Efficient Precipitation of Dyes from Dilute Aqueous Solutions of Ionic Liquids

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The addition of only ~1.7 wt% (~0.06 M) ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate to aqueous solutions of six popular cationic dyes resulted in the precipitation of almost all of the dye from the solution.

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Due to their unusual properties, ionic liquids are garnering increased attention from academic and industrial research communities alike.¹ Almost every named synthesis and many more organic/inorganic/organometallic reactions have been reported in ionic liquids.² Novel analytical applications of ionic liquids are emerging every day; effective, and in some cases unique, utilizations of ionic liquids have been demonstrated in a variety of techniques encompassing electroanalysis, separation, extraction, spectrometry, and sensing.¹ More specifically, unique features have emerged during many investigations of extraction processes involving ionic liquids.^{1,3} Some of the initial reports on the utilization of ionic liquids in extraction started to appear in the mid-to-late 1990's.⁴ These reports hint towards an unexplored potential of ionic liquids in extraction-based applications.

Optical dyestuff has diverse industrial applications. Unfortunately, as a consequence, they are often present in wastewater and give rise to potential hazards due to their inherent toxicity. For example, 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.⁵ Since most of these dyes have high water solubility, they are generally difficult to remove by the usual waste-treatment systems. Efficient, rapid, cost-effective, and environmentally-friendly removal of dyestuff from aqueous media has always been a major issue.

In this paper, we present an efficient, rapid, and remarkably-easy way of efficiently extracting cationic dyes from their aqueous solutions using popular ionic liquids. We have demonstrated that the addition of only ~1.7 wt% (~0.06 M) of ionic liquids to the aqueous solutions of six popular cationic dyes resulted in almost complete precipitation of each dye from its aqueous solution. The structures of the six cationic dyes investigated are presented in Fig. 1.

Aqueous solutions of the six dyes were prepared at three different concentrations of 75 μ M, 750 μ M, and 1.5 mM at room temperature using doubly distilled deionized water. The UV-Vis molecular absorption spectra of the dye solutions were obtained. To these dye solutions, *ca.* 1.7 wt% (0.06 M) ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF₆) was directly added. The solubility of bmimPF₆ in water under ambient conditions is *ca.* 2.1 wt%.⁶ Immediate precipitation of dyes was clearly evident in each case, as demonstrated in Fig. 2 for one of the dyes, pinacyanol chloride. As shown in Fig. 2, colored dye solutions became nearly clear upon the addition of bmimPF₆. Solid precipitated dyes were carefully removed from the solutions. Extracted solid dyes were dried at room-temperature, after which, the ¹H NMR spectra of the dyes were collected and compared with those of dyes from the stock. The ¹H NMR spectra are found to be identical, thus confirming the identity of the precipitated dyes to be the same. Further characterization of the dyes was carried out using UV-Vis molecular absorbance spectroscopy. Aqueous solutions of the recovered dyes were prepared and

Fig. 1 Structures of the six cationic dyes used in this investigation.

Fig. 2 1.5 mM aqueous solutions of pinacyanol chloride before (bottle on the left) and after (bottle on the right) addition of ~1.7 wt% (~0.06 M) bmimPF₆ under ambient conditions.

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Fig. 3 Normalized absorbance spectra of the aqueous solutions of the six dyes. MB, methylene blue; PC, pinacyanol chloride; AO, acridine orange; NR, neutral red; SO, safranin O; NB, Nile blue A. Panel A: Diluted stock solutions of the dyes. Panel B: Diluted solutions of the precipitated dyes.

their UV-Vis molecular absorbance spectra were compared with those obtained from aqueous solutions of dyes prepared using starting stock solutions at similar concentrations (Fig. 3). This further confirmed the identity of the dyes to be the same. Based on electronic absorbance values obtained from dyes in filtrate solutions, dye solutions having similar absorbance values were prepared using the stock. A comparison of the two spectra for each dye also confirmed the identity of the dye in the filtrate to be the same. On the basis of these measurements, it can be concluded that the structures of the dyes after being precipitation remained the same. However, an exchange of the anion of the dye with that of ionic liquid can not be ruled out.

Our next goal was to calculate the efficiency of this precipitation process. Recovered dyes were weighed after making sure they were moisture-free as well as bmimPF₆-free. The efficiency of the recovery was calculated as [(weight of the recovered dye/weight of the initial dye) × 100]%. The percent recovery for all six dyes at three different initial concentrations is reported in Fig. 4. It is clear that as the dye concentration increased in the aqueous solution, the percent recovery of the dye usually increased. This is expected in a precipitation process. It is worthwhile to mention that at lower concentrations (*e.g.*, ~75 μ M), the recoveries of pinacyanol chloride and neutral red were not as good as those for the other four dyes. At higher concentrations (*i.e.*, ~1.5 mM), all six dyes showed similar and very high percent recoveries (*ca.* 99%).

Next, we investigated the affect of the pH of the aqueous dye solution on the efficiency of the precipitation and dye recovery. First, 1.5 mM aqueous dye solutions of pH 4.0, 7.0, and 10.0 were prepared. The same amount of bmimPF₆ (~1.7 wt% or 0.06 M) was then added to each dye solution. It was observed that, except for Nile blue A, the percent recovery for all dyes was within $\pm 2\%$ at the three pH values investigated. For Nile blue A, while the percent recovery was ~99% at pH 7.0, it was reduced to ~80% at pH 4.0 and 10.0.

It is clear from the aforementioned data and its analysis that a small amount of an ionic liquid bmimPF₆ can induce efficient precipitation of cationic dyes. In order to generalize the outcome of our studies, as far as ionic liquids are concerned, we investigated the precipitation of the six dyes with three other ionic liquids (1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF₄), 1-butyl-3-methylimidazolium bis(trifluoromethyl-

Fig. 4 Percent recovery of dyes after the addition of ~1.7 wt% (~0.06 M) bmimPF₆ to aqueous dye solutions. Black (left), grey (middle), and dark grey (right) bars represent 75 μ M, 750 μ M, and 1.5 mM of dye, respectively. MB, PC, AO, NR, SO, NB, same as in Fig. 3. Errors with recovery are < 2%.

sulfonyl)imide (bmimTf₂N), and 1-hexyl-3-methylimidazolium bromide (hmimBr)). After the addition of ~1.7 wt% (~0.06 M) of these ionic liquids to 1.5 mM aqueous dye solutions, it was found that the precipitation efficiencies of the six dyes with bmimBF₄ and bmimTf₂N were similar to those observed for bmimPF₆. While the aqueous solubility of bmimTf₂N is comparable to that of bmimPF₆, bmimBF₄ is completely miscible in water.^{6a} Therefore, it can be suggested that the hydrophobicity of the ionic liquid does not play a part in deciding the efficiency of the dye precipitation process. The percent recovery with hmimBr was observed to be slightly less than that observed with bmimPF₆, bmimTf₂N, and bmimBF₄. We tentatively attribute this reduction in precipitation efficiency to the identity of the anion of the ionic liquid (*vide infra*).

To further explore the role of the anion and/or cation in dye precipitation, the percent recovery of the six dyes was measured using solid potassium hexafluorophosphate (KPF₆). As stated earlier, ~1.7 wt% (~0.09 M) solid KPF₆ was added to 1.5 mM aqueous dye solutions. Interestingly, while for methylene blue, acridine orange, safranin O, and pinacyanol chloride, the percent recovery was the same within 2% of that with bmimPF₆, the percent recovery was reduced by > 5% for Nile blue A and > 50% for neutral red. Apart from these reduced percent recoveries, the addition of solid KPF₆ for such extraction is inconvenient. Aqueous KPF₆ can be used, however, it introduces an additional solution preparation step.

In conclusion, a variety of dyes of industrial importance can be separated from their aqueous solutions using small amounts of ionic liquids. To the best of our knowledge, this kind of simple, effective, efficient, rapid, and clean precipitation of such dyes is unprecedented.

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References and Notes

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