

Thermal and Electrochemical Properties of Morpholinium Salts with Bromide Anion

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Abstract—The present work is a study of the thermal properties and electrochemical stabilities of N-ethyl-N-methylmorpholinium bromide ([Mor_{1,2}][Br]), N-butyl-N-methylmorpholinium bromide ([Mor_{1,4}][Br]), N-octyl-N-methylmorpholinium bromide ([Mor_{1,8}][Br]), N-dodecyl-N-methylmorpholinium bromide ([Mor_{1,12}][Br]), and N,N-dihydroxyethylmorpholinium bromide ([DHEMor][Br]). The melting points, decomposition temperatures, and electrochemical stabilities of the salts were measured by DSC (differential scanning calorimetry), TGA (thermogravimetric analysis), and CV (cyclic voltammogram), respectively. All salts were decomposed below approximately 230.00 °C and their melting points were above 100.00 °C except [DHEMor][Br], which melted at 75.17 °C. [DHEMor][Br] appeared to possess the most wide liquid-phase range between melting point and decomposition temperature. The electrochemical windows of salts ranged from 3.3 V for [Mor_{1,8}][Br] to 3.6 V for [Mor_{1,4}][Br] and thus did not show any noticeable variation with cations used for salt synthesis.

Key words: Ionic Liquid, Morpholinium Salt, DSC, TGA, CV (Cyclic Voltammogram)

INTRODUCTION

Ionic liquids (ILs) have received growing attention owing to their unique properties such as non-volatility, high ionic conductivity, wide electrochemical window, undetectable flammability, and high thermal stability [Ngo et al., 2000; Welton, 1999; Marsh et al., 2002; Kim et al., 2004a]. Recently, based on these properties, industrial applications of ILs such as electrolytes, catalysts, and stabilizers for preparing nanoparticles have been investigated [Kim et al., 2004a, b; Yoshizawa et al., 2002; Welton, 1999].

The synthesis procedures of ILs are normally divided into two steps [Kim et al., 2004a]. In the first step, the desired organic cation with a halide anion is prepared by the reaction of alkylhalide with a precursor of the cation such as 4-methylmorpholine, 1-methylimidazole, 1-methylpyrrolidinone, and many others. The synthesized salts with a halide anion have in general the undesirable characteristics of high viscosities, poor thermal properties, and narrow electrochemical windows, and therefore are hardly expected in industrial applications without overcoming these barriers. Accordingly, one of the possible methods to improve the salt's physical and electrochemical properties is for the halide anion to be converted into a proper inorganic anion such as tetrafluoroborate (BF₄), hexafluorophosphate (PF₆), and bis(trifluoromethanesulfonyl)imide (TFSI) by a metathesis reaction in the second step. However, it should be noted that not all organic salts with a halide anion have poor physical and chemical properties [Bonhote et al., 1996]. Further, the reports on the characteristics of salts with a halide anion will assist in determining metathesis reaction conditions such as proper solvents, reac-

tion temperature, reaction time, and so on. Therefore, it turns out to be essential to investigate the characteristics of the salts with an inorganic anion as well as a halide anion.

Recently, we reported an experimental result on morpholinium salts with TFSI having melting points near room temperature, wide liquid-phase range, high ionic conductivity, and wide electrochemical stability [Kim et al., 2004a]. However, there have been few reports on morpholinium salts according to the variation of anionic species and alkyl chain length of cation. In this study, we extensively investigated the thermal properties and electrochemical stabilities of morpholinium bromides having different alkyl chains of cation. The experimental results obtained through the present works might be practically useful because they will (1) assist researchers in determining whether their properties are practical for further applications, (2) will provide a useful background to investigate morpholinium salts with other anion species, and (3) will contribute to determining the various reaction conditions in a metathesis reaction.

EXPERIMENTAL SECTION

1. Materials

4-methylmorpholine (Aldrich, 99%), bromoethane (Aldrich, 99%), 1-bromobutane (Aldrich, 99%), 1-bromooctane (Aldrich, 99%), 1-bromododecane (Aldrich 99%), 4-(2-hydroxyethyl) morpholine (Aldrich, 99%), and 2-bromoethanol (Aldrich 99%) were used without other treatments. Acetonitrile (99.9%) and dichloromethane (99.9%) were obtained from Merck and used as received.

After the synthesis was finished, the final products were checked by ¹H NMR spectra from a Bruker AMX FT 500 MHz NMR spectrometer and Fab Mass spectra from High Resolution Tandem Mass Spectrometer.

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Table 1. Melting points of the [Mor_{1,2}][Br], [Mor_{1,4}][Br], [Mor_{1,8}][Br], [Mor_{1,12}][Br], and [DHEMor][Br]

	Morpholinium Salts				
	[Mor _{1,2}][Br]	[Mor _{1,4}][Br]	[Mor _{1,8}][Br]	[Mor _{1,12}][Br]	[DHEMor][Br]
Melting point/°C	189.66	208.13	155.49	141.00	75.17

2. Preparation

2-1. *N*-ethyl-*N*-methylmorpholinium Bromide ([Mor_{1,2}][Br])

For the [Mor_{1,2}][Br], 30.35 g (0.30 mol) of 4-methylmorpholine in 200 mL acetonitrile was reacted with 32.69 g (0.30 mol) of bromoethane dropwise in a round-bottom flask. Under nitrogen gas, the mixture was refluxed for 5 h. The molten salt was decanted from the hot solution in a separatory funnel, washed three times with 100 mL of dichloroethane, and dried on a rotavapor for 1 h at 70 °C under low pressure. The solid product ([Mor_{1,2}][Br]) was dried under vacuum at 40 °C for more than 48 h, and 56.7 g of the product was obtained (yield 90%).

¹H-NMR (DMSO, δ ppm, relative to TMS) 3.92-3.91 (s, 4H), 3.57-3.49 (q, 2H), 3.42-3.39 (t, 4H), 3.11 (s, 3H), 1.28-1.23 (t, 3H). FAB MS: $m/z=130.01$ [Mor_{1,2}]⁺.

2-2. *N*-butyl-*N*-methylmorpholinium Bromide ([Mor_{1,4}][Br])

The same apparatus and similar procedure as for [Mor_{1,2}][Br] were used. For [Mor_{1,4}][Br], 30.35 g (0.30 mol) of 4-methylmorpholine and 41.11 g (0.30 mol) of 1-bromobutane were used and 58.52 g of [Mor_{1,4}][Br] was obtained (yield 82%).

¹H-NMR (Acetone, δ ppm, relative to TMS) 4.12-4.05 (m, 4H), 3.68-3.61 (m, 6H), 3.38 (s, 3H), 1.94-1.87 (m, 2H), 1.48-1.41 (m, 2H), 1.00-0.97 (t, 3H). FAB MS: $m/z=158.05$ [Mor_{1,4}]⁺.

2-3. *N*-octyl-*N*-methylmorpholinium Bromide ([Mor_{1,8}][Br])

The same apparatus and similar procedure as for [Mor_{1,2}][Br] were used. For [Mor_{1,8}][Br], 30.35 g (0.30 mol) of 4-methylmorpholine and 57.94 g (0.30 mol) of 1-bromooctane were used and [Mor_{1,8}][Br] was obtained (yield 92%).

¹H-NMR (DMSO, δ ppm, relative to TMS) 3.92-3.90 (m, 4H), 3.49-3.41 (m, 6H), 3.15 (s, 3H), 1.73-1.66 (m, 2H), 1.30-1.27 (t, 10H), 0.89-0.85 (t, 3H). FAB MS: $m/z=214.08$ [Mor_{1,8}]⁺.

2-4. *N*-dodecyl-*N*-methylmorpholinium Bromide ([Mor_{1,12}][Br])

The same apparatus and similar procedure as for [Mor_{1,2}][Br] were used. For [Mor_{1,12}][Br], 10.11 g (0.10 mol) of 4-methylmorpholine and 24.92 g (0.10 mol) of 1-bromododecane were used and 14.20 g of [Mor_{1,12}][Br] was obtained (yield 40.5%).

¹H-NMR (DMSO, δ ppm, relative to TMS) 3.92-3.91 (m, 4H), 3.47-3.41 (m, 6H), 3.15 (s, 3H), 1.71-1.66 (m, 2H), 1.31-1.26 (q, 18H), 0.88-0.85 (t, 3H). FAB MS: $m/z=270.23$ [Mor_{1,12}]⁺.

2-5. *N,N*-dihydroxyethylmorpholinium Bromide ([DHEMor][Br])

The same apparatus and similar procedure as for [Mor_{1,2}][Br] were used. For [DHEMor][Br], 13.11 g (0.10 mol) of 4-(2-hydroxyethyl)morpholine and 12.51 g (0.10 mol) of 1-bromoethanol were used and 19.46 g of [DHEMor][Br] was obtained (yield 76%).

¹H-NMR (DMSO, δ ppm, relative to TMS) 5.29 (s, 2H), 3.96-3.94 (t, 4H), 3.86 (s, 4H), 3.72-3.67 (t, 4H), 3.60-3.58 (t, 4H). FAB MS: $m/z=176.06$ [DHEMor]⁺.

3. Apparatus and Procedure

3-1. Thermal Properties

Temperature-dependent phase behaviors were examined under helium gas at a heating rate of 10 °C·min⁻¹ by DSC Q1000 V9.0

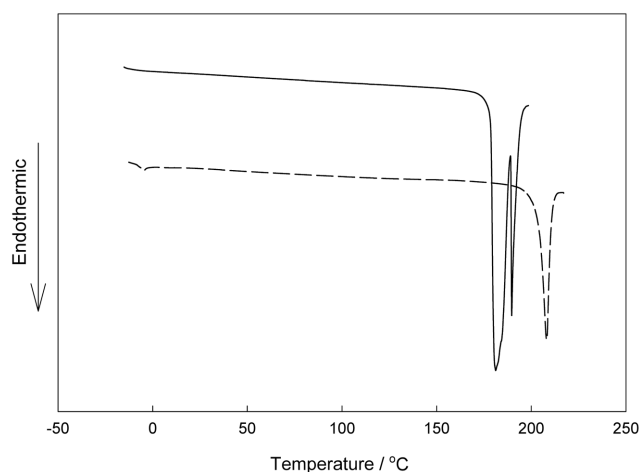
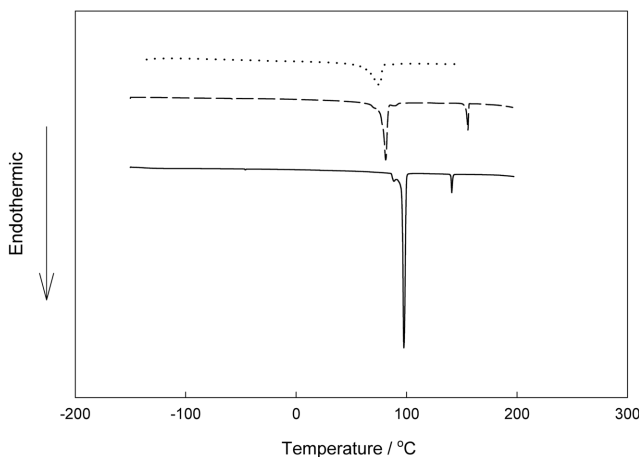
Build 275. The thermal stabilities of the salts were determined under nitrogen gas at a heating rate of 10 °C·min⁻¹ by TGA Q500 V5.0 Build 164.

3-2. Electrochemical Stabilities

Electrochemical stabilities were analyzed at room temperature by a Solartron 1287A potentiostat/galvanostat coupled to an IBM computer. A glassy carbon working electrode of 3 mm diameter was used with a platinum wire as counter electrode and a silver wire as the reference electrode.

RESULTS AND DISCUSSION

The DSC traces for the salts are presented in Figs. 1 and 2. [Mor_{1,4}][Br], and [DHEMor][Br] exhibited only one melting event, respec-

**Fig. 1. DSC results of [Mor_{1,2}][Br] (—) and [Mor_{1,4}][Br] (---).****Fig. 2. DSC results of [Mor_{1,12}][Br] (—), [Mor_{1,8}][Br] (---), and [DHEMor][Br] (···).**

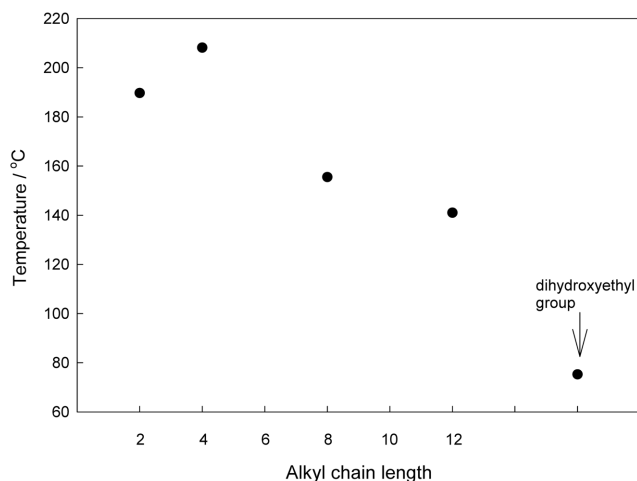


Fig. 3. Relationship between melting point and alkyl chain length: 2 (ethyl); 4 (butyl); 8 (octyl); 12 (dodecyl).

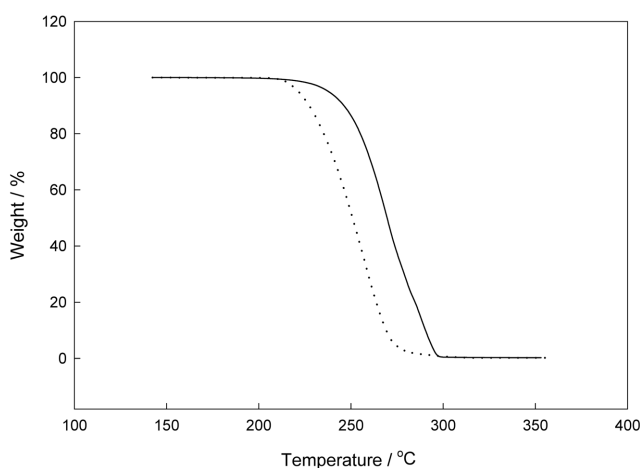


Fig. 4. TGA data of $[\text{Mor}_{1,2}][\text{Br}]$ (—) and $[\text{Mor}_{1,4}][\text{Br}]$ (---).

tively, without any multiple thermal transitions. However, $[\text{Mor}_{1,2}][\text{Br}]$, $[\text{Mor}_{1,8}][\text{Br}]$, and $[\text{Mor}_{1,12}][\text{Br}]$ showed both solid-liquid transitions and solid-solid transitions [MacFarlane et al., 1999]. All salts showed relatively high melting points above 100.00 °C except 75.17 °C for $[\text{DHEMor}][\text{Br}]$. Fig. 3 shows the relationship between melting point and alkyl chain length. The melting point was maximal for $[\text{Mor}_{1,4}][\text{Br}]$ and tended to decrease with increasing alkyl chain length. This trend between melting point and alkyl chain length was presumed by the symmetry of morpholinium cations [Forsyth et al., 2001]. $[\text{Mor}_{1,2}][\text{Br}]$ and $[\text{Mor}_{1,4}][\text{Br}]$, which are more symmetric than $[\text{Mor}_{1,8}][\text{Br}]$ and $[\text{Mor}_{1,12}][\text{Br}]$, indicated comparatively high melting points due to their more stable crystal lattice structure. However, the melting point was minimal for $[\text{DHEMor}][\text{Br}]$ which has the most symmetric structure.

Figs. 4 and 5 indicate that the decomposing temperatures were approximately 200.00 °C for $[\text{Mor}_{1,4}][\text{Br}]$, $[\text{Mor}_{1,8}][\text{Br}]$, and $[\text{Mor}_{1,12}][\text{Br}]$, 230.00 °C for $[\text{Mor}_{1,2}][\text{Br}]$, and $[\text{DHEMor}][\text{Br}]$, respectively. Among the salts, $[\text{DHEMor}][\text{Br}]$ not only had the lowest melting point but also the highest decomposition temperature. Further, $[\text{Mor}_{1,2}][\text{Br}]$ was decomposed at a higher temperature than $[\text{Mor}_{1,4}][\text{Br}]$. This

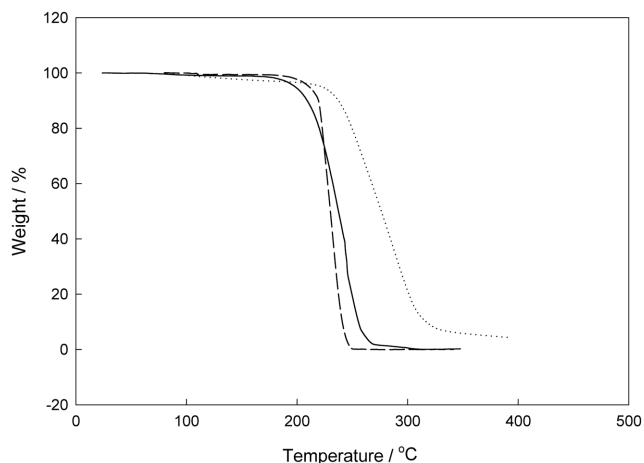


Fig. 5. TGA data $[\text{Mor}_{1,8}][\text{Br}]$ (—), $[\text{Mor}_{1,12}][\text{Br}]$ (---), and $[\text{DHEMor}][\text{Br}]$ (---).

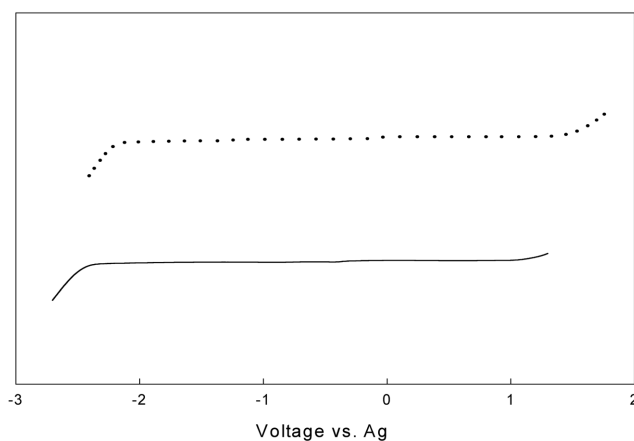


Fig. 6. CV data of $[\text{Mor}_{1,2}][\text{Br}]$ (—) and $[\text{Mor}_{1,4}][\text{Br}]$ (---).

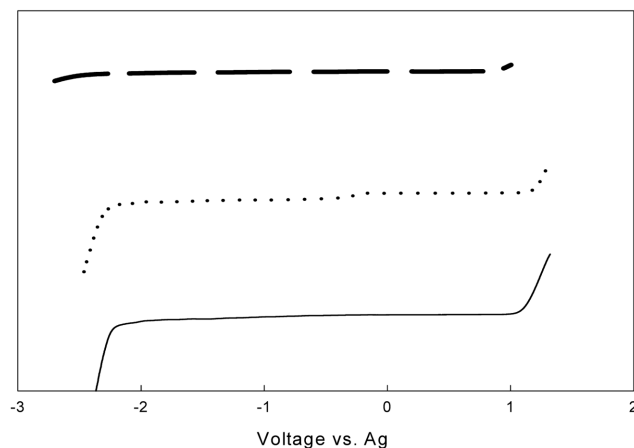


Fig. 7. CV data of $[\text{Mor}_{1,8}][\text{Br}]$ (—), $[\text{Mor}_{1,12}][\text{Br}]$ (---), and $[\text{DHEMor}][\text{Br}]$ (---).

observation is consistent with our previous results for morpholinium salts with TFSI [Kim et al., 2004a].

The results of each CV indicate a reversible behavior of the Ag/Ag^+ redox couple in the prepared salts. Figs. 6 and 7 show that the

windows of electrochemical stability between reduction and oxidation potentials were 3.4 V for the [Mor_{1,2}][Br], 3.6 V for [Mor_{1,4}][Br], 3.3 V for [Mor_{1,8}][Br], 3.5 V for [Mor_{1,12}][Br], and 3.4 V for [DHEMor][Br], respectively. In the case of [Mor_{1,4}][Br], the oxidation related to the anion commenced at the highest value, that is, approximately 1.4 V vs Ag/Ag⁺. Meanwhile, in the case of [DHEMor][Br], the reduction considered to arise from decomposition of the cation commenced at -2.6 V vs Ag/Ag⁺, which was the lowest value among all the prepared salts.

Usually, from an electrochemical point of view, the reduction potential of the cyclic voltammogram is related to the decomposition of the cation [Hagiwara et al., 2000, 2003]. However, the difference of the reduction limiting potential according to the variation of cations scarcely occurred (Figs. 6 and 7). Therefore, it is estimated that the reduction limiting potential is not significantly influenced by the alkyl chain length of the morpholinium cation.

Based on the obtained properties, the morpholinium bromides had relatively high melting points, low decomposition temperatures, narrow liquid-phase ranges, and narrow electrochemical windows, compared to morpholinium salts with TFSI [Kim et al., 2004a]. These results indicate that the thermal properties and electrochemical stabilities of morpholinium salts were dramatically enhanced only changing bromide anion into TFSI. That is, the metathesis reaction leads to outstanding improvement in the overall physical and electrochemical properties of morpholinium salts.

CONCLUSION

In this work, the thermal transitions, decomposition temperatures, and electrochemical stabilities of [Mor_{1,2}][Br], [Mor_{1,4}][Br], [Mor_{1,8}][Br], [Mor_{1,12}][Br], and [DHEMor][Br] were measured by DSC, TGA, and CV, respectively. The melting points of these salts were above 100.00 °C except for that of [DHEMor][Br]. At least, all salts were stable until approximately 200.00 °C. [Mor_{1,2}][Br] and [DHEMor][Br] decomposed at the highest temperature, roughly 230.00 °C. The electrochemical windows of the salts ranged from 3.3 V for [Mor_{1,8}][Br] to 3.6 V for [Mor_{1,4}][Br]. The obtained data indicated that [DHEMor][Br] had the best thermal properties among the prepared salts. However, the salts displayed narrow liquid-phase ranges and relatively high melting points. The results from this study will contribute to determining the appropriate conditions of metathesis reactions and investigating various morpholinium salts in subsequent researches.

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