Ionic liquids promote selective responses towards the highly hydrophilic anion sulfate in PVC membrane ion-selective electrodes

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Received (in Cambridge, UK) 3rd March 2005, Accepted 7th April 2005
First published as an Advance Article on the web 11th May 2005
DOI: 10.1039/b503154k

A remarkable enhanced response towards the hydrophilic anion sulfate using plasticized PVC membranes containing the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate and a polyazacycloalkane derivative as ionophore has been found.

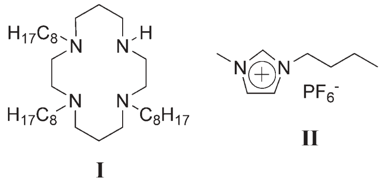
The interest in ion-selective electrodes has grown over recent years as they are easy-to-use devices that allow rapid and accurate analytical determination of chemical species at relatively low concentrations, with a reasonable selectivity and at low cost.[1] Despite the large number of ion-selective electrodes reported by now, there are still particular problems related to the design of electrodes for certain applications. This is the case of ion selective electrodes for highly hydrophilic anionic species. It is known that the relative tendency of a certain anion to enter into a membrane is the balance between two energies, one resulting from the anion–water interaction and the other reflecting the anion–membrane interactions. A large number of classical membrane-based electrodes for anions contain PVC, a plasticizer and a suitable ionophore. However, when the ionophore does not form strong interactions with the anions, the response of these membranes basically displays the well-known Hofmeister series ($ClO_4^- > SCN^- > I^- \sim$ Salicylate $> NO_3^- > Br^- > Cl^- > HCO_3^- > CH_3COO^- > SO_4^{-2} > HPO_4^{-2}$) which determines that the anion selectivity sequence is solely related to the relative anion partition coefficients between water and the PVC membrane.[2] This sequence reflects that whereas the extraction to PVC-based membranes of lipophilic anions is relatively easy, highly hydrophilic anions such as sulfate and phosphate are very poorly extracted from water solutions.

Among several possible approaches to invert the Hofmeister behaviour, the most common is the use of ionophores suitable to form strong complexes with hydrophilic anions. Among these ionophores relevant examples relaying in metal–anion and hydrogen bonding or electrostatic interactions have been reported.[3,4] Additionally, it is also apparent that an additional mode of making less unfavourable the extraction of hydrophilic anions from water to the membrane is to reduce the difference in dielectric constant between the water and the membrane phases.

As a suitable mode to significantly increase the dielectric constant of PVC-based membranes we focused our attention on the potential use of ionic liquids as membrane component. Room temperature ionic liquids have attracted much interest as suitable alternatives to volatile organic solvents in synthesis, catalysis, extraction, separation, and other related "green chemistry" technologies.[5] Ionic liquids are generally composed of an organic cation and an inorganic anion. One of the most interesting features of ionic liquids is that it is possible to optimize their characteristics *via* a choice of the anion and cation combination. Additionally, ionic liquids have many useful properties such as high thermal stability, high ionic conductivity, are non-volatile and have a negligible vapour pressure. Although there are recent examples where ionic liquids have been used in membranes for the amperometric determination of gases,[6] catalysis[7] and separation applications,[7,8] to the best of our knowledge, ionic liquids have never been used as membrane components in the development of ion-selective electrodes.

Membranes containing different PVC/plasticizer ratios were studied and finally the membrane **E1** with the following optimum composition was prepared: 41.84 wt.% of powdered PVC, 25.11 wt.% of plasticizer (NPOE), 7.11 wt.% of the polyazacycloalkane **I** (see Scheme 1) used as ionophore[9] and 25.94. wt.% of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (**II**).[10] These components were mixed in 3 ml of THF and transferred into a glass dish of 5 cm diameter. The solvent was allowed to evaporate overnight, leaving a homogeneous, flexible and transparent membrane from which small-diameter disks were cut out and incorporated into the electrode which was finally conditioned for 12 h by soaking it in a 0.1 M potassium sulfate solution. When not in use the electrode was kept immersed in the same solution. The electrode cell assembly of the following type was used: Ag–AgCl(KCl 3M)|sample solution|PVC membrane|internal solution, 0.1 M of K_2SO_4|KCl(satured)|Hg_2Cl_2, Hg.

Prior to their use as ionophore in the membrane, the ability of **I** to coordinate anions was studied in dioxane–water, 70 : 30 *v*/*v* (298 K, 0.1 mol ml^{-1} tetrabutylammonium perchlorate) from potentiometric titrations.[11] The logarithms of the stability constants for the anion sulfate are shown in Table 1. It is clear from data in Table 1 that the ionophore **I** forms quite strong



Scheme 1 Schematic representation of the polyazacycloalkane **I** and the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (**II**).

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Table 1 Logarithms of the stability constants for the interaction of **I** with sulfate in dioxane–water, 70 : 30 v/v (298 K, 0.1 mol ml^{-1} tetrabutylammonium perchlorate)

Reaction	Log$K^{a,b}$
$\mathbf{I} + H^+ + SO_4^{2-} \leftrightarrows [SO_4H\mathbf{I}]^-$	14.14(3)^a
$\mathbf{I} + 2H^+ + SO_4^{2-} \leftrightarrows [SO_4H_2\mathbf{I}]$	23.53(3)
$\mathbf{I} + 3H^+ + SO_4^{2-} \leftrightarrows [SO_4H_3\mathbf{I}]^+$	30.73(4)
$\mathbf{I} + 4H^+ + SO_4^{2-} \leftrightarrows [SO_4H_4\mathbf{I}]^{2+}$	36.48(5)
$H\mathbf{I}^+ + SO_4^{2-} \leftrightarrows [SO_4H\mathbf{I}]^-$	4.04
$H_2\mathbf{I}^{2+} + SO_4^{2-} \leftrightarrows [SO_4H_2\mathbf{I}]$	6.62
$H_3\mathbf{I}^{3+} + SO_4^{2-} \leftrightarrows [SO_4H_3\mathbf{I}]^+$	10.95
$H_3\mathbf{I}^{4+} + HSO_4^{2-} \leftrightarrows [SO_4H_4\mathbf{I}]^{2+}$	14.33

[a] Stability constants for the **I** − H$^+$ system: $\mathbf{I} + H^+ \leftrightarrows [H\mathbf{I}]^+$, log$K$ = 10.1(2); $[H\mathbf{I}]^+ + H^+ \leftrightarrows [H_2\mathbf{I}]^{2+}$, log$K$ = 6.81(2); $[H_2\mathbf{I}]^{2+} + H^+ \leftrightarrows [H_3\mathbf{I}]^{3+}$, log$K$ = 2.87(3); $[H_3\mathbf{I}]^{3+} + H^+ \leftrightarrows [H_4\mathbf{I}]^{4+}$, log$K$ = 2.37(4). Stability constant for the SO_4^{2-} − H$^+$ system: $SO_4^{2-} + H^+ \leftrightarrows HSO_4^-$, log$K$ = 2.11. [b] Values in parenthesis are standard deviations in the last significant digit.

complexes with sulfate even in the presence of an excess of perchlorate which was used as supporting electrolyte. Polyazacycloalkanes are well-known anion receptors *via* H-bonding and electrostatic interactions. Although the stability constants have been determined in dioxane–water mixtures, it would also be expected for **I** to form relatively strong complexes with sulfate into the **E1** membrane.

Preliminary studies with the membrane **E1**, containing the ionic liquid **II** and the ionophore **I**, showed a remarkable response to sulfate. Studies on the membrane response as a function of the pH in 5 × 10^{-3} M sulfate solutions were also carried out. The response remained unchanged over the 5–10 pH range, whereas in high alkaline media the potential decrease probably due to the OH$^-$ anion competition. The response of the electrode was therefore further studied at pH 6. At this pH, the electrode **E1** showed a Nernstian potentiometric response (slope 30 mV/decade) for a sulfate concentration ranging from 1 × 10^{-1} to 4 × 10^{-5} M with a detection limit of 1 × 10^{-4} M. The response time to sulfate was 8 s to a 90% response (τ_{90}). The membrane showed no decay of the slope below −26 mV/decade after at least 30 days. Fig. 1 shows the response of the electrode in the presence of selected anions as the primary anion.

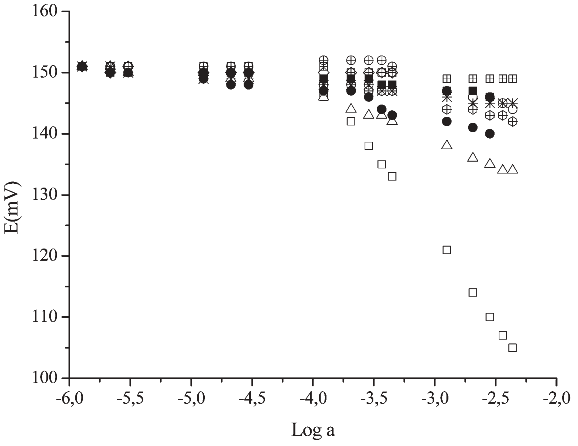

Fig. 1 Response of the membrane **E1** containing the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate and the ionophore **I** at pH 6 in the presence of different anions: (□) sulfate, (○) phosphate, (Δ) perchlorate, (◇) oxalate, (⊕) acetate, (⊞) cyanide, (*) iodide, (■) chloride, (●) bromide.

One of the most important characteristics of ion-selective electrodes is the relative response towards a certain ion over others which is expressed in terms of potentiometric selectivity coefficients. The selectivity coefficients $K^{\mathrm{POT}}_{\mathrm{sulfate,X}^-}$ were calculated by means of the fixed primary ion method[12] considering sulfate (5 × 10^{-3} M) as the principal anion. The values of $K^{\mathrm{POT}}_{\mathrm{sulfate,X}^-}$ are shown in Table 2.

The electrode responded in the following order of preference to anions: $SO_4^{-2} > ClO_4^- > Br^- \approx C_2O_4^{2-} > SCN^- > Cl^- > H_2PO_4^- \approx I^- > CH_3COO^- > CN^-$. This anion-selectivity pattern deviated remarkably from that imposed by the hydrophobicity-based Hofmeister sequence ($ClO_4^- > SCN^- > I^- \sim$ Salicylate $> NO_3^- > Br^- > Cl^- > HCO_3^- > CH_3COO^- > SO_4^{-2} > HPO_4^{-2}$). There are not many examples of anion selective electrodes for highly hydrophilic anions and in the case of sulfate, most of the reported PVC-based electrodes suffer from very serious interferences from more lipophilic anions such as perchlorate, thiocyanate, nitrate or iodide.[4]

For the sake of comparison a plasticized PVC membrane containing the ionophore without the ionic liquid was prepared (membrane **E2**: 40 wt.% of powered PVC, 50 wt.% of plasticizer (NPOE), 10 wt.% of the ionophore **I**). This membrane however showed a Nernstian response to perchlorate and all the efforts were carried out to improve the response to lipophilic anions by changing plasticizers and/or the proportion of the membrane components were unsuccessful. We also prepared NPOE plasticized PVC membranes containing only the ionic liquid **II**, however only a very poor undefined sub-Nernstian response was observed. Thus, it is apparent that only membranes containing both the ionophore **I** and the ionic liquid **II** displayed a remarkable selective response to the highly hydrophilic anion sulfate. A likely explanation of this remarkable effect could be associated with the combination of the ionophore **I**, that forms quite strong complexes with sulfate, and the expected increase of the dielectric constant in the membrane **E1** containing the ionic liquid when compared with that of the membrane **E2**.

We have measured[13] the dielectric constant of the membrane **E2** and have found a value of ε = 11. For instance, a similar value (ε = 14) has been found for NPOE plasticized PVC membranes containing tridodecylmethylammonium chloride as ionophore.[14] This is a relatively low value that has a negative effect on the extraction of hydrophilic anions from water. Thus, it is known that, among other factors, the energy of extraction depends on the difference of the dielectric constant of water (ε = 80) and the membrane. Therefore, despite the favourable coordination of sulfate with the ionophore **I** (see Table 1), the nearly null response of the membrane **E2** to this anion could be attributed to the very

Table 2 Selectivity coeficients ($K^{\mathrm{POT}}_{\mathrm{sulfate,X}^-}$) for the NPOE plasticized PVC membrane **E1** containing the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (**II**) and the ionophore **I**

Anion X$^-$	$K_{\mathrm{sulfate,X}^-}$	Anion X$^-$	$K_{\mathrm{sulfate,X}^-}$
ClO_4^-	4.3 × 10^{-1}	$H_2PO_4^-$	5.4 × 10^{-2}
Br^-	1.1 × 10^{-1}	I^-	5.3 × 10^{-2}
$C_2O_4^{2-}$	1.0 × 10^{-1}	CH_3COO^-	2.0 × 10^{-2}
SCN^-	8.9 × 10^{-2}	CN^-	1.6 × 10^{-2}
Cl^-	6.9 × 10^{-2}		

unfavourable energy of extraction from water to the lipophilic membrane. At this point it is important to note that the impact of the dielectric constant of the membrane on the value of the anion solvation energy is not linear and from the perspective of an analysis of solvation energy a medium having a dielectric constant $\varepsilon > 20$–30 is effectively nearly as polarizable as water.[15] Especially for highly hydrophilic anions, that means that a relatively low increase of the dielectric constant of the membrane can result in a significant increase in the membrane solvation energy and therefore in a more favourable anion extraction from water. At this respect we have determined the dielectric constant of the membrane **E1** and found a value of $\varepsilon = 25$. This value is remarkably larger than that of the membrane **E2** and is clearly attributed to the presence of the ionic liquid **II**. Thus, in the case of the membrane **E1** the difference in extraction energy of lipophilic anions over hydrophilic ones is much less important and the strong **I**–sulfate interaction is enough to counteract the Hofmeister lipophilicity sequence.

In summary, we have used for the first time an ionic liquid for the preparation of membranes for use in anion-selective electrodes and have found a remarkable selective response to the highly hydrophilic anion sulfate. The large number of ionic liquids known and the possibility of incorporating them as components in membranes might lead to a new generation of polymer-based ion-selective electrodes with a remarkably enhanced response towards hydrophilic anions.

We thank the Ministerio de Ciencia y Tecnología (projects REN2002-04237-C02-01, MAT2003-08568-C03-02) and the Generalitat Valenciana (GRUPOS03/035) for support. R.H.L. thanks the Generalitat Valenciana for a Doctoral Fellowship and F. S. also thanks the Ministerio de Educación y Ciencia for a Ramón y Cajal contract.

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