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Screen-printed ion-selective electrodes covered with membranes containing ionic liquids

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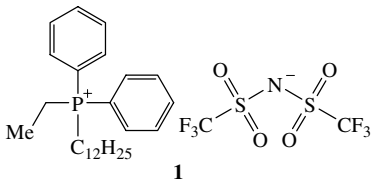
Miniature solid-contact potentiometric sensors are obtained by covering commercially available screen-printed electrodes with polymer membranes containing ionic liquids; their properties are compared to those of conventional plasticised membrane ion-selective electrodes.

Ionic liquids (ILs) are organic salts which are often melt at or below room temperature.[1] ILs have valuable physical-chemical properties: wide liquid range, high ionic conductivity, catalytic activity, *etc*. Nowadays, ILs are increasingly used in chemical science and technology and are of particular interest for chemical analysis.[2,3] Ion-exchange properties and ability to plasticise polymers may be useful in electrochemical analysis.[4,5] These properties allow one to use ILs in ion-selective electrodes (ISEs).

Previously,[6,7] we described the use of ILs as plasticisers and electrode-active components in the membranes of conventional liquid-contact ISEs. However, to construct a miniature potentiometric sensor, one has to use solid-contact ISE like coated wire or carbon paste electrodes. Here, we report on the design and properties of a solid-contact ISE based on miniature planar screen-printed electrodes (SPEs) covered with polymer membrane compositions containing ILs.



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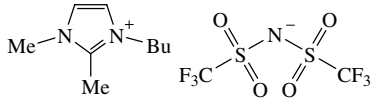

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Bistrifluoromethanesulfonimidate salts of dodecylethyldiphenylphosphonium (DEDPPTf$_2$N) **1** and 1-butyl-2,3-dimethylimidazolium (BDMImTf$_2$N) **2** were investigated as the components of plasticised membranes used for modification. Poly(vinyl chloride) (PVC) and poly(methyl metacrylate) (PMMA) were used as polymer matrices.[7] In some cases an additional plasticiser, 2-nitrophenyl octyl ether (2-NPOE) was used (Table 1). The SPEs (10 mm in width and 20 mm in length) were purchased from Elcom, Russia. Construction of SPE was of layer-by-layer printed silver, graphite and insulator inks at the polyester substrate; electrode work surface was free of insulator and no more than 0.2 cm^2. In order to estimate the stability of solid-contact electrodes characteristics in comparison with ISE with inner solution the last ones were prepared as described elsewhere.[7] The silver chloride electrode Esr-10101 (Russia) was used as a reference electrode; responses were recorded with an Orion-420A pH meter–ion meter (USA).

Table 1 Investigated membranes compositions.

Membrane	Polymer	IL	2-NPOE
I	33% PVC	67% DEDPPTf$_2$N	—
II	32% PVC	5% DEDPPTf$_2$N	63%
III	50% PMMA	50% BDMImTf$_2$N	—
IV	32% PVC	5% BDMImTf$_2$N	63%

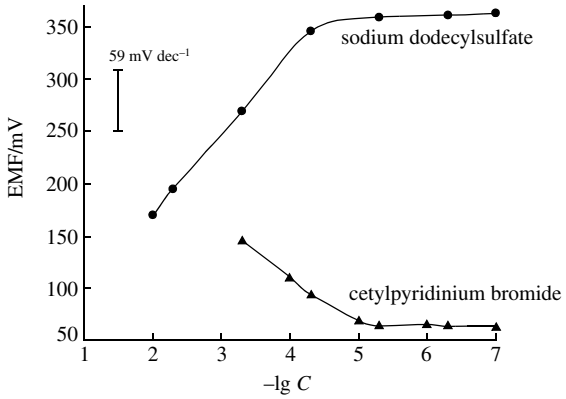

Figure 1 Potentiometric response of a solid-contact ISE (Membrane I) in salts solutions.

Potentiometric response was investigated in solutions of cetylpyridinium bromide (target is a hydrophobic cation) and sodium dodecylsulfate (target is a hydrophobic anion). Potentiometric selectivity coefficients were obtained by a separate solutions method; logarithmic values were calculated and compared.[8]

Previously, we described ISEs with inner filling solutions, which were based on polymer membranes plasticised with ILs. The potentiometric response of such ISEs to hydrophobic ions of ionogenic surfactants was close to Nernstian one in a wide concentration range.[6,7] Similar membranes appeared suitable for modifying an SPE surface leading to solid-contact potentio-

Table 2 Electrochemical characteristics of SPE modified with DEDPPTf$_2$N-based membrane composition in solutions of sodium dodecylsulfate.

ISE with inner solution		Solid-contact ISE based on SPE	
Membrane I			
S/mV dec^{-1}	C_{min}/mol dm^{-3}	S/mV dec^{-1}	C_{min}/mol dm^{-3}
62±2	1.2×10^{-5}	79±2	2.2×10^{-5}

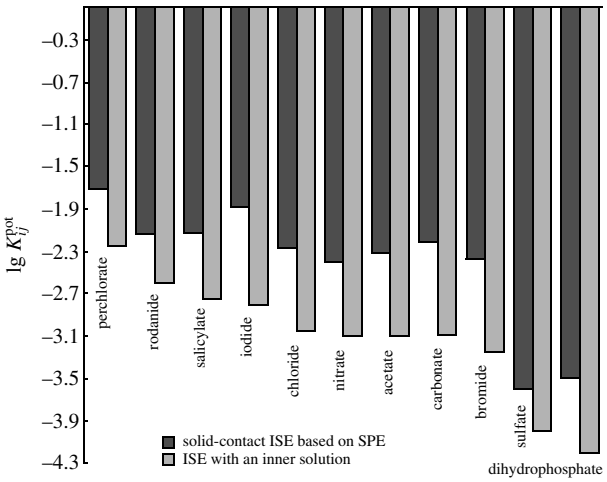

Figure 2 Comparison of potentiometric selectivities of different dodecylsulfate-selective electrodes.

metric sensors, which are miniature analogues of conventional ISEs. Covering of SPE surface with IL-based polymer membranes provides a transition from ionic to electronic type of conductivity resulting in that the sensor operates as an ISE without inner filling reference solution (solid contact).

As shown in Figure 1, the solid-contact ISE based on $DEDPPTf_2N$ (Membrane I) demonstrates nearly-Nernstian potentiometric response to both hydrophobic cations and anions. Moreover, super-Nernstian slope S of electrode function was detected for a solid-contact dodecylsulfate-selective electrode; such a deviation can be attributed to the design features of solid-contact sensors (Table 2).

Notably, the reproducibility of electrode response of a solid-contact ISE is the same as that of ISE with inner filling solution. However, detection limit C_{min} of a modified SPE is two times higher than that of ISE with inner solution. Likely, it may be explained by the transfer of primary ion from conditioned membrane to outer (analysed) solution, which leads to an increase of primary ion concentration in the diffusion layer (bulk concentration).[9] It is well known that, for the electrodes with a traditional liquid contact, this phenomenon is effectively eliminated by the decrease of primary ion concentration in the internal filling solution or by modification of the latter. Unfortunately, this is not an option in the case of solid-contact ISEs.[10]

A comparison of potentiometric selectivity of ISE with liquid contact and solid-contact ISE demonstrated that, in the latter case, the selectivity is reduced (Figure 2). This may be attributable to the absence of inner solution, which would provide nearly constant activity of primary ion in the conditioned membrane. In case of solid-contact ISE, the activity of target ion in a membrane gradually decreases because of the transfer of target ions into an outer aqueous phase; this leads to lowering the selectivity of determination in the presence of interfering ions. Anyway, selectivity coefficients for solid-contact electrodes based on IL-containing membranes are low and foreign ions do not interfere up to three orders of magnitude concentration excess. Interestingly, potentiometric selectivity does not correspond to Hoffmeister's series for both a solid-contact electrode and an electrode with inner filling solution. Difference in potentiometric selectivity coefficients is particularly leveled because of sufficient lipophilicity of ionic liquids constituent ions.

Table 3 Electrochemical characteristics of SPE modified with different membrane compositions in solutions of cetylpyridinium bromide.

Membrane I		Membrane II		Membrane III		Membrane IV	
S/mV dec^{-1}	C_{min}/mol dm^{-3}	S/mV dec^{-1}	C_{min}/mol dm^{-3}	S/mV dec^{-1}	C_{min}/mol dm^{-3}	S/mV dec^{-1}	C_{min}/mol dm^{-3}
ISE with inner solution							
57±3	4.5×10^{-6}	55±1	3.7×10^{-6}	56±3	5.0×10^{-6}	59±1	6.6×10^{-7}
Solid-contact ISE based on SPE							
45±7	7.8×10^{-6}	58±4	4.3×10^{-6}	58±6	7.2×10^{-6}	61±7	3.8×10^{-6}

In case of cation-selective electrodes characteristics of potentiometric response towards cetylpyridinium depend on ISE design even more strongly. The membrane containing $BDMImTf_2N$ responds only towards cations. Note that the use of ILs based on imidazolium derivatives allows one to obtain a cetylpyridinium-selective electrode with better characteristics (lower detection limit, higher sensitivity) than in the case of $DEDPPTf_2N$. It may be explained by lower hydrophobicity of imidazolium-derived cation and higher ion-exchange constant 'BDMIm$^+$/surfactant cation'.

Table 3 shows that detection limits C_{min} and reproducibility of response are worse in the case of solid-contact ISE. Obviously, the reasons are the same as mentioned above for anion-selective electrodes. However, an additional plasticiser, 2-NPOE, makes it possible to employ a lower amount of ILs in the membrane, which results in a decrease in the number of ionic sites in the plasticised membrane. Reducing the content of active centres able of reversible dissociation and dissolution in aqueous layer near electrode surface leads to more stable ISE operation and to lower detection limit. Interestingly, in parallel to this effect, in the case of ISE with internal filling solution the decrease of IL content in the membrane leads to significant improvement of cetylpyridinium detection limit.

In general, solid-contact ISEs based on SPE demonstrate good operational and analytical characteristics; they are characterised by short response times, high sensitivity and good selectivity. An important advantage of such sensors is miniature construction, which allows one to work with small samples (~1 ml). Absolute C_{min} values for cetylpyridinium and dodecylsulfate ions are 5.8 and 1.2 μg, respectively.

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