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Association of ionic liquids with cationic dyes in aqueous solution: A thermodynamic study

Yuanchao Pei [a], Jing Liu [a], Zhenning Yan [b], Zhiyong Li [a], Jing Fan [a], Jianji Wang [a,*]

[a] School of Chemistry and Environmental Science, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Henan Normal University, Xinxiang, Henan 453007, PR China
[b] Department of Chemistry, Zhengzhou University, Zhengzhou, Henan 450001, PR China

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ABSTRACT

In this paper, the interactions between cationic dyes and the ionic liquids (ILs) have been studied by ^{31}P nuclear magnetic resonance (NMR), UV–Vis spectroscopy and conductometric measurements at different temperatures. It was shown that a decrease in the measured specific conductance of the (dye + IL) mixtures was caused by the formation of non-conducting or less conducting (dye + IL) associates. The associates were formed by 1:1 ratio of cation of the cationic dyes and anion of the ILs by using the ^{31}P NMR and UV–Vis spectroscopy methods. The association constants were calculated by theoretical model based on the deviation from linear behavior, and the association constants were as high as 10^6 $(L \cdot mol^{-1})^2$. Thermodynamic results imply that the formation process of association was exothermic nature. It is expected that the associates reported here would have promising application as active materials for the preparation of ion-selective electrode used in the determination of ILs concentrations.

1. Introduction

There is a still growing interest in ionic liquids because of their unique properties, such as negligible volatility, non-flammability, thermal and chemical stability, and a number of possible variations in cation and anion features which allow fine-tuning of their properties. These outstanding physicochemical properties render ILs excellent candidates for potential applications in chemical synthesis, extraction and separation, electrochemistry and among others [1–5]. ILs based on 1-alkyl-3-methylimidazolium cation ($[C_n mim]$) have received much attention, such ILs may be considered as short-chain surfactants with an amphiphilicity. This type of ILs has shown unique features during many investigations involving extraction or separation.

Dyes are widely used in different industrial applications. As a result, they are often present in wastewater and give rise to potential pollutants due to their inherent toxicity. Some imidazolium-based ILs ($[C_4mim][PF_6]$, $[C_6mim][PF_6]$, $[C_8mim][PF_6]$, $[C_6mim][BF_4]$ and $[C_8mim][BF_4]$) have been successfully used to remove anionic dyes (methyl orange, eosin yellow, orange G, acid yellow RN, weak acid brilliant blue RAW, etc.) and cationic dyes (acridine orange, methylene blue, nile blue A, safranine O, neutral red and pinacyanol chloride) from aqueous media [6–10]. Previously, we described an effective separation of three anionic dyes from water by the $[PF_6]^-$ based ionic liquids [6]. Interestingly, it is found that precipitates can be formed rapidly when the $[PF_6]$ based ionic liquids are added into aqueous solutions of cationic dyes such as methylene blue and malachite green. After stirring, these precipitates can be dissolved into the ionic liquid phase. This implies that the interactions between cationic dyes and ionic liquids are strong enough to form associates with high stability.

In this paper, $[C_4mim][PF_6]$, $[C_6mim][PF_6]$, $[C_8mim][PF_6]$, methylene blue (MB) and malachite green (MG) were selected as the representative ILs and cationic dyes, respectively. The associates between the ionic liquids and the cationic dyes were prepared and purified. Then, the composition of the associates was determined by ^{31}P NMR and UV–Vis spectroscopy, and the association constants and their thermodynamic parameters were obtained by conductivity titrations. Our results suggested that these associates may be used to prepare ion-selective electrode for the concentration determination of ILs.

2. Experimental

2.1. Materials

1-Bromobutane, 1-bromohexane, 1-bromooctane (Alfa Aesar) and 1-methylimidazolium (Linhai Kaile Chem. Co. C.P.) were distilled at reduced pressure, and middle fractions of the distillates were collected. Potassium hexafluorophosphate KPF_6 (Aladdin, Shanghai), methylene blue (MB, Tianjin Guangfu Chem. Co.) and

* Corresponding author. Tel.: +86 373 3325805; fax: +86 373 3326445.
E-mail address: jwang@henannu.edu.cn (J. Wang).

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malachite green (MG, Tianjin Guangfu Chem. Co.) were used without further purification. The other reagents were of analytical reagent grade. Aqueous solutions were prepared with doubly distilled water.

$[C_4mim][PF_6]$, $[C_6mim][PF_6]$ and $[C_8mim][PF_6]$ ionic liquids were prepared and purified according to the method described previously [6]. Briefly, the freshly distilled 1-bromobutane was added dropwise into solution of 1-methylimidazolium dissolved in 1,1,1-trichloroethane under stirring. The mixture, already turbid, was refluxed for 12 h. 1-Butyl-3-methylimidazolium bromide was decanted from the hot solution in a separatory funnel, washed twice with 200 ml of trichloroethane, and then dried on a rotavapor at 343 K under reduced pressure.

Aqueous KPF_6 solution was added slowly to a magnetically stirred solution of 1-butyl-3-methylimidazolium bromide dissolved in water in a plastic bottle cooled in an ice bath. When the addition was completed, the mixture was stirred for 12 h, and then poured into separatory funnel and the two layers were separated. The organic layer was dissolved in dichloromethane and then deionized water was added. After vigorous stirring, the water layer was replaced with small amount of fresh deionized water. This procedure was repeated until no precipitation of AgBr occurred in the aqueous phase on addition of a concentrated $AgNO_3$ solution. The solvent in the organic phase was removed under reduced pressure, and the resulting ionic liquid $[C_4mim][PF_6]$ was collected. Similar procedure was applied for the preparation of $[C_6mim][PF_6]$ and $[C_8mim][PF_6]$ ionic liquids. ^1H NMR spectra data of these ILs were determined by using a Bruker AV-400 Spectrometer, and they are found to be in good agreement with those reported in literature [11]. The structures of the cationic dyes and the ionic liquids used in this work were shown in figure 1.

2.2. Preparation of the associates and determination of their composition

The associates were prepared by mixing the aqueous solutions of cationic dyes and of ILs. After filtration, the solid was washed

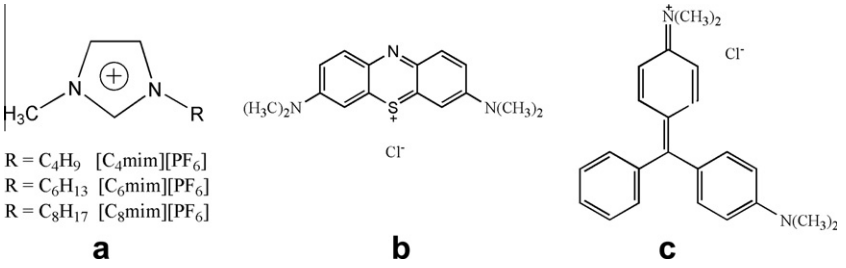

FIGURE 1. Chemical structure of the ionic liquids and cationic dyes: (a) $[C_nmim][PF_6]$ (n = 4, 6, 8); (b) methylene blue; and (c) malachite green.

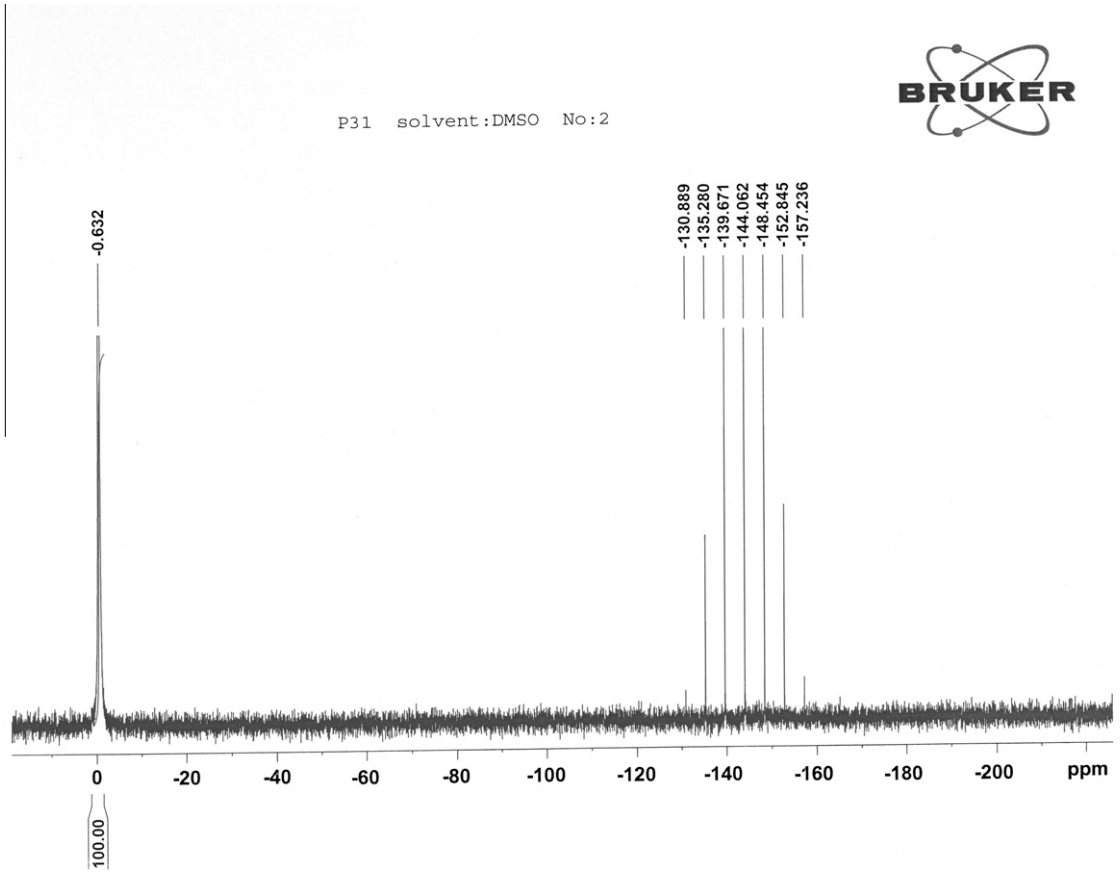

FIGURE 2. ^{31}P NMR for the methylene blue-$[C_4mim][PF_6]$ associate.