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Ion-Selective Electrodes for the Determination of Ionic Liquids in Water Using Direct Potentiometry

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Abstract—Ion-selective electrodes (ISEs) with membranes based on ion exchangers plasticized with *o*-nitrophenyl octyl ether (NPOE), diethyl sebacate (DES), or dibutyl phthalate (DBP) are used for the determination of ionic liquids (ILs) in water. The membrane composition is optimized with respect to the ion-exchanger concentration and the plasticizer.

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Ionic liquids (ILs)—low-temperature salt melts—have recently attracted the attention of researchers [1–9]. Combining nonvolatility, thermal stability, electrochemical resistivity, and low water miscibility, ILs are lucky substituents for toxic organic solvents now used in extraction, catalysis, biocatalysis, and galvanic engineering. However, some physical properties of ILs, such as miscibility with organic solvents and water solubility, remain insufficiently studied, and the available literature is frequently controversial. Inasmuch as dissolution in water during industrial use is the most likely route for ILs to enter the environment, control over the levels of ILs in water is of fundamental significance. Ionic liquids dissociate to ions; therefore, direct potentiometry by means of ion-selective electrodes (ISEs) with ion-exchanger-based membranes is the universal method for the determination of the components of ILs in water.

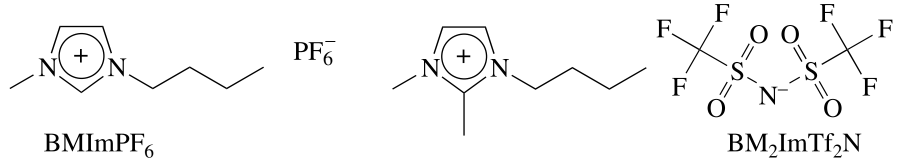
It is known that the structure of symmetrical and asymmetrical ion exchangers, which are frequently employed as electrode-active components (EACs), significantly affects the potentiometric characteristics of ISEs [10]. The components of the ILs we studied are hydrophobic ions. On one hand, hydrophobic ions are more easily determined with ISEs than hydrophilic ions [11]: for hydrophobic ions, it is not necessary to ease their transition to the membrane phase. On the other, with hydrophilic ions, ion exchange can lose reversibility as the hydrophobicity of the analyte increases. This toughens the requirements to the hydrophobicity of the EAC in the membrane phase. The EAC concentration is known to affect the electrode sensitivity and the detection limit [12]. The plasticizer also significantly affects the membrane properties. For example, lipophilic ions affect bis(2-ethylhexyl sebacate)-plasticized membranes less strongly than the membranes based on *o*-nitrophenyl octyl ether [13].

In our previous work [14], we used ion-exchanger-based ISEs for the determination of the water solubility of ILs. This work was intended to explore the electrode characteristics as dependent on the composition of poly(vinyl chloride) (PVC) membranes, the nature of the plasticizer, and the EAC concentration in the membrane composition. In so doing, our goal was to develop ISEs suitable for IL determination in water with a stable performance.

EXPERIMENTAL

The structural formulas of the ILs used in this work, namely, butylmethylimidazolium hexafluorophosphate (BMIm PF_6) and butyldimethylimidazolium bis(triflylimide) (BM_2Im Tf_2N) are indicated in Scheme 1.

Membranes were made of PVC, type S-70. The plasticizers used were *o*-nitrophenyl octyl ether (*o*-NPOE), diethyl sebacate (DES), and dibutyl phthalate (DBP), all of chemically pure grade. The EACs used were sodium tetraphenyl borate $NaB(C_6H_5)_4$



Scheme.

Table 1. Electrochemical properties of *o*-NPOE-plasticized membranes as a function of EAC concentration

EAC (TPB) concentration, %	$BMImPF_6$		BM_2ImTf_2N	
	slope, mV/dec	c_{min}, mol/L	slope, mV/dec	c_{min}, mol/L
0.5	56.6 ± 0.5	3×10^{-6}	51.6 ± 0.5	2×10^{-6}
1	56.6 ± 0.3	3×10^{-6}	48.7 ± 0.4	2×10^{-6}
2	57.4 ± 0.4	3×10^{-6}	50.6 ± 0.6	3×10^{-6}
5	57 ± 2	4×10^{-6}	48.3 ± 0.7	2×10^{-6}
EAC (TPB) concentration, %	$BMImPF_6$		BM_2ImTf_2N	
	slope, mV/dec	c_{min}, mol/L	slope, mV/dec	c_{min}, mol/L
0.5	–54 ± 1	8×10^{-7}	–53 ± 1	1×10^{-6}
1	–58 ± 2	5×10^{-7}	–55 ± 1	1×10^{-6}
2	–58 ± 2	7×10^{-7}	–59 ± 1	1×10^{-6}
5	–59.8 ± 0.8	9×10^{-7}	–58 ± 1	1×10^{-6}

(NaTPB, pure for analysis grade) as cation exchanger and tributylhexadecylphosphonium bromide $C_{16}H_{33}P(C_4H_9)_3Br$ (TBHDPBr, pure for analysis grade) as anion exchanger. The components were dissolved in freshly distilled tetrahydrofuran (THF; chemically pure grade). The internal reference solution was prepared from potassium chloride (chemically pure grade). A mixture of PVC, EAC, and the plasticizer was dissolved in THF under magnetic stirring for 15 min. The PVC concentration in the mixture was 33 wt %; the EAC concentration was varied (0.5, 1, 2, or 5%) with the overall weight of the component equal to 0.2 g. Cation-selective membranes contained TBP as the EAC; the anion-selective membranes contained TBHDP. After evaporating the solvent, the membranes were placed in the electrode housing and exposed to distilled water for 24 h. Before use, the electrodes were conditioned in a solution of the IL to be determined (1×10^{-4} mol/L). The internal solution used was a 2×10^{-5} M solution of the IL to be determined in a 0.01 M potassium chloride solution. A silver wire coated with silver chloride was used as the internal reference electrode. A silver/silver chloride reference electrode (ESr 10108) filled with a saturated potassium chloride solution was used as the external reference electrode. The measurements were carried out with the use of a robotized software–hardware potentiometric complex we developed together with OOO Econix-Expert, Ltd. [15]. The hardware part of the complex is comprised of an Expert 001 four-channel high-ohmic voltmeter (pH meter), an autosampler, and a personal computer (PC). The pH meter and autosampler are interfaced to the PC through an RS 232 (COM) asynchronous serial interface. The autosampler is equipped with an integrated magnetic stirrer; its capacity is 12 cells each 100 mL in capacity. This complex is operated by a PC using our design software. The use of this complex enabled us to automate potentiometric measurements. As a result, we achieved precision in the immersion depth of the electrode and the duration of a single measurement; this also enabled us to accomplish replicate sets of measurements followed by statistical data processing.

The slope of the electrode function was determined by the lest-squares fits. The detection limit was derived from the departure of the electrode function from the extrapolated linear portion equal to $S\log 2$, where S is the slope of the electrode function. The pH dependence was studied starting at pH 2 (0.05 M H_2SO_4) with gradually changing pH by addition of lithium hydroxide. Potentiometric selectivity coefficients were determined using the separate solutions method [16]. The foreign ions used were the most abundant inorganic cations and anions, as well as some organic cations and anions, including components of other ILs: sodium (Na^+), ammonium (NH_4^+), benzylammonium ($PhCH_2NH_2^+$), *tert*-butyl ether ± isoleucine hydrochloride, diphenyldodecylethylphosphonium ($Ph_2C_{12}H_{25}Et^+$), chloride (Cl^-), nitrate (NO_3^-), iodide (I^-), perchlorate (ClO_4^-), and picrate (Pic^-) ions.

RESULTS AND DISCUSSION

To study the electrochemical characteristics as a function of EAC percentage, we prepared cation-exchange (TBP) and anion-exchange (TBHDP) membranes plasticized with *o*-NPOE (0.5, 1, 2, 5% EAC). The results of these studies are displayed in Table 1.

For the determination of the $BMIm^+$ cation of ILs in water with the use of the TBP-based membrane, the optimal EAC concentration is 0.5–2%. Fairly high sensitivity and precision are observed within these concentration bounds; the detection limit is 3×10^{-6} mol/L.

Table 2. Electrochemical properties of membranes with various plasticizers (2% EAC, $P = 0.95$, $n = 5$)*

EAC	TPB			TBHDP		
Plasticizer	*o*-NPOE	DES	DBP	*o*-NPOE	DES	DBP
Slope, mV/dec	57.4 ± 0.4	58 ± 2	56 ± 5	–58 ± 2	–53 ± 4	–54 ± 5
c_{min}, mol/L	3×10^{-6}	3×10^{-6}	4×10^{-6}	7×10^{-7}	5×10^{-7}	7×10^{-7}

* *n*—number of replicate measurements; *P*—set confidential level.

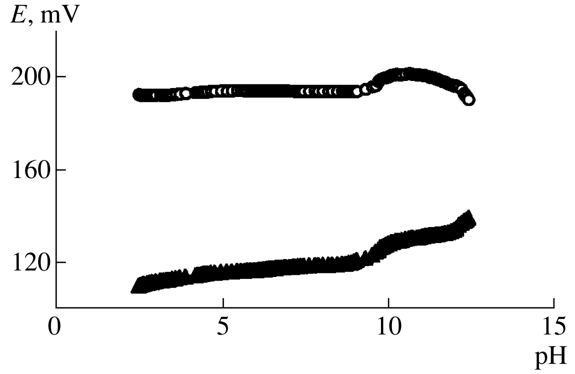


Fig. 1. Potential of the *o*-NPOE-based electrode (2 wt % EAC) vs. solution acidity.

When the EAC concentration is 5%, the detection limit is higher and the precision deteriorates.

Membranes based on anion-exchanger TBHDP are distinguished by the Nernstian slope of the electrode function in $BMImPF_6$ solutions; they have a wide linear range, low detection limits (to 5×10^{-7} mol/L), and good precision. For Tf_2N^- determination with anion-selective electrodes, an increase in the EAC concentration in the membrane appreciably increases the sensitivity: the Nernstian slope of the electrode function is reached with 2% EAC. However, the amount of the anion-exchanger in the membrane only insignificantly affects the lower detection limit and precision.

The electrochemical properties of cation- and anion-exchange PVC membranes in solutions of ILs were studied as dependent on the nature of the plasticizer for the EAC concentration in the membrane equal to 2 wt %. The plasticizers used differed in their dielectric constants ε: *o*-NPOE ($\varepsilon = 23$), DES ($\varepsilon = 5.0$), and DBP ($\varepsilon = 6.4$) [17]. The effect of the plasticizer used in the PVC membrane was studied on the following properties of the ISEs: the slope of the electrode function, selectivity to typical inorganic and some organic ions, linear range, and lower detection limit. All the electrodes tested show a potentiometric response to the components of the IL regardless of the plasticizer used. The detection limit is $n \times 10^{-6}$ to $n \times 10^{-7}$ mol/L (Table 2). For cation determination (TBP-based membranes), c_{min} and the electrode function slope are virtually independent of the plasticizer. For *o*-NPOE-plasticized membranes, however, the reproducibility of the analytical signal is far higher.

In the determination of IL anions (with TBHDP-based membranes), the Nernstian slope of the electrode function was observed only when *o*-NPOE was the plasticizer. For DES and DBP, the determination sensitivity was a little lower.

The ISE potential was studied as a function of solution acidity for cation-selective electrodes (TPB) and anion-selective electrodes (TBHDP) plasticized with *o*-NPOE in 0.001 M $BMImPF_6$ solution (Fig. 1). One can see from the plot that the potentials of electrodes with different EACs are virtually independent of solution acidity in a pH range of 2–9. For the anion-selective electrode, the solution pH has a higher influence on the membrane potential, especially in the alkaline pH range (pH > 10).

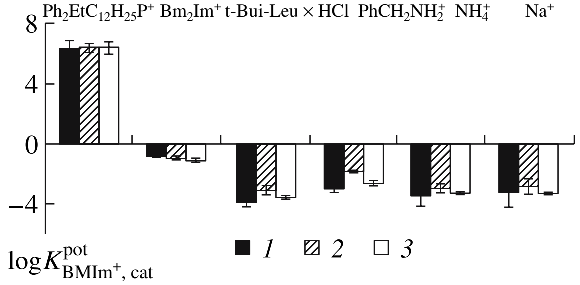


Fig. 2. Selectivity to $BMIm^+$ (2% EAC).

The electrodes have a high selectivity to the ions of the test ILs. All inorganic and some organic ions practically do not interfere with the potential of the indicator electrode (Figs. 2, 3). The effect of hydrophobic organic ions is stronger on the electrode response to potential-determining ions. However, this does not interfere with the determination of ILs in the presence of limited amounts of hydrophobic ions even such as Pic^- and ClO_4^-. DES- or *o*-NPOE-plasticized membranes have slightly higher selectivities to Tf_2N^- anion. The highly hydrophobic ion $Ph_2EtC_{12}H_{25}P^+$ most strongly interferes with the potentiometric determination of IL cations; this agrees with the mechanism of the response of cation-exchanger ISEs. The *o*-NPOE-based membrane has a higher selectivity to the desired cation in the presence of foreign ions, as in the determination of IL anions.

In summary, the membrane plasticized with *o*-NPOE and containing 2% of the TBHDP anion exchanger has the best analytical characteristics. The other membranes described in this work also give a satisfactory potentiometric response; they can also be used for IL determinations, as well as for ascertaining the water solubilities of ILs.

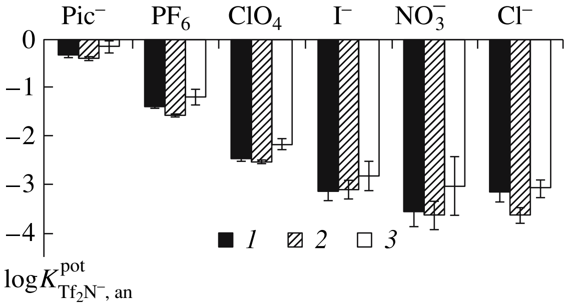


Fig. 3. Selectivity to Tf_2N^- (2% EAC (TBHDPBr)).

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