

APPLIED CHEMISTRY

New Ionic Liquids and Their Antielectrostatic Properties

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The synthesis of 3-alkoxymethyl-1-methylimidazolium, 3-alkoxymethyl-1-hexylimidazolium, and 3-alkoxymethyl-1-butoxymethylimidazolium tetrafluoroborate and hexafluorophosphate are reported. Fifty-eight salts were synthesized, and 38 of them are new ionic liquids. Trends in the properties of these liquid compounds are discussed. The prepared salts were examined according to their antielectrostatic effect; the surface resistance, half decay time, and maximum voltage induced on polyethylene film were measured. Thus, this work shows that ionic liquids have antielectrostatic properties and that their densities are linearly dependent on the length and kind of substituents in the 1 and 3 positions on the imidazole ring.

1. Introduction

Ionic liquids containing an organic cation that is a relatively large and an inorganic anion are liquid at room temperature. Some of them have been known for many years. The spectrum of their physical properties is much larger than that of classical organic solvents. The inorganic anion mainly accounts for the low melting point of the salts and the liquid range that can reach about 300 °C, making them suitable for the study of reaction kinetics at a variety of temperatures. They are good solvents for a wide range of inorganic and organic materials, have no appreciable vapor pressure at room temperature, and have moderate viscosity. The ionic liquids with BF_4^- and PF_6^- anions are air- and water-stable. Recently, they have drawn attention on a large scale because they produce no vapor emissions and are potentially environmentally friendly solvents. However, the chloroaluminate ionic liquids are water-sensitive, generating HCl on exposure to moisture.

A review providing an overview of the potential of ionic liquids as solvents for organic synthesis, with or without added metal complex catalysts, is available¹. In fact, that ionic liquids easily dissolve polar species and nonpolar organics such as benzene provides them with unique solvent capabilities. They are used as reaction media in organic and organometallic syntheses, including alkylation,^{1,2} hydroformylation¹, linear dimerization of 1-butene,^{1,3} hydrogenation,^{1,4} olefin oligomerization–dimerization–metathesis¹, Friedel–Crafts reactions,^{1,5–7} Heck reactions,^{1,8,9} Diels–Alder reactions,^{10,12} benzoin condensation,¹³ polymerization of methyl methacrylate,¹⁴ and acylative cleavage of cyclic and acyclic ethers.¹⁵ Also, they have been studied as solvents in separations^{16,17} or solvents and electrolytes

in electrochemistry.^{18,19} The industrial exploitation of ionic liquids as solvents is in its early days.

In this work, the synthesis and properties of novel ionic liquids have been investigated.

2. Experimental Methods

Chloromethyl alkyl ether was prepared by the chloromethylation of alcohols. 1-Hexylimidazole was obtained by deprotonation and nucleophilic displacement steps.²⁰ NMR spectra were recorded on a Varian model XL 300 spectrometer at 300 MHz for ^1H and 75 MHz for ^{13}C , with tetramethylsilane as the internal reference. Satisfactory elemental analyses for all prepared salts were obtained: C, ± 0.35 ; H, ± 0.30 ; and N, ± 0.24 . Melting points were determined by using an electrothermal digital-melting-point apparatus model JA 9100. A Mettler Toledo DA 110M scale was used for the mass/density measurements (temperature = 20 ± 2 °C, sample volume = 2 mL).

2.1. Preparation of 1-Butoxymethylimidazole. Triethylamine (101 g, 1 mol), chloromethyl butyl ether (122.6 g, 1 mol), and toluene (1 L) were mixed by stirring at room temperature for 15 min. Imidazole (68.1 g, 1 mol) was then added over a period of 10 min with continuous stirring. After 2 h of being heated under reflux, the cool reaction mixture was filtered. The solid crude product was triethylamine hydrochloride. The organic layer was evaporated to a yellow liquid, which was distilled to give 1-butoxymethylimidazole (100.2 g, 65% yield).

2.2. General Procedure for the Preparation of 3-Alkoxymethyl-1-alkylimidazolium Chlorides. To anhydrous 1-alkylimidazole (0.02 mol) was added chloromethyl alkyl ether (0.02 mol). The reaction was carried out for 0.5 h, and the product was purified by extraction with hot hexane. The final product was obtained mostly as a hygroscopic compound with a yield of over 95%.

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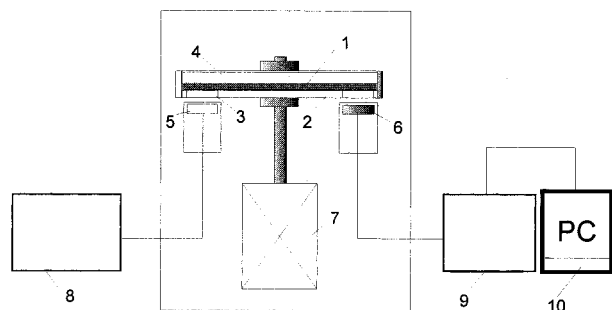


Figure 1. Experimental setup: 1, air conditioned disk; 2, earthed rotary table; 3, hole; 4, cover; 5, spike electrode; 6, probe; 7, electric motor; 8, high-voltage generator; 9, electronic equipment; and 10, personal computer.

3-Dodecyloxymethyl-1-methylimidazolium Chloride. ^1H NMR ($\text{DMSO}-d_6$) δ ppm: 9.64 (s, 1H), 7.89 (s, 1H), 7.88 (s, 1H), 5.65 (s, 2H), 3.95 (s, 3H), 3.51 (t, $J = 7$ Hz, 2H), 1.24 (m, 20H), 0.88 (t, $J = 7$ Hz, 3H). ^{13}C NMR ($\text{DMSO}-d_6$) δ ppm: 137.5, 124.2, 122.0, 78.1, 72.1, 69.3, 36.0, 31.3, 29.06, 29.01, 28.73, 28.68, 25.3, 22.12, 21.08, 13.9.

2.3. General Procedure for the Preparation of 3-Alkoxyethyl-1-alkylimidazolium Salts (1–56). To 3-alkoxymethyl-1-alkylimidazolium chloride (0.03 mol) in water or methanol (10 mL) was added sodium tetrafluoroborate (3.29 g, 0.03 mol) or sodium hexafluorophosphate (5.04 g, 0.03 mol) in 10 mL of water. The reaction was completed by gentle heating on a water bath with stirring. The organic layer was separated and washed with water to give a liquid or solid product.

3-Dodecyloxymethyl-1-methylimidazolium Tetrafluoroborate (10). ^1H NMR ($\text{DMSO}-d_6$) δ ppm: 9.12 (s, 1H), 7.70 (s, 1H), 7.67 (s, 1H), 5.54 (s, 2H), 3.96 (s, 3H), 3.47 (t, $J = 7$ Hz, 2H), 1.20 (m, 20H), 0.81 (t, $J = 7$ Hz, 3H). ^{13}C NMR ($\text{DMSO}-d_6$) δ ppm: 137.5, 124.7, 122.3, 79.0, 36.4, 32.0, 29.8, 29.7, 29.53, 29.48, 29.3, 26.0, 22.7, 14.2.

3-Dodecyloxymethyl-1-methylimidazolium Hexafluorophosphate (38). ^1H NMR ($\text{DMSO}-d_6$) δ ppm: 8.92 (s, 1H), 7.54 (s, 1H), 7.53 (s, 1H), 5.45 (s, 2H), 3.83 (s, 3H), 3.42 (t, $J = 7$ Hz, 2H), 1.14 (m, 20H), 0.74 (t, $J = 7$ Hz, 3H). ^{13}C NMR ($\text{DMSO}-d_6$) δ ppm: 137.6, 125.1, 122.5, 79.5, 70.6, 36.8, 32.4, 30.1, 29.9, 29.8, 29.7, 26.3, 23.1, 14.5.

2.4. Antielectrostatic Properties. The antielectrostatic effect was measured on a Wigofil polyethylene film with a density of 150 g/m^2 that did not contain any lubricants or antioxidants. From this 0.25-mm film, 0.125-m-diameter disks were cut out. The disks were washed in acetone and then dried by placing them in an air-conditioned room. A disk was rubbed on the surface with a cotton-bud soaked with a 0.5% chloroform solution of prepared salt. Then, the disk was hung up so that the chloroform could evaporate spontaneously. The disks, covered with 3-alkoxymethyl-1-alkylimidazolium salts, were stored for 24 h in an air-conditioned room at $20 \pm 2^\circ\text{C}$ and a relative humidity of $55 \pm 5\%$. Finally, the surface resistance, half charge decay time, and maximum voltage induced on the disk surface were measured with the equipment shown in Figure 1. The air-conditioned disk (1) is placed on the earthed rotary table (2), in which six radially displaced holes (3) had been cut. Next, the cover (4) is placed over the sample. The disk is electrically charged by a corona discharge method, with the spike electrode (5) being supplied by the high-voltage generator (8). The probe (6) transmits

Scheme 1

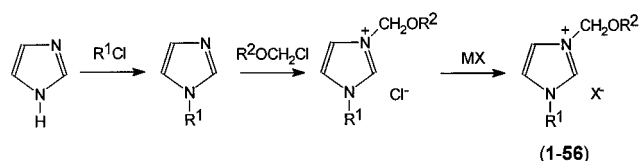


Table 1. 3-Alkoxyethyl-1-methylimidazolium (1–10), 3-Alkoxyethyl-1-hexylimidazolium (11–19), and 3-Alkoxyethyl-1-butoxymethylimidazolium Tetrafluoroborate (20–28)

salt	R1	R2	mp ($^\circ\text{C}$)	yield (%)	color
1	CH_3	C_3H_7	liquid	76	straw yellow
2	CH_3	C_4H_9	liquid	82	orange
3	CH_3	C_5H_{11}	liquid	85	straw yellow
4	CH_3	C_6H_{13}	liquid	78	colorless
5	CH_3	C_7H_{15}	liquid	86	colorless
6	CH_3	C_8H_{17}	liquid	82	colorless
7	CH_3	C_9H_{19}	liquid	87	yellow
8	CH_3	$\text{C}_{10}\text{H}_{21}$	56–57	89	white crystal
9	CH_3	$\text{C}_{11}\text{H}_{23}$	61–62	92	white crystal
10	CH_3	$\text{C}_{12}\text{H}_{25}$	62–64	80	white crystal
11	C_6H_{13}	C_3H_7	liquid	100	light-orange
12	C_6H_{13}	C_4H_9	liquid	100	orange
13	C_6H_{13}	C_5H_{11}	liquid	100	straw yellow
14	C_6H_{13}	C_6H_{13}	liquid	100	orange
15	C_6H_{13}	C_7H_{15}	liquid	99	yellow
16	C_6H_{13}	C_8H_{17}	liquid	100	yellow
17	C_6H_{13}	C_9H_{19}	liquid	98	yellow
18	C_6H_{13}	$\text{C}_{10}\text{H}_{21}$	37–39	100	orange crystal
19	C_6H_{13}	$\text{C}_{11}\text{H}_{23}$	solid	100	brown
20	$\text{C}_4\text{H}_9\text{OCH}_2$	C_3H_7	liquid	97	straw yellow
21	$\text{C}_4\text{H}_9\text{OCH}_2$	C_4H_9	liquid	98	colorless
22	$\text{C}_4\text{H}_9\text{OCH}_2$	C_5H_{11}	liquid	100	straw yellow
23	$\text{C}_4\text{H}_9\text{OCH}_2$	C_6H_{13}	liquid	100	straw yellow
24	$\text{C}_4\text{H}_9\text{OCH}_2$	C_7H_{15}	liquid	100	straw yellow
25	$\text{C}_4\text{H}_9\text{OCH}_2$	C_8H_{17}	liquid	98	straw yellow
26	$\text{C}_4\text{H}_9\text{OCH}_2$	C_9H_{19}	liquid	100	straw yellow
27	$\text{C}_4\text{H}_9\text{OCH}_2$	$\text{C}_{10}\text{H}_{21}$	15–17	98	white crystal
28	$\text{C}_4\text{H}_9\text{OCH}_2$	$\text{C}_{11}\text{H}_{23}$	21–23	97	white crystal

a signal to an electronic apparatus (9) that is programmed with a timer counter. The relative error in the determination of these three quantities did not exceed 7%.

3. Results

The alkylation and quaternization of imidazole yielded 3-alkoxymethyl-1-alkylimidazolium tetrafluoroborate (1–28) and hexafluorophosphate (29–56). The last step was the metathesis of 3-alkoxymethyl-1-alkylimidazolium chloride with the appropriate inorganic salt in water or methanol solution (Scheme 1). Chloromethyl alkyl ether was an excellent reagent but was very easily hydrolyzed. Quaternization should be conducted under strictly anhydrous conditions. The imidazolium salts (1–56) were separated readily from the aqueous solution in very high yields. 3-Alkoxyethyl-1-methylimidazolium (1–10), 3-alkoxyethyl-1-hexylimidazolium (11–19), and 3-alkoxyethyl-1-butoxymethylimidazolium (20–28) tetrafluoroborate are shown in Table 1, and 3-alkoxyethyl-1-methylimidazolium (29–38), 3-alkoxyethyl-1-hexylimidazolium (39–47), and 3-alkoxyethyl-1-butoxymethylimidazolium (48–56) hexafluorophosphate are shown in Table 2. The salts were liquids at room temperature or low-melting solids. Of the 58 products, 38 are ionic liquids with characteristic colors (Tables 1 and 2) that flow like water and refuse to mix with water. They are not air- or moisture-

Table 2. 3-Alkoxyethyl-1-methylimidazolium (29–38), 3-Alkoxyethyl-1-hexylimidazolium (39–47), and 3-Alkoxyethyl-1-butoxymethylimidazolium Hexafluorophosphate (48–56)

salt	R1	R2	mp (°C)	yield (%)	color
29	CH ₃	C ₃ H ₇	liquid	84	dark yellow
30	CH ₃	C ₄ H ₉	liquid	86	straw yellow
31	CH ₃	C ₅ H ₁₁	liquid	88	milky blue
32	CH ₃	C ₆ H ₁₃	liquid	87	straw yellow
33	CH ₃	C ₇ H ₁₅	37–38	79	white crystal
34	CH ₃	C ₈ H ₁₇	liquid	76	straw yellow
35	CH ₃	C ₉ H ₁₉	47–49	89	white crystal
36	CH ₃	C ₁₀ H ₂₁	46–47	91	white crystal
37	CH ₃	C ₁₁ H ₂₃	52–53	88	white crystal
38	CH ₃	C ₁₂ H ₂₅	61–63	93	white crystal
39	C ₆ H ₁₃	C ₃ H ₇	liquid	100	orange
40	C ₆ H ₁₃	C ₄ H ₉	liquid	99	orange
41	C ₆ H ₁₃	C ₅ H ₁₁	liquid	100	orange
42	C ₆ H ₁₃	C ₆ H ₁₃	liquid	100	yellow
43	C ₆ H ₁₃	C ₇ H ₁₅	liquid	100	yellow
44	C ₆ H ₁₃	C ₈ H ₁₇	liquid	100	yellow
45	C ₆ H ₁₃	C ₉ H ₁₉	liquid	98	light orange
46	C ₆ H ₁₃	C ₁₀ H ₂₁	liquid	100	yellow
47	C ₆ H ₁₃	C ₁₁ H ₂₃	29–31	99	straw yellow crystal
48	C ₄ H ₉ OCH ₂	C ₃ H ₇	47–49	100	white crystal
49	C ₄ H ₉ OCH ₂	C ₄ H ₉	56–58	98	white crystal
50	C ₄ H ₉ OCH ₂	C ₅ H ₁₁	36–40	100	white crystal
51	C ₄ H ₉ OCH ₂	C ₆ H ₁₃	49–51	100	white crystal
52	C ₄ H ₉ OCH ₂	C ₇ H ₁₅	56–58	100	white crystal
53	C ₄ H ₉ OCH ₂	C ₈ H ₁₇	liquid	97	colorless
54	C ₄ H ₉ OCH ₂	C ₉ H ₁₉	49–51	98	white crystal
55	C ₄ H ₉ OCH ₂	C ₁₀ H ₂₁	53–55	100	white crystal
56	C ₄ H ₉ OCH ₂	C ₁₁ H ₂₃	59–62	100	white crystal

sensitive. Tetrafluoroborates are stable during storage. The obtained salts were dried by heating at 60–50 °C in a vacuum for 4–5 h. Karl Fisher measurements showed the water contents of dried samples to be <200 ppm.

Solid imidazolium tetrafluoroborates were obtained for seven compounds with decyloxymethyl (**8**, **18**, and **27**), undecyloxymethyl (**9**, **19**, and **28**), and dodecyl-oxymethyl (**10**) substituents. This trend was also reported for 1-alkyl-3-methylimidazolium tetrafluoroborates²¹ as a result of the asymmetry of the imidazolium cation. Packing inefficiency is the single most important factor in rationalizing the low melting points of 1,3-dialkylimidazolium salts.²² The inverse trend was observed for tetraalkylammonium salts. Here, reduction of the cation symmetry is a method of lowering the melting point of the salt.²³

The structures of the new salts were established on the basis of their spectral properties and elemental analysis. The chemical shifts of the protons in the imidazole ring are anion-dependent (δ ppm = 9.64, 7.89, and 7.88 for 3-dodecyloxymethyl-1-methylimidazolium chloride; 9.12, 7.70, and 7.67 for 3-dodecyloxymethyl-1-methylimidazolium tetrafluoroborate; and 8.92, 7.54, and 7.53 for 3-dodecyloxymethyl-1-methylimidazolium hexafluorophosphate). This phenomenon has been noticed previously for the imidazole ring in 1,3-dialkylimidazolium salts.²⁴

The antielectrostatic properties of the obtained salts used in the experiments are the results of two quantities: the surface resistance and the half charge decay time. Furthermore, the maximum voltage induced on the surface was measured. The surface resistance was calculated from the formula

$$R_s = \frac{UI}{is}, \quad (\Omega)$$

Table 3. Criteria for the Estimation of the Antielectrostatic Effect Based on the Surface Resistance and Half Charge Decay Time

surface resistance log R_s (Ω)	half charge decay time $\tau_{1/2}$ (s)	antielectrostatic effect
<9	<0.5	excellent
9–10	0.5–2	very good
10–11	2–10	good
11–12	10–100	sufficient
12–13	>100	insufficient
>13		lack of antielectrostatic properties

Table 4. Surface Resistance, Half Charge Decay Time, Antielectrostatic Effect, and Maximum Voltage for Tetrafluoroborate Prepared (1–28)

salt	log R_s (Ω)	$\tau_{1/2}$ (s)	antielectrostatic effect	U_{ind} (V)
1	>15	600	lack	974
2	>15	600	lack	918
3	>15	600	lack	948
4	9.68	3.4	good	884
5	9.60	0.32	very good	62
6	8.56	0.28	excellent	116
7	8.13	0.12	excellent	18
8	8.60	0.25	excellent	32
9	8.64	0.24	excellent	105
10	>15	600	lack	960
11	14.48	600	lack	945
12	14.52	600	lack	962
13	11.54	2.43	sufficient	853
14	9.87	0.29	very good	616
15	9.56	0.26	very good	505
16	9.33	0.28	very good	434
17	8.99	0.24	excellent	156
18	8.99	0.23	excellent	260
19	8.98	0.22	excellent	214
20	10.02	0.51	good	836
21	9.82	0.25	very good	838
22	9.44	0.26	very good	403
23	9.72	0.25	very good	427
24	9.35	0.26	very good	562
25	9.97	0.97	very good	529
26	9.10	0.22	very good	171
27	9.03	0.22	very good	126
28	9.47	0.23	very good	181

where U is the applied voltage ($U = 100$ V), l is the length of electrodes ($l = 100$ mm), i is the measured current intensity, and s is the distance between the electrodes ($s = 10$ mm).

The half charge decay time was found from relation

$$\tau_{1/2} = \sqrt{\frac{\tau_{1/2(+)}^2 + \tau_{1/2(-)}^2}{2}}, \quad (\text{s})$$

where $\tau_{1/2(+)}$ and $\tau_{1/2(-)}$ are the mean half decay times of positive and negative charges, respectively.

The maximum voltage induced on the surface of the air-conditioned disks

$$U_{ind} = \sqrt{\frac{U_{ind(+)}^2 + U_{ind(-)}^2}{2}}, \quad (\text{V})$$

where $U_{ind(+)}$ and $U_{ind(-)}$ are the voltages induced by positive and negative charges, respectively.

The antielectrostatic effect was determined following the criteria listed in Table 3 and presented in Tables 4 and 5. Of the 56 obtained salts, 7 showed excellent effects, and 18 showed very good effects. The antielectrostatic effect of 3-alkoxyethyl-1-alkylimidazolium

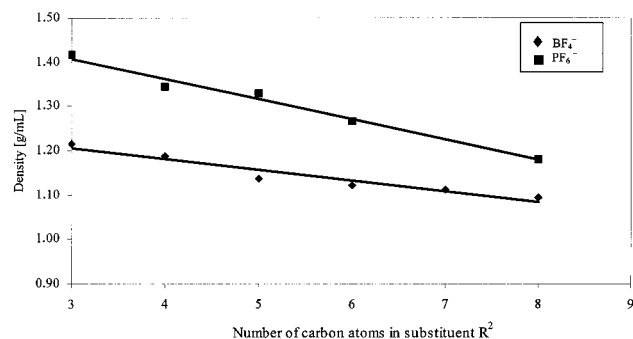


Figure 2. Density for 3-alkoxymethyl-1-methylimidazolium tetrafluoroborate (1–6) and hexafluorophosphate (29–32 and 34).

Table 5. Surface Resistance, Half Charge Decay Time, Antielectrostatic Effect, and Maximum Voltage for Hexafluorophosphate (29–56)

salt	$\log R_s$ (Ω)	$\tau_{1/2}$ (s)	antielectrostatic effect	U_{ind} (V)
29	> 15	600	lack	940
30	> 15	600	lack	897
31	> 15	600	lack	862
32	> 15	600	lack	929
33	11.25	7.55	sufficient	957
34	11.62	6.99	sufficient	904
35	11.98	4.14	sufficient	969
36	11.76	1.31	sufficient	929
37	14.24	600	lack	921
38	> 15	600	lack	915
39	14.52	600	lack	984
40	14.54	600	lack	987
41	14.46	600	lack	987
42	14.51	600	lack	888
43	9.92	0.36	very good	752
44	9.98	0.33	very good	814
45	9.90	0.26	very good	675
46	9.54	0.81	very good	627
47	9.98	0.27	very good	808
48	> 15	600	lack	990
49	13.85	600	lack	987
50	14.69	600	lack	987
51	14.77	600	lack	986
52	10.90	1.14	good	938
53	12.18	4.59	sufficient	928
54	12.71	600	lack	976
55	13.55	600	lack	979
56	12.56	600	lack	975

salts depends on the substituents on the imidazole ring and the kind of anion. The most favorable alkyl in the alkoxymethyl group contains 8–11 carbon atoms. Tetrafluoroborates are more effective than hexafluorophosphates. The measured maximum voltage induced on the surface was determined by the antielectrostatic effect only for 3-alkoxymethyl-1-methylimidazolium tetrafluoroborate (1–10), as seen in Table 4. The most reliable evidence on the mode of action of the antielectrostatic effect of ionic liquids is the adsorption of the compound on the surface. Ionic liquids penetrate the polymer surface because have unique solvent capabilities. Finally, ionic liquids dissipate the electric charge.

In Figures 2–4, we can see a linear relationship between the density and the number of carbon atoms

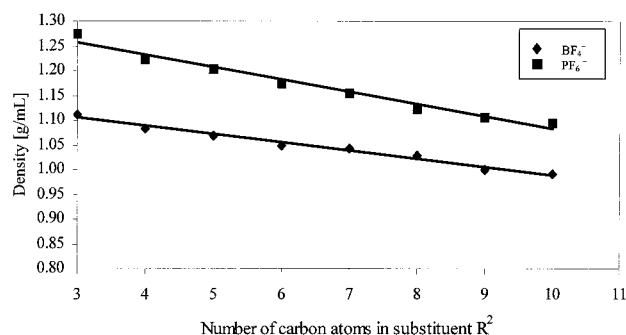


Figure 3. Density for 3-alkoxymethyl-1-hexylimidazolium tetrafluoroborate (11–17) and hexafluorophosphate (39–46).

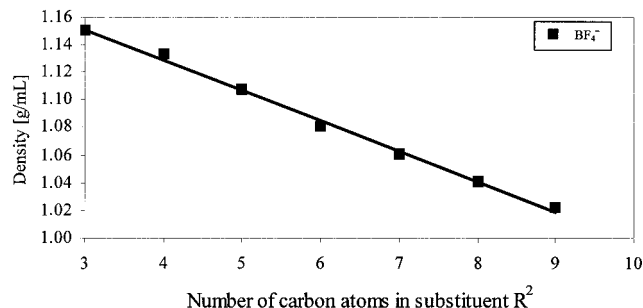


Figure 4. Density for 3-alkoxymethyl-1-methylimidazolium tetrafluoroborate (20–26).

in the alkoxymethyl substituent. The increase in molecular weight of the cation leads to a decreasing density. This is the reason for the poor crystal packing between the bulky cation and the weakly complexing symmetrical anion.²⁵ All ionic liquids prepared are heavy with water except for one. Calculation results from the correlation of the equations ($y = ax + b$) for density (y) and the number of carbon atoms in the alkoxymethyl substituent (x) are presented in Table 6.

The values of acute toxicity of 3-hexyloxymethyl-1-methylimidazolium tetrafluoroborate were assessed by the Gadumm method and found to be $LD_{50} = 1400$ mg/kg for female and $LD_{50} = 1370$ for male Wistar rats. Tetrafluoroborates can be safely used.

4. Conclusions

This investigation has shown that novel ionic liquids in the imidazolium family can be successfully prepared in high yields. We found liquid compounds with large molecular weights that were soluble in acetone, chloroform, THF, ethyl acetate, and DMF and insoluble in water. This work shows that ionic liquids have antielectrostatic properties. The antielectrostatic effect is dependent on the structure of the obtained imidazolium salt. 3-Alkoxymethyl-1-methylimidazolium tetrafluoroborates with 8–11 carbon atoms in the alkoxymethyl group have an excellent antielectrostatic effect, similar to that of the known antistatic agent Catanac 609 [American Cyanamid Co.; *N,N*-bis(2-hydroxyethyl)-*N*-(3'-dodecyloxy-2'-hydroxypropyl)methylammonium

Table 6. Values for the Parameters a and b

salt	a	b
3-alkoxymethyl-1-methylimidazolium hexafluorophosphate (29–32, 34)	–0.0432	1.5688
3-alkoxymethyl-1-methylimidazolium tetrafluoroborate (1–7)	–0.0272	1.3232
3-alkoxymethyl-1-hexylimidazolium hexafluorophosphate (39–46)	–0.0249	1.3555
3-alkoxymethyl-1-hexylimidazolium tetrafluoroborate (11–17)	–0.0160	1.7030
3-alkoxymethyl-1-butoxymethylimidazolium tetrafluoroborate (20–26)	–0.0214	1.2358

methasulfate; $\log R_s = 8.48$, $\tau_{1/2} = 0.25$ s, and $U_{\text{ind}} = 100$ V]. The presented results demonstrate that densities of these ionic liquids are linearly dependent on the length and kind of substituents in the 1 and 3 positions on the imidazole ring and the kind of anion.

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