Novel Room Temperature Inorganic Ionic Liquids

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New inorganic ionic liquids (IIL) consisting of an inorganic polyoxometalate anion with the Keggin structure and a sodium cation, that is $Na_{13}[Ln(TiW_{11}O_{39})_2]\cdot xH_2O$ [where Ln = lanthanide (type 1)], $Na_5[MTiW_{11}O_{39}]\cdot xH_2O$ and $Na_6[MTiW_{11}O_{39}]\cdot xH_2O$ [where M = transition metal (type 2)], were prepared and their physicochemical properties were investigated. These ionic liquids were characterized by NMR and IR spectroscopy and by elemental analysis. Their melting point, viscosity, conductivity, thermal stability, and miscibility with water and organic solvents were determined. When the temperature is below ambient temperature (about 298 K) these ionic liquids are almost immiscible with water. When the temperature is raised, the solubility of the new ionic liquids increases sharply. The influence of the size and of the charge density of both the cations and anions on these properties was examined. The most remarkable feature of IILs is that water is their indispensable component. The role of the water molecule in ionic liquids is similar to that of crystalline water in hydrated compounds.

Introduction

Ionic liquids constitute a large, fundamental class of fluid materials that in recent years have aroused increasing interest because of their relevance to separation technologies, manufacturing processes and catalysis in green chemistry. Their properties, in fact, are low melting point, a wide liquid range, negligible vapor pressure, good solubility characteristics, relatively low viscosity, nonflammability, a wide electrochemical window, tolerance to strong acids, and excellent thermal and chemical stability.[1−10] Since the discovery of the first ionic liquid (ethylammonium nitrate) in 1914,[11] many classes of ionic liquids have been investigated. According to the current definition, ionic liquids should become liquid at or below 373 K[1] or 423 K[4]. They are typically composed of organic cations with a variety of substituents such as quaternary ammonium cations,[12,13] heterocyclic aromatic compounds,[14] pyrrolidinium cations,[15] derivatives of natural products,[16] phosphonium,[17−18] sulfonium,[19] guanidinium[20] and some more exotic cations,[21,22] and a variety of anions such as Cl^-, Br^-, NO_3^-, I^-, BF_4^-, $AlCl_4^-$, PF_6^- and others. Such ionic liquids are commonly referred to as organic−inorganic ionic liquids.[4] Only few ionic liquids comprising organic cations and organic anions (organic ionic liquids) have been investigated.[4,23−25] However, with the exception of the supercooled ionic liquid, $[Ca(NO_3)_2]_{0.4}(KNO_3)_{0.6}$, reported by Moom and Jeong,[26] ionic liquids consisting of inorganic cations and inorganic anions (inorganic ionic liquids) have not yet appeared in the literature. Although their rapid emergence as environmentally benign solvents and catalysts has lead to a growing number of applications, the basic understanding and study of their physical and chemical properties has lagged behind. A significant barrier to the widespread use of ionic liquids is the lack of understanding of such properties and of the suitable manufacturing processes. It is very important to accumulate a substantial body of scientific and technological data for these fascinating fluid materials, so that their true potential as solvents and catalysts in chemical synthesis and separation processes can be realized. Here, we report the synthesis and characterization of several new inorganic ionic liquids consisting of an inorganic polyoxometalate anion with the Keggin structure and a sodium cation, that is $Na_{13}[Ln(TiW_{11}O_{39})_2]\cdot xH_2O$ [where Ln = lanthanide(type 1)], $Na_5[MTiW_{11}O_{39}]\cdot xH_2O$ and $Na_6[MTiW_{11}O_{39}]\cdot xH_2O$ [where M = transition metal (type 2)]. These materials have allowed us to further explore the formation mechanism of ionic liquids with lower melting points and to reveal the relationship between the structural features of an ionic liquid and its useful properties. Their incorporation into ionic liquids may expand the utility of ionic liquids and open up a new field of ionic liquid chemistry.

Results and Discussion

The syntheses of the novel inorganic ionic liquids were carried out in a mixture comprising an aqueous solution of sodium tungstate, tetrachlorotitanium and the related transition-metal salts (or lanthanide nitrate) at 333 K.[27] The

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ionic liquids synthesized have high solubility in water at high temperatures but they are almost immiscible below ambient temperature; we were therefore able to separate the water from the synthetic mixture at low temperatures. These ionic liquids can change into amorphous powders when they are mixed with anhydrous acetone or ethanol, due to the loss of constituent water from the ionic liquids to the organic solvent. The molar ratios of the constituent elements in the investigated ionic liquids, Na:Ti:Ln:W = 13:2:1:22 (type 1), Na:Ti:M:W = 5:1:1:11 (when M = Fe, or Cr), Na:Ti:M:W = 6:1:1:11 [when M = Mn, Zn(type 2)], were determined by inductively coupled plasma-emission spectrometry. The Keggin structure characteristic of the anions was evidenced by IR spectroscopy. These results illustrate that the anion of type 1 is twice as large as that of type 2, but the charge density on the surface of the anion has no significant difference.

The most remarkable trait of IILs is that water is their indispensable component. The water content of the new ionic liquids was estimated by Karl Fischer analysis and is showed in Table 1. Although various amounts of water were also present in previously known ionic liquid systems,[4] in our IILs system water is a necessary component. Upon heating in air and in the absence of organic solvents, such ionic liquids could change into mudlike solids after loss of constituent water. This phenomenon is reminiscent of the dehydration process in crystalline solids containing crystallization water. The difference between the two phenomenona is that ionic liquids change into mudlike solids while crystals change into amorphous powders.

Table 1. Water content of the inorganic ionic liquids

Compound	H_2O (wt.-%)	x
$Na_{13}[La(TiW_{11}O_{39})_2]\cdot xH_2O$	11.18	40.0
$Na_{13}[Ce(TiW_{11}O_{39})_2]\cdot xH_2O$	9.16	32.6
$Na_{13}[Pr(TiW_{11}O_{39})_2]\cdot xH_2O$	10.08	36.3
$Na_{13}[Sm(TiW_{11}O_{39})_2]\cdot xH_2O$	10.92	39.8
$Na_{13}[Gd(TiW_{11}O_{39})_2]\cdot xH_2O$	7.72	27.1
$Na_{13}[Dy(TiW_{11}O_{39})_2]\cdot xH_2O$	8.22	29.1
$Na_{13}[Er(TiW_{11}O_{39})_2]\cdot xH_2O$	10.76	39.2
$Na_{13}[Tm(TiW_{11}O_{39})_2]\cdot xH_2O$	9.26	33.2
$Na_{13}[Yb(TiW_{11}O_{39})_2]\cdot xH_2O$	11.83	43.7
$Na_5[CrTiW_{11}O_{39}]\cdot xH_2O$	15.95	30.2
$Na_6[MnTiW_{11}O_{39}]\cdot xH_2O$	15.75	30.0
$Na_5[FeTiW_{11}O_{39}]\cdot xH_2O$	17.62	34.0
$Na_6[ZnTiW_{11}O_{39}]\cdot xH_2O$	14.70	27.2

One of the most important criteria for the evaluation of an ionic liquid is its melting point. The solid−liquid phase transition of the new inorganic ionic liquids was examined with a PerkinElmer DSC and a YAN-1 melting point apparatus and the results are summarized in Table 2. The DSC curve for $Na_{13}[Ce(TiW_{11}O_{39})_2]\cdot 33H_2O$, at a heating rate of 10 K/min, is shown in Figure 1. The DSC measurements show two distinct peaks, which demonstrate that two liquid phases, an aqueous phase and an ionic liquid phase, can be formed when the solid melts.[28] The presence of little free-water in the sample is indeed confirmed by a small shoulder peak at 272.4 K. However, the main peak at 260.5 K shows that the highly hydrated inorganic ionic liquid of $Na_{13}[Ce(TiW_{11}O_{39})_2]\cdot 33H_2O$ exists in a pure phase. The results in Table 2 illustrate that all the ionic liquids possess a very low melting point and are liquid below room temperature. In general, the melting point of an ionic liquid is correlated with the symmetry, size and charge density of the component ion.[4] Hydrogen bonding and Van Der Waals interactions have also a slight influence on the melting point.[2] The low melting point of the new ionic liquids (shown in Table 2) is ascribed to the absence of hydrogen bonding between the anions and the cations and to the lower charge density on the surface of the anions.

Table 2. Melting point (T_m) of the inorganic ionic liquids

Compound	T_m (K)	Compound	T_m (K)
$Na_{13}[La(TiW_{11}O_{39})_2]$	253.0	$Na_{13}[Tm(TiW_{11}O_{39})_2]$	260.2
$Na_{13}[Ce(TiW_{11}O_{39})_2]$	263.0	$Na_{13}[Yb(TiW_{11}O_{39})_2]$	267.2
$Na_{13}[Pr(TiW_{11}O_{39})_2]$	253.0	$Na_5[CrTiW_{11}O_{39}]$	261.5
$Na_{13}[Sm(TiW_{11}O_{39})_2]$	256.0	$Na_5[MnTiW_{11}O_{39}]$	253.0
$Na_{13}[Gd(TiW_{11}O_{39})_2]$	265.1	$Na_5[FeTiW_{11}O_{39}]$	257.6
$Na_{13}[Dy(TiW_{11}O_{39})_2]$	265.2	$Na_6[ZnTiW_{11}O_{39}]$	257.4
$Na_{13}[Er(TiW_{11}O_{39})_2]$	261.0		

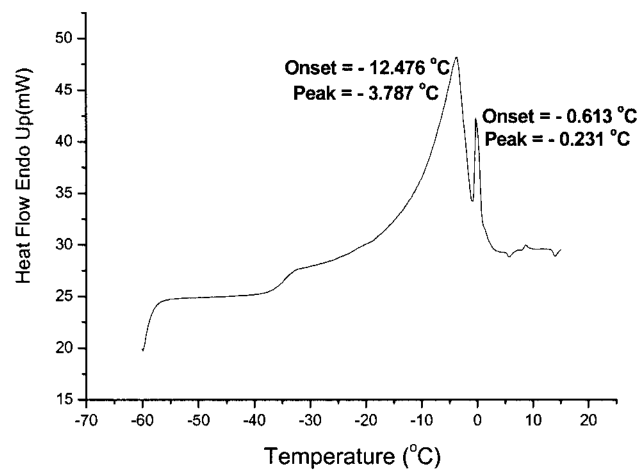

Figure 1. DSC analysis curve of $Na_{13}[Ce(TiW_{11}O_{39})_2]\cdot 33H_2O$

The viscosity measurement of the new inorganic ionic liquids was carried out with an NEX-11 rotational viscosimeter. The lower viscosity (42.5−82.5 cps at 298 K) found in these ionic liquids is similar to that of [emim][BF_4](43 cps at 293 K)[29] and [bmim][CF_3SO_3](90 cps at 293 K).[30] It appears from the examination of a number of organic ionic liquids that the viscosity of the corresponding ionic liquids is related to the structure and the size of the component ions, to their tendency to form hydrogen bonding and to the strength of their van der Waals interactions.[1,31] In the inorganic ionic liquids the structures of all the component ions are very simple. For example, the cation is sodium Na^+ or hydrated sodium $Na^+(H_2O)_x$, the anion is the spherical ion with the Keggin structure $[MTiW_{11}O_{39}]^{5-}$ or $[MTiW_{11}O_{39}]^{6-}$ (where M = Cr, Mn, Fe, Zn) or the dumbbell complex ion with a double lacunary Keggin structure

Table 3. Specific conductivity of measurable samples at 298 K

Compound	σ (×10^4μS/cm)	Compound	σ (×10^4μS/cm)
$Na_{13}[La(TiW_{11}O_{39})_2]$	1.10	$Na_5[CrTiW_{11}O_{39}]$	1.62
$Na_{13}[Ce(TiW_{11}O_{39})_2]$	2.02	$Na_6[MnTiW_{11}O_{39}]$	1.80
$Na_{13}[Pr(TiW_{11}O_{39})_2]$	1.85	$Na_5[FeTiW_{11}O_{39}]$	2.66
$Na_{13}[Sm(TiW_{11}O_{39})_2]$	2.24	$Na_{13}[Tm(TiW_{11}O_{39})_2]$	1.59
$Na_{13}[Er(TiW_{11}O_{39})_2]$	1.68	$Na_{13}[Yb(TiW_{11}O_{39})_2]$	1.77
$Na_{13}[Gd(TiW_{11}O_{39})_2]$	2.30	$Na_6[ZnTiW_{11}O_{39}]$	2.01
$Na_{13}[Dy(TiW_{11}O_{39})_2]$	1.92		

$[Ln(TiW_{11}O_{39})_2]^{13-}$, which has the largest ionic radius and the lowest charge density on it. The tendency to form hydrogen bonds between the cations and the anions of ionic liquids may be completely suppressed. Therefore, the viscosity in these inorganic ionic liquids is simply governed by a weak electrostatic interaction force.

The conductivity of an ionic liquid can been described by the equation below:[31]

$$\sigma = yF^2d(6\pi N_A FW\eta)[(\zeta_a r_a)^{-1} + (\zeta_{ac} r_c)^{-1}] \quad (1)$$

and can be related to its viscosity (η), formula weight (FW), density (d), ion radii (r_a and r_c) and to the specific interactions between the mobile ions (ζ_a and ζ_c) in an ionic liquid. The conductivity of the new inorganic ionic liquids was measured with a DDS-11 conductivitimeter and the results are shown in Table 3. Following on from the equation above, the ionic liquid containing the smallest ion should provide the highest conductivity but in our results (see Table 3) both type 1 and type 2 have some conductivity around 2×10^4 μS/cm. This phenomenon can be attributed to the similar charge density on the anionic surface of the type 1 and type 2 ionic liquids and it illustrates that one must not only focus on viscosity, molecular weight, or density, but also keep in mind the importance of the charge density on the iron when searching for highly conducting ionic liquids.

The thermal stability of the new ionic liquids in air or nitrogen was examined by Mettler Toledo thermogravimetric analysis at a heating rate of 2 K/min. Figure 2 shows the TG and SDTA data for $Na_{13}[Ce(TiW_{11}O_{39})_2]\cdot32.6H_2O$. It is important to note that this ionic liquid is only stable up to 308 K in N_2. The two steps of water-loss and the accompanying endothermal process were observed in the TG and SDTA curves in the temperature range 291−673 K. In order to clarify the thermal behavior, the conductivity of $Na_{13}[Ce(TiW_{11}O_{39})_2]\cdot32.6H_2O$ was measured at various temperatures after heating for 1 h in air. The experimental results are shown in Figure 3. The conductivity of this ionic liquid is almost constant in the temperature range 308−328 K and it decreases rapidly as the temperature increases, which leads to loss of constituent water. This result shows that the new ionic liquid is much less stable and possesses a liquid range of about 65 K with a melting point of around 263 K (see Table 2).

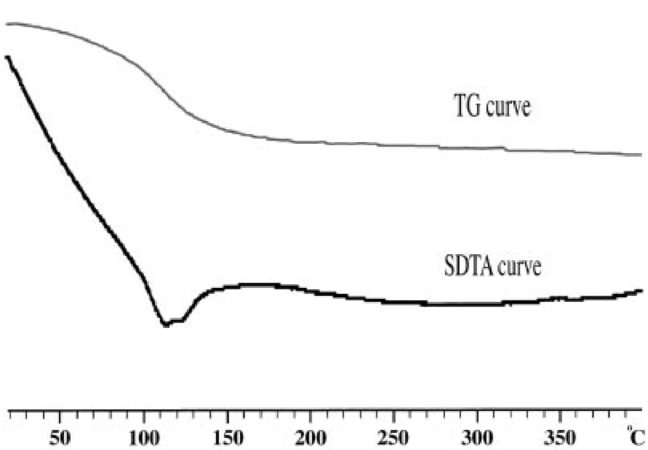

Figure 2. Thermal gravimetric curve and scanning differential thermal analysis curve of $Na_{13}[Ce(TiW_{11}O_{39})_2]\cdot32.6H_2O$

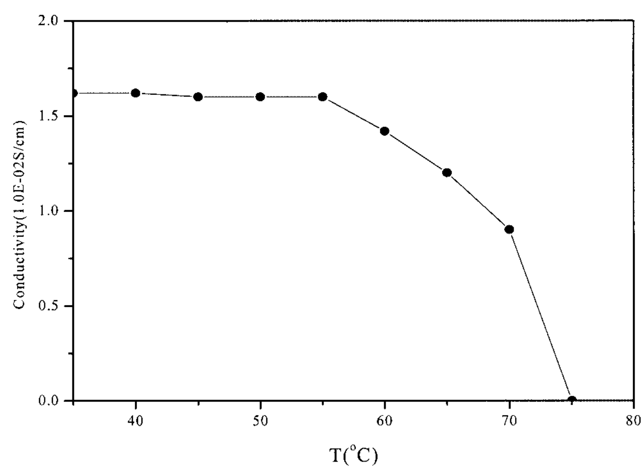

Figure 3. Specific conductivity of $Na_{13}[Ce(TiW_{11}O_{39})_2]\cdot32.6H_2O$ at different temperatures after heating for 1h

All the investigated ionic liquids are immiscible with organic solvents having low, medium and high dielectric constants (ε): cyclohexane (ε = 2.02), benzene (ε = 2.284), carbon tetrachloride (ε = 2.238), toluene (ε = 2.379), diethyl ether (ε = 4.22), chloroform (ε = 4.724), ethyl acetate (ε = 6.02), ethanol (ε = 25.2), methanol (ε = 32.63)and acetonitrile (ε = 37.4), and so forth. They are only miscible with water but their solubility in water varies drastically depending on the temperature. When the temperature is below ambient temperature (about 293 K) these ionic liquids are almost immiscible with water. However, if the temperature is raised , the solubility of the new ionic liquids in water increases. Most of the known ionic liquids are miscible with common organic solvents and with water, which leads us to believe that these ionic liquids may play an unexpected role in some fields such as separation and biphasic catalysis.

In order to determine the structure of the anion, the ^{183}W NMR and IR spectra of the new ionic liquids were recorded on a Bruker DRX400 nuclear magnetic resonance spectrometer, and on a Nicolet NEXUS 670 FT-IR spectrometer. The ^{183}W NMR and IR spectra of $Na_{13}[Ce(TiW_{11}O_{39})_2]\cdot 32.6H_2O$ and $Na_6(ZnTiW_{11}O_{39})\cdot 27.2H_2O$ are shown in Figures 4 and 5. The ^{183}W NMR (Figure 4) and IR (Figure 5) spectra of $Na_6(ZnTiW_{11}O_{39})\cdot 27.2H_2O$ reveal six very strong, well-resolved resonance lines and four infrared bands in the $400-1200 cm^{-1}$ range, in accordance with eleven tungsten atoms involved in the expected Keggin structure (C_s symmetry) with a lacunary site.[32] The infrared spectra of $Na_{13}[Ce(TiW_{11}O_{39})_2]\cdot 32.6H_2O$ is virtually identical to that of $Na_6(ZnTiW_{11}O_{39})\cdot 27.2H_2O$, which proves that the ligand with a mono-vacant Keggin structure $(TiW_{11}O_{39})^{8-}$ consists of the new ionic liquid $Na_6(ZnTiW_{11}O_{39})\cdot 27.2H_2O$ and $Na_{13}[Ce(TiW_{11}O_{39})_2]\cdot 32.6H_2O$. However, there is a marked difference between the ^{183}W NMR spectra of $Na_6(ZnTiW_{11}O_{39})\cdot 27.2H_2O$ and that of $Na_{13}[Ce(TiW_{11}O_{39})_2]\cdot 32.6H_2O$ (see Figure 4). Ten stronger well-resolved resonance lines and some weaker resonance lines were observed in the ^{183}W NMR spectra of $Na_{13}[Ce(TiW_{11}O_{39})_2]\cdot 32.6H_2O$. This phenomenon may be due to the presence of the paramagnetic center Ce^{III} and of the isomer with a different configuration[33] or to the small magnitude of the other anionic component in the ionic liquid $Na_{13}[Ce(TiW_{11}O_{39})_2]\cdot 32.6H_2O$, as was observed in [emim]Cl-$AlCl_3$[34−36] ionic liquids.

In summary, a new series of inorganic ionic liquids consisting of an inorganic polyoxometalate anion with the Keggin structure and a sodium cation were prepared and investigated. They are the first examples of inorganic ionic liquids containing only one kind of inorganic compound and possessing different physicochemical properties from those of the known organic-inorganic ionic liquids or organic ionic liquids. Some of the characteristics of these new ionic liquids are not so desirable but they can enrich the

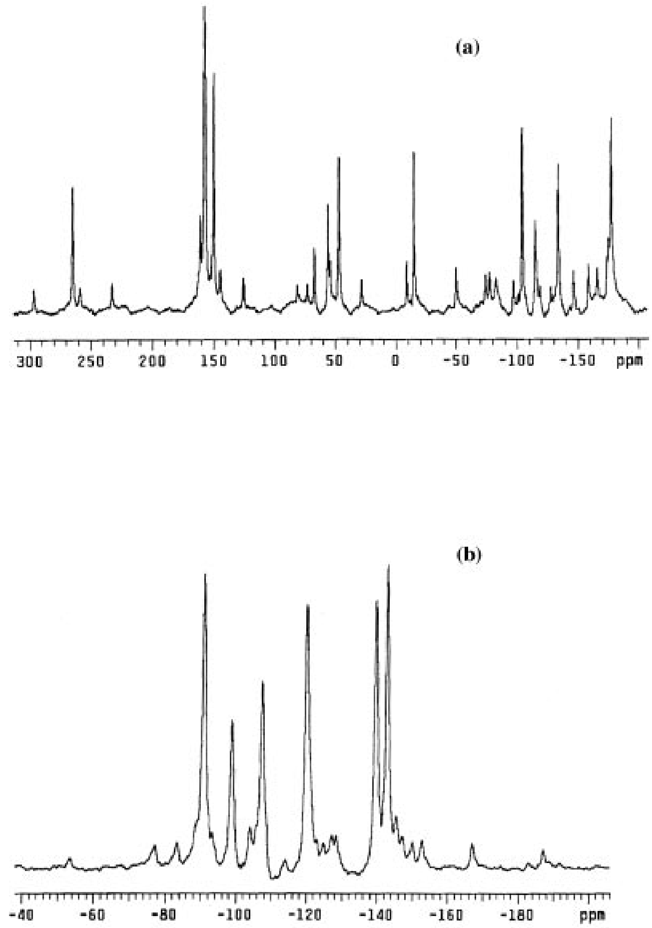

Figure 4. ^{183}W NMR spectra of $Na_{13}[Ce(TiW_{11}O_{39})_2]\cdot 32.6H_2O$ (a) and $Na_6(ZnTiW_{11}O_{39})\cdot 27.2H_2O$ (b)

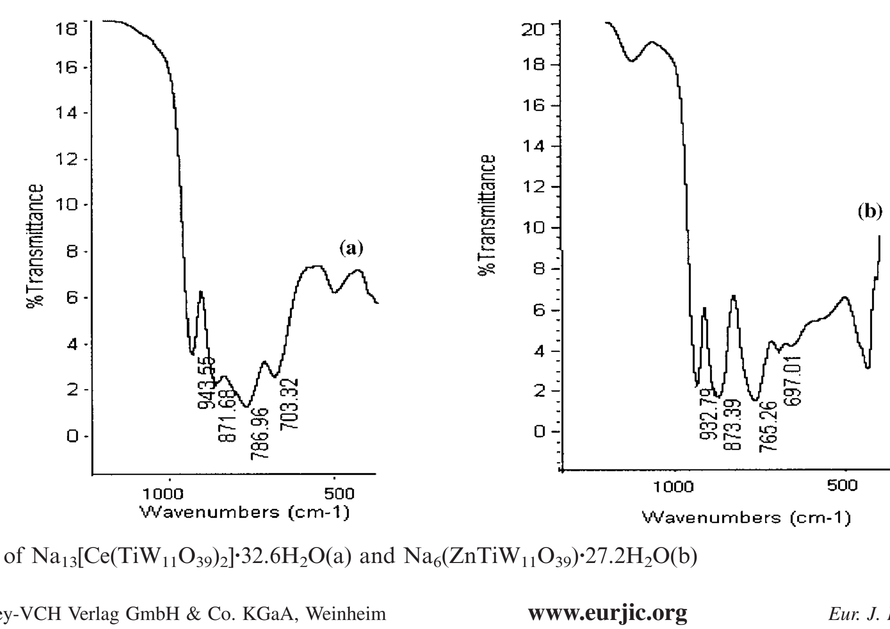

Figure 5. IR spectra of $Na_{13}[Ce(TiW_{11}O_{39})_2]\cdot 32.6H_2O$(a) and $Na_6(ZnTiW_{11}O_{39})\cdot 27.2H_2O$(b)

chemistry of ionic liquids and open up new opportunities for further research in this field. It is extremely important to be able to access tailor-made ionic liquids for biphasic catalysis and novel separation techniques.

Experimental Section

Preparation of the Inorganic Ionic Liquids: $Na_{13}[Ln(TiW_{11}O_{39})_2]\cdot xH_2O$ (Ln = lanthanide) were prepared by dissolving sodium tungstate (36.3 g, 0.11 mol) in water (200 mL). $TiCl_4$ (1.099 mL, 0.01 mol) was added to the solution with stirring violently. The pH was adjusted to 6 with glacial acetic acid. The mixture was refluxed at 333 K for half an hour, then about 5 mL of a solution containing 0.005 mol of $Ln(NO_3)_3$ was added to the hot mixture. After stirring for 2.5 h at 333 K, the mixture was filtered and the filtrate was cooled to room temperature in a beaker. Anhydrous ethanol (50 mL) was added to the cool filtrate. The product, a colored oil, was collected at the bottom of the beaker.

The method of preparation of $Na_5[MTiW_{11}O_{39}]\cdot xH_2O$ and $Na_6[MTiW_{11}O_{39}]\cdot xH_2O$, (M = transition metal; type 2) is similar to that of type 1. The difference between the two is only the amount of metal salt used as a starting material. In the case of a transition metal, the amount of salt added is 0.01 mol, rather than 0.005 mol of the lanthanide salt.

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