An unusual effect of charcoal on the purification of alkylimidazolium iodide room temperature ionic liquids

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Activated charcoal, commonly used for purification of ionic liquids is found, for the first time, to severely contaminate 1-butyl 3-methyl imidazolium iodide with iodine species during the conventional purification process. Surprisingly, the contaminants which includes I$_3^-$, reduces the viscosity of the ionic liquid considerably as compared to externally added molecular iodine, making it extremely promising for electrochemical applications.

Keywords: Ionic liquids, Room temperature ionic liquids, Activated charcoal, Purification, Iodine

Ionic liquids (ILs) raise considerable research interest, not only as promising new solvents for the replacement of conventional solvents in synthesis, but also as new liquid materials. Like in many other materials, purity is a major concern for applications, especially in spectroscopic and biological studies. Identification of the impurity in the ILs is of importance since their presence is found to have a strong impact on the physico-electro-chemical properties$^1$. In general, ILs have very low vapor pressure making it difficult to purify these liquids through distillation$^5$. The usual practice is to treat the samples with sorbents such as activated carbon, alumina and silica$^{1,3,4}$. These procedures have been found to be useful in removing organic and coloured impurities$^{5,6}$. Very recently, Clare and coworkers$^7$ have reported the complicacy that may arise out of using sorbents. In their significant paper they have revealed that the use of alumina or silica (to a lesser extent, charcoal) may introduce small particles of sorbents which can not be removed using normal procedures. Further, they have shown that alumina and silica particles are not innocent on the physical properties and may have non-negligible effects on spectroscopic and electrochemical properties.

Among various room temperature ILs, iodide containing ILs have been extensively considered as nonvolatile substitutes for liquid iodide electrolyte solution in dye-sensitized photoelectrochemical cells$^{8,10}$. It has been found that the performance of such cells is greatly influenced by the type of ILs and their structure and properties. Addition of molecular iodine (I$_2$) is required for constituting the I/I$_3^-$ redox couple (I$^-$+I$_3^-$⇌I$_2$+I$^-$). Depending upon the concentration of added I$_2$, various polyiodide species with high ionic conductivity can form, which actually contributes to the observed high short circuit currents in dye-sensitized photoelectrochemical cells. This basically compensates for the detrimental effect of high viscosity associated with RTIL containing iodine$^{11}$.

Herein, we report for the first time that charcoal, a sorbent used commonly, is found not to be innocent in nature. For a specific ionic liquid having iodide as anion, it causes colorization instead of decolorization. More interestingly, this apparent color impurity is found to be iodine or iodine containing complex anion. This in situ-generated species can actually be a benefit for electrochemical applications of iodide containing ILs as discussed later.

Materials and Methods

The N-methylimidazole (Sigma Aldrich, redistilled, >99 %) and iodobutane (Merck, Germany) were used as received for the synthesis. Activated charcoals were procured from Sigma Aldrich, (Norit carbon) and Merck, Germany. Iodine (granular, resublimed, >99 %) was procured from Merck, Germany, while sodium thiosulphate pentahydrate (98.5 %), copper
sulphate pentahydrate (99 %) and potassium iodide (99 %) were procured from Merck, India, and were used as received. Acetonitrile (HPLC grade) was procured from Merck, Germany, while diethyl ether and ethyl acetate (LR grade) were obtained from Merck, India, and were used after purification following standard procedures.

UV-visible spectra were recorded on a Cary 100 BIO UV-visible spectrophotometer, which has photometric linearity till absorbance 3. The 300 MHz (Jeol) and 400 MHz (Bruker) NMR instruments were used to record the $^1$H NMR and $^{13}$C NMR spectra respectively. The bulk viscosities of ILs at different temperatures were measured by a LVDV-III Ultra Brookfield Cone and Plate viscometer connected to a Julabo water circulator (model F32) for variable temperature measurements.

**Synthesis of bmimI**

The N-methylimidazole (12.75 ml, 161 mmol) was dissolved in 20 ml of dry acetonitrile followed by slow addition of butyliodide (20 ml, 176 mmol) at 0 °C with constant stirring under N$_2$ atmosphere in dark. The solution was left at 0 °C for 2 h and then stirred for 72 h while keep the temperature below 40 °C. Acetonitrile was then evaporated at reduced pressure at the same temperature. A pale yellow colored viscous liquid was obtained (yield: 94 %) which was then washed with dry ethyl acetate and dry diethyl ether and further dried under reduced pressure for 5 h. Special precautions were taken to eliminate the presence of water or organic solvents in the ILs. The product was confirmed by NMR and IR spectra. We also followed the reported procedure$^{8,10}$ (which uses higher temperature, 70 °C) of synthesizing bmimI, but found that the produced ILs is considerably darker in color.

**Estimation of iodine**

The bmimI (6.0 g) was diluted with 10 ml dry acetonitrile and stirred with 4.0 g of activated charcoal for 10 min under nitrogen atmosphere. Then it was filtered through Celite and PTFE membranes (0.2 µm). During these processes or due to the passage through charcoal column, some amount of ionic liquids is always lost. The acetonitrile was evaporated under reduced pressure at 40 °C and the sample was kept under high vacuum for 5 h to obtain a brown colored liquid (referred as charcoal treated bmimI in the text). This brown liquid (4.45 g) was taken in a stoppered conical flask for the iodimetric titration. Separately, sodium thiosulphate (hypo) solution was prepared and standardized by known strength of copper sulphate solution and excess potassium iodide. This standardized hypo solution was used for the estimation of dissolved iodine in the brown solution by iodimetric titration using freshly prepared starch solution as an indicator. Iodine dissolved in the brown solution was found to be 5.37 g/l (±12 %). Prior to this iodimetric titration, we tested the bmimI and charcoal treated bmimI with an iodine indicator starch paper and observed the color change to dark blue for the latter, indicating the presence of dissolved iodine. Though bmimI has a very pale yellow color, neither the iodine indicator nor the iodimetric titration indicated presence of any dissolved iodine. Since bmimI was found to be light sensitive, all the sample preparation and handling were done either in dark or in least possible light and air exposure.

**Results and Discussion**

**Coloration instead of decoloration**

In order to purify bmimI by the usual method, the pale yellow colored sample (bmimI) is passed through a column packed with activated charcoal. As soon as it passes through the column, a brown colored liquid comes out. The prominent difference in color, as shown in (Fig. 1) clearly indicates that the iodide IL undergoes some kind of change during the passage through the activated charcoal packed column. Various activated charcoals procured from different sources have been used to check whether the observation is source specific or not. It has been observed that this colorization of iodide IL takes place with different kinds of charcoal that have been tested.

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![Passing through column containing activated charcoal](image)

Fig. 1 — Darkening of bmimI when passed through the column containing activated charcoal.
The colorization process is reasonably fast and the depth of the color does not change much when the IL is stirred over night with activated charcoal.

To know whether the color change is due to change in cation (such as loss of proton from C2 carbon to form any iodide adduct) or anion moiety, $^1$H NMR and IR spectra of the untreated bmimI and charcoal treated bmimI were recorded. Other than the small changes in chemical shifts for the interacting (with anion) protons, no change in NMR spectrum (included as Supplementary data) was found in the spectrum of the charcoal treated bmimI, indicating that cation (bmim) is unaffected by the charcoal treatment. The small changes in the chemical shift for the imidazolium ring protons further indicate that there is indeed a change in the type of anion. We have also performed a comparative experiment with KI solution passing through the column having the same activated charcoal but did not observe any change of color indicating that the colorization process is specific to ILs. Further, a number of other imidazolium cation based iodide ILs have been tested for activated charcoal mediated purification process and have been found to produce darker ILs.

**UV-visible spectrum**

Since there is clear difference of color of the samples, UV-visible spectra of the bmimI (i.e., charcoal untreated), and the brown colour IL (charcoal treated bmimI) were recorded (Fig. 2). As seen in the figure, the absorption maxima for charcoal treated bmimI is considerably red-shifted. In addition to a hump at 380 nm, the maxima appear at 497 nm. The reason for pale yellow color in bmimI is not very clear though reported earlier$^{12}$. Theoretical calculation indicates that the color is due to the weak charge transfer transition ($n \rightarrow \pi^*$) between I$^-$ and cation moiety$^{13}$. The reason for passing the ILs through charcoal even though we are aware that it should have pale yellow color is that charcoal absorbs the colored organic impurity that may get involved during the process of synthesis as is the case with other imidazolium halide ILs.

The large red shift on charcoal treatment indicates the possible involvement of I$_2$. To confirm the presence of iodine as well as for its estimation, iodimetric titration (vide experimental section) was carried out. While, as expected, bmimI did not respond to the iodometric titration, charcoal treated bmimI was found to contain iodine (free or complexed), which was available to thiosulphate to get reduced. The estimated iodine was found to be 5.4 g/l ($\pm$12 %). In addition, the presence of I$_2$ (as well as I$_3^-$) is also confirmed in the NIR-Raman spectrum of charcoal treated bmimI$^{14}$.

Having confirmed the in situ generation of iodine due to the charcoal treatment, we looked for plausible reasons. The presence of active oxygen in activated charcoal is thought to be a possible reason for oxidation of iodide to iodine. It is known that during the process of activating the charcoal, oxygen gas is released which gets trapped in the minute pores of charcoal. It is likely that the activated charcoal oxidizes the iodide anion to iodine when iodide anion gets trapped in the pores. So, it is the active oxygen residing in the pores which oxidizes the iodide$^{15}$. It appears that oxygen adsorbed on the surface is not responsible for the colorization since reheating the charcoal in an oven under nitrogen atmosphere did not make any difference. That the simple oxygen molecule is not responsible for coloration is also clear from the fact that not much change in color was observed when oxygen gas was bubbled for 15 min through bmimI IL. Another alternative possible mechanism for the generation of I$_3^-$ species has recently been suggested by Gardner et al.$^{16}$ According to this mechanism, iodine atom is formed via the oxidation of iodide anion which reacts with another I$^-$ to produce short lived intermediate I$_2^-$ (di-iodide) species. This generated I$_2^-$ reacts with another I$^-$ leading to the formation of I$_3^-$. 

![Fig. 2 — UV-visible spectra of bmimI and charcoal treated bmimI. [1, bmimI; 2, charcoal treated bmimI.]](image-url)
Viscosity measurements

During the course of investigation, we also observed that the charcoal treated bmimI (brown bmimI) is considerably less viscous than the bmimI. This is quite surprising in view of the reports in the literature that the presence of excess amount of chloride enhances the viscosity of IL\textsuperscript{17}. To compare the viscosity of charcoal treated bmimI with that of bmimI having the same amount of I\textsubscript{2} added externally, we prepared a bmimI solution having approximately 5.4 g/l dissolved iodine. Viscosities of the bmimI, charcoal treated bmimI, externally added I\textsubscript{2} in bmimI (hence forth represented as bmimI-I\textsubscript{2}) were measured between 10 °C and 70 °C. The viscosity of bmimI was found to be 448 cP at 25 °C and with decrease in temperature the viscosity increases rapidly (at 15 °C, the viscosity doubled). With increase in temperature, a similar sharp decrease in viscosity is observed (at 40 °C, viscosity drops to 117 cP), but at higher temperature the dependence is much less pronounced (16 % change on changing the temperature from 60 to 70 °C). This temperature effect is clearly depicted in Fig. 3. Similar temperature dependence of viscosity for ILs have also been reported by Majer and coworker\textsuperscript{18}.

When I\textsubscript{2} is added externally, a slight increase in viscosity is observed as expected. We have also observed that if the synthesis of bmimI is carried out at elevated temperature, a darker yellow colored bmimI having higher viscosity is obtained.

Surprisingly, the charcoal treated bmimI, having \textit{in situ} generated iodine species possesses significantly lower viscosity at all the temperatures. The viscosity at 25 °C (133 cP) is about 70 % less than the untreated bmimI (448 cP). This drastic decrease is almost uniform (50-60 %) throughout the temperature range. It clearly indicates that the generated iodine species is not the same as that in the case of externally added iodine. This significant decrease in viscosity of charcoal treated bmimI having \textit{in situ} generated iodine species can have considerable significance from the point of view of electrochemical application such as dye-sensitized photo electrochemical cells. Further, the unique local structure of IL\textsuperscript{19} efficiently stabilizes these complex anions. There are examples of this kind where the unique local structures of ILs helped in stabilizing various unstable species. These complex anions make the local structure considerably smaller, thereby reducing the viscosity.

In order to get the activation energy associated with these viscous materials, we have used an Arrhenius-like equation as shown in Eq. (1), which correlates viscosity with temperature,

$$\eta = \eta_{\infty} \exp\left(-\frac{E_a}{RT}\right)$$  \hspace{1cm} \text{...(1)}

where $\eta_{\infty}$ is the viscosity at infinite temperature and $E_a$ is the activation energy. The activation energies were determined from the best fit of the equation to the experimental data. The $E_a$ for the bmimI is found to be 59.35 kJ/mol which is close to that of bmimI-I\textsubscript{2} (63.92 kJ/mol). These values are considerably higher than that of charcoal treated bmimI ($E_a = 48.88$ kJ/mol). Another advantage of the charcoal treated bmimI for use in electrochemical cell is that it is found to be more stable than the bmimI solution of externally added I\textsubscript{2}, as evident from the temperature dependent viscosity measurements. Hence, this \textit{in situ} generated iodine species containing bmimI is a more promising IL than the presently used combination of IL and externally added I\textsubscript{2} solution.

We now also think that activated charcoal disturbs the chloride and bromide anions. Since the chlorine is colorless and bromine is light colored, it may have been overlooked. This may require a revisit. We are in the process of studying this charcoal treated bmimI by Raman and NMR spectroscopy to understand the structural aspects of cation and anions and identification of other anionic species.\textsuperscript{20}

![Fig. 3 — Viscosities of bmimI, charcoal treated bmimI and bmimI containing added iodine as a function of temperature. The lines correspond to the best fit of the data by Eq. 1. [1, bmimI; 2, charcoal treated bmimI; 3, bmimI + added iodine].](image)
Conclusions
Herein, we report for the first time, that activated charcoal is not suitable for the purification of iodide based imidazolium ILs. Instead of removing the color impurity, it \textit{in situ} generates iodine species. This \textit{in situ}-generated iodine species surprisingly reduces the viscosity of IL to a large extent, making it a very promising medium for electrochemical cells. The purification with activated charcoal is used so commonly that this report may raise caution about the validity of the method for purifying the ionic liquids.

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Supplementary Data
Supplementary data including NMR and Raman spectra may be obtained from the authors on request.

References
13 Since the sample (charcoal treated bmimI) is dark brown in colour, we have used NIR laser for getting the Raman spectrum of the sample. The spectrum showed peaks at 100 cm\(^{-1}\) and 140 cm\(^{-1}\) which are assigned to symmetric and asymmetric stretching \(I_3^\text{-}\) respectively (vide Supplementary Data).
14 It is well known that for a normal reduction process involving one mole of O\(_2^\text{-}\), two moles of water molecules are required. It may appear that water molecules intruded in the ionic liquid system are responsible. We have specially dried the solvents and carried out the reaction and workup in dry conditions to rule out the possibility of interference of water. The result that we obtained using dry condition is same, i.e., darkening of bmimI on passing through the charcoal. Moreover, we have not observed any change in IR spectra of charcoal treated in comparison to untreated bmimI.
19 As oxidation of two iodide anions generates one \(I_2^\text{-}\), it is obvious that some other species is reduced in the process and balances the net charge of the system. However, as of now, we have not been able to identify this species. Work in this direction is currently underway.