Synthesis, Physicochemical Properties, and Toxicity Data of New Hydrophobic Ionic Liquids Containing Dimethylpyridinium and Trimethylpyridinium Cations[†]

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Hydrophobic ionic liquids containing 1-butyl-2,3-dimethylpyridinium [B2M3MPYR], 1-butyl-3,5-dimethylpyridinium [B3M5MPYR], 1-butyl-2-methyl-5-ethylpyridinium [B2M5EPYR], 1-butyl-2,3,5-trimethylpyridinium [B2M3M5MPYR], 1-octyl-2,3-dimethylpyridinium [O2M3MPYR], 1-octyl-3,5-dimethylpyridinium [O3M5MPYR], 1-octyl-2-methyl-5-ethylpyridinium [O2M5EPYR], or 1-octyl-2,3,5-trimethylpyridinium [O2M3M5MPYR] as the cation and bis(trifluoromethanesulfonyl)imide [NTf_2], trifluoromethanesulfonate [TfO], dicyanamide [$N(CN)_2$], thiocyanate [SCN] or iodide as the anion have been synthesized, and their physicochemial properties have been studied. Thermal properties, solubilities in water and water contents, UV−vis spectra, densities, refractive indices, electrochemical windows, and toxicities on *Vibrio fischeri* have been measured. These ionic liquids, most of which are liquid at room temperature, exhibit high refractive indices and increased hydrophobicity. Despite high toxicity values toward *V. fischeri*, ionic liquids containing a dialkylpyridinium or trialkylpyridinium cation with an octyl chain represent good alternatives to extracting solvents.

Introduction

Ionic liquids, a new class of molten salts that exhibit melting temperatures below 100 °C, have been intensively studied for over a decade. They are usually composed of linear or cyclic ammonium cations. Among them, imidazolium and pyridinium cations have been the most common cations reported in the literature.[1−6] Fewer reports have dealt with ionic liquids containing pyrrolidinium, piperidinium, or morpholinium cations[7−9] or other cations such as phosphonium[10−12] or sulfonium.[13,14]

It is known that ionic liquids exhibit extremely low vapor pressure,[15] thermal stability up to 400 °C, and relatively low flammability. Therefore, ionic liquids are often considered as promising solvent replacements for volatile organic compounds (VOCs). Besides, their physicochemical properties, such as melting temperature, density, viscosity, solubility in solvents, conductivity, and solvent properties, are dramatically modified by simple changes in the nature of the cation or anion. In view of the number of potential combinations of cations and anions that yield ionic liquids, much work still needs to be done in order to extend the existing ionic liquid database and gain better insight into the physicochemical properties of such compounds.

Because of their wide variety of properties, ionic liquids have been applied in past years in most fields of chemistry and chemical engineering, including organic synthesis and catalysis,[16−20] biochemistry,[21−24] electrochemistry,[7,25−28] extraction,[29−34] and industrial processes.[35] For the specific application of metal extraction from wastewater, ionic liquids with low melting temperatures, moderate to low viscosities, and, most of all, solubilities in water that are as low as possible are required.

Extraction of heavy metals with hydrophobic ionic liquids has been reported in numerous works.[29−34] Most reports, however, have used ionic liquids containing imidazolium cations that exhibit high solubility in water, typically around 0.01 in mass fraction.[36] Moreover, distribution coefficients of metal ions between water and ionic liquid phases have been found to be small, typically less than 1, for "generic" ionic liquids containing a simple alkyl chain appended to the cation.[33,37]

The use of so-called task-specific ionic liquids (TSILs), which incorporate functional groups appended either to the cation alkyl chain[31,33] or the anion,[34] has also been explored. In these studies, various ionic liquids containing functional groups such as nitrile, sulfide, sulfur, and urea were found to yield high extraction capabilities and high selectivities toward metallic ions such as mercury,[29,33] cadmium,[29,34] americium,[31] copper, palladium, and silver ions.[33]

In order to investigate potential new ionic liquid candidates for extraction applications, the syntheses and properties of ionic liquids containing the cations 1-octylpyridinium [OPYR], 1-octyl-2-methylpyridinium [2MOPYR], and 1-octyl-4-methylpyridinium [4MOPYR] were recently reported.[5] These ionic liquids were synthesized starting from water-soluble pyridine or picoline reactants. In the present work, the properties of ionic liquids

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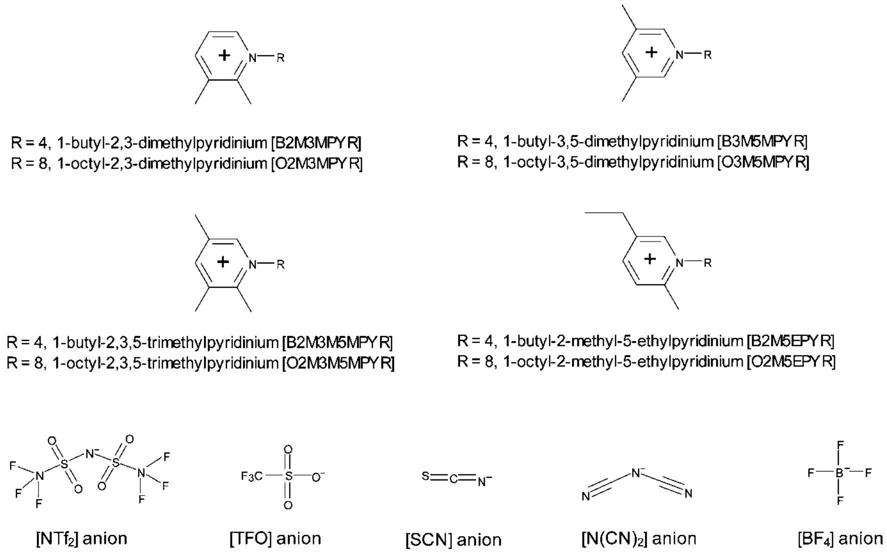

Figure 1. Cation and anion structures used in this study.

based on pyridinium cations are investigated further. The objective of this work is to provide ionic liquids with increased hydrophobicity and reduced hygroscopicity in comparison with ionic liquids containing imidazolium cations. Therefore, reported here are the syntheses and physicochemical properties of new hydrophobic ionic liquids based on reactants exhibiting limited solubility in water: 2,3-dimethylpyridine, 3,5-dimethylpyridine, 2-methyl-5-ethylpyridine, and 2,3,5-trimethylpyridine.

The ionic liquids reported here contain 1-butyl-2,3-dimethylpyridinium [B2M3MPYR], 1-butyl-3,5-dimethylpyridinium [B3M5MPYR], 1-butyl-2-methyl-5-ethylpyridinium [B2M5EPYR], 1-butyl-2,3,5-trimethylpyridinium [B2M3M5MPYR], 1-octyl-2,3-dimethylpyridinium [O2M3MPYR], 1-octyl-3,5-dimethylpyridinium [O3M5MPYR], 1-octyl-2-methyl-5-ethylpyridinium [O2M5EPYR], or 1-octyl-2,3,5-trimethylpyridinium [O2M3M5MPYR] as the cation and iodide [I], tetrafluoroborate [BF_4], trifluoromethanesulfonate [TfO], dicyanamide [$N(CN)_2$], thiocyanate [SCN], or bis(trifluoromethanesulfonyl)imide [NTf_2] as the anion.

Experimental Section

Synthesis. Syntheses of ionic liquids were performed according to previously reported procedures.[5,38] Briefly, 1-bromoalkane or 1-iodoalkane was mixed with 2,3-dimethylpyridine, 3,5-dimethylpyridine, 2-methyl-5-ethylpyridine, or 2,3,5-trimethylpyridine in ethyl acetate or acetonitrile for 2 days under reflux to synthesize corresponding bromide or iodide ionic liquid. Bromide or iodide anion was then replaced by mixing with the appropriate sodium or potassium salt in water, acetonitrile, or acetone, which yielded the ionic liquid containing [BF_4], [TfO], [$N(CN)_2$], [SCN], or [NTf_2] as the anion. Purities were checked with NMR and IR spectroscopy. ^{1}H and ^{13}C NMR spectra were recorded at (300 and 75.57) MHz, respectively, on a Bruker spectrometer (Houston, TX). Ionic liquids successfully passed nitrate tests for bromide impurities. IR spectra were recorded on a Nicolet 380 FTIR spectrometer from Thermo Electron corporation. Details are collected in the Supporting Information. Figure 1 shows the structures and abbreviations of all the ions used in this study.

Glass-Transition, Crystallization, and Melting Temperatures. Glass-transition, crystallization, and melting temperatures were measured with a Thermal Analysis DSC 2920 modulated differential scanning calorimetry (DSC) apparatus. Each sample was prepared by adding a small amount of the ionic liquid (typically 6 mg) to an aluminum pan. Next, the sample was heated in the DSC apparatus at 125 °C for 10 min to remove all traces of water and then cooled to −100 °C. Heating and cooling curves were then recorded at a rate of 10 °C/min. Melting, crystallization, and glass-transition temperatures were then measured from the second heating curve. Results are given in degrees Celsius. The uncertainty of each temperature measurement was ± 1 °C.

Thermogravimetric Analysis. Prior to each measurement, the sample was dried overnight under vacuum and then vacuumed and flushed with argon three times in the apparatus. A thermal analyzer (TG 209 F1 Iris, Netzsch) was used for the thermogravimetric analysis. The experiments were performed under a helium atmosphere at a heating rate of 10 °C/min from 30 to 800 °C. Decomposition temperature onsets and decomposition temperatures corresponding to (1 and 5) % mass loss were measured. The uncertainty of the decomposition temperature measurement was ± 1 °C.

Additionally, isothermal thermogravimetric experiments were carried out on a homemade apparatus consisting of a microbalance from Mettler Toledo connected to a computer and a high-temperature oven monitored with the help of an electronic temperature controller (Eurotherm). Typically, 100 mg of sample was dried under vacuum overnight and put into an alumina pan, after which it was heated to 225 °C at a rate of 3 °C/min under air and kept at 225 °C for 5 h.

Solubility in Water. Solubilities in water were measured according to previously reported protocols.[5] An aqueous solution saturated with an ionic liquid was first prepared by mixing the ionic liquid and water in a tube in suitable amounts to obtain two phases. Calibration solutions were then prepared by adding known amounts of the ionic liquid to water. UV−vis spectra of the calibration and IL-saturated aqueous solutions were then recorded between (200 and 500) nm using a Cary 50 spectrophotometer (Varian) and a 2 mm thick quartz cell. For each of the ionic liquids, an absorption band characteristic of the corresponding trialkylpyridinium or tetraalkylpyridinium cation was observed. Absorption intensities at the maximum absorption wavelength (λ_{max}) were then recorded. The saturation concentration of the ionic liquid in water was then obtained with the help of the Beer−Lambert law.

Table 1. Glass-Transition Temperatures (t_g), Crystallization Temperatures (t_{cc}), Melting Temperatures (t_m), Heat Capacity Changes (ΔC_p), Enthalpies of Fusion ($\Delta_{fus}H$), Thermal Decomposition Temperatures at the Onset Point (t_{onset}), Thermal Decomposition Temperatures at 1 % Weight Loss ($t_{1\%}$), and Thermal Decomposition Temperatures at 5 % Weight Loss ($t_{5\%}$) for the Ionic Liquids Studied in This Work

	t_g / °C	t_{cc} / °C	t_m / °C	ΔC_p / ($J \cdot g^{-1} \cdot K^{-1}$)	$\Delta_{fus}H$ / ($kJ \cdot mol^{-1}$)	t_{onset} / °C	$t_{1\%}$ / °C	$t_{5\%}$ / °C
[O3M5MPYR][I]	−41	−11	82	0.1153	25.45	234	202	220
[O2M5EPYR][I]	−33	8	87	−	30.87	211	194	208
[O2M3M5MPYR][I]	−31	−	−	0.4211	−	224	188	210
[B3M5MPYR][NTf_2]	−73	−	−	0.3195	−	327	264	302
[B2M3MPYR][NTf_2]	−81	−	−	0.2684	−	316	261	289
[B2M5EPYR][NTf_2]	−81	−	−	0.3358	−	305	266	292
[B2M3M5MPYR][NTf_2]	−74	−	−	0.3256	−	364	266	296
[O3M5MPYR][NTf_2]	−78	−	−	0.2875	−	375	288	334
[O2M3MPYR][NTf_2]	−70	−	−	0.3857	−	328	260	301
[O2M5EPYR][NTf_2]	−78	−	−	0.3049	−	324	255	284
[O2M3M5MPYR][NTf_2]	−72	−	−	0.3812	−	362	283	318
[B3M5MPYR][TfO]	−	−	91	−	28.50	345	281	317
[B2M3MPYR][TfO]	−69	−30	17	0.2669	16.88	332	305	322
[B2M3M5MPYR][TfO]	−	−	74	−	20.97	338	294	319
[O3M5MPYR][TfO]	−	−	76	−	24.81	349	288	329
[O2M3MPYR][TfO]	−63	−	−	0.3241	−	322	295	315
[O2M3M5MPYR][TfO]	−56	−	−	0.3927	−	335	300	321
[B3M5MPYR][$N(CN)_2$]	−80	−32	−1	0.4926	3.85	267	227	254
[B2M3MPYR][$N(CN)_2$]	−72	−	−	0.5793	−	259	226	252
[O3M5MPYR][$N(CN)_2$]	−78	−	−	0.4453	−	266	231	257
[O2M5EPYR][$N(CN)_2$]	−59	22	53	0.3772	−	241	205	231
[B3M5MPYR][SCN]	−57	−	13	0.1543	16.04	253	212	239
[O3M5MPYR][SCN]	−74	−	−38	0.2265	6.39	249	219	236
[O2M3MPYR][SCN]	−65	−	−	0.5040	−	234	206	221
[O2M3M5MPYR][SCN]	−58	−10	20	0.5226	14.66	236	204	223
[O3M5MPYR][BF4]	−	−	56	−	28.07	401	312	349

Experiments were performed in triplicate. Results are given as the mass fraction of ionic liquid in water (w_{IL}) with a relative uncertainty of ± 5 % of the final mass fraction value.

Density. Densities of the ionic liquids exposed to air at 20 °C were measured by weighing the ionic liquids in a 1 cm^{-3} volumetric flask. The water contents of the ionic liquids were measured prior to these measurements. Results are given in grams per cubic centimeter with an uncertainty of ± 0.01.

Water Content. Water contents were measured for the air-saturated ionic liquids with the help of a Metrohm coulometric Karl Fischer (KF) 831KF titration apparatus. Prior to the measurements, the ionic liquids were left five weeks in contact with air. Each water content was then measured by introducing a few milligrams of the ionic liquid in the apparatus with the help of a needle.

Experiments were performed in triplicate. Results are given in mass fraction of water in the ionic liquid (w_{water}). The relative uncertainty in the water content measurements was estimated to be that given by the coulometric KF method, namely, ± 7 % of the value of the mass fraction measured.

Refractive Index. Refractive indices were measured with an automatic digital refractometer (Atago RX-7000α). Prior to the measurements, the ionic liquids were dried under vacuum for 12 h. Water contents for all of the ionic liquids were then measured and found to be less than $w = 0.0005$. Measurements were carried out in triplicate at (20 ± 0.2) °C, using a Peltier unit to control the temperature. The uncertainty in the refractive index measurements was ± 0.0005.

Electrochemical Window. Electrochemical measurements were performed using a PJT24-1 potentiometer monitored by a PIL101T function generator (Tacussel). A glassy carbon working electrode, a platinum auxiliary electrode, and a Ag/AgCl pseudoreference wire were used. Measurements were performed with 1 cm^3 ionic liquid samples. The ionic liquid, stirring bar, and electrodes were put into an electrochemical cell and set under vacuum for 1 h prior to the each measurement. The water content was measured by the KF titration method prior to the electrochemical window measurement and found to be less than $w = 0.0002$ for each of the ionic liquids studied here. The ionic liquid was then set under a continuous flow of argon during the measurement. All of the electrochemical window determinations were performed in duplicate. Cathodic and anodic potentials correspond to a current density of 100 $\mu A \cdot cm^{-2}$. The uncertainty of each potential measurement was ± 50 mV.

Toxicity Bioassays. The toxicities of the ionic liquids were assessed using the bioluminescent bacteria *Vibrio fischeri*. The light emission is related to the bacterial metabolism, and its inhibition is an indicator of the toxicity level. This method has been widely used in environmental-level ecotoxicology assays and standardized.[39] The strain *V. fischeri* (formerly *Photobacterium phosphoreum*) was purchased from DSMZ GmbH (DMS 2167). Bacteria were cultivated in an optimized NY liquid growth medium.[40] IL solution (100 μL) was introduced into three wells (replicates) of a black 96-well microplate; 50 μL of NaCl solution at 2 % final concentration and 50 μL of bacterial suspension were added, and the luminescence signal was recorded after an exposure time of 15 min by a plate reader (Hidex Chameleon, ScienceTec). Inoculums of bacterial suspension were mixed with different concentrations of ionic liquid. Toxicities are expressed as $EC_{50\_15\ min}$ (effective concentration), which is the concentration at which a 50 % reduction of the light emission was observed after an exposure time of 15 min. EC_{50} values were then calculated on the basis of the best-fit linear regression models assessing the concentration−effect relationship. The error was estimated at the 95 % confidence interval.

Results and Discussion

Glass-Transition, Crystallization, and Melting Temperatures. Glass-transition temperatures (t_g), crystallization temperatures (t_{cc}), and melting temperatures (t_m) were measured for all of the ionic liquids synthesized here. The results are collected in Table 1. Figure S1 in the Supporting Information shows DSC curves obtained for selected ionic liquids.

Four types of DSC thermograms were observed: (a) those containing only a glass-transition temperature, with no melting or crystallization temperature observed upon heating; (b) those exhibiting a glass-transition temperature and a melting temperature upon heating, corresponding to most room-temperature ionic liquids; (c) those showing a glass-transition temperature, a crystallization temperature, and a melting temperature upon heating; and (d) those showing only a melting temperature, which are usually observed for ionic liquids exhibiting high melting temperatures, such as ionic liquids containing halogen, triflate, or large-sized anions. Details will be discussed below.

Most of the ionic liquids studied here exhibit glass-transition temperatures, with the t_g values ranging from −31 °C for [O2M3M5MPYR][I] to −81 °C for [B2M3MPYR][NTf_2]. Because the spherical shape of iodide anion increases the symmetry and ordering in ionic liquids, ionic liquids containing this type of anion exhibit the highest glass-transition temperatures measured here. In agreement with previous observations concerning ionic liquids containing [NTf_2] anions, the glass-transition temperatures are low,[1,4,5] varying between (−72 and −81) °C for [O2M3M5MPYR][NTf_2] and [B2M3MPYR][NTf_2], respectively. For ionic liquids containing dicyanamide anions, the glass-transition temperatures are close to previously reported values. [B2M3MPYR][$N(CN)_2$] and [O3M5MPYR]-[$N(CN)_2$] exhibited values of (−72 and −80) °C, respectively. Values of (−69, −79, and −80) °C were previously reported for [4MBPYR][$N(CN)_2$], [4MOPYR][$N(CN)_2$], and [OMIM]-[$N(CN)_2$], respectively.[5] Except for [B3M5MPYR][NTf_2], [O3M5MPYR]NTf_2], [B3M5MPYR][SCN], and [O3M5MPYR]-[SCN], for the same anion and pyridinium ring, the ionic liquids containing butyl chains exhibit lower t_g values than those containing octyl chains. This is probably due to the fact that when a shorter chain is present, the electrostatic interactions between the ions are stronger. Additionally, lateral packing and van der Waals forces increase with the alkyl chain length, giving rise to an increase in the cohesive energy of the ionic liquid. Changing from a methyl group to an ethyl group appended to the cation, such as in going from [O2M3MPYR] to [O2M5EPYR], increases the short-range interactions, further increasing the glass-transition temperatures.

In this study, six of the 12 ionic liquids exhibiting melting temperatures also exhibited crystallization temperatures (t_{cc}). The appearance of a crystallization temperature is favored by the presence of multiple methyl or ethyl groups appended to the pyridinium ring. The appearance of such thermal transitions happened with all types of cations and anions used here, and no clear trend in terms of influence of the cation or anion structure on the crystallization point can be established.

As expected, ionic liquids containing iodide anions, such as [O3M5MPYR][I] and [O2M5EPYR][I], are solid at room temperature. Despite the presence of three methyl substituents on the pyridinium cation, [O2M3M5MPYR][I] is a liquid at room temperature, though it is very viscous. Previous work had reported that addition and the position of methyl substituents around imidazolium or pyridinium cations in many cases yield ionic liquids exhibiting melting temperatures higher than those for ionic liquids containing no alkyl substituents.[1,4,5]

Because the [NTf_2] anion presents a highly delocalized charge and a rodlike shape, all of the ionic liquids containing butyl chains and [NTf_2] anions exhibited glass-transition temperatures and no melting temperature, whatever the alkyl chain or cation ring used.

As reported previously,[5] cation symmetry has a significant influence on the melting temperatures of ionic liquids containing [TfO] anions. Here, [B2M3MPYR][TfO] exhibits a melting temperature approximately 70 °C lower than that of [B3M5MPYR][TfO]. This is even more clear for [O2M3MPYR][TfO], which exhibits only a glass-transition temperature, whereas [O3M5MPYR]-[TfO] exhibits a melting temperature of 76 °C.

Except for [O2M5EPYR][$N(CN)_2$], all of the ionic liquids containing [$N(CN)_2$] anion were found to be liquids at room temperature. This is due to the high delocalization of charge and the rodlike shape of the anion. Here again, cation symmetry influences the melting temperature. [B3M5MPYR][$N(CN)_2$] exhibits a melting temperature of −1 °C, which is close to that for [4MBPYR][$N(CN)_2$] (−5 °C).[38] As expected, when longer octyl chains are used, only glass-transition temperatures and no melting temperaures are observed.

Similar to dicyanamide anion, thiocyanate is a small anion with significant electron delocalization among the atoms. As expected, changing the alkyl chain length from butyl to octyl lowers the melting temperature. In addition, more symmetrical cations, such as in [O3M5MPYR][SCN] compared with [O2M3MPYR][SCN], yield ionic liquids with higher melting temperatures. Unlike ionic liquids containing [TfO] anions, addition of an extra methyl group, such as in [O2M3M5MPYR][SCN], increases melting temperature.

Thermogravimetric Analysis. Temperatures of decomposition onset (t_{onset}) and decomposition temperatures at (1 and 5) % mass loss, denoted as $t_{1\%}$ and $t_{5\%}$ respectively, were measured for all of the ionic liquids reported here. Results are shown in Table 1, and plots of thermal degradation of selected ionic liquids are shown in Figures S2 and S3 in the Supporting Information.

In agreement with previous observations, degradation of ionic liquids is mostly influenced by the nature of the anion. For any cation studied here, the decomposition temperatures of the ionic liquids are in the following anion order:

$$[\mathrm{I}] < [\mathrm{SCN}] < [\mathrm{N(CN)_2}] < [\mathrm{NTf_2}] \leq [\mathrm{TfO}] < [\mathrm{BF_4}]$$

The temperatures of decomposition onset measured here agree well with those obtained by Crosthwaite et al.[4] [O3M5MPYR][BF_4] exhibits the highest t_{onset} value, 401 °C, which is similar to those reported for imidazolium cations.[6] For the same anion, the presence of two methyl groups at positions 3 and 5 on the pyridinium ring, that is, in the cations [B3M5MPYR], [O3M5MPYR], [B2M3M5MPYR] and [O2M3M5MPYR], appears to yield higher t_{onset} values. As expected, t_{onset} is significantly higher than $t_{1\%}$ or even $t_{5\%}$, which underlines the fact that ionic liquid undergo significant decomposition at temperatures below the t_{onset} value usually reported in the literature. Therefore, $t_{1\%}$ and $t_{5\%}$ values will mainly be discussed here.

Ionic liquids containing iodide anion exhibit the lowest degradation temperatures, with $t_{1\%}$ ranging from (188 to 200) °C. In contrast, the highest decomposition temperature is obtained for [O3M5MPYR][BF_4]. Because of the high thermal stability of [TfO] and [NTf_2] anions, ionic liquids containing these anions exhibit high $t_{1\%}$ values ranging from (260 to 300) °C. Because of the presence of cyanide groups in both thiocyanate and dicyanamide anions, the thermal stabilities obtained for ionic liquids containing [$N(CN)_2$] or [SCN] anion are close and relatively low. Ionic liquids containing thiocyanate anions exhibit $t_{1\%}$ values ranging from (220 to 240) °C, and values from (205 to 230) °C are observed for [$N(CN)_2$]-containing ionic liquids, in agreement with previous results obtained for 1-octyl-4-methylpyridinium dicyanamide (228 °C).[5]

As illustrated in Figure S2 in the Supporting Information, the thermal degradation of ionic liquids containing [N(CN)$_2$] anions occurs in a two-step process, probably as a result of the decomposition of [N(CN)$_2$] into [CN] followed by the decomposition of [CN] anion.

Interestingly, the ($t_{5\%} - t_{1\%}$) values appear to be mostly influenced by the nature of the anion. For ionic liquids containing [SCN] anions, the values of ($t_{5\%} - t_{1\%}$) range between (15 and 20) °C. For ionic liquids containing [N(CN)$_2$] anions, ($t_{5\%} - t_{1\%}$) is 26 °C. Less thermally stable ionic liquids are also those that exhibit highest decomposition rates. For ionic liquids containing [TfO] and [NTf$_2$] anions, the ($t_{5\%} - t_{1\%}$) values are higher, typically ranging from (20 to 45) °C. Despite lower $t_{1\%}$ values, ionic liquids containing [NTf$_2$] anion appear to decompose less rapidly than ionic liquids containing [TfO] anions. These observations are clearly represented by the plot of $t_{5\%}$ as a function of $t_{1\%}$ shown in Figure S3 in the Supporting Information. The ionic liquids are clearly separated into five groups according to the nature of the anion.

The influence of the cation on thermal stability is not so clear. For a given anion, the values of $t_{1\%}$ are not easily correlated with the cation structure. Nevertheless, except for [O3M5MPYR][TfO], for a given anion, the ionic liquid containing the [O3M5MPYR] cation exhibits a decomposition temperature 5 °C higher than that for other anion homologues. Also for a given anion, ionic liquid based on the [O2M5EPYR] cation exhibits thermal stability that is approximately 20 °C lower than for the other anion homologues. The ethyl substituent appears to be the weak link in these molecules. Furthermore, the temperature variation between $t_{1\%}$ and $t_{5\%}$ appears to be the largest when the cations [B3M5MPYR] and [O3M5MPYR] are used. For instance, the ($t_{5\%} - t_{1\%}$) values for [B3M5MPYR][NTf$_2$] and [B3M5MPYR][TfO] are 38 and 36 °C, respectively. This type of cation therefore appears to yield most thermally stable ionic liquids.

Additionally, isothermal thermogravimetric analysis was performed by exposing the ionic liquids to a temperature of 225 °C for 5 h in air. The ionic liquids [B3M5MPYR][TfO], [B3M5MPYR][NTf$_2$], [O3M5MPYR][TfO], and [O3M5MPYR]-[NTf$_2$] were tested. Surprisingly, the ionic liquids containing [NTf$_2$] anion underwent some decomposition, losing approximately 5 % of their mass after 5 h at 225 °C and turning from a clear to a dark color. Ionic liquids containing [TfO], on the other hand, did not exhibit any color change, and no significant weight loss was observed. These results are surprising, considering the similar thermal stabilities obtained from the decomposition temperatures. This tends to show that the ionic liquids containing [TfO] anions studied here are the most stable ionic liquids for use at high temperatures over long periods of time.

Density and Refractive Index. Densities and refractive indices were measured for various ionic liquids exhibiting melting temperatures below 20 °C. The water contents of all the ionic liquids studied here were measured prior to the density measurements. Refractive indices were measured after the ionic liquids had been dried under vacuum, and the water contents were found to be less than $w = 0.0005$. Densities, water contents, and refractive indices of the ionic liquids are collected in Table 2.

Table 2. Densities (ρ), Water Contents (w_{water}) Prior to Density Measurements, and Refractive Indices (n_D) for Selected Room-Temperature Ionic Liquids at 20 °C

ionic liquid	ρ/(g·cm^{-3})	100 w_{water}[b]	n_D[c]
[4MBPYR][NTf$_2$]	1.35[a]	–	–
[B3M5MPYR][NTf$_2$]	1.39	0.076	1.4559
[B2M3MPYR][NTf$_2$]	1.37	0.078	1.4497
[B2M5EPYR][NTf$_2$]	1.37	0.046	1.4552
[B2M3M5MPYR][NTf$_2$]	1.37	0.048	1.4583
[OPYR][NTf$_2$]	1.31	0.18	1.4476
[O3M5MPYR][NTf$_2$]	1.28	0.022	1.4526
[O2M3MPYR][NTf$_2$]	1.29	0.040	1.4571
[O2M5EPYR][NTf$_2$]	1.28	0.050	–
[O2M3M5MPYR][NTf$_2$]	1.28	0.040	1.4617
[B2M3MPYR][TfO]	–	–	1.4748
[O2M3MPYR][TfO]	1.18	0.085	1.4725
[B3M5MPYR][N(CN)$_2$]	–	–	1.5278
[B2M3MPYR][N(CN)$_2$]	–	–	1.5403
[O3M5MPYR][N(CN)$_2$]	1.00	0.335	1.5196
[O3M5MPYR][SCN]	1.00	0.290	1.5415
[O2M3MPYR][SCN]	1.02	0.276	1.5489
[O2M3M5MPYR][I]	–		1.5776

[a] Data taken from ref 32. [b] Measured prior to density measurements. [c] The mass fractions of water in all of the ionic liquids during the refractive index measurements were always less than $w = 0.0005$.

In agreement with previous reports, ionic liquids with [NTf$_2$] anions exhibit the highest densities.[1,3,38] This is confirmed here, as the highest density was measured for [B3M5MPYR][NTf$_2$]. Densities of ionic liquids containing butyl chains are approximately 0.10 g·cm^{-3} higher than those for ionic liquids containing octyl chains. In addition, except for the ionic liquids containing [NTf$_2$] anions, the presence of two methyl groups increases the density of the ionic liquids relative to those obtained for 1-butyl-4-methylpyridinium or 1-octyl-4-methylpyridinium homologues.[5] As reported previously,[1,3] ionic liquids containing triflate anion exhibit densities lower than that for [NTf$_2$] anion. Because of the absence of trifluoromethyl groups on the anion, ionic liquids containing dicyanamide or thiocyanate anions exhibit low densities close to or less than that of water. Hydrophobic [O3M5MPYR][N(CN)$_2$] and [O3M5MPYR][SCN], for instance, are slightly less dense than water, since each ionic liquid remains above water upon mixing.

The refractive indices range from 1.4476 to 1.5776. The results show that for a given anion, the refractive indices of the ionic liquids measured here are higher than those reported elsewhere for ionic liquids based on imidazolium or tetrahydrothiophenium cations.[3,10] For instance, the refractive index for [O2M3M5MPYR][I] is higher than that reported elsewhere for 1-methyl-4-butylimidazolium iodide (1.572).[3] Anions have the most significant influence on the refractive index: the smaller the anion, the higher the refractive index. For the same cation, refractive indices increase in the following anion order: $n(\text{NTf}_2) < n(\text{TfO}) < n(\text{N(CN)}_2) < n(\text{SCN}) < n(\text{I})$. The high refractive indices found for dicyanamide or thiocyanate anions are consistent with previous results[41] and are related to the high mobility of electrons in the anion. Despite the fact that ionic liquids containing pyridinium cations generally exhibit higher refractive indices, the influence of the cation is not clear. Increasing the alkyl chain length or adding methyl groups on the pyridinium have no systematic influence on refractive indices.

Solubility in Water. Solubilities in water were obtained by measuring the intensity at the maximum absorption wavelength ($\lambda_{\max}$) of pyridinium-based ionic liquids in water. UV−vis spectra of several ionic liquids are plotted in Figure S4 in the Supporting Information. Maximum absorption wavelengths and molecular extinction coefficients for selected ionic liquids are collected in Table 3. For a given cation, the $\lambda_{\max}$ values are equal whatever the anion used.

Unlike 1-methylimidazole, pyridine, or picoline reactants, the compounds 2,3-dimethylpyridine, 3,5-dimethylpyridine, and 2,3,5-trimethylpyridine that are fragments of the ILs studied here

Table 3. Maximum Absorption Wavelengths and Molecular Extinction Coefficients for Selected Ionic Liquids Containing Trialkylpyridinium or Tetraalkylpyridinium Cations in Water

ionic liquid	M_w/(g·mol^{-1})	λ/nm	ε/(L·mol^{-1}·cm^{-1})
[B3M5MPYR][NTf$_2$]	444.42	271	6771
[B2M3MPYR][NTf$_2$]	444.42	271	4783
[B2M5EPYR][NTf$_2$]	458.44	273	6036
[B2M3M5MPYR][NTf$_2$]	458.44	277	6552
[O3M5MPYR][NTf$_2$]	500.53	271	5192
[O2M3MPYR][NTf$_2$]	500.53	271	5778
[O2M5EPYR][NTf$_2$]	514.55	273	6554
[O3M5MPYR][TfO]	369.45	271	5051
[O2M3M5MPYR][TfO]	383.48	277	6599

Table 4. Solubilities of Ionic Liquids in Water (w_{IL}) and Water Contents (w_{water}) for Several Ionic Liquids Exposed to Air at (16 ± 1) °C

ionic liquid	100 w_{IL}[a]	100 w_{water}[b]
[O2M5EPYR][I]	2.386	–
[O2M3M5MPYR][I]	2.871	–
[B3M5MPYR][NTf$_2$]	0.339	0.169
[B2M3MPYR][NTf$_2$]	0.278	–
[B2M5EPYR][NTf$_2$]	0.249	0.151
[B2M3M5MPYR][NTf$_2$]	0.166	0.117[d]
[O3M5MPYR][NTf$_2$]	0.031	0.091
[O2M3MPYR][NTf$_2$]	0.040	0.106
[O2M5EPYR][NTf$_2$]	0.026	0.097[c,d]
[O2M3M5MPYR][NTf$_2$]	–	0.135[e]
[OPYR][NTf$_2$]	–	0.264
[O2M3MPYR][TfO]	1.487	0.937
[O3M5MPYR][TfO]	0.975	–
[O2M3M5MPYR][TfO]	1.092	–
[O3M5MPYR][N(CN)$_2$]	2.000	2.758
[O2M3MPYR][N(CN)$_2$]	–	2.766
[O2M5EPYR][N(CN)$_2$]	1.524	–
[O2M3M5MPYR][N(CN)$_2$]	–	2.571
[O3M5MPYR][SCN]	1.053	3.133
[O2M3MPYR][SCN]	0.972	3.291
[O2M3M5MPYR][SCN]	–	2.942

[a] Solubility of the ionic liquid in water, reported as the mass fraction. [b] Water content of the ionic liquid, expressed as the mass fraction. Each ionic liquid was exposed to air for 5 weeks at (28 ± 1) % relative humidity, unless otherwise specified. [c] Value obtained for the ionic liquid after 2 weeks of exposure to air at (29 ± 1) % relative humidity. [d] A single datum was measured. [e] Value obtained for the ionic liquid after 1 week of exposure at (29 ± 1) % relative humidity.

have limited solubilities in water. The water solubilities of the ionic liquids based on 2,3-dimethylpyridine, 3,5-dimethylpyridine, and 2,3,5-trimethylpyridine are therefore expected to be lower than those previously reported for ionic liquids based on pyridine or picoline compounds.[5]

In agreement with previous reports showing that ionic liquids containing octylpyridinium cation are hydrophobic,[5] all of the ionic liquids studied here that contain an octyl chain form two phases when they are in contact with water. Except for those containing [NTf$_2$] anions, the ionic liquids containing butyl chains are soluble in water. The results are all reported in Table 4.

Here, the ionic liquids containing iodide anion are found to be hydrophobic. To the best of our knowledge, this is the first example of hydrophobic ionic liquids based on iodide reported to date. Solubility measurements were carried out in dark vials to avoid reaction of iodide with water. The solubilities in water obtained for these ionic liquids are high but similar to those previously reported for other ionic liquids containing 1-octyl-3-methylimidazolium [OMIM], [OPYR], or 1-octyl-4-methylpyridinium [O4MPYR] as the cation and [TfO], [N(CN)$_2$], or even [BF$_4$] as the anion.[5]

Furthermore, because of the increased hydrophobicity of the cation, the water solubilities of the ionic liquids containing dicyanamide or triflate anions are lower than those of their [OPYR] and [O4MPYR] homologues. For instance, [OPYR][TfO] exhibits a solubility in water of $w = 0.0159$,[13] compared with 0.00975 and 0.00109 for [O3M5MPYR][TfO] and [O2M3M5MPYR][TfO], respectively. The solubility in water for [O4MPYR][N(CN)$_2$] has been reported to be greater than $w = 0.0500$.[13] Here, values of 0.0200 and 0.0152 were found for [O3M5MPYR][N(CN)$_2$] and [O2M5EPYR][N(CN)$_2$], respectively. Ionic liquids containing thiocyanate anion and an octyl chain exhibit solubility in water of approximately $w = 0.0100$ and are in the range of those obtained for triflate.

Among all of the ionic liquids studied here, those containing [NTf$_2$] anions exhibit lowest solubilities in water, which range from $w = 0.00339$ to $w = 0.00166$ for the butyl-based ionic liquids and from $w = 0.00040$ to $w = 0.00026$ for the octyl-based ionic liquids. As previously reported, changing the chain from butyl to octyl yields a 10-fold decrease in the solubility of ionic liquids in water. [B2M3M5MPYR][NTf$_2$] and [O2M5EPYR][NTf$_2$] exhibit the lowest solubilities in water for butyl and octyl NTf$_2$-containing ionic liquids, respectively. This shows that the hydrophobicity increases with the number of alkyl substituents on the cation ring. Furthermore, the water solubilities of the ionic liquids studied here are approximately half those obtained for the 1-butyl-4-methylpyridinium homologues.[5] The solubility in water for [B4MPYR][NTf$_2$] was previously reported to be $w = 0.00480$, compared to $w = 0.00166$ obtained here for [B2M3M5MPYR][NTf$_2$].

With a longer alkyl chain length, however, the results are not similar to those obtained for the butyl-based ionic liquids. When the ionic liquid is very hydrophobic because of the anion and a longer alkyl chain, the influence of the cation ring is less pronounced. Therefore, no significant differences in water solubility were found between [OPYR][NTf$_2$] ($w = 0.00035$)[5] and [O3M5MPYR][NTf$_2$] ($w = 0.00031$), [O2M3MPYR][NTf$_2$] ($w = 0.00040$), or [O2M5EPYR][NTf$_2$] ($w = 0.00026$).

It appears that using a cation ring with increased hydrophobicity to synthesize ionic liquids has a significant influence on the water solubility of the resulting ionic liquids when used with hydrophilic anions and a short alkyl chain length. For ionic liquids containing a hydrophobic anion such as [NTf$_2$] and a long alkyl chain, however, the influence of the trialkylpyridinium or tetraalkylpyridinium cation on the solubility in water is rather small.

Water Content. Water contents of several ionic liquids synthesized in this work were measured with the help of a coulometric KF apparatus. Prior to the measurements, the samples were left in contact with air for 5 weeks under vigorous stirring. The results are collected in Table 4.

The water content (i.e., hygroscopicity) of ionic liquids is primarily related to the nature of the anion. For every cation studied here, the water content follows the trend $w(\mathrm{NTf_2}) < w(\mathrm{TfO}) < w[\mathrm{N(CN)_2}] < w(\mathrm{SCN})$. Ionic liquids containing [NTf$_2$] anions exhibit lowest water contents. The lowest water content is $w = 0.00091$ for [O3M5MPYR][NTf$_2$]. As expected, the presence of extra methyl groups appended to the cation ring or a longer alkyl chain yields a lower water content. The water content for [OPYR][NTf$_2$] ($w = 0.00264$) is higher than those measured for [O3M5MPYR][NTf$_2$] ($w = 0.00091$), [O2M3MPYR][NTf$_2$] ($w = 0.00106$), and [O2M5EPYR][NTf$_2$] ($w = 0.00097$). The water content for [O2M3MPYR][TfO] ($w = 0.00937$) is higher than those obtained for [NTf$_2$]-based ionic liquids, in agreement with previous results.[1,5]

When a more hydrophilic anion such as [SCN] or [N(CN)$_2$] is used, the water contents is higher, ranging from $w = 0.0257$ for [O3M5MPYR][N(CN)$_2$] to $w = 0.0329$ for[O2M3MPYR]-

Table 5. Reduction Potentials (E^{red}), Oxidation Potentials (E^{ox}), and Electrochemical Windows (ΔE) for Several Ionic Liquids Containing Pyridinium Cations (All Data Were Recorded with a Ag/AgCl Pseudoreference Electrode at 20 °C)

ionic liquid	E^{red}/V^a	E^{ox}/V^a	ΔE/V
[O2M3MPYR][NTf$_2$]	−1.0	2.6	3.9
[O2M5EPYR][NTf$_2$]	−1.2	2.9	4.2
[O2M3M5MPYR][NTf$_2$]	−1.3	3.0	4.1
[O3M5MPYR][NTf$_2$]	−1.3	2.6	4.2
[OPYR][NTf$_2$]	−1.0	2.5	3.5

[a] Potential vs Ag/AgCl pseudoreference electrode obtained for a current density of $i = 100\ \mu\text{A}\cdot\text{cm}^{-2}$.

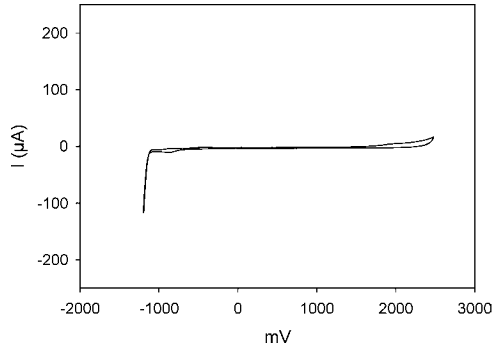

Figure 2. Electrochemical window for [O2M5EPYR][NTf$_2$].

[SCN]. Interestingly, it appears that ionic liquids containing [SCN] are more hygroscopic than their [N(CN)$_2$] homologues, despite the fact that the latter ionic liquids exhibit higher solubilities in water.

Electrochemical Properties. Electrochemical windows were recorded for five ionic liquids, namely, [OPYR][NTf$_2$], [O2M3MPYR][NTf$_2$], [O3M5MPYR][NTf$_2$], [O2M5EPYR] [NTf$_2$], and [O2M3M5MPYR][NTf$_2$]. The results are given in Table 5. A plot of the electrochemical window for [OPYR]-[NTf$_2$] is shown in Figure 2. All of the other electrochemical windows are shown in the Supporting Information.

In order to gain some insight into the reduction potentials of ionic liquids containing pyridinium cations and the influence of methyl substituents on the reduction potentials of such ionic liquids, the electrochemical windows of ionic liquids containing [NTf$_2$] anion and the cations [O2M3MPYR], [O3M5MPYR], [O2M5EPYR], and [O2M3M5MPYR] were measured. [NTf$_2$] anion was used because it is a well-known anion exhibiting increased electrochemical stability. Furthermore, all of the ionic liquids studied here that contain this anion are liquids at room temperature. Moreover, cations containing octyl chains were used because it has been reported elsewhere that ionic liquids containing long linear alkyl chains are slightly less subject to reduction than those containing shorter alkyl chains.[7]

Previous reports revealed that the reduction potential of an ionic liquid is mostly due to the nature of the cation.[1,9] Ionic liquids containing saturated heterocyclic cations such as pyrrolidinium (PYRRO) or piperidinium (PIP) are subject to reduction at much more negative potentials than ionic liquids containing unsaturated imidazolium heterocycles. For instance, reduction potentials below −3 V versus Ag/AgCl have been reported for [OMPYRRO][NTf2] (OMPYRRO = 1-methyl-1-octylpyrrolidinium)[7] and [OMPIP][NTf$_2$] (OMPIP = 1-methyl-1-octylpiperidinium)[9] and below −2 V for [OMIM][NTf$_2$].[1] Oxidation potentials, on the other hand, were found to be mostly influenced by the nature of the anion, whatever the cation used.[7,8,27] Very few works have reported electrochemical windows for pyridinium ionic liquids. The value of −1.0 V for 1-butyronitrilepyridinium bis(trifluoromethanesulfonyl)imide ([BCNPYR][NTf$_2$]) has been reported, consistent with the fact that hydrogens present on the pyridinium cation, which is aromatic, are easily reduced.[41]

Table 6. Toxicities (EC$_{50}$) for Several Ionic Liquids on *V. fischeri*

ionic liquid	EC$_{50}$/(mol·L^{-1})	EC$_{50}$ standard deviation/(mol·L^{-1})	log EC$_{50}$
[B3M5MPYR]$^+$[Br]$^-$	$3.10\cdot10^{-4}$	$1.32\cdot10^{-5}$	−3.51
[B2M3M5MPYR]$^+$[Br]$^-$	$3.01\cdot10^{-4}$	$1.67\cdot10^{-5}$	−3.52
[O3M5MPYR]$^+$[Br]$^-$	$1.33\cdot10^{-5}$	$5.04\cdot10^{-7}$	−4.88
[O2M3MPYR]$^+$[Br]$^-$	$1.19\cdot10^{-5}$	$4.11\cdot10^{-7}$	−4.92
[O2M3M5MPYR]$^+$[Br]$^-$	$4.38\cdot10^{-6}$	$7.84\cdot10^{-8}$	−5.36
[B3M5MPYR]$^+$[NTf$_2$]$^-$	$7.18\cdot10^{-5}$	$4.28\cdot10^{-6}$	−4.14
[B2M3M5MPYR]$^+$[NTf$_2$]$^-$	$3.65\cdot10^{-5}$	$4.07\cdot10^{-6}$	−4.44
[O3M5MPYR]$^+$[NTf$_2$]$^-$	$2.27\cdot10^{-6}$	$2.48\cdot10^{-7}$	−5.64
[O2M3M5MPYR]$^+$[NTf$_2$]$^-$	$4.20\cdot10^{-6}$	$3.18\cdot10^{-7}$	−5.38

Our results show that the electrochemical window for [OPYR]-[NTf$_2$] is similar to that reported previously for [BCNPYR][NTf$_2$].[41] As observed for imidazolium cations,[27] when methyl groups are added on pyridinium cations, reduction occurs at slightly lower potentials. Reduction potentials of (−1.2, −1.3, and −1.3) V versus Ag/AgCl were obtained for [O2M5EPYR][NTf$_2$], [O3M5MPYR] [NTf$_2$], and [O2M3M5MPYR][NTf$_2$], respectively. Only [O2M3-MPYR][NTf$_2$] exhibits a reduction potential similar to that of [OPYR][NTf$_2$]. The presence of methyl groups appended to the pyridinium cation appears to have some small influence on the electrochemical stability of the cation, because of the number of unsaturated carbons bound to hydrogen that are still available for reduction. Additionally, it appears that the presence of more than two methyl substituents (i.e., in the cation [O2M5EPYR] or [O2M3M5MPYR]) significantly increases the oxidation potential of the ionic liquid, which is related to the electrochemical stability of the anion. Such a stability increase is probably due to stronger interactions between the anion and the cation via hydrogen bonding. Such observations have been reported previously for [BCNPYR][NTf$_2$].[41]

This study shows that ionic liquids containing the stable [NTf$_2$] anion and pyridinium cations exhibit high reduction potentials. Because it is commonly accepted that the reduction potential of ionic liquids is mainly due to reduction of the cation, this tends to show that pyridinium-based ionic liquids are electrochemical solvents that generally exhibit high reduction potentials. Nevertheless, their high oxidation stability and thermal stability can be useful in high-temperature electrochemical applications involving oxidative species, such as ruthenium complexes in dye-sensitized solar cells (DSSC), for instance.

Toxicity. In addition to the physicochemical properties, the toxicities of several of the ionic liquids on a marine bacterium, *V. fischeri*, have been studied. In order to compare the influences of the cation and anion on the toxicity of the ionic liquids, five water-soluble ionic liquids containing bromide anion and four hydrophobic ionic liquids containing NTf$_2$ anion were tested. The results of these toxicity measurements (including standard deviations) are shown in Table 6.

As expected, the toxicity increases with alkyl chain length. For instance, [O3M5MPYR][Br] is more toxic than [B3M5MPYR] [Br]. For the latter, the toxicity value measured here is consistent with that from a previous publication [EC$_{50}$ = $(4.9 \pm 2)\cdot10^{-4}$ mol·L^{-1}].[42] The position of the methyl groups on the pyridinium cation has a very limited influence on the toxicity, as observed for [O3M5MPYR][Br] and [O2M3MPYR][Br], while adding an extra substituent leads to a significant increase in toxicity, as seen for [O2M3M5MPYR][Br]. Therefore, the values reported here are significantly higher than those for other ionic liquids containing the same alkyl chain length and a pyridinium ring.[42] Moreover, since ionic liquids based on imidazolium or another saturated cation such as pyrrolidinium or piperidinium have been found to be less toxic than their pyridinium homologues, the ionic liquids reported here are among most toxic ionic liquids reported in the literature.[42,43]

In agreement with previous reports,[42,43] the hydrophobic ionic liquids synthesized here that contain a butyl chain and the [NTf$_2$] anion exhibit higher toxicity (lower EC$_{50}$ values) than the water-soluble bromide homologues. The toxicity of [B3M5MPYR][NTf$_2$] is one order of magnitude higher than that obtained for [B3M5MPYR][Br]. Similarly, [O3M5MPYR][NTf$_2$] and [O3M5MPYR][Br] exhibit EC$_{50}$ values of ($2.27 \cdot 10^{-6}$ and $1.33 \cdot 10^{-5}$) mol·L^{-1}, respectively.

On the contrary, ionic liquids containing [O2M3M5MPYR] cations exhibit similar toxicities regardless of whether bromide or [NTf$_2$] anion is used. [O2M3M5MPYR][Br] and [O2M3M5MPYR][NTf$_2$] exhibit EC$_{50}$ values of ($4.38 \cdot 10^{-6}$ and $4.20 \cdot 10^{-6}$) mol·L^{-1} respectively. In this case, the ionic liquid toxicity is determined by the most toxic element of the ionic liquid (i.e., [O2M3M5MPYR], a cation containing a long alkyl chain and many methyl substituents). This implies that the toxic effects of cations and anions are not always additive.

Conclusion

Hydrophobic ionic liquids have been synthesized starting from hydrophobic alkylpyridine reactants. Some properties, such as glass-transition and melting temperatures, densities, and water contents, are similar to those obtained for ionic liquids containing imidazolium or pyridinium cations, while many others, such as solubilities in water, refractive indices, and electrochemical windows, are significantly different. Most of the ionic liquids are liquids at room temperature, despite the increase in the number of methyl groups appended to the cation. Decomposition temperatures are similar to those previously reported for ionic liquids containing pyridinium cations. It must be pointed out that when the ionic liquids were exposed to high temperatures over longer periods of time, those containing triflate anions were found to be more stable than those based on [NTf$_2$] anions. The electrochemical windows are narrow, similar to those obtained for other pyridinium homologues and significantly narrower than those reported for ionic liquids containing imidazolium cations. The densities are slightly lower than those obtained for other pyridinium homologues. Water contents are lower and refractive indices significantly higher than those reported for other ionic liquids.

Most importantly, however, all of the ionic liquids containing an octyl chain, even those containing an iodide anion, are immiscible with water. Except for the ionic liquids containing an octyl chain and the [NTf$_2$] anion, the solubilities in water are lower than those for their methylpyridinium homologues. Ionic liquids such as [O3M5MPYR][NTf$_2$] and [O3M5MPYR][I] might therefore serve as new ionic liquids with increased hydrophobicity for various processes such as liquid−liquid extraction or purification of atmospheric gases. In the case of extraction of metal ions from wastewater, though, the increased toxicity related to the presence of extra methyl groups implies that an efficient removal of the ionic liquid from the water after the extraction procedure must be carried out.

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Supporting Information Available:

Experimental details, including synthesis procedures and ^{1}H NMR, ^{13}C NMR, and IR spectral data, and DSC and TGA curves, plots of decomposition temperatures, UV−vis spectra, and electrochemical windows. This material is available free of charge via the Internet at http://pubs.acs.org.

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