Dye Redissolution after Precipitation with a Water-miscible Ionic Liquid

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Redissolution of five popular cationic dyes with a water-miscible ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate after their near quantitative precipitation from aqueous solutions is observed. The behavior of the ionic liquid is similar to that of a salt at lower concentrations, while it acts like a cosolvent at higher concentrations.

Ionic liquids (ILs) are gathering increased attention from both academic and industrial researchers mainly due to their unusual properties.[1–8] Interesting and unique applications of ILs have been demonstrated in many sub-disciplines of analytical chemistry, such as, electroanalysis, separation, extraction, spectrometry, and sensing.[1–3,9–12] Among these, the most unusual features of ILs, in our opinion, have emerged from the investigations in the area of extraction processes involving ILs.[1–3,9,12–24]

Dyestuff has diverse and important industrial applications. Unfortunately, as a consequence, they are unavoidably present in wastewaters giving rise to potential hazards due to their inherent toxicity. Significant amounts of synthetic textile dyes that are highly water-soluble are lost into waste-streams during the manufacturing of dyestuff and other textile processing operations.[25] Because of their high water solubility, these dyes are generally fairly difficult to remove by usual waste-treatment operations. Efficient, rapid, cost-effective, and environmentally friendly treatment of dyestuff from real aqueous matrices has always been a major issue. In this letter, we demonstrate unique aspects of a completely water-miscible IL 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF_4) in resolubilization of popular cationic dyes after their efficient precipitation from aqueous solutions. The structures of the five cationic dyes investigated are presented in Figure 1.

Aqueous solutions of the five dyes were prepared at 0.075, 0.75, and 1.5 mM using doubly distilled deionized water. UV–vis molecular absorption spectra of these dye solutions were obtained (Figure S1A).[26] As soon as 1.5 wt % IL bmimBF_4 was added to each of these dye solutions almost quantitative precipitation of all the dyes occurred, and the intensely colored dye solutions turned clear. Precipitated dyes are characterized by ^{1}H NMR spectra which were found to be identical to those of the stock dyes. UV–vis molecular absorbance spectra of aqueous solutions of the precipitated dyes were compared with those obtained earlier for stock dyes and found to be similar (Figure S1B).[26] Efficiency of the precipitation process was calculated as % recovery (=[(weight of the recovered dye/weight of the initial dye) × 100]%), and is reported for all five dyes at three different initial concentrations in Figure 2. It is clear that as the dye concentration increases in the aqueous solution, % recovery of the dye increases in general. Dependence of bmimBF_4 wt % on % recovery of the dyes was also investigated by varying bmimBF_4 wt % from 0.5 to 20 for 1.5 mM MB solution. Surprisingly, no significant changes were observed in % recovery as bmimBF_4 wt % is changed. While a minimum % recovery of 95.0 ($\pm$1.0)% was observed for 0.5 and 20 wt % added bmimBF_4, maximum % recovery was 97.5 ($\pm$1.0)% for ca. 2 wt % added bmimBF_4 (Figure S2).[26] It can be inferred that addition of small amounts of water-miscible bmimBF_4 can induce almost quantitative precipitation of these dyes.

The most interesting feature of our studies was the redissolution of these dyes as the bmimBF_4 wt % was increased. Depending upon the dye and its concentration, at a certain bmimBF_4 wt % the dye completely redissolves. Figure 3 shows the redissolution of MB as bmimBF_4 wt % is increased. Further, the amount of bmimBF_4 required to redissolve the dye was

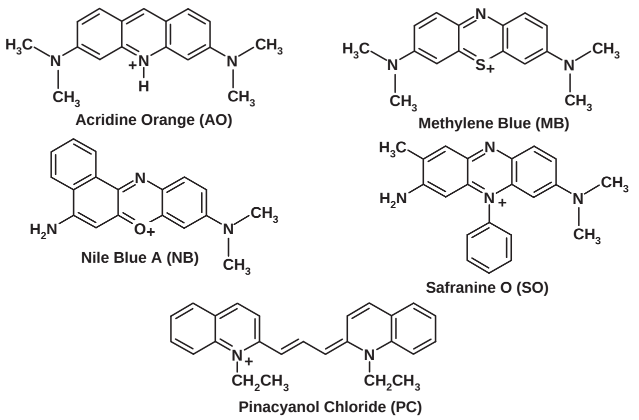

Figure 1. Structures of the five cationic dyes used in this investigation.

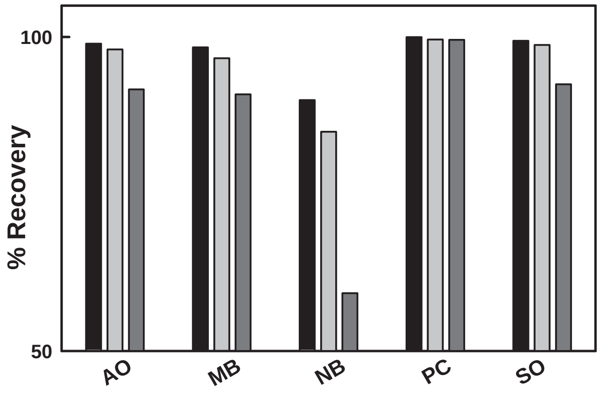

Figure 2. % Recovery of dyes after addition of 1.5 wt % bmimBF_4 to aqueous dye solutions at ambient conditions. Bars from left to right represent 1.5, 0.75, and 0.075 mM of dye, respectively. Errors with recovery are <2%.

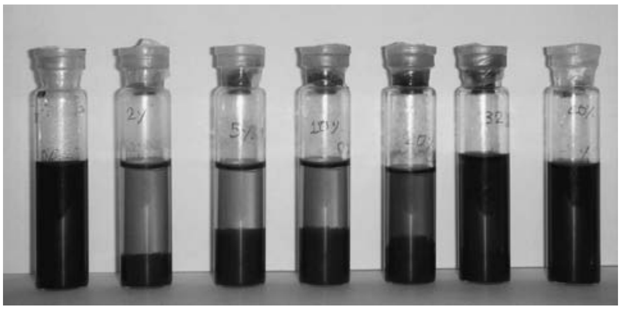

Figure 3. Aqueous solutions of MB after addition of (from left) 0, 2, 5, 10, 20, 32, and 40 wt % $bmimBF_4$ at ambient conditions.

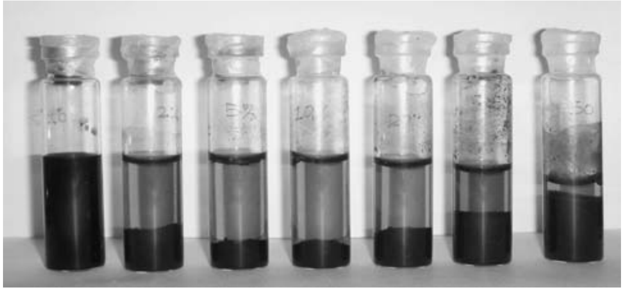

Figure 4. Aqueous solutions of MB after addition of (from left) 0, 2, 5, 10, 20, 25, and 50 wt % KBF_4 at ambient conditions.

found to strongly depend on the aqueous dye concentration. The dependence of wt % $bmimBF_4$ needed to redissolve MB on molar concentration of MB is shown in Figure S3.[26] As the concentration of dye is increased, the amount of $bmimBF_4$ required to redissolve the dye also increases. Interestingly, an acceptable linear behavior can be proposed between wt % $bmimBF_4$ required to redissolve MB and log [MB] ($r^2 = 0.9882$ was recovered from the linear regression analysis, Figure S3).[26] It is important to mention that although the cause of the precipitation of the dyes described earlier could be attributed largely to the exchange of anions of the dyes with that of IL $bmimBF_4$, redissolution of the dyes was found to be IL specific (% recoveries of the dyes were observed to be similar with KBF_4, redissolution of the dyes could not be observed even with very high concentrations of aqueous KBF_4 (Figure 4)). Further, addition of aqueous KBF_4 introduces an additional solution preparation step in such extraction processes, while usage of solid KBF_4 is inconvenient. It can be suggested that at lower IL concentrations the role of $bmimBF_4$ is similar to that of a salt in the solution, whereas at higher concentrations, the IL behaves more like a cosolvent, and hence, helps in redissolution of the dyes.

We also investigated the effect of pH, ionic strength, and temperature of the aqueous dye solution on the efficiency of precipitation and dye recovery with this water-miscible IL. 1.5 mM aqueous dye solutions of pH 3.2, 6.6, and 11.1 were prepared and 1.5 wt % $bmimBF_4$ was added to each of the dye solution. It was observed that for most dyes, % recoveries were within ±2% at the three pH investigated (Figure S4).[26] Changes in the ionic strength of the dye solutions also resulted in almost no significant alterations in the % recoveries of dyes (a decrease and an increase to some extent with increasing ionic strength in % recoveries were observed for 1.5 mM AO and NB with addition of 1.5 wt % $bmimBF_4$, respectively (Figure S5)).[26] Dye precipitation at ca. 4 °C showed similar % recoveries as compared to those at ambient temperature; % recovery appeared to increase slightly for 1.5 mM NB after the addition of 1.5 wt % $bmimBF_4$ at ca. 4 °C (Figure S6).[26]

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26 Supporting Information is available electronically on the CSJ-Journal website, http://www.csj.jp/journals/chem-lett/.