

# Synthesis and Physical Properties of Tunable Aryl Alkyl Ionic Liquids (TAAILs)

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**Abstract:** Tunable aryl alkyl ionic liquids (TAAILs) based on the imidazolium cation were first reported in 2009. Since then, a series of TAAILs with different properties due to the electron-donating or -withdrawing effect of the substituents at the aryl ring has been developed. Herein, a wide variety of those ionic liquids (ILs) is presented in terms of their cation structure. The authors synthesized ILs containing the bromide

or bis(trifluoromethane)sulfonimide anion and 1-aryl-3-alkyl imidazolium cations with various substituents in the ortho and/ or para position of the phenyl ring and alkyl chains of different lengths varying from butyl to dodecyl. The differences of their physical properties (melting point, thermal decomposition, viscosity, electro-chemical window) of these ILs are reported according to their structure.

## Introduction

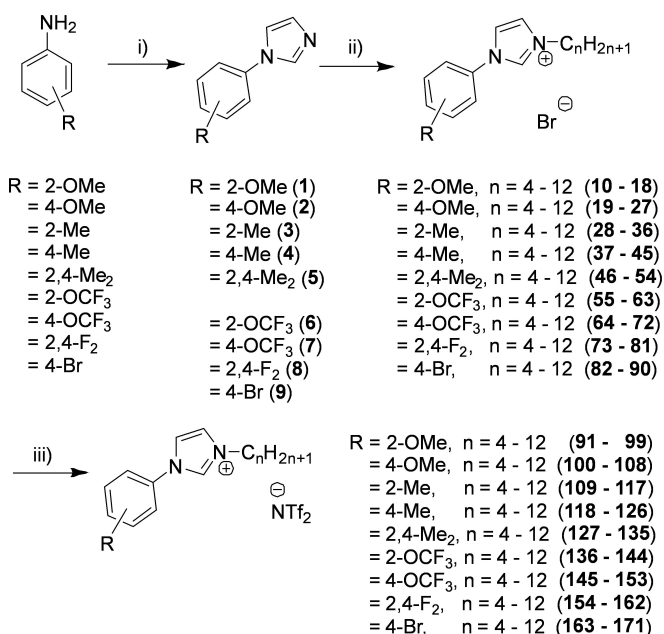
Ionic liquids (ILs) are generally defined as salts with melting points below 100 °C.<sup>[1]</sup> In the last two decades, these compounds developed from an unexpected curiosity<sup>[2,3]</sup> to commercially available compounds<sup>[4]</sup> used as solvents,<sup>[5]</sup> catalysts or catalyst carriers,<sup>[6,7]</sup> electrolytes,<sup>[8–10]</sup> for phase separation<sup>[11,12]</sup> and are discussed as drug carriers.<sup>[13,14]</sup> Their main differences compared to standard organic solvents lie in their high thermal<sup>[15]</sup> and chemical stability,<sup>[16]</sup> their negligible vapor pressure<sup>[17]</sup> and their immiscibility with both water and unpolar solvents.<sup>[18–20]</sup> In general, ILs consist of an inorganic bulky and non-coordinating anion<sup>[21,22]</sup> and an organic cation, for example tertiary ammonium, phosphonium, pyridinium or imidazolium cations.<sup>[23]</sup> In 2009, 1-aryl-3-alkyl-imidazolium based ILs which we named tunable aryl alkyl ionic liquids (TAAILs) were introduced by our group.<sup>[24]</sup> Since then, their application in transition metal catalysis,<sup>[25,26]</sup> metal extraction<sup>[27,28]</sup> and for the synthesis of metal nano particles has been reported.<sup>[29]</sup> This new structural motive allows for the modification not only of its anion and alkyl substitution of the cation, but also by the aryl substitution giving rise to additional ways of controlling the physical and chemical properties of an ionic liquid. Even though we have, so far, reported numerous different structural motives,<sup>[30,31]</sup> no comprehensive summary has been given in which way a modification of the cation structure alters the

physical properties of a TAAIL. Herewith we want to close this gap and give an overview of the correlation between the structure of a TAAIL cation and its influence on the resulting IL.

## Results and Discussion

### Synthesis

TAAILs are accessible by a well-known three-step synthesis starting from commercially available aniline derivatives (see Scheme 1). In the first step, aniline is reacted with formaldehyde



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**Scheme 1.** Synthesis of ionic liquids: i) 1.1 equiv. glyoxal, 2.1 equiv. formaldehyde, 2 equiv. NH<sub>4</sub>Cl, cat. H<sub>3</sub>PO<sub>4</sub>, MeOH, 60 °C, 24 h; ii) 1.1 equiv. alkyl bromide (C<sub>n</sub>H<sub>2n+1</sub>Br), THF, 70 °C, 2–7 d; iii) 1.1 equiv. LiNTf<sub>2</sub>, DCM/ MeOH/ H<sub>2</sub>O, rt, 24 h.

**Table 1.** Melting points of bromide salts 10–90, in °C, n: alkyl chain length, R: aryl substituent, <rt: below room temperature.

n/R	2-OMe	4-OMe	2-Me	4-Me	2,4-Me <sub>2</sub>	2-OCF <sub>3</sub>	4-OCF <sub>3</sub>	2,4-F <sub>2</sub>	4-Br
4	<rt	<rt	36	32	84	<rt	84	107	159
5	66	52	<rt	41	57	26	46	68	87
6	<rt	49	<rt	45	53	44	78	70	69
7	<rt	<rt	37	<rt	53	47	57	46	42
8	<rt	<rt	39	50	52	45	74	56	73
9	58	<rt	72	72	<rt	43	91	47	38
10	42	<rt	<rt	84	38	36	97	59	89
11	45	48	43	59	76	45	98	55	83
12	45	49	57	44	54	41	101	62	59

**Table 2.** Thermal decomposition point at 5% mass loss, in °C, n: alkyl chain length, R: aryl substituent.

n/R	2-OMe	4-OMe	2-Me	4-Me	2,4-Me <sub>2</sub>	2-OCF <sub>3</sub>	4-OCF <sub>3</sub>	2,4-F <sub>2</sub>	4-Br
4	372	369	402	334	373	348	363	347	395
8	367	314	390	367	285	354	346	333	368
12	335	333	311	375	359	341	296	206	341

and glyoxal under acidic conditions giving the 1-arylimidazoles 1–9.<sup>[32]</sup> Subsequently, alkylation using an alkyl bromide in THF is performed to give the bromide salts 10–90. The anion exchange reaction using lithium bis(trifluoromethan) sulfonimide (LiNTf<sub>2</sub>) yields TAAIL 91–171 with the NTF<sub>2</sub> anion that are, with only a few exceptions, liquid at room temperature. This synthesis proved to be very robust tolerating numerous substituted anilines and alkyl chain lengths and is reliable even on a multigram scale (see detailed synthetic procedures and analytical data in the Supporting Information).

### Thermal properties

The melting points of bromide salts 10–90 are given in Table 1. Most of these ILs already meet the definition of an ionic liquid having a melting point below 100 °C.

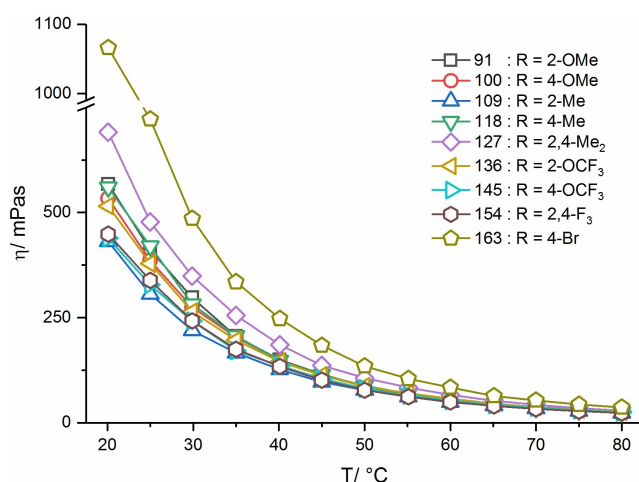
The bromide anion is bulky but also coordinates well to the cation.<sup>[33]</sup> This is why crystallization of the IL occurs regularly. In contrast, if crystallization is not observed at room temperature, this can be contributed to the asymmetry of the cation or the degree of free rotation of its phenyl substituents. For instance, TAAILs with methoxy moieties tend to crystallize less. Also, TAAILs with *ortho*-substituted phenyl rings tend to crystallize less than their *para*-substituted isomers. ILs with fluorinated moieties in *para*-position have higher melting points than their non-fluorinated homologues. This trend is reversed for ILs with *ortho*-substituted methoxy groups. Generally, ILs with fluorinated or di-substituted phenyl rings crystallize better than their non-fluorinated or mono-substituted counterparts. For increasing alkyl chain lengths, there are no general trends of melting point changes deducible. This is different from the standard ILs with two alkyl groups at the imidazolium core and can be attributed to two different physical trends: with increasing chain length, the molar mass rises and van-der-Waals (VdW) interactions increase, therefore melting points are expected to increase as well. But longer alkyl chains may get entangled,

hindering the formation of a crystal lattice, hence causing lower melting points or even prevent crystallization.

As noted above, all TAAILs with the NTF<sub>2</sub> anion are liquid at room temperature with the exception of the 4-bromido-substituted IL 165 (n=6). Their thermal decomposition temperatures lie between 206 °C (TAAIL 162) and 402 °C for IL 109 (see Table 2, Figures S1–S17). In general, thermal decomposition occurs at higher temperatures for short alkyl chains and TAAILs with fluorinated cations are thermally in general as stable as their non-fluorinated analogues. TAAILs with the bromido-substituent show high thermal decomposition temperatures that, again, decrease for longer alkyl chains.

### Viscosity measurements

The viscosities of TAAILs with different aryl substitutions and the butyl chain are shown in Figure 1 (see also Table S1). At

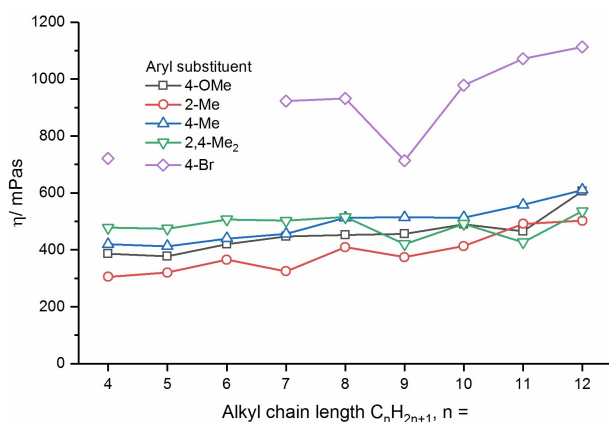
**Figure 1.** Temperature-dependent viscosity measurement of TAAILs with butyl chain and different aryl substitutions R.

20 °C, there are two groups of TAAILs with almost the same viscosity. The lowest values of around 400 mPas were measured for ILs with 2-methyl (**109**), 4-OCF<sub>3</sub> (**145**) and 2,4-F<sub>2</sub> (**154**) substitutions. The second group, with viscosities between 500 and 650 mPas at 20 °C consists of ILs **91** (2-OMe), **100** (4-OMe), **118** (4-Me) and **136** (2-OCF<sub>3</sub>). The TAAILs with the 2,4-methyl (**127**) and the 4-Br (**163**) substitution have the highest viscosities with 690 mPas and 1066 mPas, respectively. At 45 °C, the first two groups have similar viscosities of approximately 100 mPas, above 70 °C, there is no difference seen between the viscosities of all TAAILs displayed.

To examine the viscosities of TAAILs in dependence of the length of the alkyl chain,<sup>[34]</sup> Figure 2 (Table S2) shows the viscosities of TAAILs with different aryl substituents at 25 °C. Again, due to the increasing molar mass, an increase in viscosity is expected. This trend can be seen for TAAILs of the two groups of Figure 1. For TAAILs with the 2,4-dimethyl substitution, the alkyl chain has almost no influence on the viscosity indicating that the aryl moiety of the cation has a greater influence on the viscosity than the additional mass contributed by the alkyl chain.

The viscosities of TAAILs with the 4-bromido-substituted cations are very different. They are in general significantly higher compared to all other systems and additionally the viscosity increases with the exception of the TAAIL with n=9 (**168**) when the alkyl chain gets longer. These buckles are, to a smaller extent, also seen for TAAILs with 2-methyl (n=7, **112**) and 2,4-dimethyl (n=9, **132** and n=11, **134**) substitutions. These spikes cannot be explained, but may be attributed to complex interactions<sup>[35,36]</sup> between several chains of different cations forming nonpolar domains within the liquid.

The water content plays an important role in the measurement of viscosities.<sup>[37–39]</sup> The water content of the TAAILs was determined prior to all measurements to be below 100 ppm. The influence of the water content was studied for TAAIL **101** (R=4-OMe, n=5). Without drying, this IL has a water content of 1100 ppm and a viscosity of 494 mPas at 20 °C. After drying in high vacuum at room temperature, the water content was decreased to 121 ppm and the viscosity increased to 555 mPas.



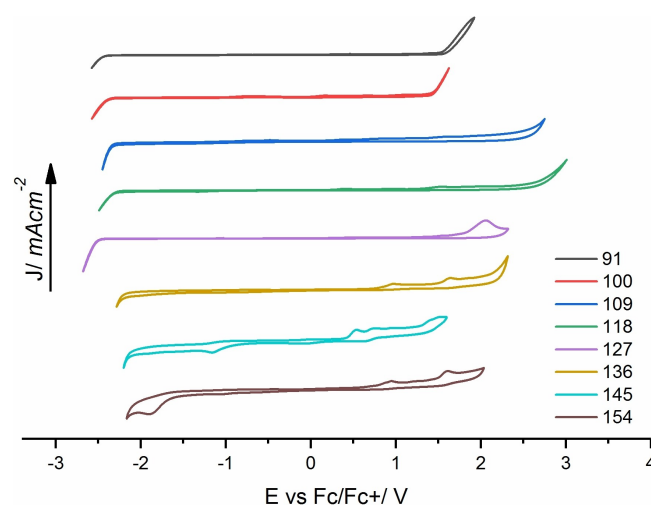
**Figure 2.** Viscosities of different TAAILs depending on their alkyl chain lengths and aryl substitution at 25 °C.

After drying in high vacuum at 70 °C, the water content was measured to be 23 ppm and the viscosity at 20 °C was 590 mPas (see Supporting Information (Figure S18) for the temperature dependence of these measurements).

### Electrochemical behavior

In order to use TAAILs either in electrochemical applications or as solvents in redox reactions,<sup>[40]</sup> their electrochemical stability has to be evaluated.<sup>[41–43]</sup> Figure 3 shows the electrochemical windows (EWs) of TAAILs with different aryl substitutions and the butyl chain.

Cyclic voltammograms were measured using a three-electrode setup with a glassy carbon working electrode, Pt counter electrode and a Ag/Ag<sup>+</sup> pseudo reference electrode. The sweep rate was 100 mV/s and the cut-off current density was set to 1 mA/cm<sup>2</sup>. The values are references vs. the ferrocene redox pair (Fc/Fc<sup>+</sup>). As seen in Figure 3, TAAILs **91** and **100** with methoxy-substituted cations have EWs of 3.8 V and 3.3 V, respectively. TAAILs **109** and **118** with one methyl group have considerably broader EWs of 4.1 V and 4.4 V, respectively. IL **127** with the 2,4-dimethylphenyl substitution has an EW of 4.0 V and is therefore comparable to the other two methyl-substituted TAAILs. There is no difference of EWs between ILs with cations with *ortho*- and *para*-substituted phenyl rings. Formally, the fluorinated TAAILs **136**, **145** and **154** have EWs of 4.4 V, 3.6 V and 3.9 V, but several irreversible redox reactions can be seen for all three salts. Their electrochemical stability is therefore lower than the stability of TAAILs with methoxy- or methyl substitutions. These values for the electrochemical window of ionic liquids lie in the same range as commercially available ILs with the NTf<sub>2</sub> anion, for example [EMIm]NTf<sub>2</sub> and [BMIm]NTf<sub>2</sub> with EWs of 4.4 V and 4.3 V, respectively.<sup>[44]</sup> In order to increase the EWs of TAAILs, the use of the dicyanamide anion<sup>[45]</sup> has been proven to be beneficial.<sup>[28]</sup>



**Figure 3.** Electrochemical windows of TAAILs with different aryl substitutions, butyl chain and NTf<sub>2</sub> anion, current density J vs. potential E vs. Fc/Fc<sup>+</sup> redox pair.

## Conclusions

With this work, we report the physical properties of more than 160 different 1-aryl-3-alkyl imidazolium-based tunable aryl alkyl ionic liquids (TAAILs) with the bromido or the bis-(trifluoromethane)sulfonimide anion (NTf<sub>2</sub>). The aryl moieties of the cation carry methoxy-, methyl-, trifluoromethoxy-, fluoro- or bromide-substituents and the alkyl chain length was varied from butyl to dodecyl. Most ILs were found to be liquid at room temperature with thermal decomposition temperatures ranging from 206 °C (TAAIL 162) to 402 °C (TAAIL 109). Their thermal stability is higher in case of shorter alkyl chains. The viscosity of TAAILs is strongly dependent on the aryl substitution and generally increases with longer alkyl chains. Whether the substituent is in ortho or para position has no predictable influence on the viscosity. As known from the standard alkyl-substituted ILs, water has a strong effect on the viscosity of TAAILs. The electrochemical windows of TAAILs lie between 3.3 V and 4.4 V with the highest stability for ILs with 2- or 4-methylphenyl substituted cations.

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## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** electrochemical window · ionic liquids · TAAIL · thermal properties · viscosity

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