)
[C_{14}MIM]Cl	10.29 (s, 1H), 7.69 (s, 1H), 7.49 (s, 1H), 4.12 (s, 3H), 4.29-4.33 (t, *J* = 7.34, 7.40 Hz, 2H), 1.88-1.91 (m, 2H), 1.30-1.33 (m, 4H), 1.23-1.25 (m, 18H), 0.85-0.89 (t, *J* = 6.59, 6.65 Hz, 3H)
[C_{16}MIM]Cl	10.29 (s, 1H), 7.68 (s, 1H), 7.46 (s, 1H), 4.12 (s, 3H), 4.29-4.33 (t, *J* = 7.32, 7.40 Hz, 2H), 1.88-1.91 (m, 2H), 1.31-1.33 (m, 4H), 1.23-1.25 (m, 22H), 0.85-0.89 (t, *J* = 6.64, 6.71 Hz, 3H)

TABLE-3
MELTING POINT DATA OF IONIC LIQUIDS

Ionic liquid	m.p. (ºC)	Ionic liquid	m.p. (ºC)
[BMIM]Cl	Below freezing	[C_{12}MIM]Cl	36.5
[HMIM]Cl	Below freezing	[C_{14}MIM]Cl	52.2
[OMIM]Cl	2.5	[C_{16}MIM]Cl	64.8
[C_{10}MIM]Cl	19.2		

The surface tension of ionic liquids have been obtained with dilution method at different density at the room temperature (25 ºC). The result of surface tension was the mean value by 5 times measures and the test precision reached 0.1 mN/m. Surface tension data was shown in Fig. 1. It is readily apparent from Fig. 1, that the surface tension of ionic liquids decrease with higher the concentration of them in aqueous solution. However, there is a decrease in surface tension with an increasing substituting alkyl chain length in the 1-position of N of the cation. Moreover, this result is consistent with Law[15]. The structures of ionic liquids are similar to the surfactant, so the changes of surface tension are also consistent with the surfactant.

Water adsorption properties: We took a spot of dried ionic liquids into the glass-surface vessel, respectively, spread out as far as possible, recorded the weight of them with a time interval and calculated the water absorption of them within 24 h at the room temperature (25 ºC). The result was shown in Fig. 2.

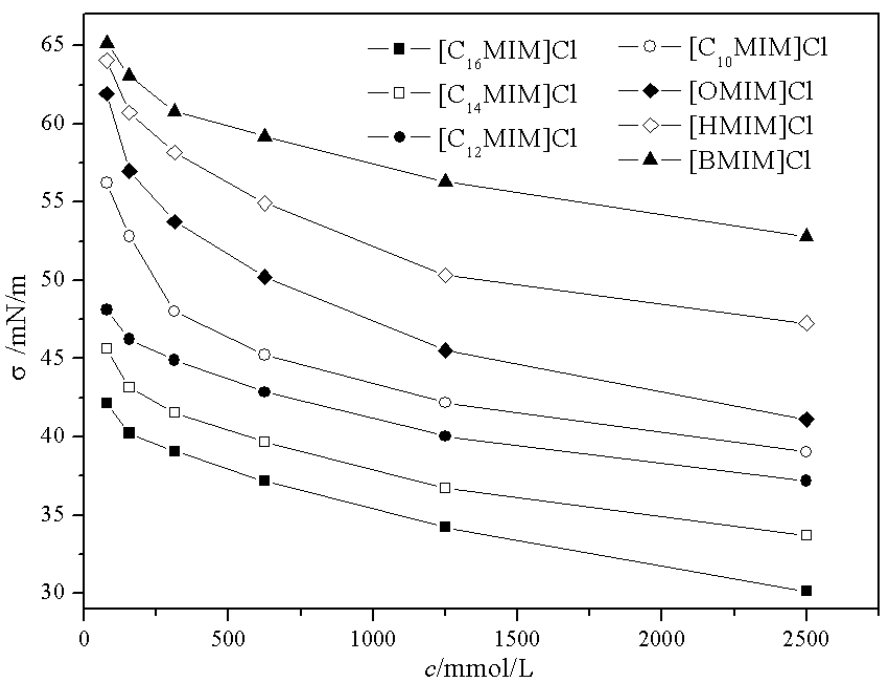

Fig. 1. Surface tension data of ionic liquids at different concentrations at 25 ºC

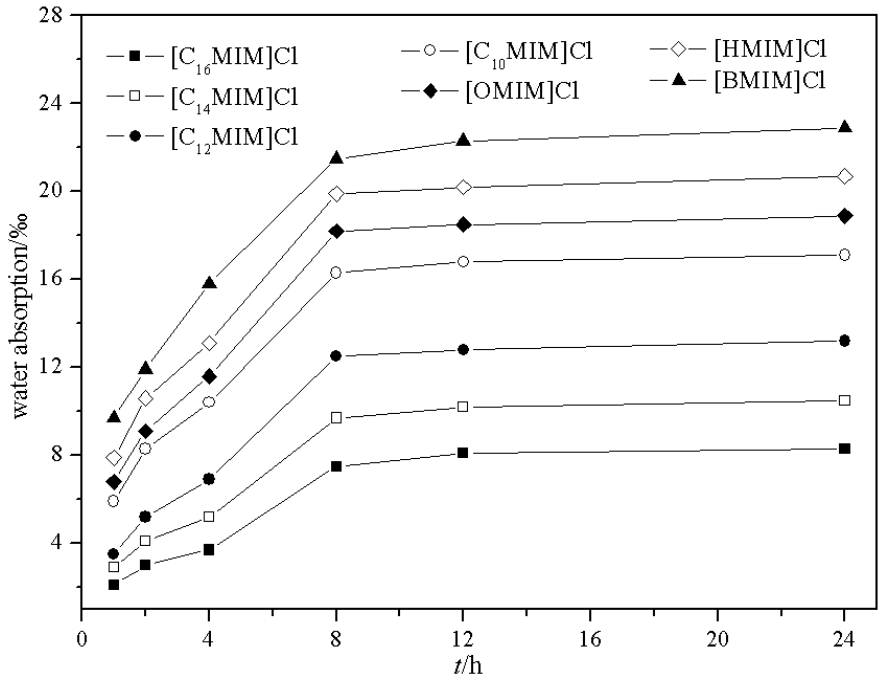

Fig. 2. Bibulous ability of ionic liquids within 24 h at 25 ºC

It is readily apparent from Fig. 2, that the several ionic liquids have significant water absorption. The rate of water absorption of [B, H, O, C_{10}MIM]Cl is appreciably faster than [C_{12}, C_{14}, C_{16}MIM]Cl that is inseparable with their carbon chain structure. There is also a decrease in water adsorption with an increasing substituting alkyl chain length in the 1-position of N of the cation. And the water absorption of them is general saturation after 12 h.

Conclusion

In this paper, seven N-alkyl-N-methylimidazolium chloride ionic liquids were synthesized under the organic-solvent-free condition with microwave irradiation. The structures were characterized and confirmed by ^{1}H NMR and melting points were determined by DSC. Their surface tensions and water adsorption properties were measured at room temperature. The results showed that there was a decrease in surface tension and water adsorption with an increasing substituting alkyl chain length in the 1-position of N of the cation. But, melting points increased with an increasing substituting alkyl chain length of the N of the cation.

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