ISSN 0027-1314, Moscow University Chemistry Bulletin, 2007, Vol. 62, No. 4, pp. 200–203. © Allerton Press, Inc., 2007.
Original Russian Text © V.V. Sviridov, O.A. Avramenko, A.A. Raeva, I.V. Pletnev, V.E. Baulin, N.V. Shvedene, 2007, published in Vestnik Moskovskogo Universiteta. Khimiya, 2007, No. 4, pp. 245–249.

Nitrate-Containing Ionic Liquids as Active Membrane Components of Nitrate-Selection Electrodes

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Received October 10, 2006

Abstract—Two dialkylimidazolium nitrate ionic liquids (ILs) have been tested for use as an active component of plasticized PVC membranes in nitrate ion selective electrodes (ISEs). The potentiometric reversibility and the main electrochemical characteristics of the ISEs in KNO_3 solutions have been studied. The test membranes contain 5% of the active component and demonstrate a near-Nernstian response to NO_3^-. The use of a more hydrophobic IL based on dioctadecylimidazolium increases the sensitivity and decreases the detection limit: the slope of the electrode function is 57 mV/p*C*, and $C_{\min} = 3.7 \times 10^{-6}$ mol/L. The pH range of the membrane performance has been studied, and the potentiometric selectivity to NO_3^- in the presence of several foreign anions has been determined. The new electrode exceeds the commercially available analogue (an ELIT 021 nitrate-selective electrode) in the detection limit and response time. The utility of the new electrode for the direct potentiometric determination of nitrate ILs in aqueous solutions has been demonstrated.

DOI: 10.3103/S0027131407040062

Virtually all state-of-the-art plasticized-membrane nitrate ion-selective electrodes (ISEs) in their performance use associations of hydrophobic organic cations with NO_3^- anions [1]. In the vast majority of ISEs, anion exchangers are alkylammonium or alkylphosphonium salts. During the conditioning in a solution of the potential-determining ion, NO_3^- is extracted to the lipophilic membrane, whose extraction selectivity and, therefore, potentiometric selectivity correlate with the Hoffmeister lipophilicity raw [2]. Anion-exchange membrane electrodes were proposed for use in the pH-metric determination of relatively hydrophobic organic anions, such as ClO_4^-, BF_4^-, SCN^-, and NO_3^- [3, 4]. The electrode-active component (EAC) is formed on the membrane surface via association as a result of long conditioning in a solution of the potential-determining ion. We think that ISEs with the hydrophobic association containing the target ion being embedded directly into membranes have a higher potential [5, 6].

The analytical application of ionic liquids (ILs), which are ionic organic compounds in a molten state, is continually widening [7, 8]. Most often, compounds with melting temperatures not higher than 100°C are classified as ILs. Ionic liquids are used as solvents, diluents, and extracting agents in liquid–liquid extraction [9–11], voltammetry [12], capillary electrophoresis, and chromatography [13–15]. The feasibility of using ILs as EACs and plasticizers of polymer binders in ISE membranes has been documented [16].

In this work, we tested two ILs based on 1,3-dialkylimidazolium cations ($C_8C_{12}ImNO_3$ and $(C_{16})_2ImNO_3$) for use as the active components of PVC membranes for nitrate-reversible ISEs.

EXPERIMENTAL

Solutions and Reagents

Ionic liquids, namely, 1-octyl-3-dodecylimidazolium nitrate $C_8C_{12}ImNO_3$ (a liquid at room temperature) and 1,3-dihexadecylimidazolium nitrate $(C_{16})_2ImNO_3$ (a solid at room temperature; T_m = 68.5°C) were synthesized as described previously [17] (Table 1). *o*-Nitrophenyl octyl ether (*o*-NPOE; $\varepsilon = 24.5$; from Sigma) was used as a solvent and plasticizer in the manufacture of plasticized membranes. Poly(vinyl chloride) (S-70 grade) was used as the polymer matrix.

KNO_3 stock solutions and IL solutions were prepared by dissolving exactly weighed aliquots in distilled water. Weaker solutions were prepared by consecutive dilution. Solutions of foreign anions for potentiometric-sensitivity studies (1×10^{-3} mol/L; SO_4^{2-}, Cl^-, Br^-, I^-, CH_3COO^-, and ClO_4^-) were prepared by dissolving an exactly weighed aliquot of an alkali-metal (sodium, potassium, or lithium) salt, of reagent or analytical grade, in distilled water.

Table 1. Ionic liquids as electrode-active compounds

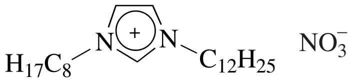
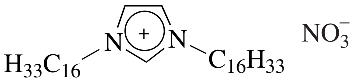
Name	Structural formula	Membrane notation
1-Dodecyl-3-octylimidazolium nitrate $C_8C_{12}Im^+NO_3^-$		I
1,3-Dihexadecylimidazolium nitrate $(C_{16})_2Im^+NO_3^-$		II

Table 2. Electrochemical properties of test membranes

Electrode	Electrode parameter				
	slope, mV	linear range, mol/L	$C_{min} \times 10^6$, mol/L	response time (10^{-1} mol/L), min	working pH range
I	–51 ± 5	1×10^{-1}–1×10^{-5}	5.0	2.5	3–10
II	–57.1 ± 0.8	1×10^{-1}–1×10^{-5}	3.7	2.5	3–10
ELIT 021	–58 ± 1	1×10^{-1}–1×10^{-5}	5.9	4.0	2–9

Manufacturing of Plasticized ISE Membranes

Film ISE membranes were manufactured using known technology [18] via dissolving PVC, a plasticizer, and an EAC in tetrahydrofuran while stirring. The EAC, plasticizer, and PVC concentrations were 5.0, 63.5, and 31.5 wt %, respectively. The IL was added directly to the membrane composition to serve as an EAC (ion exchanger).

The e.m.f. of a galvanic cell with transference was measured in order to study the electrochemical properties of the membranes. The cell was as shown below.

Ag/AgCl	Inner standard solution	Plasticized membrane	Test solution	AgCl/Ag

An Expert 001 pH meter was used to measure the e.m.f. The external reference electrode used was an

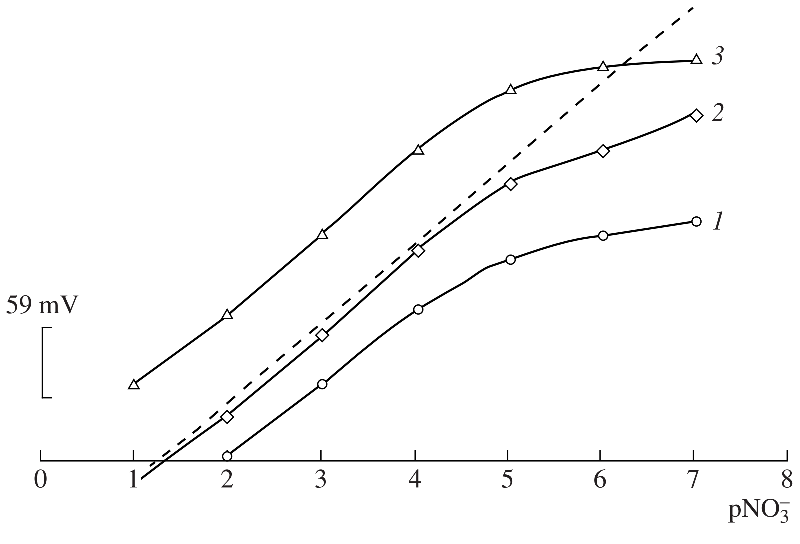


Fig. 1. Response of electrodes I, II, and ELIT 021 to KNO_3: (*1*) electrode I, (*2*) electrode II, and (*3*) ELIT 021. The dashed line is the Nernstian function.

Table 3. Potentiometric selectivity of electrodes

$\log K^{\text{pot}}_{X,\,NO_3^-}$	Electrode	
	II	ELIT 021
SO_4^{2-}	–3.41	–3.39
Ac^-	–2.04	–1.97
Cl^-	–1.45	–1.36
Br^-	–0.94	–0.69
Sal^-	0.99	1.38
I^-	1.01	1.06
ClO_4^-	2.55	2.81

EVL-1 M3 silver/silver chloride electrode. The potentiometric selectivity coefficient ($\log K^{\text{pot}}_{X,\,NO_3^-}$) was estimated using the bionic potentials technique with the main and interfering ion concentrations equal to 1 × 10^{-3} mol/L. The main performance parameters of the test electrode were compared to the parameters of an ELIT 021 nitrate-selective electrode, which is produced by Niko-Analit research and production company.

RESULTS AND DISCUSSION

Electrochemical Characteristics of IL-Based ISEs

The potentiometric response of the membranes containing dialkylimidazolium-based ILs and NO_3^- ions was studied (Table 1). All test ISEs in KNO_3 solutions respond to NO_3^-; the electrode function has a near-Nernstian slope (Fig. 1). The response time of the electrode is not longer than 2 min. The membrane potential is independent of solution acidity in a pH range of 3.0–10.0. The use of $(C_{16})_2ImNO_3$ (the more hydrophobic IL) increases the sensitivity and decreases the detection limit for NO_3^- (Table 2).

The electrochemical properties of IL membranes were compared to those of a commercially available ELIT 021 electrode. The IL-based ISEs exceed their commercial analogue in the detection limit $C_{\min}$ and the response time, the other parameters being competitive (Table 2).

Nitrate-Ion Selectivity of Membranes

In order to study the potentiometric selectivity of IL membranes, the potentiometric selectivity coefficients were measured in salt solutions containing 1×10^{-3} mol/L of the following foreign anions: sulfate, chloride, bromide, iodide, acetate, and perchlorate. The selectivity coefficients thus obtained are listed in Table 3.

The effect of the tested foreign ions on the response to NO_3^- increases in the order

$$SO_4^{2-} < Ac^- < Cl^- < Br^- < Sal^- < I^- < ClO_4^-.$$

The highest selectivity is observed in the presence of SO_4^{2-}; ClO_4^- most strongly interferes with the potentiometric determination of NO_3^-.

Response of Nitrate-Selective Electrodes in IL Solutions

The electrodes equipped with ILs as active components were used for the ionometric determination of

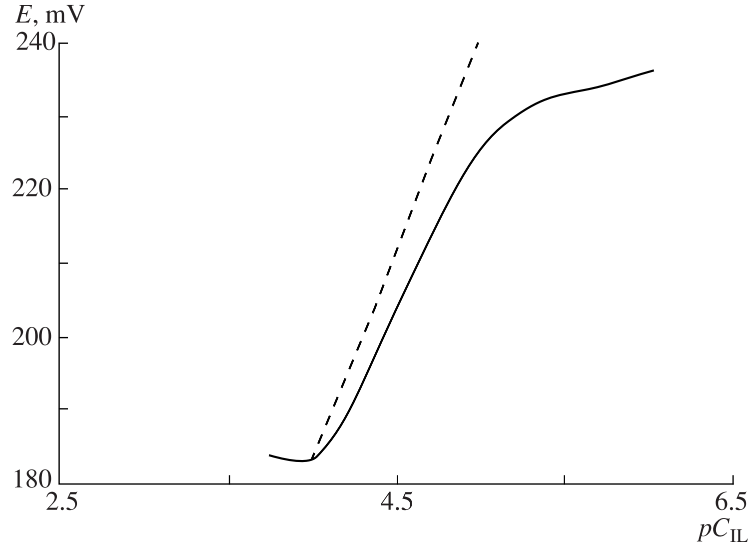


Fig. 2. Response of an ISE equipped with membrane II in a $C_8C_{12}ImNO_3$ aqueous solution. The dashed line is the Nernstian function.

NO_3^- in $C_8C_{12}ImNO_3$ IL solutions. The ISE in these solutions behaved differently than in KNO_3 solutions. The presence of dialkylimidazolium $C_8C_{12}Im^+$ (a large and hydrophobic cation) in the test solution substantially affected the response to NO_3^-. The NO_3^- sensitivity within a narrow concentration range was found only for membrane II, in which imidazolium $(C_{16})_2Im^+$ (a more hydrophobic cation) was the anion exchanger. For low IL concentrations (below 1×10^{-4} mol/L), an incomplete anionic function was observed with a slope of (43 ± 3) mV/pC; C_{min} was equal to 6.3×10^{-6} mol/L (Fig. 2). Such a sub-Nernstian electrode function is likely due to the presence of imidazolium hydrophobic cations, which penetrate the membrane and decrease its nitrate sensitivity. At higher IL concentrations (above 2×10^{-4} mol/L), the membrane loses its anion sensitivity; the electrode function is reversed to the anionic one, also because of the effect of the hydrophobic cation. In a narrow IL concentration range (1×10^{-4} to 1×10^{-5} mol/L), however, the electrode potential is well reproducible, making it possible to recommend the ISE for use in the selective determination of nitrate ILs, in particular, for evaluating the water solubility of such ILs.

Determination of the Water Solubility of $C_8C_{12}ImNO_3$

Electrode II, equipped with a $(C_{16})_2ImNO_3$ membrane, was used to determine the IL ($C_8C_{12}ImNO_3$) concentration in water. The ISE was calibrated in a $C_8C_{12}ImNO_3$ solution. The saturated solution was prepared using a previously described procedure [19]. Equal volumes of the IL and distilled water were shaken for 10 min. After the liquids separated, a 1-mL aliquot of the aqueous phase was sampled, diluted with distilled water (1 : 10), and measurements were carried out. The IL concentration was determined by direct potentiometry. The $C_8C_{12}ImNO_3$ solubility was determined as 5.6×10^{-4} mol/L.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 05-03-32976).

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