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Selective electrodes for $[PF_6]^-$ and $[BF_4]^-$ anions based on the associates formed by ionic liquid and cationic dyes

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ABSTRACT

The feasibility of the newly synthesized ionic associates L1 and L2 formed by ionic liquid $[C_4mim][PF_6]$ and cationic dyes (malachite green and methylene blue) has been tested as a novel ionophore for the preparation of anion-selective polymeric membrane electrodes. The electrode exhibits Nernstian response and enhanced potentiometric selectivity towards $[PF_6]^-$ compared to many other anions. The influence of some experimental parameters such as membrane composition, nature of plasticizer and amount of additive on the potential response of the $[PF_6]^-$ sensor are investigated. Under the optimized conditions, the response slopes of the membrane electrodes towards $[PF_6]^-$ are 59.7 ± 0.5 and 58.1 ± 0.5 mV/decade based on ionophore L1 and L2, respectively, in 1.0×10^{-5}–1.0×10^{-1} or 1.0×10^{-6}–1.0×10^{-1} mol/L concentration range. Interestingly, the optimized electrodes based on ionophores L1 and L2 also exhibit Nernstian response characteristics (60.3 ± 0.5 and 56.0 ± 0.5 mV/decade) for tetrafluoroborate anion $[BF_4]^-$ in a wide concentration range. Thus, the proposed sensor has been used for the determination of $[PF_6]^-$ and $[BF_4]^-$ in aqueous ionic liquids samples and the solubility of the $[PF_6]^-$ and $[BF_4]^-$ based ionic liquids in water. The satisfactory results are obtained.

1. Introduction

One of the most challenging problems in modern chemistry is the development of environmentally friendly processes for both industrial and laboratory-scale usage. Room temperature ionic liquids (ILs) have attracted wide interest in these aspects including chemical synthesis, extraction and separation, electrochemistry and among others [1–5] in recent years, due to their "greener" characteristics, such as negligible volatility, non-flammability, thermal stability, and a number of possible variations in cation and anion features which allow fine-tuning of their properties. Among the ionic liquids, the $[PF_6]^-$ and $[BF_4]^-$ based ionic liquids are the most popular ILs and have found potential applications in many fields. However, the production, application and waste management of these ionic liquids will inevitably lead to the discharge into the water ecosystems although they can avoid the atmosphere pollution. On the other hand, solubility of ILs is one of the important parameters that need to be quantified when designing their applications and biphasic IL-based separations. Thus, the accurate measurements of ILs' concentration and solubility remained in aqueous media are very important for the evaluation of their environmental impact and the rational design of novel ILs. In addition, $LiPF_6$ is the commonly used lithium salt in the research and development of lithium-ion battery because of its excellent specific energy and energy density [6]. The quantitative concentration measurements of $LiPF_6$ are critical for the quality control of lithium battery. Because $[PF_6]^-$ and $[BF_4]^-$ are the components of the $[PF_6]^-$ and $[BF_4]^-$ based ionic liquids and $LiPF_6$, the method of detecting $[PF_6]^-$ and $[BF_4]^-$ anions may be used to determine the content of these compounds in water.

Although the UV-spectroscopy [7], electrospray ionization mass spectrometry [8], Fisher titration [9] and cloud point methods [10–12] have been reported to determine the concentration or the solubility of ionic liquids in aqueous solutions, all of these methods have some drawbacks and the measurements require the use of some standard instrumentation. To overcome the drawbacks of the above mentioned methods, one of the most convenient, cheap and fast analytical methods: potentiometry with ion-selective electrode (ISE) is introduced in this work. The only equipment required for the analysis is a conventional potentiometer and easily fabricated electrodes. This method has been used to measure the solubility of ionic liquid in aqueous solutions. Pletnev and his co-workers [13] developed a polyvinyl chloride-plasticized membrane ion-selective electrode based on conventional ion-exchangers tributylhexadecylphosphonium bromide (anion-exchanger) and sodium tetraphenylborate (cation-exchanger) to determine the solubility of alkylimidazolium ionic liquids in water. Their proposed electrodes response to ionic constituents of ILs, including $[PF_6]^-$. Pungor et al. [14] have reported $[PF_6]^-$ — selective electrode

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based on the tetradecylphosphonium hexafluorophosphate ion-pair complex as an ionophore. However, few information on the selectivity and application of the electrode was given in their study. To the best of our knowledge, there are only these two reports on the determination of $[PF_6]^-$ concentration by ion-selective electrode.

Herein, the present study was undertaken to develop a simple quantitative method ISE for measurement of $[PF_6]^-$ anion. The ionophores are the associates formed by $[C_4mim][PF_6]$ and cationic dyes. In our previous work aiming to extract cationic dyes, such as methylene blue and malachite green, from water by using the $[PF_6]^-$ based ionic liquids [15], we found that precipitate can be formed rapidly when the ionic liquids were added into the aqueous cationic dye solutions. After stirring, these precipitates can be dissolved into the lower ionic liquid phase. This implies that the interactions between cationic dyes and ionic liquid are strong enough to form associates. Recently, we determined the association constants of these cationic dyes with 1-alkyl-3-methylimidazolium hexafluorophosphate ($[C_nmim][PF_6]$, n = 4, 6, 8) by conductometric measurements [16]. It was found that the association constants were as high as 10^6 $(L/mol)^2$. So in this work, the associates formed by $[C_4mim][PF_6]$ and cationic dyes (malachite green and methylene blue) have been used as a novel ionophore to prepare PVC polymeric selective electrodes for $[PF_6]^-$ anion. The composition of the electrode membranes was optimized, and the response time, electrode's lifetime, and electrode's selectivity against some other anions were investigated. Interestingly, the optimized electrodes based on ionophores L1 and L2 also exhibit Nernstian response to $[BF_4]^-$ anion. The developed electrodes have been successfully used to determine the concentration of $[PF_6]^-$ and $[BF_4]^-$ in aqueous ionic liquids samples and the solubility of the $[PF_6]^-$ and $[BF_4]^-$ based ionic liquids in water.

2. Experimental

2.1. Chemicals and reagents

1-Bromobutane (Alfa Aesar) and 1-methylimidazolium (Linhai Kaile Chem. Co., C. P.) were distilled at reduced pressure, and middle fractions of the distillates were collected. Sodium hexafluorophosphate $NaPF_6$ (Shanghai Chem. Co.) was purified through a twice recrystallization process with deionized water. Methylene blue (MB) and malachite green (MG) (Tianjin Guangfu Chem. Co.) as well as 2-nitrophenyloctyl ether (o-NPOE) (Alfa Aesar) and tridodecylmethylammonium chloride (TDMACl) (Fluka) were used without further purification. Dibutylphthalate (DBP), bis(2-ethylhexyl)sebacate (DOS), tetrahydrofuran (THF) (dried by sodium and distilled prior to use) and poly (vinylchloride) (PVC) of high molecular mass were obtained from Shanghai Chem. Co. The other reagents were of analytical reagent grade. All aqueous solutions were prepared with doubly deionized and distilled water.

$[C_4mim][PF_6]$ and the IL-dye associates were prepared and purified according to the method described previously [15,16]. The structure of the cationic dyes and the ionic liquid $[C_4mim][PF_6]$ was shown in Fig. 1. The associates formed by $[C_4mim][PF_6]$ with malachite green and methylene blue as ionophores are named as L1 and L2, respectively.

2.2. Electrodes preparation and potentiometric measurements

1 wt.% of the ionophore (i.e. the associate), 33 wt.% of PVC, 66 wt.% of plasticizer (o-NPOE, DBP or DOS) and 0–50 mol% TDMACl versus the ionophore were used to prepare the membranes. For this purpose, the membrane components (about 281 mg in total) were dissolved into 5 ml of THF. The solution was poured into a glass ring with a diameter of 18 mm, which was fixed tightly on a glass plate. The solvent THF was allowed to evaporate at room temperature for two days. The resulting membrane of about 0.4 mm thickness was cut into small disks. A disk with diameter of 10 mm was removed carefully from the glass plate and sealed onto the end of the Ag/AgCl electrode barrel with the help of a 5 wt.% PVC solution in THF. For all the electrodes, a solution of 0.01 mol/L $NaPF_6$ + 0.01 mol/L NaCl was used as the internal reference solution. Before potentiometric measurements, the electrodes were conditioned in a 0.01 mol/L $NaPF_6$ solution overnight.

Potentials and pH values were measured by using a pXS-215 ion-meter (Leici Instruments Corporation, Shanghai) and a 6071 pH-meter (JENCO Electronics, LTD, Shanghai), respectively. All potentials were measured relative to an Hg/Hg_2Cl_2 double liquid junction reference electrode with 0.1 mol/L lithium acetate in the outer compartment and saturated potassium chloride in the inner compartment. The potentiometric measurements were made with the following electrochemical cell:Hg/Hg_2Cl_2/KCl(saturated)/0.1 mol/L LiAc/sample solution//PVC membrane//0.01 mol/L $NaPF_6$ + 0.01 mol/L NaCl /Ag/AgCl.

Performance of the electrodes was investigated by measuring their potential in $NaPF_6$ solutions in the concentration range from 1.0×10^{-1} to 1.0×10^{-7} mol/L which was obtained by serial dilution of the stock solution (0.1 mol/L). The solutions were stirred and potential readings were recorded when stable values were reached. The data were plotted as the observed potentials versus the logarithm of the anion activity. Detection limit was determined according to the IUPAC recommendations [17].

3. Results and discussion

3.1. Influence of membrane composition

According to the structural characteristics and high association constants of the two associates reported in our previous work [16], L1 and L2 were used as neutral ionophores in $[PF_6]^-$ membrane electrodes. The experimental results have showed that the electrodes work well over a wide linear range with Nernstian responses for $[PF_6]^-$. It is well known that sensitivity, linearity and selectivity obtained for a given ionophore depend significantly on membrane composition, nature of plasticizer and amount of additive used [18]. Thus, the influence of membrane potential response of the $[PF_6]^-$ electrode was investigated, and the results are summarized in Table 1. To compare the effect of various plasticizers on response

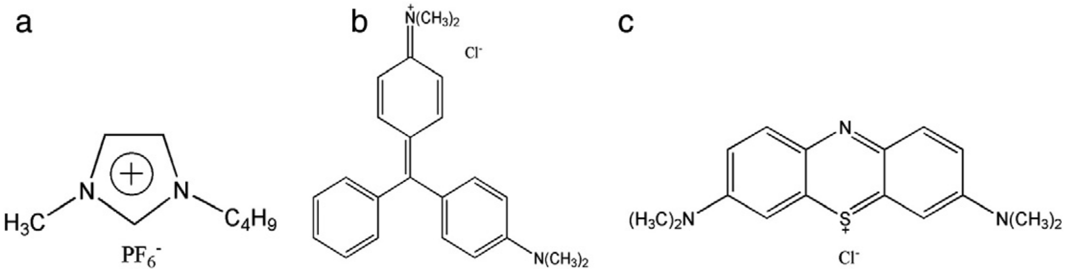

Fig. 1. Chemical structure of the ionic liquid and cationic dyes: (a) $[C_4mim][PF_6]$, (b) malachite green, (c) methylene blue.