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Ionic Liquids

Expanding the Electrochemical Window: New Tunable Aryl Alkyl Ionic Liquids (TAAILs) with Dicyanamide Anions

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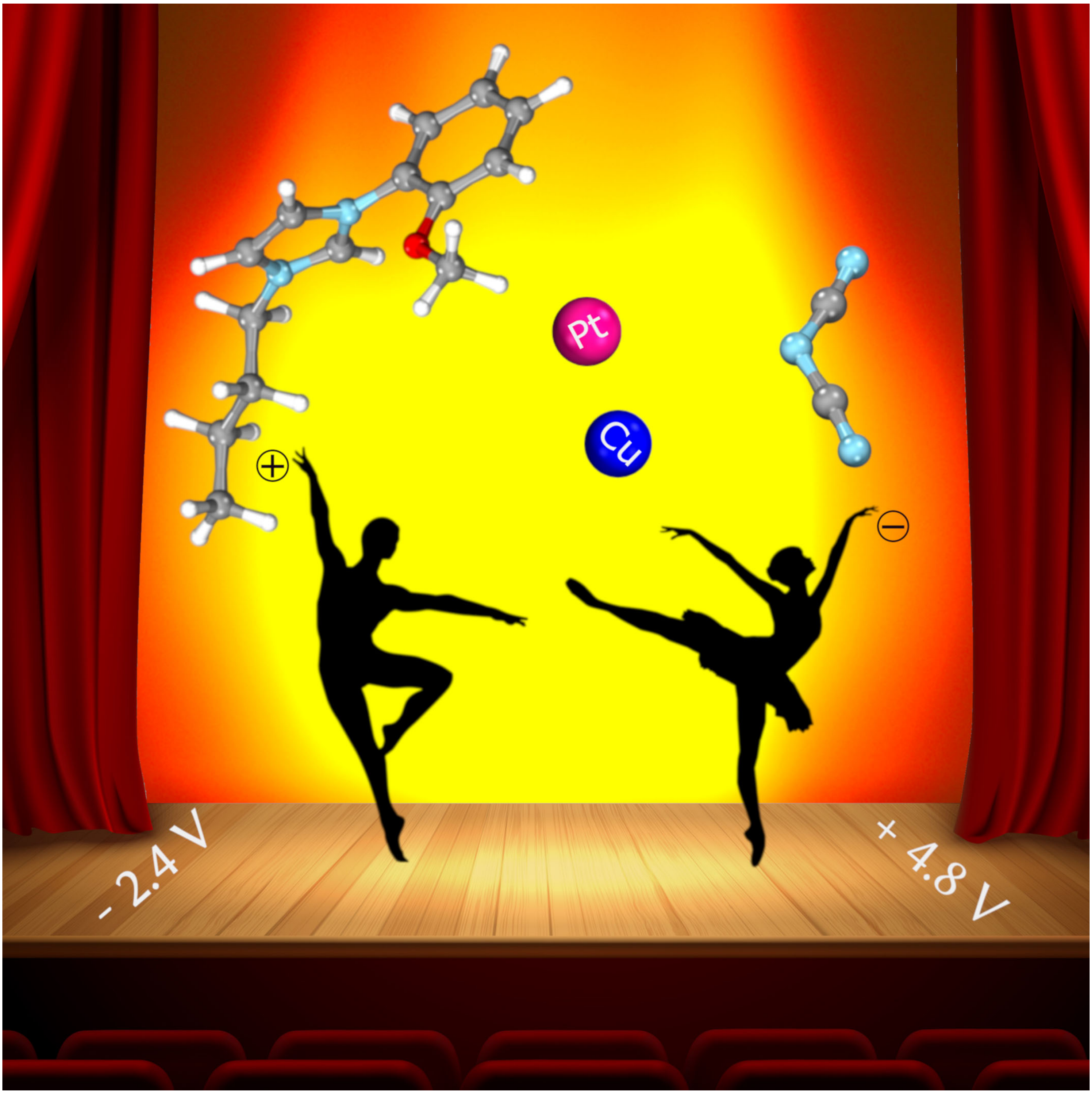

Abstract: A set of new tunable aryl alkyl ionic liquids (TAAILs) based on the 1-aryl-3-alkyl imidazolium motif has been synthesized, in which the following variables were systematically changed: alkyl chain length, aryl substitution (group and position), and counter ion. TAAILs with dicyanamide (DCA) and bis(trifluoromethylsulfonyl)imide ($N(SO_2CF_3)_2$, NTf_2) anions showed remarkable differences of their physical properties: NTf_2 ionic liquids were found to have high decomposition temperatures and viscosities well below those of the DCA TAAILs. In contrast, the dicyanamide anion increased the electrochemical stability leading to TAAILs with an extremely wide electrochemical window of up to 7.17 V. Additionally, both classes of TAAILs extract transition metals from aqueous solutions: TAAILs with the DCA anion extract both platinum and copper while TAAILs with the NTf_2 anion are selective towards platinum. This demonstrates that minor changes of the molecular structure lead to TAAILs with drastically changed physicochemical properties.

Introduction

Over the past decades, ionic liquids (ILs) have attracted attention due to their unique physicochemical properties. They can be used as solvents in organic synthesis,[1,2] as a catalyst in homogeneous catalysis,[3–8] in dye-sensitized solar cells,[9,10] as electrolytes in batteries or supercapacitors,[11–17] for the extraction[18–26] and deposition[27–31] of metals, and for the stabilization of nanoparticles.[32–35] They have also been used as lubricants[36,37] and in nanoelectronics.[38] Per definition, these salts have a melting point below 100 °C, are conductive, have a negligible vapour pressure and show an extremely high thermal stability.

ILs are composed of organic cations and organic or inorganic anions, which allows for a great variability of structural motifs and hence of their physical properties.[39,40] Common cations used are all-alkyl ammonium-, phosphonium- or imidazolium-based moieties.

In 2009, we introduced a new class of imidazolium-based ionic liquids, the so called tunable aryl alkyl ionic liquids (TAAILs, Figure 1).[41,42] Over the past years, we demonstrated that the phenyl ring not only alters melting points and thermal stabilities, but also allows to fine tune the physicochemical properties according to one's requirements.[43] In collaboration with the Krossing group, we combined the weakly coordinating tetrakis- (1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)borate ($B(CH_2(CF_3)_2)_4$, B(hfip)$_4$) anion with TAAIL cations, yielding ionic liquids with remarkable low glass transition points.[44] The Janiak group used TAAILs for the synthesis of ruthenium and iridium nanoparticles.[45] They observed that both nanoparticle size and size distribution are drastically influenced by the aryl substitution of the TAAIL cation. TAAILs also proved to be suitable solvents in transition metal catalysis, for example, the hydrosilylation[46] or the hydroamination and hydroarylation.[47] By introducing palladium-containing anions, we extended the range of catalytically active ionic liquids.[48]

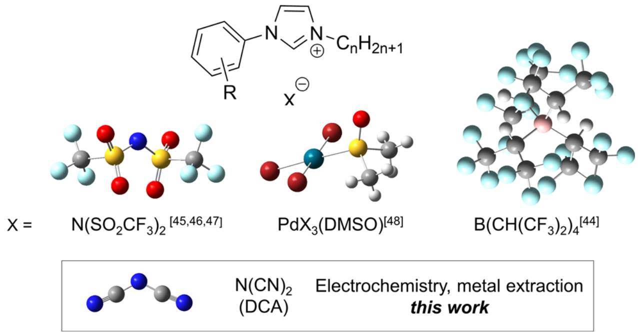

Figure 1. General structure of TAAILs and recent applications featuring different anions.

Recently, it was reported that the dicyanamide (DCA) anion led to remarkable improvements of the viscosity and electrochemical window (EW) of ammonium-, phosphonium- and imidazolium-based ionic liquids leading to be promising candidates for the applications mentioned above.[54–57]

Therefore, we were interested in the combination of the dicyanamide anion with different TAAIL cations and its influence on the physicochemical properties of the resulting materials. To further investigate the structure–property correlation, we synthesized a set of TAAILs with different aryl substituents in the *ortho*- and *para*-position and different alkyl chain lengths (butyl, octyl and dodecyl) with both the DCA anion and the bis(trifluoro-methylsulfonyl)imide ($N(SO_2CF_3)_2$, NTf_2) anion for comparison. We examined the thermal properties, electrochemical stability, viscosities and metal extraction performance of these two classes of ionic liquids.

Results and Discussion

Synthesis

TAAILs are accessible by a three-step synthesis starting from commercially available aniline derivates (see Scheme 1). In the first step, a ring-closing reaction is performed using aniline, formaldehyde, glyoxal and ammonium chloride. The reaction can be done in a 6 L batch reactor on a scale of up to 0.5 kg of aniline, yielding substituted aryl imidazoles **1**–**4**. The follow-

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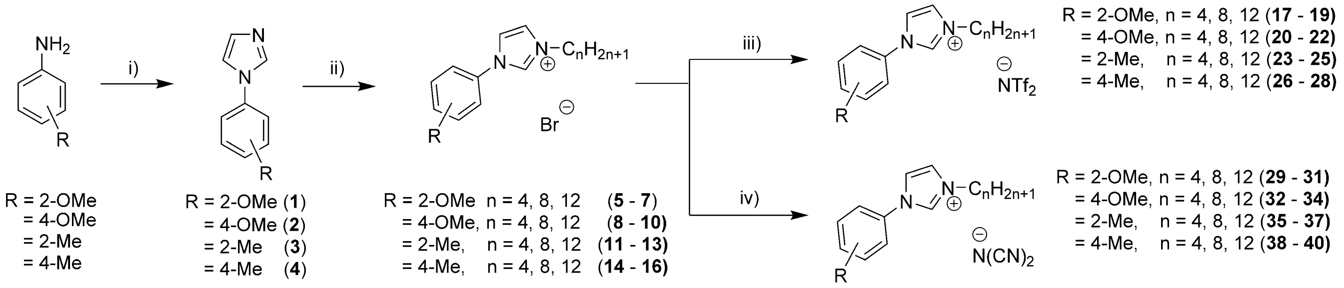

Scheme 1. Synthesis of ionic liquids: i) 1.1 equiv. glyoxal, 2.1 equiv. formaldehyde, 2 equiv. NH_4Cl, cat. H_3PO_4, MeOH, 60 °C, 24 h; ii) 1.1 equiv. alkyl bromide ($C_nH_{2n+1}Br$), THF, 70 °C, 2–7 d; iii) 1.1 equiv. $LiNTf_2$, DCM/MeOH/H_2O, rt, 24 h; vi) 1.5 equiv. $NaN(CN)_2$, H_2O, rt, 24 h.

ing alkylation with different alkyl bromides gives TAAILs **5**–**16** with bromide counterion, synthesized as previously reported by our group in multi-molar scale.[47] Anion exchange with lithium bis(trifluoromethylsulfonyl)imide ($LiNTf_2$) afforded the corresponding TAAILs **17**–**28**.

Dicyanamide ILs are generally obtained by the reaction of the chloride or bromide salt with $AgN(CN)_2$.[49,50,53] To avoid any silver contamination, TAAILs **29**–**40** were synthesized following a modified protocol of Boudesocque and co-workers.[54] The corresponding bromide salt is suspended in sodium dicyanamide solution in water (1.5 equivalents) and stirred at room temperature for 24 hours. The crude product is then extracted with dichloromethane three times. For complete anion exchange, the organic layer is washed with sodium dicyanamide solution (1 equivalent) and twice with water. After removal of the solvent, the ionic liquids were dried in high vacuum for 16 hours. All TAAILs described were obtained as liquids at room temperature, thus belonging to the class of room temperature ionic liquids (RTILs). The synthetic procedures, analytical data, and NMR spectra of TAAILs **5**–**40** are given in the Supporting Information.

Thermal properties

Glass transition points of TAAILs **17**–**40** were measured via differential scanning calorimetry (DSC) in the range of 20 °C to −80 °C with a scanning rate of $1\,K\,min^{-1}$ using a Mettler Toledo DSC1. Thermal decompositions (T_d) were measured via thermogravimetric analysis (TGA) using a Netzsch STA 409 PC/PG measuring between 30 °C and 500 °C with a heating rate of $5\,K\,min^{-1}$. The T_d is given at 5 % mass loss. The results are given in Table 1, TG and DSC plots are given in the Supporting Information.

For ILs with a short or medium alkyl chain, very low glass transition points were observed ranging between −50 °C and −71 °C which is in the same order as those reported for TAAILs with the $B(hfip)_4$ anion.[44] TAAILs with the long dodecyl chain show different solidification characteristics: for DCA TAAILs **37** and **40** crystallization temperatures were found at −36 °C and −13 °C upon heating, respectively. For TAAILs **19**, **22** and **31**, no solidification could be observed upon cooling, but upon heating, a crystallization was observed. TAAILs **25**, **28** and **34** show no solidification at temperatures above −80 °C.

Table 1. Physicochemical data of TAAILs **17**–**40**. T_g(h/c): glass transition point upon heating/cooling in [°C], t_d: thermal decomposition temperature in [°C], [a] crystallization temperature.

TAAIL	T_g(h/c)	T_d	TAAIL	T_g(h/c)	T_d
17	−61/−61	372	**29**	−57/−59	265
18	−63/−60	367	**30**	−59/−60	270
19	−13[a]/< −80	335	**31**	−24[a]/< −80	264
20	−61/−62	369	**32**	−58/−60	270
21	−61/−61	314	**33**	−61/−60	256
22	−9[a]/< −80	333	**34**	< −80	279
23	−66/−67	402	**35**	−62/−63	279
24	−71/−71	390	**36**	−65/−67	270
25	< −80	311	**37**	−36/−27[a]	267
26	−56/−58	334	**38**	−60/−62	267
27	−61/−61	367	**39**	−60/−61	277
28	< −80	375	**40**	−13/−41[a]	264

Thermal decomposition occurs between 311 °C and 402 °C for NTf_2 salts and between 256 °C and 279 °C for DCA salts. Thus, ILs with the NTf_2 anion are thermally more stable than their dicyanamide analogues. Still, TAAILs with the DCA anion show a higher thermal stability than other unsymmetrical 1,3-dialkyl imidazolium salts where the decomposition temperature is between 220 °C and 240 °C.[51] For most ILs with the NTf_2 anion, the decomposition temperature decreases with longer alkyl chains. This trend is not seen in DCA ILs where the decomposition temperature does not change significantly with either aryl substitution or alkyl chain length.

Electrochemical behavior

The electrochemical properties of ionic liquids depend strongly on the molecular structure of the salt. The cathodic limit is dependent on the cation and the anodic limit is determined by the anion.[55–59] For imidazolium cations, the alkyl chain length has only a minor influence on the electrochemical stability.[59] Therefore, all eight TAAILs with the butyl chain were chosen for electrochemical measurements as their properties can be compared to the well investigated and commercially available 1-butyl-3-methyl-imidazolium analogues. Cyclic voltammograms were measured using a three-electrode set up (glassy carbon working electrode, Pt counter electrode and an Ag/Ag^+ pseudo reference electrode). Table 2 shows the cathodic and

Table 2. Electrochemical windows (EW) of TAAILs with different aryl substitutions and anions at a sweep rate of 100 $mV\,s^{-1}$ and a cut-off current density of 1 $mA\,cm^{-2}$, vs. the Fc/Fc^{+} redox pair.

TAAIL	Cathodic limit	Anodic limit	EW	TAAIL	Cathodic limit	Anodic limit	EW
17	−2.43	+1.44	3.87	**29**	−2.42	+4.75	7.17
20	−2.33	+0.96	3.28	**32**	−2.47	+3.46	5.93
23	−2.33	+1.78	4.11	**35**	−2.53	+2.98	5.51
26	−2.13	+1.26	3.39	**38**	−2.45	+2.96	5.41

anodic limits and the electrochemical window (EW) of these compounds, complete cyclic voltammograms are shown in Figures S71–S78 in the Supporting Information.

The NTf_2 salts **17**, **20**, **23** and **26** have an EW between 3.28 V and 4.11 V at a cut-off current density of 1 $mA\,cm^{-2}$, a little smaller than the EW of the corresponding 1-butyl-3-methylimidazolium NTf_2 IL (4.6 V).[60] The electrochemical stability of TAAILs increases drastically with the DCA anion. TAAILs **29**, **32**, **35** and **38** have extremely wide EWs between 5.41 V and 7.17 V (for comparison, the well-known 1-butyl-3-methylimidazolium DCA IL only has an EW of 4.7 V).[29]

In Figure 2, cyclic voltammograms of ILs **17** and **29** are shown. As both contain the same cation, their cathodic limit is nearly the same with −2.43 V for IL **17** and −2.42 V for IL **29** against the ferrocene redox pair at a cut-off current density of 1 $mA\,cm^{-2}$. The NTf_2 anion leads to an anodic limit of +1.44 V against Fc/Fc^{+}. But we were surprised to learn that the change of the anion to DCA shifts this limit drastically by more than 3 V to +4.75 V vs. Fc/Fc^{+} leading to an EW of 7.17 V. To the best of our knowledge, this is the widest electrochemical window reported for ionic liquids on a glassy carbon electrode so far.[61–64]

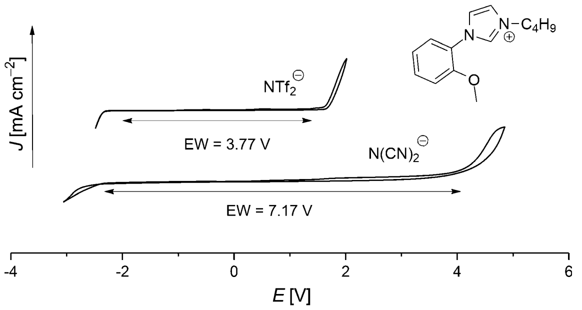

Figure 2. Electrochemical windows of TAAILs **17** (top) and **29** (bottom) with a sweep rate of 100 $mV\,s^{-1}$ and a cut-off current density of 1 $mA\,cm^{-2}$ (vs. Fc/Fc^{+} redox pair).

Viscosity measurements

Viscosities were measured between 20 °C and 80 °C in 5 K steps (see Supporting Information for detailed procedure). In general, viscosities of TAAILs are higher in comparison to common all-alkyl ILs as for example, $[EMIm]NTf_2$ or [EMIm]DCA. This is a result of the higher molecular weight and of the additional π–π interactions of the aryl moieties in the cation.

Figure 3 shows the viscosity of TAAILs **17**–**28** with the NTf_2 anion between 20 °C and 80 °C. The viscosities range between 419 $mPas^{-1}$ for IL **23** and 884 $mPas^{-1}$ for compound **28** at 20 °C. The substitution pattern of the methoxy-substituted ILs has only a minor influence on the viscosity, whereas the *ortho*-methyl substituted ILs **23**–**25** have a lower viscosity in comparison to their *para*-substituted isomers **26**–**28**. More pronounced, the increase of the alkyl chain length results in an increase of viscosity which is in agreement with literature findings and is a result of the increasing molar mass and of the van der Waals interactions of the alkyl chains.[40,65] At 80 °C, the viscosities decrease to values between 25 and 36 $mPas^{-1}$.

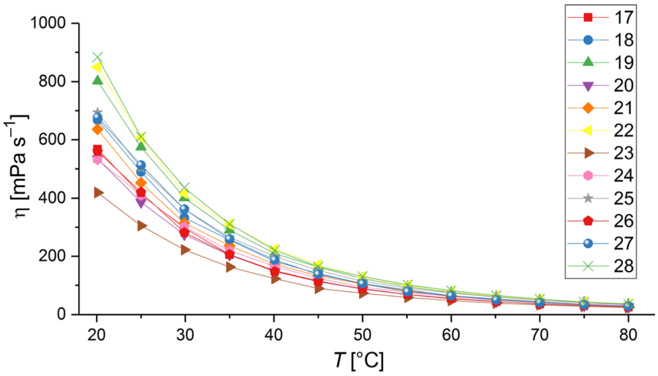

Figure 3. Viscosities of NTf_2 TAAILs **17**–**28** between 20 and 80 °C.

The DCA anion generally leads to an increase of viscosity in comparison to its NTf_2 analogues. Graphic representations of the viscosities of the dicyanamide TAAILs **29**–**40** are shown in Figure S80 (see supporting information). This finding can be explained by additional strong π–π interactions between the phenyl ring and the π-bonds of the cyano groups present in the DCA anion which is known from ILs with the $C(CN)_3$ anion.[66]

Selective extraction of transition metals

The extraction percentage $E\%$ is used to quantify an extraction process and can be calculated using Equation (1)[54] with C_i and C_f defined as the initial and final metal concentration in the aqueous layer.

$$E\% = \frac{C_i - C_f}{C_i} * 100 \tag{1}$$

The extraction of metal ions from an aqueous solution or waste waters is known for TAAILs with the NTf_2 anion. There, long alkyl chains proved to be beneficial for the extraction of platinum.[66] Therefore, different dodecyl substituted NTf_2 (**22** and **28**) and DCA TAAILs (**34**, **37** and **40**) were tested on their extraction behavior towards a 1 mM solution of three transition metal salts (K_2PtCl_4, $CuSO_4$, $NiCl_2$) in water (see Supporting Information for detailed procedure).

The selectivity and extraction efficiency are strongly dependent on the anion (see Table 3). Without further additives, all ILs bearing the NTf_2 anion (**22**, **28**) selectively extract platinum (29 % and 90 %, respectively) and show no extraction of neither copper nor nickel. The DCA ILs **34**, **37** and **40** extract platinum quantitatively and copper with an efficiency of up to 51 % for IL **37**. The extraction of nickel is negligible for all TAAILs under investigation.

Table 3. Extraction efficiency (in %) of TAAILs towards aqueous solutions of the Pt^{II}, Cu^{II} and Ni^{II} salts.

TAAIL	**22**	**28**	**34**	**37**	**40**
Pt	29	90	100	100	100
Cu	0	0	35	51	19
Ni	0	0	3	0	0

ILs **34** ($R=4$-OMe, $n=12$, X=DCA) and **37** ($R=2$-Me, $n=12$, X=DCA) were chosen for successive extraction as they both extract platinum quantitatively. Additionally, TAAIL **37** was tested on the extraction of copper (see Figure 4).

TAAIL **34** extracts platinum quantitatively for the first two runs. Then, the extraction efficiency decreases slowly to 80 % at the 6th run. TAAIL **37** performs slightly better with a complete extraction of platinum for the first three runs and a decrease to 83 % over the following three runs. 72 % of copper is extracted by TAAIL **37** from a 0.5 mM solution of copper(II) chloride, but the extraction efficiency drops to 13 % for the second run and stays almost constant in the following two runs (12 % and 11 %, respectively).

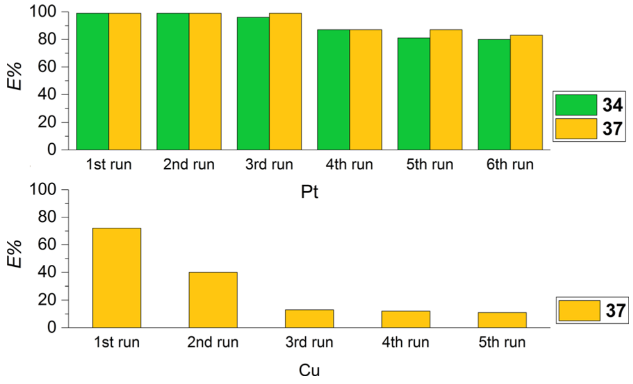

Figure 4. Extraction of Pt^{II} and Cu^{II} with TAAILs **34** and **37**.

Conclusions

New tunable aryl alkyl ionic liquids (TAAILs) with the dicyanamide anion (DCA) and for comparison the bis(trifluoromethylsulfonyl)imide anion (NTf_2) were synthesized leading to ILs with a broad range of physicochemical properties. Thermal analysis (DSC and TGA) revealed glass transition points of below −50 °C for both NTf_2 and DCA TAAILs together with a high thermal stability of up to 402 °C. The electrochemical window is extraordinary wide for DCA TAAILs with an EW of up to 7.17 V. The selective extraction of transition metal cations from an aqueous solution was feasible by the right choice of ionic liquid, depending both on the anion and the aryl substitution. This comparative study emphasizes the versatility of TAAILs: by changing either the anion, the aryl substitution or the alkyl chain length, physicochemical properties as thermal stability, electrochemical window or viscosity, can be modulated as well as the metal extraction behavior can be adjusted.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: dicyanamide anion · electrochemical window · ionic liquids · metal extraction · viscosity

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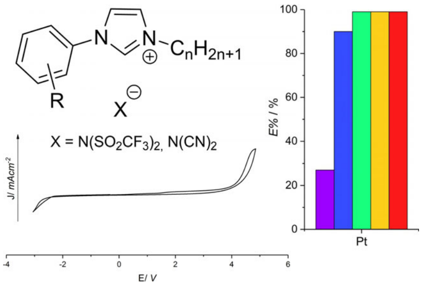
FULL PAPER

Broadening horizons: Different 1-aryl-3-alkyl imidazolium ionic liquids (tunable aryl alkyl ionic liquids, TAAILs) with spectacular electrochemical properties are presented. By changing the molecular system, ILs with thermal stability of up to 402 °C, an electrochemical window of up to 7.17 V and glass transition points below −60 °C could be obtained. Depending on the anion, transition metals were extracted selectively from aqueous solution using different TAAILs.



Ionic Liquids

*S. Lerch, T. Strassner**

■■ – ■■

Expanding the Electrochemical Window: New Tunable Aryl Alkyl Ionic Liquids (TAAILs) with Dicyanamide Anions

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Like two dancers on stage, the anion and cation of an ionic liquid (IL) interact with each other, each one contributing its own properties. With the combination of a 1-aryl-3-alkyl-imidazolium-based cation (TAAIL) and the dicyanamide anion, the authors were able to expand the electrochemical window of these ILs. Furthermore, a compound was synthetized that is able to repeatedly extract transition metals from aqueous solutions. For more details see the Full Paper by T. Strassner et al. on page ■ ■ ff.