Phosphonium Acesulfamate Based Ionic Liquids

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We present a new class of solvents containing nonfluorous, well-established, nontoxic organoanions that can be used as "green" alternatives to volatile organic solvents in a variety of applications such as solvent extraction, antielectrostatic agents, and as electrolytes in solar-cell applications. The acesulfamate anion is an effective substitute for very expensive bis(trifluoromethylsulfonyl)imide

Introduction

Ionic liquids (ILs), in the form of organic salts, exhibit many interesting properties such as a negligible vapor pressure, low melting point, an extensive liquid range, thermal and electrochemical stability, favorable solvation behavior (they dissolve many organic, organometallic, and inorganic compounds), a wide electrochemical window, and high ionic conductivity. Further, they are nonflammable, easy to handle in a variety of standard experimental procedures, and are recyclable. Some of the more widely studied ILs consist of a heterocyclic cation based on a substituted pyridine or imidazole. It is also possible to alter their properties simply by changing the length of the side chains or the nature of the organic cation and the inorganic or organic anion. Consequently, ILs have successfully replaced traditional organic solvents (OS) in chemical processes including bio- and chemical catalysis, in aqueous/OS biphasic extraction systems, OS/scCO$_2$ extraction, as the solvent/base electrolyte in solar-cell applications, and as components in electrochemical capacitors. The physical and chemical properties and potential applications of ILs have been extensively reviewed recently.[1–16] In these reviews, ILs containing a quaternary phosphorus cation are listed but few studies are available on applications of these liquids. Recently, a review has been published on the synthesis and application of phosphonium-based ILs.[17] That report unequivocally demonstrates that the application potential of these salts is just as high as that of the more commonly studied imidazolium-, pyridinium-, and ammonium-based ILs.

Results and Discussion

The studies conducted in our labs since 2003 on new phosphonium-based ILs containing nonfluorous organoanions with well-established toxicological profiles have turned our attention to the acesulfamate anion. Recently, a publication has appeared on ILs containing a quaternary nitrogen center with a sweetener (acesulfamate and saccharinate)-based anion.[18] These imidazolium, pyridinium, pyrrolidinium, and ammonium acesulfamate ILs are soluble in water, which is consistent with results from our laboratory. The only cation group that contains members that are relatively insoluble in water is that of the phosphonium acesulfamates, which are the topic of this report.

Alkyltrihexylphosphonium acesulfamates were obtained in high yields by a metathesis route, starting with alkyltrihexylphosphonium chlorides or bromides (products of Cytec Industries) and the commercially available acesulfamate potassium salt (Figure 1). Chlorides proved to be a better starting material than bromides, probably due to the different solubilities of KCl and KBr in water. Water proved to be a very convenient solvent since both the substrates and by-product (KCl) are readily soluble in water, in contrast to the acesulfamate phosphonium salts. Also, anhydrous acetone is a very good solvent for ion exchange. KCl is completely insoluble in anhydrous acetone as opposed to phosphonium acesulfamates. Ten acesulfamates were synthesized, which contained ethyl to hexadecyl alkyl groups. All these salts are room-temperature ionic liquids (RTILs), even those containing the long hexadecyl substituent.

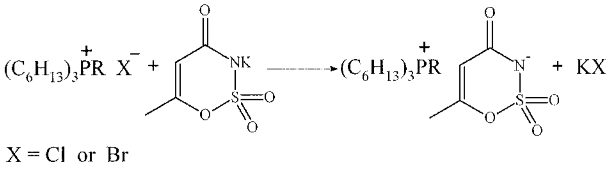

Figure 1. Alkyltrihexylphosphonium acesulfamates **1**–**10**

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The densities, viscosities, and thermal-degradation temperatures for the anhydrous RTILs are presented in Table 1. The water content was estimated to be lower than 500 ppm after heating the samples in vacuo. The phosphonium acesulfamates are stable in air and in common organic solvents such as acetone, $CHCl_3$, CH_3OH, toluene, ethyl acetate, DMF, and DMSO, in which they are highly soluble. They are immiscible with hexane and water but, when anhydrous, they quickly absorb water upon exposure to air. At room temperature and at 50% humidity, the maximum water content in the ILs is 2.07, 1.91, 1.80, 1.57, 1.48, 1.40, 1.27, 1.19, 1.11, and 1.06% and at 90% humidity 6.42, 6.31, 6.22, 6.15, 6.13, 5.95, 5.75, 5.68, 4.80, and 4.06% for **1**–**10**, respectively. The capacity to absorb water depends on the atmospheric relative humidity and on the size of the phosphonium cation. The RTILs behave as desiccants: they easily absorb and release water. Their solubility in water at room temperature is less than 0.5 g L^{-1}.

Their densities range from 1.0597 to 0.9576 g mL^{-1}. As is typical for RTILs, as the number of carbon atoms in the phosphonium cation increases the RTIL density decreases, and at the higher carbon content the density is lower than that of water. Over the range 20–30 °C, the temperature effect on density does not exceed 3%.

Table 1. Densities, viscosities, and thermal-degradation temperatures (T_d) of the prepared RTILs

RTIL	R	Density[a] [g mL^{-1}]	Viscosity [mPa]	T_d [°C]
1	C_2H_5	1.0597	630	184
2	C_3H_7	1.0422	500	185
3	C_4H_9	1.0237	490	186
4	C_6H_{13}	1.0160	510	212
5	C_7H_{15}	1.0087	490	220
6	C_8H_{17}	1.0021	520	194
7	$C_{10}H_{21}$	0.9903	470	213
8	$C_{12}H_{25}$	0.9801	505	203
9	$C_{14}H_{29}$	0.9685	630	196
10	$C_{16}H_{33}$	0.9576	650	210

[a] At 20 °C.

Table 2. Thermal data, surface resistance R_S (Ω), and half-charge decay time ($t_{1/2}$) of the prepared RTILs

RTIL	DSC analysis		Antielectrostatic properties[a]		
	T_G[b] [°C]	Dc_p[c] [J g^{-1} °C^{-1}]	log R_S	$t_{1/2}$ [s]	effect
1	–73	0.36	11.30	>600	lack
2	–72	0.39	11.48	>600	lack
3	–71	0.40	11.35	>600	lack
4	–66	0.43	11.30	>600	lack
5	–69	0.42	10.95	>600	lack
6	–70	0.45	9.70	0.51	very good
7	–70	0.44	8.90	0.35	excellent
8	–72	0.43	8.30	0.25	excellent
9	–71	0.47	8.00	0.15	excellent
10	–70	0.43	8.95	0.20	excellent

[a] At room temperature and 63% humidity. [b] Glass-transition temperature determined as the onset temperature in the heating mode (10 °C min^{-1}). [c] Heat capacity jump.

The salts are viscous and their viscosity is strongly affected by humidity, temperature, and is also very sensitive to solutes. The addition of solvents and reactants can be expected to further reduce the viscosity. The same effect of chloride, water, and organic solvents on the viscosity of imidazolium ILs has been observed by Seddon et al.[19] The thermal-degradation temperatures, estimated by using a Büchi model B-545 automatic boiling point apparatus, range from 184 to 220 °C (no color change), which indicates the temperature range for their applications. Thermogravimetric analysis showed that the salts decompose at temperatures above 300 °C. However, we note that dynamic thermal stabilities normally reported for ILs are typically much higher then static thermal stabilities. These salts are also nonvolatile and nonflammable.

These acesulfamates form long-lived supercooled phases; that is, they can be cooled from the liquid state down to low temperatures without crystallizing. The glass-transition temperatures for the RTILs are shown in Table 2, along with their antielectrostatic properties. The antielectrostatic effect is related to the length of the alkyl substituent. This effect was determined by the criteria listed in Table 3. Of the ten acesulfamates, four show excellent antistatic properties, which means that they penetrate the polymer surface and finally dissipate the electric charge. This effect was unexpected since the other phosphonium salts manifest antistatic properties to a lesser degree; for example, in the RTILs with a $(C_6H_{13})_3P^+C_{14}H_{29}$ cation and BF_4^-, Tf_2N^-, NO_3^-, and $(CN)_2N^-$ anions the effect was very good, but with the PF_6^- anion there was no apparent antielectrostatic property.

Table 3. Criteria for the estimation of the antielectrostatic effect based on the surface resistance R_S (Ω) and half-charge decay time $t_{1/2}$

log R_S	$t_{1/2}$ [s]	Antielectrostatic effect
<9	<0.5	excellent
9–9.99	0.51–2	very good
10–10.99	2.1–10	good
11–11.99	10.1–100	sufficient
12–12.99	>100	insufficient
>13	>600	lack of antielectrostatic properties

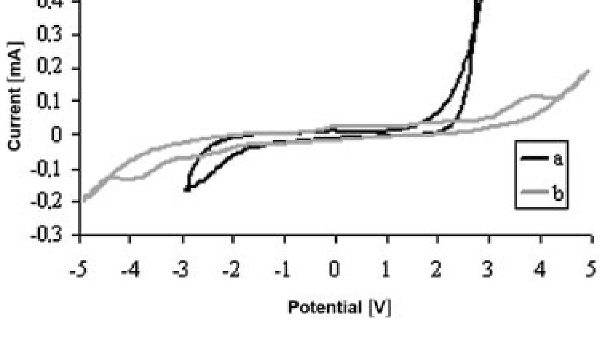

Figure 2. Cyclic voltammograms of (a) 1 M tetraethylammonium tetrafluoroborate in CH_3CN, and (b) RTIL **3** (scan rate = 10 mV s^{-1})

The RTILs also manifest a wide electrochemical window. Cyclic voltammograms for a commercially available solvent and for RTIL **3** are presented in Figure 2.

The water-immiscible phosphonium acesulfamates are not oxidized in an aqueous solution of $KMnO_4$, which is usually an effective method for the decomposition of ILs.[20]

Experimental Section

Alkyltrihexylphosphonium chloride (0.1 mol) was dissolved in water (10 mL). A stoichiometric amount of potassium acesulfamate was then slowly added in three portions to the stirred solution. The reaction mixture was stirred at room temperature for 2 h to afford a heterogeneous mixture. After separation of the phases, the aqueous phase was decanted and the IL, obtained with a yield of 90%, was washed with distilled water until chloride ions could no longer be detected with $AgNO_3$, and then dried for 10 h at 60 °C in vacuo (8 Torr).

Ethyltrihexylphosphonium Acesulfamate: ^{1}H NMR ([D$_6$]DMSO): cation: $\delta = 2.21$ (m, 8 H), 1.43 (m, 12 H), 1.28 (m, 12 H), 1.12 (dt, $J_{H,P} = 18$, $J_{H,H} = 7.6$ Hz, CH_3), 0.88 (t, $J_{H,H} = 6$ Hz, $3CH_3$) ppm; anion: $\delta = 5.30$ (q, $J_{H,H} = 0.85$ Hz, 1 H), 1.9 (d, $J_{H,H} = 0.8$ Hz, CH_3) ppm. ^{13}C NMR ([D$_6$]DMSO): cation: $\delta = 30.3$ (3 CH_2), 29.7 (d, $J_{C,P} = 15$ Hz, $3CH_2$), 21.8 (3 CH_2), 20.5 (d, $J_{C,P} = 4$ Hz, 3 CH_2), 17.2 (d, $J_{C,P} = 47$ Hz, 3 CH_2), 13.9 (3 CH_3), 11.4 (d, $J_{C,P} = 49$ Hz, CH_2CH_3), 5.4 (d, $J_{C,P} = 5$ Hz, CH_3) ppm; anion: $\delta = 167.5$ (CO), 159.6, 101.7, 19.4 ppm. ^{31}P NMR ([D$_6$]DMSO): $\delta = 40.2$ ppm. $C_{24}H_{48}NO_4PS$ (477.63): calcd. C 60.34, H 10.13, N 2.93; found C 61.55, H 10.47, N 3.01.

Trihexyltetradecylphosphonium Acesulfamate: ^{1}H NMR ([D$_6$]-DMSO): cation: $\delta = 2.18$ (m, 8 H), 1.43 (m, 16 H), 1.25 (m, 32 H), 0.88 (t, $J_{H,H} = 6$ Hz, $4CH_3$) ppm; anion: $\delta = 5.27$ (q, $J_{H,H} = 0.85$ Hz, 1 H), 1.90 (d, $J_{H,H} = 0.8$ Hz, CH_3) ppm. ^{13}C NMR ([D$_6$] DMSO): cation: $\delta = 31.3$, 30.4, 29.7 (d, $J_{C,P} = 15$ Hz, 3 CH_2), 29.06, 29.03, 29.0, 28.7 (d, $J_{C,P} = 4.6$ Hz, CH_2), 28.1, 22.1, 21.8, 20.5 (d, $J_{C,P} = 4$ Hz, 4 CH_2), 17.5 (d, $J_{C,P} = 47$ Hz, 3 CH_2), 17.4 (d, $J_{C,P} = 47$ Hz, CH_2), 13.9 (CH_3), 13.8 (3 CH_3) ppm; anion: $\delta = 167.5$ (CO), 159.6, 101.8, 19.4 ppm. ^{31}P NMR ([D$_6$]DMSO): $\delta = 38.4$ ppm. $C_{36}H_{72}NO_4PS$ (646.00): calcd. C 66.93, H 11.23, N 2.17; found C 66.07, H 11.61, N 2.22.

The antielectrostatic effect was measured on a 0.25-mm-thick polyethylene film with a density of 150 g m^{-2} that did not contain any lubricants or antioxidants. Disks with a diameter of 0.125 m were cut from this film. The surface of a disk was rubbed with a cotton-wool bud soaked with a 0.5% chloroform solution of the phosphonium acesulfamate. The disk was hung so that the chloroform could evaporate and was stored for 24 h in an air-conditioned box at 20 °C and a relative humidity of 55%. Finally, the surface resistance and half-charge decay time were measured by a method described earlier.[21]

For the electrochemical characterization, the cyclic voltammetry measurements were performed using MacPile-Biologic (France) and ARBIN Instruments (USA). The working and counter electrodes were steel.

For water content, the samples were stored for 10 d in an air-conditioned box at room temperature and humidities of 50 and 90%. The mass increments were then measured.

Acknowledgments

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