

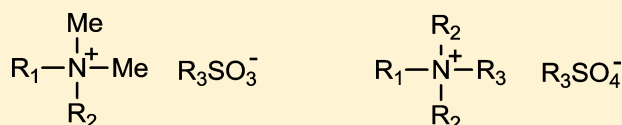
Physicochemical Characterization of New Sulfonate and Sulfate Ammonium Ionic Liquids

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ABSTRACT: In this work we describe the synthesis and thermal properties of nine new salts derived from ammonium that incorporate alkanesulfonate and alkanesulfate anions. Their structures were confirmed by ¹H and ¹³C NMR and HRMS-ESI. Their thermal properties were determined by differential scanning calorimetry (DSC). Three of the synthesized salts have been shown to be room temperature ionic liquids: *N*-ethyl-*N*-(2-hydroxyethyl)-*N,N*-dimethylammonium butanesulfonate, *N*-ethyl-*N,N*-dimethylbutylammonium ethylsulfate, and *N*-ethyl-*N*-(2-hydroxyethyl)-*N,N*-dimethylammonium ethylsulfate. Experimental densities, speeds of sound, dynamic viscosities, and refractive indices of these three ionic liquids were measured at *T* = 298.15 K.



INTRODUCTION

Ionic liquids (IL) have received increasing interest during the last decades as novel nonvolatile organic compounds.¹ A broad range of possible cations and anions allows us to create diverse ILs, tailored to various needs.² Their general properties such as nonvolatility, nonflammability, chemical and thermo stability, and environmentally friendly nature make them ideal candidates for new lubricants.^{3–12} The potential use of ILs as lubricants was first proposed in 2001.⁶ A significant number of articles and patents on this topic have been published, implying widespread interest from fundamental and industrial points of view.¹⁰ However, there is little knowledge about the appropriate formulation of a lubricant based on ILs.

In this work, a family of salts based on alkanesulfonate and alkanesulfate anions and ammonium cations, where lengths of the linear alkyl side chains were varied independently, were prepared (Figure 1). Their structures were selected according to the physical properties, toxicity, and tribological behavior of previously described ILs.¹³ Nine of them were synthesized for the first time. Their phase transition temperatures were determined by differential scanning calorimetry (DSC). Experimental densities, speeds of sound, refractive indices and dynamic viscosities of those that have been shown to be room temperature ILs were measured at *T* = 298.15 K. These ILs are new and could be further applied in tribology tests.

EXPERIMENTAL SECTION

Materials and Methods. *N,N*-Dimethylbutylamine (≥ 99.0 %), *N,N*-dimethylethanolamine (≥ 99.5 %), 1-octanesulfonyl chloride (≥ 97.0 %), and triethylamine (≥ 99.0 %) were purchased from Aldrich and used as received. 1-Butanesulfonyl chloride (98.0 % mass fraction) was purchased from Acros Organics. Diethyl sulfate (≥ 99.0 %) is commercially available (Fluka). Toluene (≥ 99.9%), dichloromethane (≥ 99.9 %), ethyl acetate (≥ 99.5 %), hexane (≥ 99.9 %), and diethyl ether (≥ 99.9 %) were purchased from Merck. Methanol and ethanol

were received from Quimivita. *N,N,N*-Trimethylbutylammonium methanesulfonate (**11**) and *N*-(2-hydroxyethyl)-*N,N,N*-trimethylammonium methanesulfonate (**12**) were purchased from IoLiTec and dried under high vacuum for 24 h. The rest of the salts studied in this work (**6**–**14**) were synthesized for the first time as shown below and dried under high vacuum for 24 h. All ILs were obtained with more than 99 % of purity. Solvents were dried with suitable drying agents and distilled under argon.

Reactions progress were monitored by thin layer chromatography using precoated plates with stationary phase 0.2 mm SilicaGel. ¹H and ¹³C NMR spectrum were measured on a Bruker ARX 400 and Electrospray MS were recorded on a Bruker FTMS APEX/Qe mass spectrometer.

Preparation of Alkanesulfonate Esters. Alkane sulfonate esters were prepared according to the literature.¹⁴ The structures of methyl butanesulfonate (**1**) and methyl octanesulfonate (**2**) were confirmed by comparison of their ¹H and ¹³C NMR data with those previously reported,¹⁵ whereas ethyl methanesulfonate (**3**), ethyl butanesulfonate (**4**), and ethyl octanesulfonate (**5**) are described for the first time.

Ethyl Methanesulfonate (3). Colorless liquid. ¹H NMR (400 MHz, CDCl₃, ppm, δ): 1.42 [t, 3H, *J* = 7.1 Hz, OCH₂CH₃], 3.0 [s, 3H, SCH₃], 4.30 [q, 2H, *J* = 7.1 Hz, OCH₂CH₃]. ¹³C NMR (100.6 MHz, CDCl₃, ppm, δ): 15.0, 37.4, 66.4.

Ethyl Butanesulfonate (4). Colorless liquid. ¹H NMR (400 MHz, CDCl₃, ppm, δ): 0.98 [t, 3H, *J* = 7.4 Hz, S(CH₂)₃-CH₃], 1.42 [t, 3H, *J* = 7.1 Hz, OCH₂CH₃], 1.50 [sex, 2H, *J* = 7.4 Hz, S(CH₂)₂CH₂], 1.86 [quin, 2H, *J* = 7.7 Hz, SCH₂CH₂], 3.11 [t, 2H, *J* = 7.7 Hz, SCH₂], 4.31 [q, 2H, *J* = 7.1 Hz, OCH₂]. ¹³C NMR (100.6 MHz, CDCl₃, ppm, δ): 13.5, 15.2, 21.5, 25.4, 50.2, 65.9.

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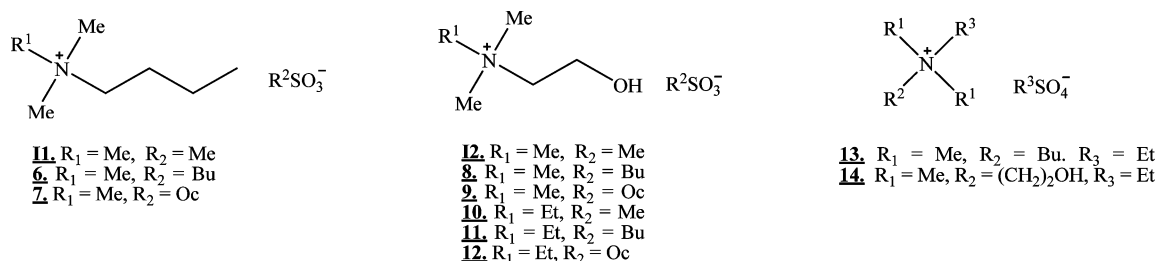


Figure 1. Ammonium salts studied in this work: **6**, $[\text{BM}_3\text{N}][\text{BSO}_3]$; **7**, $[\text{BM}_3\text{N}][\text{OSO}_3]$; **8**, $[\text{M}_3\text{N}(\text{CH}_2)_2\text{OH}][\text{BSO}_3]$; **9**, $[\text{M}_3\text{N}(\text{CH}_2)_2\text{OH}][\text{OSO}_3]$; **10**, $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}][\text{MSO}_3]$; **11**, $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}][\text{BSO}_3]$; **12**, $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}][\text{OSO}_3]$; **13**, $[\text{BEM}_2\text{N}][\text{ESO}_4]$; **14**, $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}][\text{ESO}_4]$; **11**, $[\text{BM}_3\text{N}][\text{MSO}_3]$; **12**, $[\text{M}_3\text{N}(\text{CH}_2)_2\text{OH}][\text{MSO}_3]$. Compounds **6–14** were synthesized for the first time; compounds **11** and **12** were supplied by IoLiTec.

Ethyl Octanesulfonate (5). Colorless liquid. ^1H NMR (400 MHz, CDCl_3 , ppm, δ): 0.88 [t, 3H, $J = 6.4$ Hz, $\text{S}(\text{CH}_2)_7\text{CH}_3$], 1.28 [m, 10H, $\text{S}(\text{CH}_2)_2(\text{CH}_2)_5$], 1.40 [t, 3H, $J = 7.1$ Hz, OCH_2CH_3], 1.85 [quin, 2H, $J = 7.7$ Hz, SCH_2CH_2], 3.07 [t, 2H, $J = 7.7$ Hz, SCH_2], 4.29 [q, 2H, $J = 7.1$ Hz, OCH_2]. ^{13}C NMR (100.6 MHz, CDCl_3 , ppm, δ): 14.0, 15.1, 22.6, 23.4, 28.2, 28.9, 31.7, 50.5, 65.8.

General Procedure for the Synthesis of Ammonium Alkanesulfonate Ionic Liquids. The desired tertiary amine was added dropwise to a solution of equal molar amounts of previously prepared alkanesulfonate ester ($\text{C}_m\text{H}_{2m+1}\text{SO}_3\text{C}_n\text{H}_{2n+1}$) in ethyl acetate (3 mL). The reaction mixture was stirred at room temperature (in case of compounds **6–9**) or under reflux (in case of compounds **10–12**) until reaction completion. Ethyl acetate was removed under low pressure. The product was washed with diethyl ether and solvent was removed by decantation. After washings, remaining diethyl ether was eliminated under reduced pressure and the product was dried under high vacuum for 24 h.

N,N,N-Trimethylbutylammonium Butanesulfonate $[\text{BM}_3\text{N}][\text{BSO}_3]$ (6). Reagents: *N,N*-dimethylbutylamine (0.1 mL, 0.72 mmol) and methyl butanesulfonate (**1**) (109.6 mg, 0.72 mmol). Reaction time: 12 h. The yield was 73% (133.7 mg of a white powder). ^1H NMR (400 MHz, CDCl_3 , ppm, δ): 0.91 [t, 3H, $J = 7.3$ Hz, $\text{S}(\text{CH}_2)_3\text{CH}_3$], 1.00 [t, 3H, $J = 7.3$ Hz, $\text{N}(\text{CH}_2)_3\text{CH}_3$], 1.43 [m, 4H, $\text{S}(\text{CH}_2)_2\text{CH}_2$ and $\text{N}(\text{CH}_2)_2\text{CH}_2$], 1.70 [m, 2H, SCH_2CH_2], 1.78 [m, 2H, NCH_2CH_2], 2.80 [t, 2H, $J = 7.6$ Hz, SCH_2], 3.35 [s, 9H, $\text{N}(\text{CH}_3)_3$], 3.49 [m, 2H, NCH_2]. ^{13}C NMR (100.6 MHz, CDCl_3 , ppm, δ): 13.7, 13.9, 19.6, 22.2, 25.0, 27.5, 51.9, 53.0, 66.4. HRMS-ESI m/z (%): 369.31475 $[(\text{BM}_3\text{N})_2(\text{BSO}_3)]^+$ ($\text{C}_{18}\text{H}_{45}\text{N}_3\text{O}_3\text{S}$ requires 369.31454, 100), 370 $[(\text{BM}_3\text{N})_2(\text{BSO}_3) + 1]^+$ (21), 371 $[(\text{BM}_3\text{N})_2(\text{BSO}_3) + 2]^+$ (6), 622.48622 $[(\text{BM}_3\text{N})_3(\text{BSO}_3)_2]^+$ ($\text{C}_{29}\text{H}_{72}\text{N}_3\text{O}_6\text{S}_2$ requires 622.48570, 53), 623 $[(\text{BM}_3\text{N})_3(\text{BSO}_3)_2 + 1]^+$ (19).

N,N,N-Trimethylbutylammonium Octanesulfonate $[\text{BM}_3\text{N}][\text{OSO}_3]$ (7). Reagents: *N,N*-dimethylbutylamine (0.17 mL, 1.21 mmol) and methyl octanesulfonate (**2**) (251.6 mg, 1.21 mmol). Reaction time: 20 h. The yield was 63% (235.9 mg of a white powder). ^1H NMR (400 MHz, CDCl_3 , ppm, δ): 0.86 [t, 3H, $J = 6.8$ Hz, $\text{S}(\text{CH}_2)_7\text{CH}_3$], 0.99 [t, 3H, $J = 7.3$ Hz, $\text{N}(\text{CH}_2)_3\text{CH}_3$], 1.26 [m, 8H, $\text{S}(\text{CH}_2)_3(\text{CH}_2)_4$], 1.34 [m, 2H, $\text{S}(\text{CH}_2)_2\text{CH}_2$], 1.42 [sex, 2H, $J = 7.4$ Hz, $\text{N}(\text{CH}_2)_2\text{CH}_2$], 1.70 [m, 2H, SCH_2CH_2], 1.75 [m, 2H, NCH_2CH_2], 2.78 [t, 2H, $J = 6.7$ Hz, SCH_2], 3.34 [s, 9H, $\text{N}(\text{CH}_3)_3$], 3.49 [m, 2H, NCH_2]. ^{13}C NMR (100.6 MHz, CDCl_3 , ppm, δ): 13.7, 14.1, 19.6, 22.6, 24.9, 25.5, 28.9, 29.1, 29.4, 31.8, 52.2, 52.9, 66.4. HRMS-ESI m/z (%): 425 $[(\text{BM}_3\text{N})_2(\text{OSO}_3)]^+$ (100), 734 $[(\text{BM}_3\text{N})_3(\text{OSO}_3)_2]^+$ (50), 1043 $[(\text{BM}_3\text{N})_4(\text{OSO}_3)_3]^+$ (5).

N-(2-Hydroxyethyl)-N,N,N-trimethylammonium Butanesulfonate $[\text{M}_3\text{N}(\text{CH}_2)_2\text{OH}][\text{BSO}_3]$ (8). Reagents: *N,N*-dimethylethanolamine (0.07 mL, 0.66 mmol) and methyl butanesulfonate (**1**) (101.0 mg, 0.66 mmol). Reaction time: 24 h. The yield was 71% (114.2 mg of a white powder). ^1H NMR (400 MHz, CDCl_3 , ppm, δ): 0.92 [t, 3H, $J = 7.3$ Hz, $\text{S}(\text{CH}_2)_3\text{CH}_3$], 1.41 [sex, 2H, $J = 7.4$ Hz, $\text{S}(\text{CH}_2)_2\text{CH}_2$], 1.74 [quin, 2H, $J = 7.8$ Hz, SCH_2CH_2], 2.78 [t, 2H, $J = 6.7$ Hz, SCH_2], 3.34 [s, 9H, $\text{N}(\text{CH}_3)_3$], 3.71 [t, 2H, $J = 6.7$ Hz, NCH_2], 4.08 [m, 2H, NCH_2CH_2], 5.52 [bs, 1H, $\text{NCH}_2\text{CH}_2\text{OH}$]. ^{13}C NMR (100.6 MHz, CDCl_3 , ppm, δ): 13.8, 22.0, 27.3, 51.8, 54.4 [t, $J(\text{C},\text{N}) = 3.3$ Hz], 56.4, 67.8. HRMS-ESI m/z (%): 345.24159 $\{[\text{M}_3\text{N}(\text{CH}_2)_2\text{OH}]_2[\text{BSO}_3]\}^+$ ($\text{C}_{14}\text{H}_{37}\text{N}_2\text{O}_5\text{S}$ requires 345.24177, 100), 346 $\{[\text{M}_3\text{N}(\text{CH}_2)_2\text{OH}]_2[\text{BSO}_3] + 1\}^+$ (18), 586.37685 $\{[\text{M}_3\text{N}(\text{CH}_2)_2\text{OH}]_3[\text{BSO}_3]\}^+$ ($\text{C}_{23}\text{H}_{60}\text{N}_3\text{O}_9\text{S}_2$ requires 586.37655, 32), 587 $\{[\text{M}_3\text{N}(\text{CH}_2)_2\text{OH}]_3[\text{BSO}_3]_2 + 1\}^+$ (12), 588 $\{[\text{M}_3\text{N}(\text{CH}_2)_2\text{OH}]_3[\text{BSO}_3]_2 + 2\}^+$ (5).

N-(2-Hydroxyethyl)-N,N,N-trimethylammonium Octanesulfonate $[\text{M}_3\text{N}(\text{CH}_2)_2\text{OH}][\text{OSO}_3]$ (9). Reagents: *N,N*-dimethylethanolamine (0.24 mL, 2.40 mmol) and methyl octanesulfonate (**2**) (500.0 mg, 2.40 mmol). Reaction time: 16 h. The yield was 82% (590.0 mg of a white powder). ^1H NMR (400 MHz, CDCl_3 , ppm, δ): 0.87 [t, 3H, $J = 7.2$ Hz, $\text{S}(\text{CH}_2)_7\text{CH}_3$], 1.26 [m, 8H, $\text{S}(\text{CH}_2)_2(\text{CH}_2)_4$], 1.36 [m, 2H, $\text{S}(\text{CH}_2)_6\text{CH}_2$], 1.76 [quin, 2H, $J = 7.8$ Hz, SCH_2CH_2], 2.77 [t, 2H, $J = 6.8$ Hz, SCH_2], 3.34 [s, 9H, $\text{N}(\text{CH}_3)_3$], 3.70 [m, 2H, NCH_2], 4.08 [m, 2H, NCH_2CH_2], 5.52 [bs, 1H, $\text{NCH}_2\text{CH}_2\text{OH}$]. ^{13}C NMR (100.6 MHz, CDCl_3 , ppm, δ): 14.0, 22.6, 25.2, 28.8, 29.1, 29.3, 31.7, 52.1, 54.3, 56.4, 67.8. HRMS-ESI m/z (%): 401 $\{[\text{M}_3\text{N}(\text{CH}_2)_2\text{OH}]_2[\text{OSO}_3]\}^+$ (60), 698 $\{[\text{M}_3\text{N}(\text{CH}_2)_2\text{OH}]_3[\text{OSO}_3]\}^+$ (100), 995 $\{[\text{M}_3\text{N}(\text{CH}_2)_2\text{OH}]_4[\text{OSO}_3]_3\}^+$ (17).

N-Ethyl-N-(2-hydroxyethyl)-N,N-dimethylammonium Methanesulfonate $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}][\text{MSO}_3]$ (10). Reagents: *N,N*-dimethylethanolamine (0.15 mL, 1.45 mmol) and ethyl methanesulfonate (**3**) (180.0 mg, 1.45 mmol). Reaction time: 20 h. The yield was 73% (225.6 mg of a white powder). ^1H NMR (400 MHz, CDCl_3 , ppm, δ): 1.40 [t, 3H, $J = 7.3$ Hz, NCH_2CH_3], 2.70 [s, 3H, SCH_3], 3.24 [s, 6H, $\text{N}(\text{CH}_3)_2$], 3.60 [q, 2H, $J = 7.3$ Hz, NCH_2CH_3], 3.65 [m, 2H, $\text{NCH}_2\text{CH}_2\text{OH}$], 4.07 [m, 2H, $\text{NCH}_2\text{CH}_2\text{OH}$], 5.51 [bs, 1H, $\text{NCH}_2\text{CH}_2\text{OH}$]. ^{13}C NMR (100.6 MHz, CDCl_3 , ppm, δ): 8.4, 39.6, 51.1 [t, $J(\text{C},\text{N}) = 3.3$ Hz], 56.1, 61.1, 65.1. HRMS-ESI m/z (%): 331.22751 $[(\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH})_2(\text{MSO}_3)]^+$ ($\text{C}_{13}\text{H}_{35}\text{N}_2\text{O}_5\text{S}$ requires 331.22612, 100), 544.32741 $[(\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH})_3(\text{MSO}_3)_2]^+$ ($\text{C}_{20}\text{H}_{54}\text{N}_3\text{O}_9\text{S}_2$ requires 544.32960, 33).

N-Ethyl-N-(2-hydroxyethyl)-N,N-dimethylammonium Butanesulfonate $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}][\text{BSO}_3]$ (11). Reagents: *N,N*-dimethylethanolamine (0.14 mL, 1.34 mmol) and ethyl butanesulfonate (**4**) (222.8 mg, 1.34 mmol). Reaction time: 72 h.

The yield was 83% (280.0 mg of a slightly yellow liquid). ^1H NMR (400 MHz, CDCl_3 , ppm, δ): 0.93 [t, 3H, $J = 7.3$ Hz, $\text{S}(\text{CH}_2)_3\text{CH}_3$], 1.43 [m, 5H, $\text{S}(\text{CH}_2)_2\text{CH}_2$ and NCH_2CH_3], 1.78 [m, 2H, SCH_2CH_2], 2.82 [t, 2H, $J = 6.9$ Hz, SCH_2], 3.28 [s, 6H, $\text{N}(\text{CH}_3)_2$], 3.63 [q, 2H, $J = 7.3$ Hz, NCH_2CH_3], 3.69 [m, 2H, $\text{NCH}_2\text{CH}_2\text{OH}$], 4.13 [m, 2H, $\text{NCH}_2\text{CH}_2\text{OH}$], 5.62 [bs, 1H, $\text{NCH}_2\text{CH}_2\text{OH}$]. ^{13}C NMR (100.6 MHz, CDCl_3 , ppm, δ): 8.4, 13.8, 22.0, 27.3, 51.0, 51.8, 56.1, 61.0, 65.1. HRMS-ESI m/z (%): 373.27198 $[(\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH})_2(\text{BSO}_3)]^+$ ($\text{C}_{16}\text{H}_{41}\text{N}_2\text{O}_3\text{S}$ requires 373.27362, 100), 628.42456 $[(\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH})_3(\text{BSO}_3)_2]^+$ ($\text{C}_{26}\text{H}_{66}\text{N}_3\text{O}_9\text{S}_2$ requires 628.42405, 54), 884 $[(\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH})_4(\text{BSO}_3)_3]^+$ (38), 1139 $[(\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH})_5(\text{BSO}_3)_4]^+$ (11), 1394 $[(\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH})_6(\text{BSO}_3)_5]^+$ (9). The mass fraction of water was found to be 5×10^{-5} (determined by 756 Karl Fischer coulometer).

***N*-Ethyl-*N*-(2-hydroxyethyl)-*N,N*-dimethylammonium Octanesulfonate $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}][\text{OSO}_3]$ (12).** Reagents: *N,N*-dimethylethanolamine (0.23 mL, 2.25 mmol) and ethyl octanesulfonate (5) (500.3 mg, 2.25 mmol). Reaction time: 48 h. The yield was 79% (554.0 mg of a white powder). ^1H NMR (400 MHz, CDCl_3 , ppm, δ): 0.86 [t, 3H, $J = 6.0$ Hz, $\text{S}(\text{CH}_2)_7\text{CH}_3$], 1.25 [m, 8H, $\text{SCH}_2\text{CH}_2(\text{CH}_2)_4$], 1.39 [m, 5H, NCH_2CH_3 , and $\text{S}(\text{CH}_2)_6\text{CH}_2$], 1.76 [m, 2H, SCH_2CH_2], 2.77 [t, 2H, $J = 8.0$ Hz, SCH_2], 3.25 [s, 6H, $\text{N}(\text{CH}_3)_2$], 3.60 [q, 2H, $J = 7.3$ Hz, NCH_2CH_3], 3.64 [m, 2H, $\text{NCH}_2\text{CH}_2\text{OH}$], 4.07 [m, 2H, $\text{NCH}_2\text{CH}_2\text{OH}$], 5.58 [bs, 1H, $\text{NCH}_2\text{CH}_2\text{OH}$]. ^{13}C NMR (100.6 MHz, CDCl_3 , ppm, δ): 8.4, 14.1, 22.6, 25.3, 28.9, 29.2, 29.4, 31.8, 51.1, 52.1, 56.1, 61.0, 65.1. HRMS-ESI m/z (%): 429 $[(\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH})_2(\text{OSO}_3)]^+$ (100), 740 $[(\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH})_3(\text{OSO}_3)_2]^+$ (77), 1052 $[(\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH})_4(\text{OSO}_3)_3]^+$ (6).

General Procedure for the Synthesis of Ammonium Alkanesulfates Ionic Liquids. Ammonium alkanesulfates were prepared according to a procedure previously described.¹³

***N*-Ethyl-*N,N*-dimethylbutylammonium Ethylsulfate $[\text{BEM}_2\text{N}][\text{ESO}_4]$ (13).** Reagents: *N,N*-dimethylbutylamine (3.0 mL, 19.6 mmol) and diethyl sulfate (2.6 mL, 19.6 mmol). Reaction time: 5 h. The yield was 98% (4.9 g of a colorless liquid). ^1H NMR (400 MHz, CDCl_3 , ppm, δ): 0.86 [t, 3H, $J = 7.4$ Hz, $\text{N}(\text{CH}_2)_3\text{CH}_3$], 1.14 [t, 3H, $J = 7.1$ Hz, OCH_2CH_3], 1.25 [t, 3H, $J = 7.3$ Hz, NCH_2CH_3], 1.29 [sex, 2H, $J = 7.4$ Hz, $\text{N}(\text{CH}_2)_2\text{CH}_2$], 1.58 [m, 2H, NCH_2CH_2], 3.03 [s, 6H, $\text{N}(\text{CH}_3)_2$], 3.22 [m, 2H, NCH_2], 3.38 [q, 2H, $J = 7.3$ Hz, NCH_2CH_3], 3.90 [q, 2H, $J = 7.1$ Hz, OCH_2CH_3]. ^{13}C NMR (100.6 MHz, CDCl_3 , ppm, δ): 8.3, 13.6, 15.2, 19.5, 24.4, 50.1 [t, $J(\text{C},\text{N}) = 3.5$ Hz], 59.2, 62.9, 63.2. HRMS-ESI m/z (%): 385.30843 $[(\text{BEM}_2\text{N})_2(\text{ESO}_4)]^+$ ($\text{C}_{18}\text{H}_{43}\text{N}_2\text{O}_4\text{S}^+$ requires 385.30891, 100), 640 $[(\text{BEM}_2\text{N})_3(\text{ESO}_4)_2]^+$ (25), 895 $[(\text{BEM}_2\text{N})_4(\text{ESO}_4)_3]^+$ (12), 1151 $[(\text{BEM}_2\text{N})_5(\text{ESO}_4)_4]^+$ (3), 1406 $[(\text{BEM}_2\text{N})_6(\text{ESO}_4)_5]^+$ (3). The mass fraction of water was found to be 4×10^{-5} (determined by 756 Karl Fischer coulometer).

***N*-Ethyl-*N*-(2-hydroxyethyl)-*N,N*-dimethylammonium Ethylsulfate $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}][\text{ESO}_4]$ (14).** Reagents: *N,N*-dimethylethanolamine (6.2 mL, 61.6 mmol) and diethyl sulfate (8.1 mL, 61.6 mmol). Reaction time: 5 h. The yield was 88% (13.2 g of a colorless liquid). ^1H NMR (400 MHz, CDCl_3 , ppm, δ): 1.29 [t, 3H, $J = 7.1$ Hz, OCH_2CH_3], 1.40 [t, 3H, $J = 7.3$ Hz, NCH_2CH_3], 3.23 [s, 6H, $\text{N}(\text{CH}_3)_2$], 3.59 [m, 4H, $\text{NCH}_2\text{CH}_2\text{OH}$ and NCH_2CH_3], 3.95 [m, 2H, $\text{NCH}_2\text{CH}_2\text{OH}$], 4.07 [q, 2H, $J = 7.1$ Hz, OCH_2CH_3], 4.96 [bs, 1H, $\text{NCH}_2\text{CH}_2\text{OH}$]. ^{13}C NMR (100.6 MHz, CDCl_3 , ppm, δ): 8.4, 15.2, 51.1, 56.3, 61.2, 63.7, 65.2. HRMS-ESI m/z (%): 361.23548 $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}]_2[\text{ESO}_4]^+$ ($\text{C}_{14}\text{H}_{37}\text{N}_2\text{O}_6\text{S}$ requires

361.23723, 100), 604.34935 $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}]_3[\text{ESO}_4]_2^+$ ($\text{C}_{22}\text{H}_{58}\text{N}_3\text{O}_{11}\text{S}_2$ requires 604.35128, 32), 847 $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}]_4[\text{ESO}_4]_3^+$ (45), 1091 $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}]_5[\text{ESO}_4]_4^+$ (23), 1334 $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}]_6[\text{ESO}_4]_5^+$ (21). The mass fraction of water was found to be 6×10^{-5} (determined by 756 Karl Fischer coulometer).

Apparatus and Procedures. DSC. The thermal analysis of the pure salts synthesized in this work was performed using a Mettler-Toledo differential scanning calorimeter (DSC), model DSC822^c, with Mettler-Toledo STAR^c software version 8.01. Zinc and indium reference sample (provided by Mettler-Toledo) were used for the calibration of the temperature and heat flow. The sample pan and empty pan reference were placed within the furnace and they were exposed to a flowing N_2 atmosphere. The method used for the thermal analysis consisted in cooling the samples from (393 to 233) K, at a rate of $10^\circ\text{C}\cdot\text{min}^{-1}$, followed by heating from (233 to 423) K at a rate of $10^\circ\text{C}\cdot\text{min}^{-1}$. Because the presence of volatiles affects the glass transition and melting temperature,^{16,17} the samples were heated at $T = 393.15$ K for 30 min inside the furnace of the DSC. The uncertainty of the temperature measurement was ± 1 K, and the uncertainty of the transition enthalpies was ± 4 $\text{J}\cdot\text{g}^{-1}$, which were determined by using a common procedure consisting in three consecutive scans of the same sample and three scans removing and replacing the sample carried out by different operators.

The heat capacities of the compounds were determined by using the sapphire sample. Aluminum pans of 100 μL with ± 80 mg of the sample were used. The rate for the heat capacities measurements was $20^\circ\text{C}/\text{min}$ and the uncertainty in experimental measurements of heat capacity was ± 1 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

Physical Properties. The apparatus used for the determination of density, speed of sound, refractive index and dynamic viscosity of the pure salts were described elsewhere.¹³ Briefly, an Anton Paar DSA-5000 M digital vibrating-tube densimeter was employed for the density and speed of sound determination. It is important to remark that the influence of viscosity on the density measurement is automatically corrected. The uncertainties in the density and speed of sound experimental measurements were $\pm 2 \times 10^{-6}$ $\text{g}\cdot\text{cm}^{-3}$ and ± 0.3 $\text{m}\cdot\text{s}^{-1}$, respectively.

The refractive indices were measured with an automatic refractometer Abemat-HP Dr. Kernchen; the uncertainty in its measurement was $\pm 4 \times 10^{-5}$.

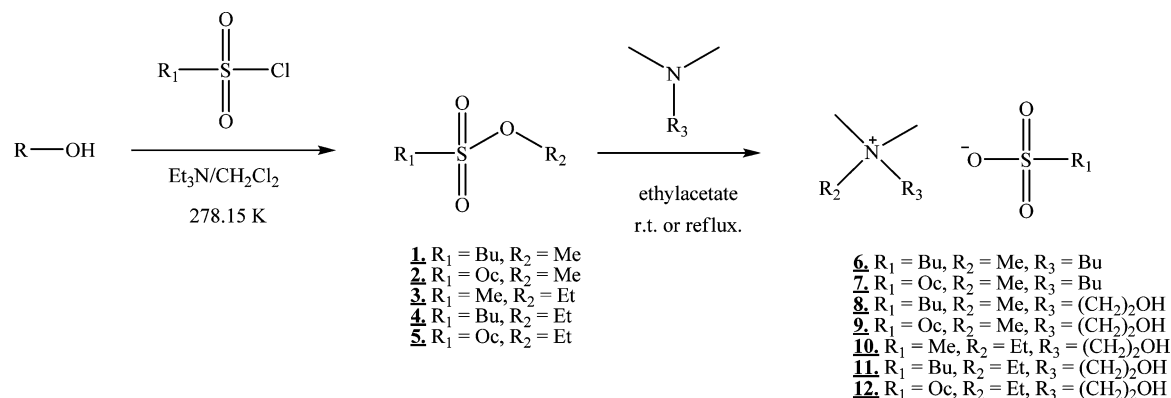
The dynamic viscosities were determined by using an automatic viscosimeter Lauda PVS1 with two Ubbelohde capillary microviscosimeters of (3×10^{-3} and 4.7×10^{-3}) m diameter (the uncertainty in experimental measurement was ± 1 and ± 3 mPa·s respectively).

RESULTS AND DISCUSSION

Synthesis of ILs. Ammonium alkanesulfonate salts were synthesized by alkylation of the corresponding tertiary amines with alkyl sulfonates ($\text{C}_m\text{H}_{2m+1}\text{SO}_3\text{C}_n\text{H}_{2n+1}$), which were prepared by simple treatment of alcohols ($\text{C}_n\text{H}_{2n+1}\text{OH}$, $n = 1, 2$) with alkanesulfonyl chlorides ($\text{C}_m\text{H}_{2m+1}\text{SO}_2\text{Cl}$, $m = 1, 4, 8$) in the presence of a base (Scheme 1). Ammonium alkanesulfates salts were synthesized by alkylation of the corresponding tertiary amines with alkyl sulfates.¹³

Thermal Properties. Thermal data derived from DSC traces are summarized in Table 1. In this table, the melting temperature (T_m), the cold crystallization temperature (T_{cc}), and the solid–solid transition temperature (T_{s-s}) are taken to be the

Scheme 1. Synthesis of Ammonium Alkanesulfonates

Table 1. Thermal Properties for Pure Salts^a

compound	T_m (K) and ΔH (J·g ⁻¹)	T_f (K) and ΔH (J·g ⁻¹)	T_g (K) and ΔH (J·g ⁻¹)	T_{ss} (K) and ΔH (J·g ⁻¹)	T_{cc} (K) and ΔH (J·g ⁻¹)	T_x (K) and ΔH (J·g ⁻¹)
[BM ₃ N][MSO ₃] (11)	442	349 (-18.42)	404			
[BM ₃ N][BSO ₃] (6)	335 (11.86)	328 (-12.27)				
[BM ₃ N][OSO ₃] (7)	484 ^b			347 (10.62) 413 (1.60)	246 (-24.18)	409 (-1.22) 340 (-13.49)
[M ₃ N(CH ₂) ₂ OH][MSO ₃] (12)	393 (24.83)	378 (-25.13)		350 (29.48) 365 (13.65)		360 (-18.64) 323 (-33.50)
[M ₃ N(CH ₂) ₂ OH][BSO ₃] (8)	324 (103.59)	305 (-103.40)				
[M ₃ N(CH ₂) ₂ OH][OSO ₃] (9)	390 (15.46)	387 (-14.99)		307 (22.16) 337 (17.65) 346 (17.65)		342 (-21.65) 323 (-41.47) 279 (-21.65) 307 (-15.89)
[EM ₂ N(CH ₂) ₂ OH][MSO ₃] (10)	317 ^c (94.03)	318 ^d (-63.10)				
[EM ₂ N(CH ₂) ₂ OH][BSO ₃] (11)	293 (93.08)					
[EM ₂ N(CH ₂) ₂ OH][OSO ₃] (12)	320 (95.89)	326 (-101.80)				
[BEM ₂ N][ESO ₄] (13)	307 ^e (45.71)					
[EM ₂ N(CH ₂) ₂ OH][ESO ₄] (14)						

^a T_m , melting temperature (K); T_f , freezing temperature (K); T_g , glass-transition temperature (K); T_{ss} , solid–solid transition temperature (K); T_{cc} , cold crystallization temperature (K); T_x , phase-transition temperature on cooling (K); ΔH , enthalpy (J·g⁻¹). ^bExhibits cold crystallization (crystallization on heating) at 259.09 K (24.07 J·g⁻¹). ^cExhibits endothermic transition on heating at 337.64 K (7.34 J·g⁻¹). ^dExhibits two exotherms on cooling at 317.2 K (-9.02 J·g⁻¹) and 309.28 K (-1.41 J·g⁻¹). ^eExhibits endothermic transition on heating at 334.58 K (5.31 J·g⁻¹).

peak of an endothermic curve on heating; the freezing temperature (T_f) and the phase-transition temperature on cooling (T_x) are taken to be the peak of an exothermic curve on cooling; and the glass-transition temperature (T_g) is the midpoint of a small heat capacity change on heating from the amorphous glass state to a liquid state. The cold crystallization temperature is defined as the midpoint of an exothermic peak on heating from a subcooled liquid state to a crystalline solid state.²¹ It should also be noted that the DSC scans were always started at 233 K and finished at 423 K for all salts studied in this work. Because [BM₃N][MSO₃] (**11**) and [BM₃N][OSO₃] (**7**) melting points were not observed, DSC scans from 298 to 523 K were performed.

Illustrative DSC thermograms obtained on cooling and heating are shown in Figures 2–14. Figure 2 showed a glass-transition at 404 K and freezing point at 349 K for [BM₃N][MSO₃] (**11**), whereas a melting transition was not observed. However, Figure 3 showed a melting point at 442 K. [BM₃N][BSO₃] (**6**) (Figure 4) and [M₃N(CH₂)₂OH][BSO₃] (**8**) (Figure 8) present distinct freezing points [(328 and 305) K, respectively] on cooling and distinct melting points [(335 and 324) K, respectively] on heating.

Multiple solid–solid transitions are shown before melting points for compounds [BM₃N][OSO₃] (**7**) (Figures 5 and 6), [M₃N(CH₂)₂OH][MSO₃] (**12**) (Figure 7), and [M₃N(CH₂)₂OH][OSO₃] (**9**) (Figure 9). The melting point of [BM₃N][OSO₃] (**7**) can be seen in Figure 6 at 484 K. Thus, the DSC thermogram of this compound showed a cold crystallization temperature at 246 K; two solid–solid transition temperatures at (347 and 413) K before the melting point and two phase-transition temperatures on cooling [(409 and 340) K]. The broadness of the final melting peak observed for [M₃N(CH₂)₂OH][MSO₃] (**12**) at 393 K could indicate the onset of one or more solid–solid transitions coincident with the melting point.¹⁸ This compound also showed two solid–solid phase-transitions at (350 and 365) K, following with a melting point at 393 K and phase-transition temperatures at (359 and 323) K on cooling. Thermogram of [M₃N(CH₂)₂OH][OSO₃] (**9**) showed three solid–solid transitions at (307, 336, and 346) K before melting point (390 K); a freezing point at 387 K, and three phase-transition temperatures on cooling at (342, 323, and 279) K.

The [EM₂N(CH₂)₂OH][MSO₃] (**10**) thermogram (Figure 10) showed a broad melting peak on heating at 317 K, where coincidence of solid–solid transition with melting point is

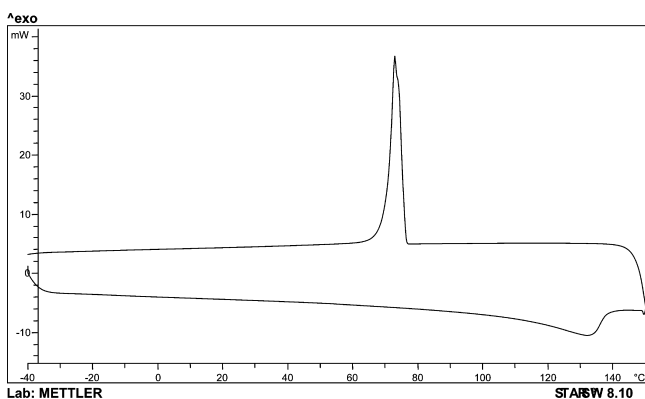


Figure 2. DSC scan for $[\text{BM}_3\text{N}][\text{MSO}_3]$ (11); upper curve is cooling and lower curve is heating.

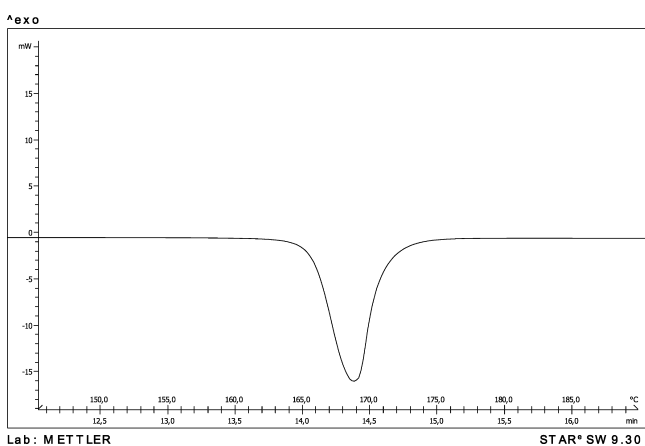


Figure 3. DSC scan from (298 to 523) K for $[\text{BM}_3\text{N}][\text{MSO}_3]$ (11).

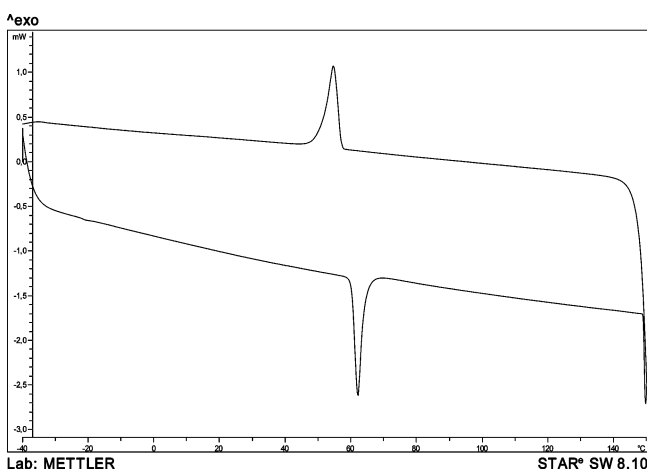


Figure 4. DSC scan for $[\text{BM}_3\text{N}][\text{BSO}_3]$ (6); upper curve is cooling and lower curve is heating.

observed again.¹⁹ The freezing point was registered at 318 K and one phase-transition at 307 K.

The $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}][\text{OSO}_3]$ (12) DSC (Figure 12) analysis was quite complicated as several weak endothermic (and/or exothermic) transitions were observed. We could suppose that the DSC thermogram shows endothermic transition (337 K) from the crystalline to the isotropic liquid state. When the compound was cooled from the isotropic liquid state to the crystalline state,

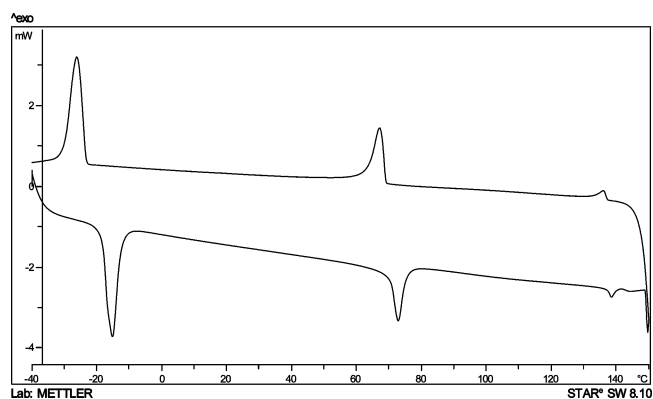


Figure 5. DSC scan for $[\text{BM}_3\text{N}][\text{OSO}_3]$ (7); upper curve is cooling and lower curve is heating.

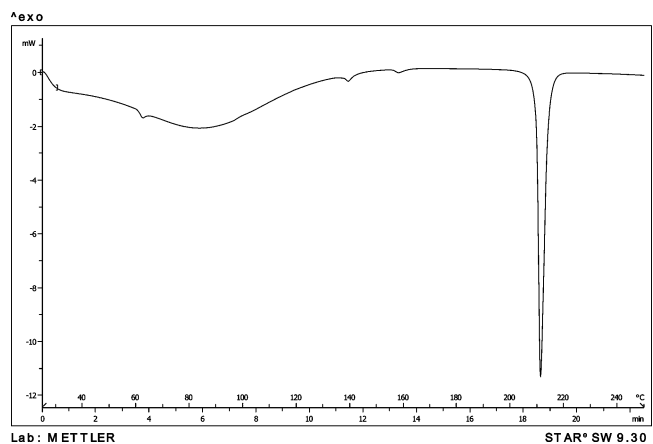


Figure 6. DSC scan from (293 to 523) K for $[\text{BM}_3\text{N}][\text{OSO}_3]$ (7).

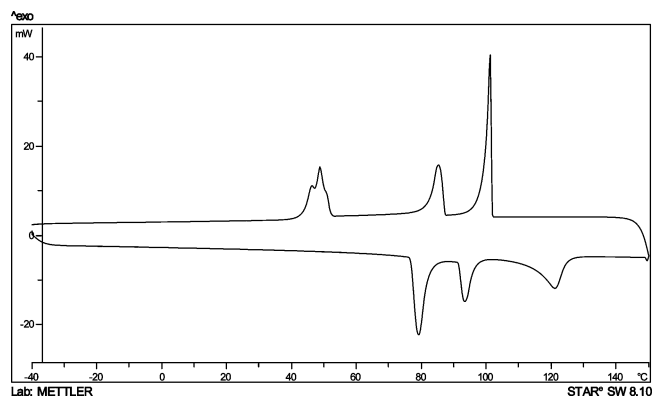


Figure 7. DSC scan for $[\text{M}_3\text{N}(\text{CH}_2)_2\text{OH}][\text{MSO}_3]$ (12); upper curve is cooling and lower curve is heating.

its DSC curve exhibited two exotherms at (317 and 309) K, corresponding to the subsequent transitions from the isotropic liquid to the crystalline state.²⁰ The broadness of melting peak showed coincidence of solid–solid transition with the melting point at 320 K. The freezing point was registered at 326 K.

Compounds $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}][\text{BSO}_3]$ (11), $[\text{BEM}_2\text{N}][\text{ESO}_4]$ (13) and $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}][\text{ESO}_4]$ (14) were shown to be room temperature ILs. The $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}][\text{BSO}_3]$ (11) (Figure 11) DSC thermogram showed one melting peak at 293 K and no peaks on cooling. The $[\text{BEM}_2\text{N}][\text{ESO}_4]$ (13) (Figure 13) DSC thermogram showed a melting point at 307 K and an endothermic transition at 334 K. The onset melting

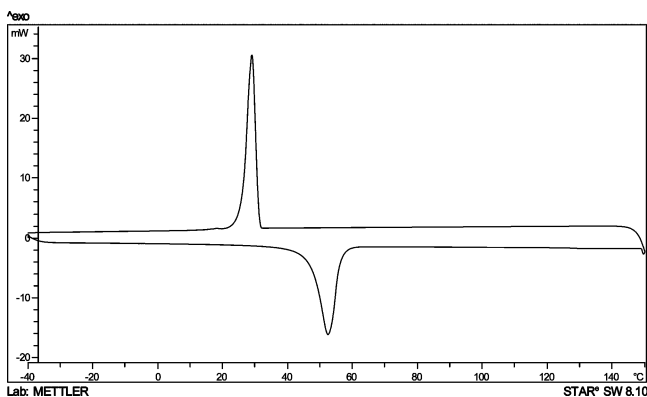


Figure 8. DSC scan for $[M_3N(CH_2)_2OH][BSO_3]$ (8); upper curve is cooling and lower curve is heating.

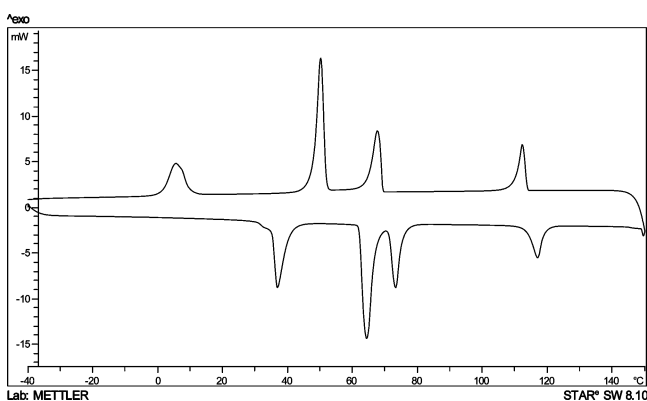


Figure 9. DSC scan for $[M_3N(CH_2)_2OH][OSO_3]$ (9); upper curve is cooling and lower curve is heating.

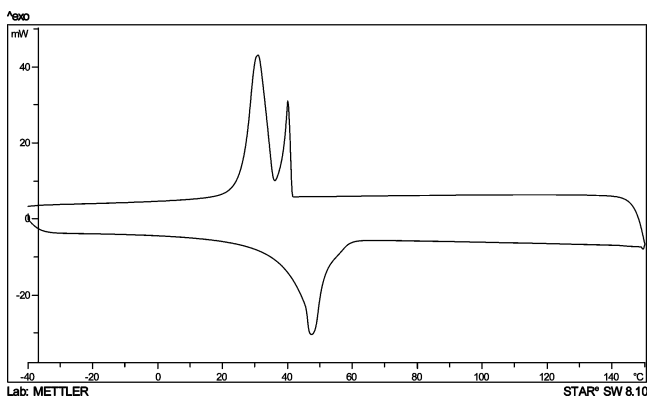


Figure 10. DSC scan for $[EM_2N(CH_2)_2OH][MSO_3]$ (10); upper curve is cooling and lower curve is heating.

temperature of this compound was 293 K. Therefore, this IL is liquid at room temperature. In the case of $[EM_2N(CH_2)_2OH][ESO_4]$ (14) no peaks were observed.

It is well-known that thermal properties of ILs depend on the structure of cation and anion.² As it can be observed in Figure 15, when the anion alkyl chain length increase from $n = 1$ to $n = 4$, the melting point decrease. However, when the anion alkyl chain length increase from $n = 4$ to $n = 8$, the melting point increase. Figure 15 also shows the melting point variation for sulfonates when the anion alkyl chain increase. The influence of cation asymmetry on the melting point is also observed. As the

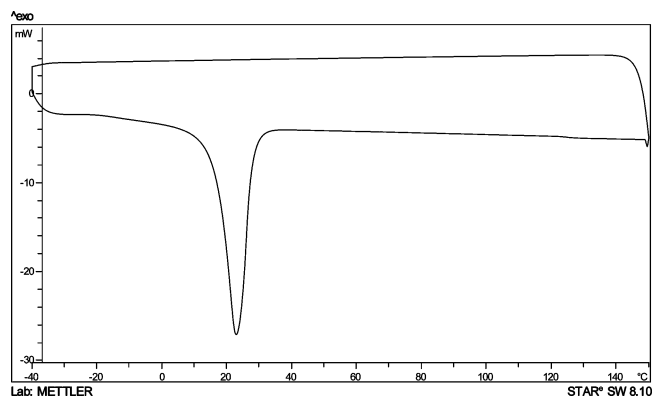


Figure 11. DSC scan for $[EM_2N(CH_2)_2OH][BSO_3]$ (11); upper curve is cooling and lower curve is heating.

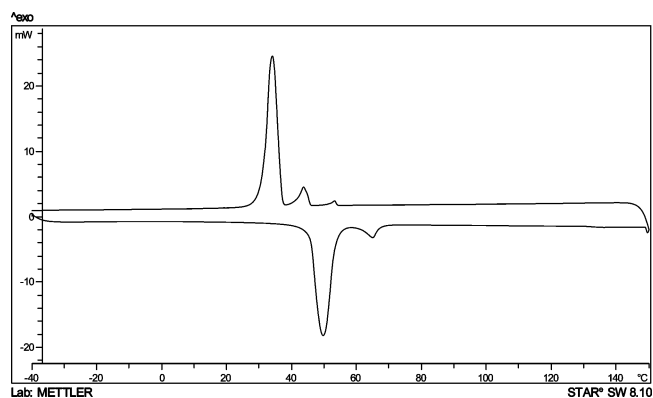


Figure 12. DSC scan for $[EM_2N(CH_2)_2OH][OSO_3]$ (12); upper curve is cooling and lower curve is heating.

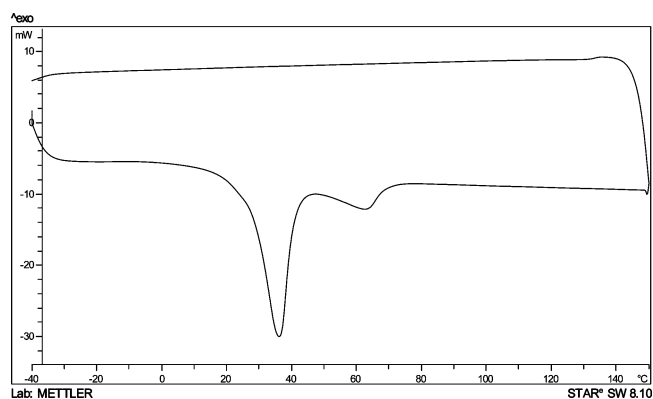


Figure 13. DSC scan for $[BEM_2N][ESO_4]$ (13); upper curve is cooling and lower curve is heating.

cation asymmetry increase (12 versus 10, 8 versus 11, and 9 versus 12) melting point decreases.

Heat Capacities. Heat capacities of some salts with melting points below $T = 373$ K were measured in different temperature ranges. The next polynomial equation was used to adjust them, where T is temperature and a , b , and c are adjustable parameters

$$C_p = aT^2 + bT + c \quad (2)$$

The characteristic parameters a , b , and c are given in Table 2 together with temperature ranges of measurements and the

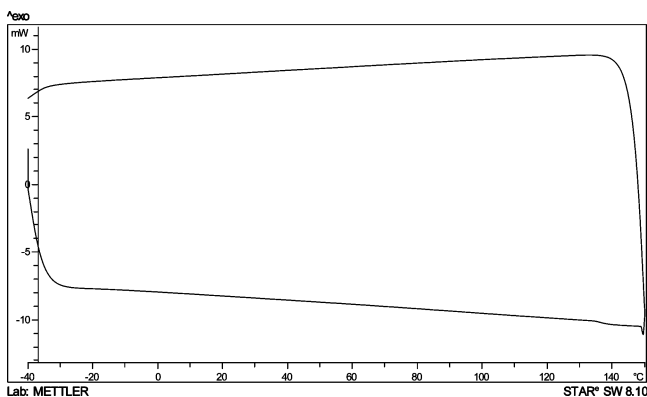


Figure 14. DSC scan for $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}][\text{ESO}_4]$ (14); upper curve is cooling and lower curve is heating.

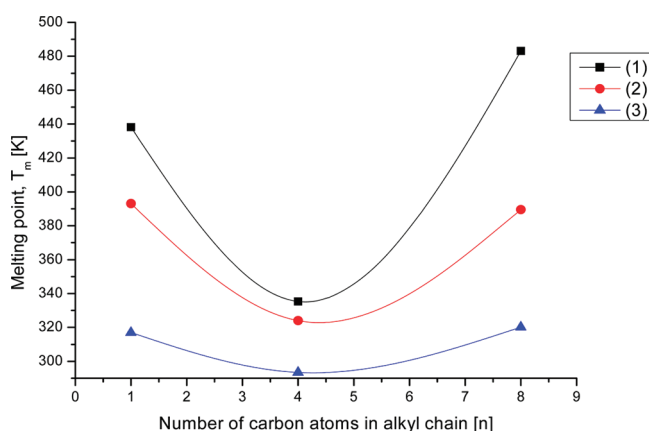


Figure 15. Melting point variation with the anion alkyl chain length of alkanesulfonate salts: N,N,N -trimethylbutylammonium alkanesulfonate (■), N -(2-hydroxyethyl)- N,N,N -trimethylammonium alkanesulfonate (red circle), and N -ethyl- N -(2-hydroxyethyl)- N,N -dimethylammonium alkanesulfonate (blue triangle).

Table 2. Fitting Coefficients of eq 2 of Some Ammonium Salts (6, 8, and 10–14)

salt	ΔT (K)	C_p ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)		
		a	b	c
6: $[\text{BM}_3\text{N}][\text{BSO}_3]$	360–400	−0.0043	4.3421	−300.86
8: $[\text{M}_3\text{N}(\text{CH}_2)_2\text{OH}][\text{BSO}_3]$	360–400	0.0020	−1.1947	691.36
10: $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}][\text{MSO}_3]$	351–397	−0.0041	3.8245	−430.53
11: $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}][\text{BSO}_3]$	352–400	−0.0011	1.0622	−147.81
12: $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}][\text{OSO}_3]$	355–398	−0.0027	3.0380	−22.604
13: $[\text{BEM}_2\text{N}][\text{ESO}_4]$	360–390	−0.0314	25.111	−4518.9
14: $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}][\text{ESO}_4]$	300–360	−0.0017	1.5388	−238.00

experimental heat capacities for each temperature are summarized in Table 3.

Physical Properties. The density, speed of sound, dynamic viscosity, and refractive index of $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}][\text{BSO}_3]$ (11), $[\text{BEM}_2\text{N}][\text{ESO}_4]$ (13), and $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}][\text{ESO}_4]$ (14) ILs were experimentally measured at $T = 298.15$ K. The obtained values are summarized in Table 4.

Table 3. Experimental Heat Capacities [C_p ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)] as a Function of Temperature of Some Ammonium Salts (6, 8, and 10–14)

T (K)	C_p ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)						
	6	8	10	11	12	13	14
300.15							451
305.15							456
310.15							461
315.15							466
320.15							470
325.15							474
330.15							477
335.15							481
340.15							485
345.15							489
350.15							491
355.15			406	93	711		494
360.15	701	518	411	94	715	451	497
365.15	706	519	415	95	720	467	500
370.15	711	520	419	97	725	478	504
375.15	717	521	422	98	730	485	507
380.15	723	523	425	99	736	491	
385.15	728	525	428	100	740	496	
390.15	733	527	432	101	744	500	
395.15	736	528	435	102	748		
400.15	741	529		104			

Table 4. Density, ρ , Refractive Index, n_D , Speed of Sound, u , and Dynamic Viscosity, η , of $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}][\text{BSO}_3]$, $[\text{BEM}_2\text{N}][\text{ESO}_4]$, and $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}][\text{ESO}_4]$ at 298.15 K

IL	ρ ($\text{g}\cdot\text{cm}^{-3}$)	$10^3 \eta$ ($\text{Pa}\cdot\text{s}$)	n_D	u ($\text{m}\cdot\text{s}^{-1}$)
$[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}][\text{BSO}_3]$ (11)	1.11157	1354	1.45985	1694.0
$[\text{BEM}_2\text{N}][\text{ESO}_4]$ (13)	1.20810	333	1.46252	1817.9
$[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}][\text{ESO}_4]$ (14)	1.12566	1617	1.47303	1714.0

CONCLUSIONS

In this work we designed and synthesized nine new ammonium salts: seven ammonium alkanesulfonates and two ammonium alkanesulfates. The selection of their structures was made according to the physical properties, toxicity, and tribological behavior of previously described ILs, in order to obtain new ILs as potential lubricants. Ammonium alkanesulfonates $[\text{BM}_3\text{N}][\text{BSO}_3]$, $[\text{BM}_3\text{N}][\text{OSO}_3]$, $[\text{M}_3\text{N}(\text{CH}_2)_2\text{OH}][\text{BSO}_3]$, $[\text{M}_3\text{N}(\text{CH}_2)_2\text{OH}][\text{OSO}_3]$, $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}][\text{MSO}_3]$, $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}][\text{BSO}_3]$, and $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}][\text{OSO}_3]$ were prepared by alkylation of the corresponding tertiary ammine with an alkyl sulfonate. Ammonium alkanesulfates $[\text{BEM}_2\text{N}][\text{ESO}_4]$ and $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}][\text{ESO}_4]$ were prepared by simple quaternization of the corresponding tertiary ammine with diethyl sulfate. Three of the synthesized salts shown to be room temperature ILs: $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}][\text{BSO}_3]$, $[\text{BEM}_2\text{N}][\text{ESO}_4]$, and $[\text{EM}_2\text{N}(\text{CH}_2)_2\text{OH}][\text{ESO}_4]$. Their density, speed of sound, dynamic viscosity, and refractive index were experimentally measured at room temperature.

The thermal properties of the synthesized compounds were determined by differential scanning calorimetry (DSC). Illustrative DSC thermograms obtained on cooling and heating showed several solid–solid transitions in salts with melting

point higher than 373 K such as $[\text{BM}_3\text{N}][\text{OSO}_3]$, $[\text{M}_3\text{N}(\text{CH}_2)_2\text{OH}][\text{MSO}_3]$, and $[\text{M}_3\text{N}(\text{CH}_2)_2\text{OH}][\text{OSO}_3]$.

The anion alkyl chain length influence on the ammonium salts thermal properties was also determined. When the anion alkyl chain length increased from $n = 1$ to $n = 4$, the melting point decreased. However, when the anion alkyl chain length increased from $n = 4$ to $n = 8$, the melting point increased. As expected, an influence of the cation asymmetry on the melting point was also observed: when the asymmetry of the cation increased, the melting temperature decreased.

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