

# Ionic Liquid Based on a Quaternary Phosphonium Cation as a Plasticizer and an Electrode-Active Component of Ion-Selective Electrode Membranes

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**Abstract**—The dodecylethylidiphenylphosphonium bis(trifluoromethylsulfonyl)imide ionic liquid (IL) can behave as both a plasticizer and an electrode-active component in the membranes of ion-selective electrodes (ISEs). A stable potentiometric response to cationic surfactants is observed. The slope of the electrode function is close to the Nernstian value for cetylpyridinium (CP) bromide and cetyltrimethylammonium (CTMA) bromide; the detection limits are  $(5.0 \pm 1.0) \times 10^{-6}$  and  $(1.3 \pm 0.3) \times 10^{-5}$  mol/l, respectively. The membrane potential does not depend on pH in the range from 3 to 11. The possibility of determining the critical micelle concentration (CMC) with the ISEs is demonstrated.

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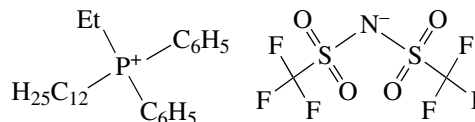
Search for new environmentally sound organic solvents has become topical [1]. Ionic liquids (ILs) are one class of such solvents. The nonvolatility, inflammability, thermostability [2], and frequently water-immiscibility make ILs suitable for use in synthesis, catalysis, extraction [3–6], chromatography [7–9], and electrophoresis [10–12]. The voltammetric applications of ILs are due to their ionic nature, a wide electrochemical window, and high ionic conductivity [13–16]. Recently, ILs have been used as solvents for preparing polymers with various physicochemical properties. Polymerization in ILs proceeds more rapidly and efficiently than in conventional solvents; ILs can behave as plasticizers, solvents, or both [18]. The extremely low volatility of ILs (compared to that of ethers and esters, which are conventional plasticizers) can in future provide basis for the design of plastic polymers with improved performance parameters. Ionic liquids both have ion-exchange properties and can plasticize some polymers. The combination of these properties makes it possible to use ILs as both plasticizers and electrode-active components in the manufacturing of membranes of ion-selective electrodes (ISEs). Here, we intend to verify this possibility.

## EXPERIMENTAL

### Reagents

Polyvinyl chloride, grade C-70, was used as a binder in the manufacturing of plasticized ISE membranes. The electrode-active component (ion-exchanger) and plasticizer both were dodecylethylidiphenylphosphonium bis(trifluoromethylsulfonyl)imide, the first-synthesized ionic liquid (IL):

ium bis(trifluoromethylsulfonyl)imide, the first-synthesized ionic liquid (IL):



Solutions of potential-determining ions (PDIs) and foreign ions were prepared from exact weights with consecutive dilutions. For this purpose, the following reagents were used: cetylpyridinium (CP) bromide ( $C_{16}H_{33}-N-C_5H_5Br$ ), cetyltrimethylammonium (CTMA) bromide ( $C_{16}H_{33}-N-(CH_3)_3Br$ ), benzylammonium hydrochloride ( $C_6H_5-CH_2NH_2HCl$ ), ammonium chloride ( $NH_4Cl$ ), potassium chloride (KCl), sodium chloride (NaCl), and lithium chloride (LiCl).

### Instruments and Techniques

Plasticized film membranes were manufactured using the procedure described in work [19]: the IL and PVC were one-by-one dissolved in tetrahydrofuran under stirring (for 2–3 h) and gentle heating (at 60°C). The weight ratio PVC : IL was varied from 1 : 1 to 1 : 2 (membrane weight, 0.3 g; diameter, 40 mm); the optimal ratio was determined by trial and error. Before measurements, the membrane was conditioned for 1.5–3 h in a PDI solution; then, direct potentiometric measurements were carried out on an Orion 420A ionometer/pH-meter. The external reference electrode used was an EVL-1M3T silver/silver chloride electrode (Russia) filled with a saturated KCl solution. The electrochemical properties of the test membranes were



Scheme 1.

studied by measuring the emf of the galvanic circuit with transference (Scheme 1).

The detection limit ( $c_{\text{min}}$ ) was estimated, in accordance with the IUPAC recommendations, as the deviation ( $S \log 2$ ) of the extrapolated linear portion of the electrode function from the experimental curve. Potentiometric selectivity coefficients were determined by the two-ion potential method [19].

pH control was accomplished on an Econix-expert model 001-3 (Russia) ionometer/pH-meter using an ESK-10601/7 (Russia) combination glass electrode. The potential was determined as a function of pH as follows: to a PDI solution acidified with strong  $\text{H}_2\text{SO}_4$  to pH 2, a 0.1 M NaOH solution was dropped.

The critical micelle concentration (CMC) was determined as follows. A series of CP bromide solutions with concentrations far higher than the suggested CMC were prepared from exact weights. Cetylpyridinium solutions with concentrations lower than the CMC were prepared by consecutive dilutions of a  $5 \times 10^{-3}$  M solution. The CMC was found as the point of the intersection of extrapolated linear portions of the electrode function in the region of high surfactant concentrations.

## DISCUSSION

In a search for the optimal membrane composition, we tested the PVC : IL ratios of 1 : 1, 1 : 1.5, and 1 : 2. In all cases, dodecylethylphenylphosphonium bis(trifluoromethylsulfonyl)imide plasticized PVC; the physical and performance parameters of the membrane improved with increasing IL proportion in the mem-

brane. The membrane with PVC : IL = 1 : 2 was a homogeneous, flexible, elastic, and transparent membrane.

Potential-determining ions (PDIs) were sought in order to study the electrochemical properties of the membrane. The highest potentiometric response was found in the solutions of salts of cations that have surfactant properties. Further, the membranes were investigated in their relation to CP bromide and CTMA bromide.

The electrode functions in the solutions of these surfactants have near-Nernstian slopes. The electrode has good performance parameters toward CP: the slope is  $57 \pm 3$  mV/dec;  $c_{\text{min}} = (5 \pm 1) \times 10^{-6}$  mol/l. In CTMA solutions, the test membrane also has the Nernstian response and the reproducibility of the potential is good ( $59.5 \pm 0.2$ ) mV/dec, but  $c_{\text{min}}$  is slightly worse:  $(1.3 \pm 0.3) \times 10^{-5}$  mol/l (Fig. 1).

In order to decrease  $c_{\text{min}}$ , we varied the concentration of the CP and CTMA inner solutions. A decrease in the PDI concentration in the inner solution from  $5 \times 10^{-6}$  to  $1 \times 10^{-6}$  mol/l leads to an abrupt decrease in the slope of the calibration curve but only insignificantly decreases  $c_{\text{min}}$ . The optimal surfactant concentration in the inner solution is  $5 \times 10^{-6}$  mol/l.

The potentiometric selectivity coefficients of the membrane toward PDIs in the presence of foreign ions were determined by the two-ion potential method (Fig. 2). The ISE membrane has a high selectivity to cationic surfactants. Alkali-metal and ammonium cations, and well as low-hydrophilic benzylammonium

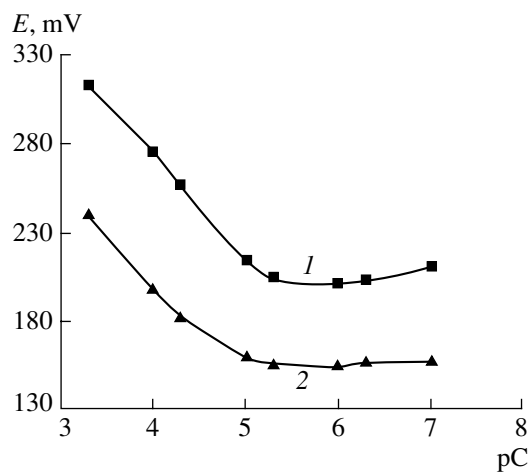


Fig. 1. Electrode functions of ISEs in solutions of (1) CP bromide and (2) CTMA bromide.

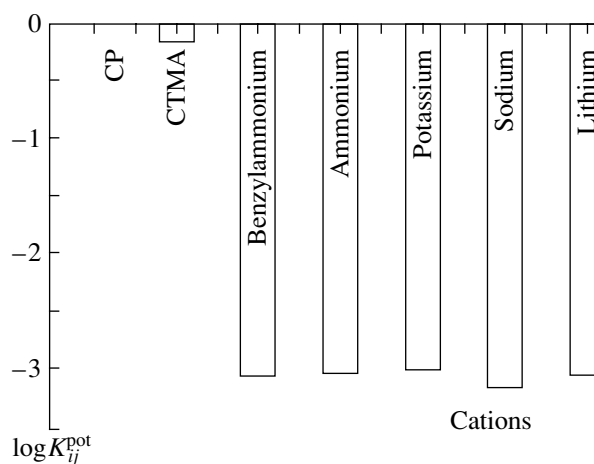


Fig. 2. Potentiometric selectivity of ISEs toward CP in the presence of foreign ions (CP-sensitive electrode).

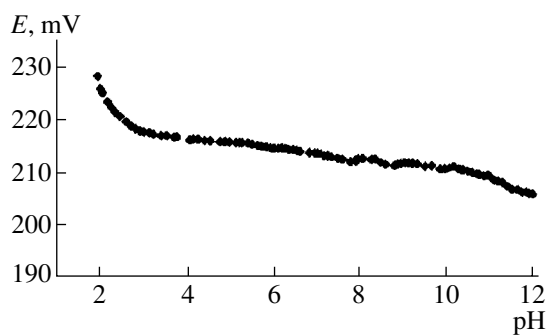


Fig. 3. ISE potential vs. pH ( $1 \times 10^{-4}$  mol/l CP).

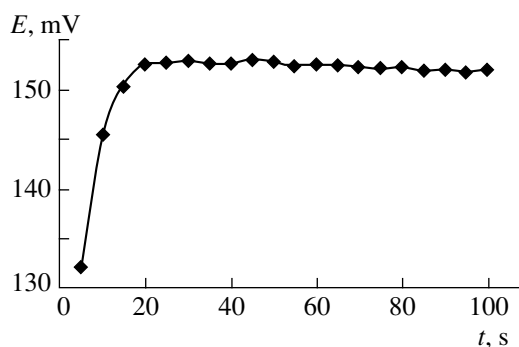


Fig. 4. Response time of the ISE membrane in a CP solution ( $5 \times 10^{-5}$  mol/l).

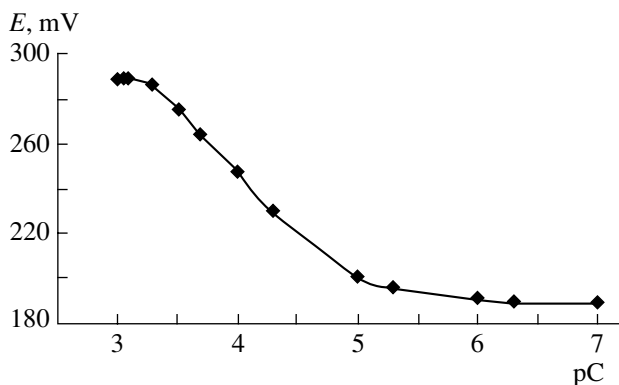


Fig. 5. Electrode function of the ISE for CMC determination for CP.

cations, practically do not affect the CP or CTMA determinations. The membrane has a slightly higher affinity to CP than to CTMA, but the difference is not great.

The membrane potential is independent of pH over a wide range from 3 to 11. The slight decrease in the potential at pH > 10 is likely due to the error of the glass electrode at high alkaline pHs. The abrupt ascent of the pH curve at acidic pHs is more difficult to interpret. Likely, this ascent is due to the acid–base properties of

the electrode-active component, e.g., the protonation of the bis(trifluoromethylsulfonyl)imide anion (Fig. 3).

A significant advantage of our membranes is the retention of the stability and precision of their electrochemical characteristics even after several months; this is on account of the extremely low volatility of ILs. It is noteworthy that the weekly measurements of the membrane potential in solutions of cationic surfactants yield unchanged values of the slope of the electrode function (only absolute values of the potential insignificantly change); this means that the test ISE has good performance parameters. When the ISE is stored properly (when it is immersed, together with the inner solution, in a dilute solution of PDIs), it retains its electrochemical properties during long periods of time. The potentiometric response time even in dilute solutions of cationic surfactants is not longer than 20 s (Fig. 4).

It is known that direct potentiometry with ISEs is a method for measuring ion activities (equilibrium concentrations); the CMC can be derived from the slope of the electrode function in the region of high surfactant concentrations (Fig. 5). A value of  $(5.37 \pm 0.20) \times 10^{-4}$  mol/l was determined for the cetylpyridinium CMC with the use of the ISE designed. This result matches the literature data [20].

In summary, we have shown that dodecylethyl-diphenylphosphonium bis(trifluoromethylsulfonyl)imide is suitable for manufacturing new compositions for ISE membranes; this IL behaves both as an electrode-active component and solvent/plasticizer. The application perspective of the electrode is on account of the high sensitivity, precision, and selectivity of surfactant determination. The short response time, simple implementation, and high precision of the analytical signal allows us to recommend this ISE for use as a potentiometric detector in in-flow analysis and in chromatography.

#### ACKNOWLEDGMENTS

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