Purification or contamination? The effect of sorbents on ionic liquids†

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Commonly used for purification, alumina and silica are found to contaminate ionic liquids with particles; these particles cannot be removed easily and can have a non-negligible impact on the electrochemical, spectroscopic and physical properties of an ionic liquid, including its nucleation and crystallisation kinetics.

The popularity of ionic liquids (ILs) as solvents and electrolytes has risen greatly over the last twenty years. Two properties that make ILs especially appealing, in some cases, are low or non-existent freezing points and negligible vapour pressures.[1] It is these two properties, however, that make ILs difficult to purify by traditional crystallisation and distillation techniques. For this reason, sorbents such as activated carbon, alumina and silica are commonly used, and have proven useful in the removal of organic and/or coloured impurities.[2] The assumption that sorbents are easily and completely removed is so widespread that, in most cases, very little experimental detail is given regarding their use, or the techniques employed for their removal. Recently, evidence has arisen that alumina is left behind as a trace level contaminant in certain ILs, and that this contamination has an impact on subsequent electrochemical responses.[3] Trace sorbents are also likely to have an impact on the physical, spectroscopic and catalytic properties of an IL; it is therefore essential to determine the nature and level of contamination caused by common sorbents.

Contrary to the usual lack of information regarding the use of sorbents, Passerini and co-workers[4] undertook an extensive study on the use of alumina and carbon to decolourize 1-methyl-1-butylpyrrolidinium bis(trifluoromethylsulfonyl)-amide. The methods developed in their studies were used as a basis for the work in this article.‡

To investigate particulate contamination, dynamic light scattering (DLS) experiments were performed. These experiments produced average count rates, in kilocounts per second (kcps), where:

$$\text{Average count rate} \propto (\text{diameter of particles})^6 \times (\text{number of particles})$$

The average count rates for 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([C$_4$mim][NTf$_2$]), 1-hexyl-3-methyl-imidazolium bromide ([C$_6$mim][Br]) and 1-ethyl-1-methyl-pyrrolidinium dicyanamide ([C$_2$mpyr][DCA]) before and after exposure to alumina, silica and carbon are shown in Table 1. The noise level for the experiments was approximately 20 kcps, as evidenced by the average count rates for [C$_4$mim][NTf$_2$] (14 kcps) and [C$_6$mim][Br] (19 kcps) before exposure to any sorbents. [C$_2$mpyr][DCA], however, showed an above average noise level of 56 kcps before exposure. This IL was synthesized *via* a metathesis reaction between [C$_2$mpyr][Br] and AgDCA to precipitate AgBr. The AgBr was removed by passing the sample through a 200 nm filter; however, the average count rate strongly suggests that some AgBr particles remained. These particles are a concern, and are likely to have an impact on subsequent physicochemical measurements. All ILs showed significant increases in their average count rates after exposure to alumina and silica, with silica-exposed [C$_6$mim][Br] showing the highest level at 846 kcps. Interestingly, samples exposed to carbon did not show a significant increase in particle content. As discussed further below, there is differential scanning calorimetry (DSC) evidence of the presence of particles in the carbon-exposed sample, but in this case, it appears that DLS is not sensitive to these particles at the low levels involved.

The effective diameters, as determined by DLS measurements, of the alumina and silica particles were typically between 100 and 1000 nm. These diameters suggested the particles may be removed by a 200 nm PTFE filter. Table 2 shows the average count rates for samples after filtration through a 200 nm PTFE filter. As expected, 200 nm filtration did not affect the particle content of the non-exposed and carbon-exposed samples. While 200 nm filtration did significantly decrease the number of alumina and silica particles, only alumina-exposed [C$_4$mim][NTf$_2$] showed a negligible average count rate after 200 nm filtration, demonstrating that even after this filtration, most ILs were still contaminated with a significant quantity of particles.

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Table 1 DLS count rates for different ILs before and after exposure to sorbents

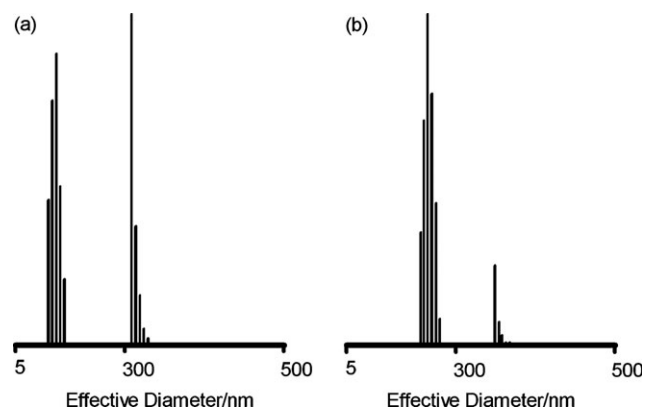| IL	—	Average count rate (kcps ± 9%) after exposure to:		
		Alumina	Silica	Carbon
[C$_4$mim][NTf$_2$]	14	67	517	22
[C$_6$mim][Br]	19	816	846	18
[C$_2$mpyr][DCA]	56	131	666	56

Table 2 DLS count rates for different ILs before and after exposure to sorbents—after 200 nm filtration

	Average count rate (kcps ± 9%) after exposure to:			
IL	—	Alumina	Silica	Carbon
$[C_4mim][NTf_2]$	21	21	226	20
$[C_6mim][Br]$	20	173	184	12

Table 3 ICP-OES analysis of $[C_4mim][NTf_2]$

Sorbent	Decontamination method	Aluminium content/ppm	Silicon content/ppm
—	Celite	<10	<5
	200 nm filter	<10	<5
Alumina	Celite	<10	<5
	200 nm filter	<10	<5
Silica	Celite	<10	190
	200 nm filter	<10	<5

Fig. 1 shows the multimodal size distribution graphs for silica-exposed $[C_6mim][Br]$ after filtration through Celite (Fig. 1(a)) or a 200 nm filter (Fig. 1(b)). These graphs show two distributions of particle size, above and below 300 nm.

This bimodal size distribution makes it difficult to accurately determine particle size; however, as expected, the graphs clearly show that 200 nm filtration decreases the proportion of particles larger than 300 nm relative to those smaller than 300 nm.

Samples of $[C_4mim][NTf_2]$ were analysed for silicon and aluminium content by inductively coupled plasma-optical emission spectroscopy (ICP-OES), and Table 3 shows the results of these analyses. Before 200 nm filtration, the silica-exposed sample showed a considerably high silicon content of 190 ppm; after 200 nm filtration, however, this level decreased to <5 ppm. All the remaining samples showed silicon and aluminium contents below the detection limits of 5 ppm (Si) and 10 ppm (Al).
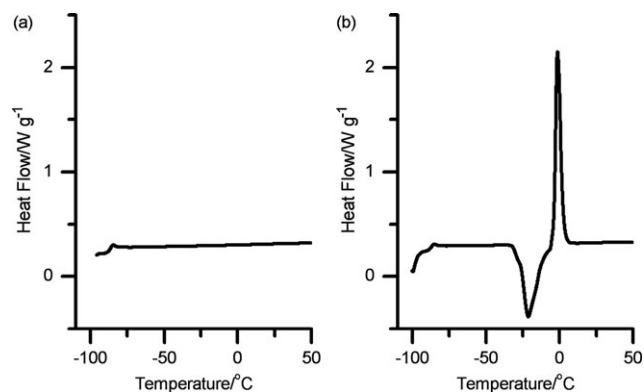
The above results show that alumina and silica contaminate ILs with particles. While in most cases the contamination level is low (<10 ppm), it has already been shown that this contamination can affect the electrochemical properties of an IL.[3] DLS shows that the particles scatter light, and will therefore affect the spectroscopic and optical properties of an IL. To demonstrate the effect of sorbent contamination on the physical properties of an IL, carbon-, alumina- and silica-exposed $[C_4mim][NTf_2]$ samples were analysed by DSC. Broadly speaking, there is a strong effect of all of the sorbents on the kinetics of the crystallisation and melting transitions of the ILs; the non-exposed samples did not show any tendency to freeze during DSC cooling, nor melt on subsequent warming, and therefore exhibited no melting transition. The samples therefore appeared to be good glass formers. After filtration through Celite, all of the sorbent-exposed samples showed strong

Fig. 1 Multimodal size distribution for silica-exposed $[C_6mim][Br]$ (a) before and (b) after 200 nm filtration.

Fig. 2 DSC traces for $[C_4mim][NTf_2]$ (a) before and (b) after exposure to alumina (after 200 nm filtration in both cases).

crystallisation and melting points, indicating that the nanoparticles act as potent crystal nucleation agents for these ILs.

Fig. 2 shows the DSC traces for unexposed and alumina-exposed $[C_4mim][NTf_2]$. After 200 nm filtration, there was a sharpening of the crystallisation and melting points for the carbon- and alumina-exposed samples. The silica-exposed sample once again showed no tendency to freeze or melt, indicating that the filtration, though leaving a fraction of the particles, removed those capable of inducing nucleation.†

In conclusion, ILs exposed to alumina or silica sorbents are contaminated with ppm levels of sorbent particles, even after 200 nm filtration. The complete removal of these particles may require advanced synthetic techniques, such as distillation[5] or zone melting.[6] DLS appears to be a useful means for detecting their presence in the cases of alumina and silica. The DLS experiments do not indicate the presence of particles in the case of carbon; however, the DSC results clearly suggest that such particles are, nonetheless, present. Due to their impact on the physicochemical properties of ILs, it is hoped that this Communication will encourage more thorough reporting on the use and removal of sorbents during the synthesis of ILs.

Notes and references

‡ *Experimental:* $[C_6mim][Br]$,[7] $[C_4mim][NTf_2]$[8] and $[C_2mpyr][DCA]$[9] were synthesized as previously described. Activated alumina (acidic, Brockmann I, Aldrich), silica gel (60 230-400 mesh ASTM, Merck), activated carbon (SAJ first grade, Aldrich) and Celite (Celpure® P65,

Aldrich) were used as received. All solvents were HPLC grade and passed through a 0.2 μm PTFE membrane before use.

Contamination experiments: In a typical experiment, 5 g IL was dissolved in 5 mL 2-propanol; sorbent (either no sorbent, 2.5 g alumina, 2.5 g silica or 1 g carbon) was then added and the sample left to stir for 5 h at room temperature (10 h at 70 °C for carbon exposure). The slurry was then filtered through Celite and the volatiles removed *in vacuo*. Due to its insolubility in 2-propanol, all [C$_2$mpyr][DCA] samples were dissolved in ethyl acetate.

Dynamic light scattering: A zeta potential analyser (BI-ZETAPALS, Brookhaven) equipped with a BI 90 correlator board was used to evaluate particulate matter within the samples. All samples were diluted to 25 wt% in 2-propanol (ethyl acetate for [C$_2$mpyr][DCA] samples) before analysis. Samples were run in triplicate, giving a 9% error in average count rates.

ICP analysis: 0.2 g samples were prepared in 4 mL concentrated nitric acid and made up to a volume of 10 mL with water. The homogeneous solutions were then diluted 5-fold with water and analysed using a Varian VISTA ICP-OES.

Differential scanning calorimetry: Measurements were made with a Perkin-Elmer DSC7 calorimeter at a scanning rate of 10 °C min^{-1}. All samples were prepared and run in duplicate, with consistent results.

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