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Ionic liquids based on quaternary phosphonium cation as active components of solid-state iodide selective electrode

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ABSTRACT

The two ionic liquids (ILs) which melt above room temperature were used as active components of solid-state ion-selective electrodes (ISEs). The both ILs are composed of quaternary phosphonium cation and fluorinated anion, namely bis(trifluoromethylsulfonyl)imide and hexafluorophosphate. Molten and then solidified ILs were used to cover solid-state screen printed electrodes with an ion-sensing layer. The sensors show the response towards iodide. The addition of tetrakis(*tert*-butyl)phthalocyaninatocobalt (III) iodide to ion-sensing composition significantly improved the operational characteristics. The resulting ISE demonstrates good sensitivity and detection limit: $S = -(58.0 \pm 0.8)$ mV/dec, $C_{min} = 6 \times 10^{-5}$ M; response time is ca. 15 s. A high selectivity towards iodide over number anions is observed. The ISE could be used for at least a month without any deterioration of signal.

1. Introduction

Analytical chemists are always interested in novel materials which favorably influence the existing applications and give rise to the novel ones. Due to their unique properties, ionic liquids (ILs) belong to the field of promising innovative materials. They are extensively applied in various fields of analytical chemistry [1,2]. Thus, ILs are used as solvents and extractants in separation [3,4]; as components of mobile or stationary phase in chromatography [5,6]. Solid matrixes incorporating IL are used in MALDI mass-spectrometry [7]. Various electrochemical analytical procedures [8], particularly, potentiometry with ion-selective electrodes are among the most promising applications of ILs.

To date, there appeared only a few publications devoted to the use of ILs in ionometry. In general, IL-based sensors are characterized by fast response time, high sensitivity, good selectivity and reproducibility of the analytical signal. Most often ionic liquids were used as electrode active compounds of the plasticized membrane of the ion-selective electrode (ISE) [8–13]. The most important properties which affect IL applicability in electrochemical sensors are hydrophobicity, (in)solubility in water, solvating and polymer plasticizing properties. Notably, it was shown that IL can act both as ionophore and plasticizer in poly(vinyl chloride) membrane ion-selective electrodes (electrode for sulfate [14], electrodes for cationic and anionic surfactants [9–11], for nitrate [12]). Methods of ionometric determination of a number of organic and inorganic ions have been developed (bromide, iodide, nitrate, phenolates, anionic surfactants, etc.).

An attention has been recently drawn to ILs that melt slightly above room temperature [15,16]. When molten, such organic salts may be used to cover the indicator surface of the electrode; the covering becomes solid after cooling. This approach allows one to use such ILs to form ion-sensitive layer of solid-state planar printed sensors (provided that IL exhibits ability to ion exchange with the ions of aqueous solutions). Notably, even the ILs which do not exhibit good ion-exchange properties themselves (e.g., due to high hydrophobicity of the constituent ions) may be used as a solid matrix to embed a suitable non-IL–ionophore.

Noteworthy is mentioning that the stability and ion-to-electron transduction are well-known problems in the design of solid-state sensors [17]. The most explored way to overcome the related issues is application of various polymers acting as an intermediate layer between the electronic conductor and the ionic-conductive ion-selective membrane [18]. It was recently shown [15,16] that ionic liquids may also be helpful, in this relation.

Herein, we report on the study of two ILs with diphenylbutylethylphosphonium cation and fluorinated anions, bis(trifluoromethylsulfonyl)imide and hexafluorophosphate, as ISE components. Melting points of both ILs lie above room temperature; this allowed to use them for the creation of solid-state sensors. Due to hydrophobicity of IL cation, the expected role of ILs is primarily an anion-exchanger (though some ability to cation-exchange may also be expected for bis(triflyl)imide salt).

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2. Material and methods

2.1. Reagents and equipment

Ionic liquids (Table 1) diphenylbutylethylphosphonium bis(trifluoromethylsulfonyl)imide (DPBEP–Tf_2N m.p. 72 °C) and hexafluorophosphate (DPBEP–PF_6 m.p. 130.0 °C) were synthesized by Dr. V. Baulin, Institute of Physiologically Active Compounds RAS, Chernogolovka; tetrakis(*tert*-butyl)phthalocyaninatocobalt(III) iodide (Co(TBPC)I, Table 1) was synthesized at the department of organic chemistry of Moscow University by Prof. L.Tomilova.

All aqueous solutions for potentiometric measurements were prepared with distilled/deionized water. The silver chloride electrode Esr-10101 (Russia) was used as reference electrode. Potentiometric measurements were performed with pH-meter/ionomer Expert-001 (Econiks-Expert, Russia) at 20 ± 2 °C.

2.2. Modification of the solid-state electrode

The screen-printed electrodes, SPE (for further modification), were purchased from Elcom, Russia. The SPE has a layered design with silver, graphite and insulator ink layers printed at the polyester substrate; electrode work surface (which is not more than 0.2 cm^2) is free of insulator.

Modification of SPEs was performed by putting a piece of solid IL to the electrode's surface and heating for a few seconds so IL melted and flowed over the surface; after removing from heat, solidified IL formed a layer on the surface. In the case of IL and ionophore mixture, electrode's surface was modified through an alternative procedure. Appropriate amounts of the both substances were dissolved in 2–3 drops of tetrahydrofuran (THF) and a droplet of the solution was placed onto the graphite surface of electrode. After THF evaporated, IL/ionophore composition formed a solid layer on the surface. The whole procedure of preparation of modified solid-state electrodes (SSE) requires approximately 3 min. The electrodes may be used immediately after preparation.

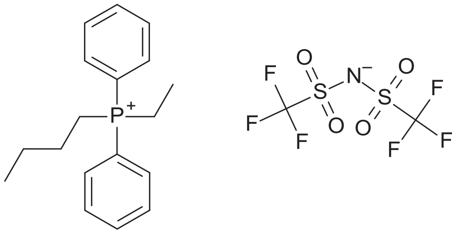
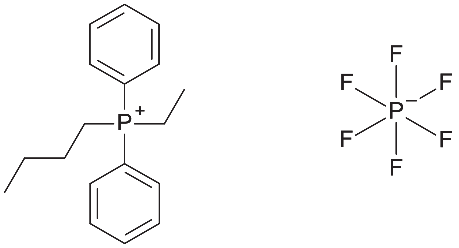
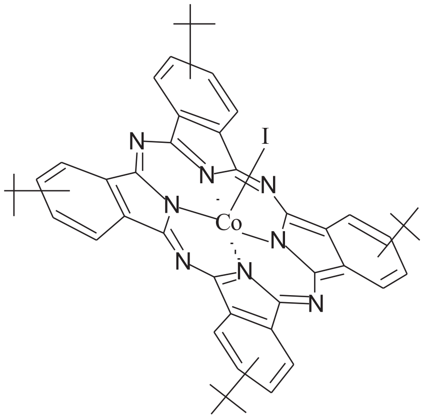
2.3. Preparation of plasticized membrane electrode

For the preparation of the plasticized membrane, powdered high molecular weight poly(vinyl chloride) (PVC; Fluka) as the polymer matrix and 2-nitrophenyloctyl ether (2-NPOE; Fluka, ≥ 99%) as the plasticizer were used. Weighed amounts of DPBEP–PF_6, Co(TBPC)I, PVC, and 2-NPOE were dissolved in freshly distilled THF, mixed for several hours, transferred into a glass dish, and kept overnight for solvent evaporation; a homogeneous flexible film was obtained. Disk-shaped membranes were cut and incorporated into an electrode Teflon body with 10 mm internal diameter. The electrode was filled with an internal solution containing 10^{-3} M potassium chloride and 10^{-3} M potassium iodide.

2.4. Measurement of potential

The response was monitored in 1×10^{-6} M to 1×10^{-1} M aqueous iodide solution. The solutions were stirred and potential

Table 1
Compounds studied in the present work.

Name	Structure formula
Diphenylbutylethylphosphonium bis(trifluoromethylsulfonyl)imide (DPBEP–Tf_2N)	
Diphenylbutylethylphosphonium hexafluorophosphate (DPBEP–PF_6)	
Tetrakis(tert-butyl)phthalocyaninatocobalt(III) iodide (Co(TBPC)I)	

readings recorded when they reached steady state. The EMF was measured in the electrochemical cell: Ag/AgCl, KCl || test solution | modifier | SSE. Potentiometric selectivity coefficients were determined by a separate solutions method.

3. Results and discussion

3.1. *ISEs based on DPBEP–Tf$_2$N and DPBEP–PF$_6$*

The response of electrode covered with DPBEP–Tf$_2$N was tested in solutions of various salts. Preliminary screening revealed no response to cations (a weak response of poor reproducibility of potential and low sensitivity with slope 20 mV/decade was detected towards tetradecyltrimethylammonium, Fig. 1). Only iodide produced a sub-Nernstian response among anions (Fig. 1). However, anionic function is characterized by poor reproducibility and rather moderate slope, -18 mV/decade. Such a behavior may be attributed to the too high hydrophobicity of IL's anion which negatively affects the ability of ion-exchange (also, it may be related to the too high association degree of IL ions).

One can expect that DPBEP–PF$_6$ IL is a better anion-exchanger than DPBEP–Tf$_2$N, and that the corresponding ISE has better characteristics because hexafluorophosphate anion is significantly less hydrophobic than bis(trifluoromethylsulfonyl)imide [19]. Indeed, the experimental data confirmed this suggestion. The DPBEP–PF$_6$ solid-state ISE showed response to anions and absolutely no response towards cations (including quite hydrophobic tetradecyltrimethylammonium and cetylpyridinium cations). The results are showed in Table 2.

The iodide produced the best response among the studied anions (chloride, bromide, nitrate, iodide, salicylate, thiocyanate, dodecylsulfate, benzoate; cation is K^+ or Na^+). Despite the results obtained with PF$_6$–IL are superior to those with Tf$_2$N–IL, the slopes of electrode function are still far from theoretical (Table 3).

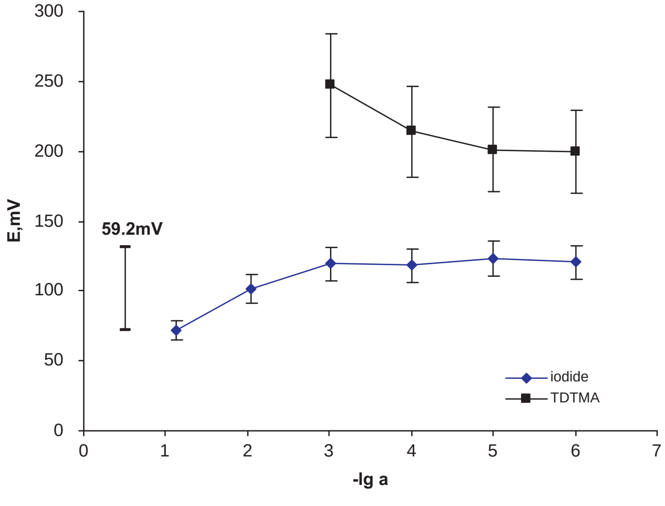


Fig. 1. Potentiometric response of solid-state electrode modified with DPBEP–Tf$_2$N towards iodide and tetradecyltrimethylammonium (TDTMA).

Table 2
Potential of electrode based on DPBEP-PF$_6$ in the solution of salts with various anions.

Anion	Cl^-	Br^-	NO_3^-	I^-	Sal^-	SCN^-
E (mV)	86	84	87	48	75	78

Table 3
The characteristics of iodide-selective electrodes ($n=3$, $P=0.95$).

Composition (wt %)		Slope (mV/decade)	Detection limit, M	Linear range, M	Response time (s)
DPBEP–PF$_6$	Co(TBPC)I				
100	0	-37 ± 5	4.0×10^{-4}	1×10^{-1}–8×10^{-3}	50
80	20	-58 ± 1	6.2×10^{-5}	1×10^{-1}–1×10^{-4}	15

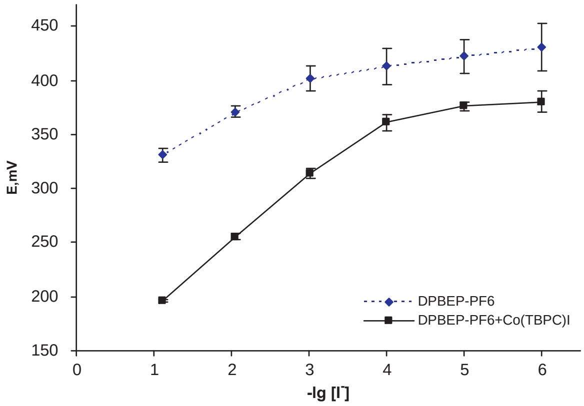


Fig. 2. Potentiometric response of solid-state electrode modified with DPBEP–PF$_6$ towards iodide.

To improve the sensor characteristics, the solid-state electrode was modified by composition containing an additional ionophore, Co(TBPC)I (IL:ionophore ratio=4:1 by weight). It was expected that ionic liquid will act as a matrix (possessing also mild anion-exchange properties), while Co(TBPC)I will specifically interact with target ion, iodide (literature data: [20]). Noteworthy is mentioning that Co(TBPC)I can provide a smooth transition from ionic to electronic conductivity, which positively affects the sensor's properties.

Indeed, the presence of metallated phthalocyanine significantly improved characteristics of the solid-state electrode: the linear range of electrode function has expanded, reproducibility of the potential has improved, and the limit of detection has reduced (see Table 3).

One may explain these effects by the contribution of iodide exchange processes $I^-_{solution}\leftrightarrow I^-{}_{ionophore}$ to the formation of analytical signal. Interaction between iodide and Co(TBPC)I can proceed along two different paths: an extra-coordination of additional iodide to Co(III)I which coordination number increases up to 6:

$$CoLI_{(o)}+X^-_{(aq)}\rightarrow CoLIX^-_{(o)} \tag{1}$$

and simple exchange of ionophore's coordinated iodide with the anion of solution:

$$CoLI_{(o)}+X^-_{(aq)}\rightarrow CoLX_{(o)}+I^-_{(aq)} \tag{2}$$

where $X^-=I^-$.

At the moment, we cannot deduce ultimately which of these two mechanisms – "neutral carrier" (1) or "charged carrier" (2) [16] – is operative Fig. 2.

As for the response time of the electrode modified with DPBEP–PF$_6$ and Co(TBPC)I a stable potential was reached in 15 s.

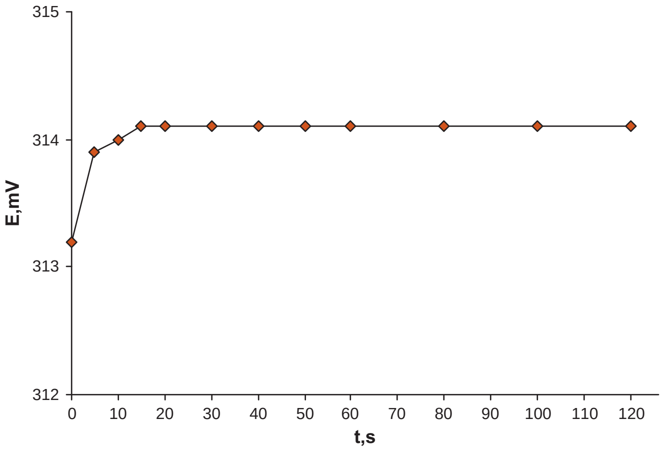


Fig. 3. Dependence of the potential on the response time of solid-state iodide-selective electrode modified with composition DPBEP–PF$_6$+Co(TBPC)I ($C_{\text{iodide}} = 1 \times 10^{-4}$ M).

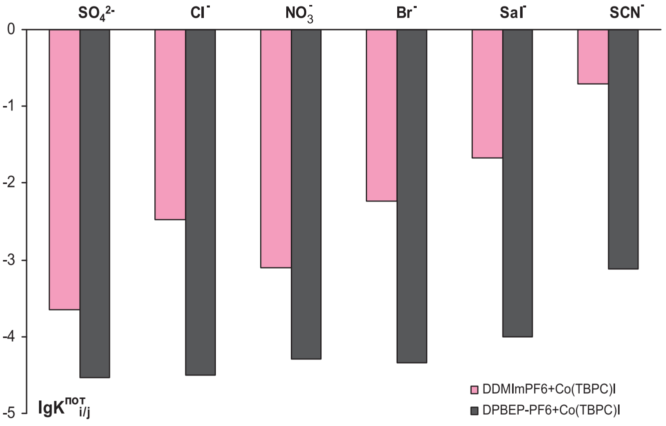


Fig. 4. Potentiometric selectivity of iodide-selective electrodes containing Co(TBPC)I and various ILs (1-1-dodecyl-3-methylimidazolium hexafluorophosphate (DDMIm–PF$_6$), [16]; 2-DPBEP–PF$_6$).

(Fig. 3). The studied ISE has stable potential which practically does not drift for a long time, at least 1 month.

3.2. Potentiometric selectivity

The potentiometric selectivity of solid-state iodide-selective electrode based on DPBEP–PF$_6$–Co(TBPC)I composition was studied. The ISE demonstrated an anti-Hofmeister selectivity order, as seen in Fig. 4. What is more interesting, sensor exhibited high selectivity towards iodide not only in the presence of hydrophilic anions, such as sulfate and chloride, but also such hydrophobic anions as Sal^-, SCN^- (which typically interfere determination of iodide). All the selectivity coefficients are lower than n-10^{-3}. As a result, the determination of iodide is possible in the presence of more than 1000-fold amounts of thiocyanate and more than 10,000-fold amounts of salicylate.

It is worth mentioning that the selectivity of SSE modified with DPBEP–PF$_6$–Co(TBPC)I composition is superior to previously described sensor [16], which also contained cobalt phthalocyanine embedded into solidified matrix formed by another IL, 1-dodecyl-3-methylimidazolium hexafluorophosphate. Most probably, the difference in selectivity should be attributed to worse anion-exchange properties of substituted quaternary phosphonium (this work) cation, as compared to imidazolium [16] one; as a result, the specific interaction of cobalt phthalocyanine with iodide may have a larger role for phosphonium–IL based sensing environment. Moreover, the worse properties of imidazolium IL electrode may be related to more significant leaching of IL cation into aqueous phase thereby reducing the sensitivity to iodide (we are grateful to the anonymous reviewer for suggesting this point).

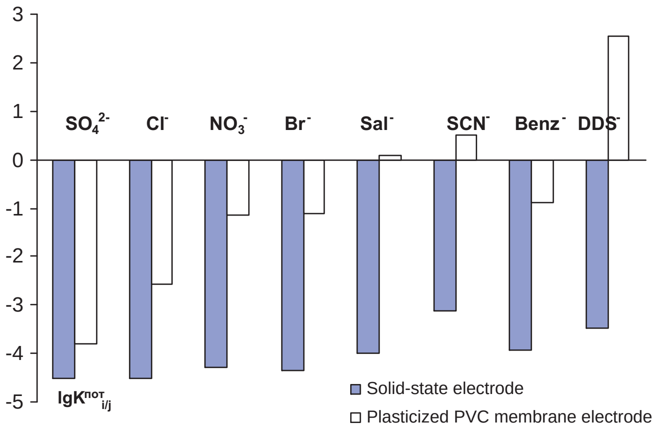


Fig. 5. Potentiometric selectivity of iodide-selective solid-state electrode vs. PVC-membrane one. The both electrodes contain the same active components, Co(TBPC)I and DPBEP–PF$_6$.

To compare results the plasticized PVC membrane electrode based on the same IL:Co(TBPC)I (4:1 by weight) composition was prepared and studied. This electrode does exhibit the response to iodide. However, the slope of electrode function $-(40 \pm 1)$ mV/decade is significantly below the theoretical value and the limit of detection is not better than 2×10^{-4} M. Most importantly, the selectivity of this ISE generally follows to Hoffmeister series (Fig. 5). In particular, significant interferences in iodide determination were found in the presence of relatively lipophilic salicylate, thiocyanate and dodecylsulfate anions. All in all, solid-state ISE shows much better characteristics than the PVC-membrane one.

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References

[1] D.W. Armstrong, P. Sun, Anal. Chim. Acta 661 (2010) 1–16.
[2] T. Torimoto, T. Tsuda, K. Okasaki, S. Kuwabata, Adv. Mater. 22 (2010) 1196–1221.
[3] I.V. Pletnev, S.V. Smirnova, K.S. Khachatryan, V.V. Zernov, Ross. Khim. Zh. 48 (2004) 51–58.
[4] J. Wang, D. Cheng, X. Chen, Z. Du, Z. Fang, Anal. Chem. 79 (2007) 620–625.
[5] T. Payagala, Y. Zhang, E. Wanigasekara, K. Huang, Z.S. Breitbach, P.S. Sharma, L.M. Sidisky, D.W. Armstrong, Anal. Chem. 81 (2009) 160–176.
[6] C. Giaginis, A. Tsantili-Kakoulidou, Biomed. Chromatogr. 25 (2011) 606–612.
[7] A. Tholey, M. Zabet-Moghaddam, E. Heinzle, Anal. Chem. 78 (2006) 291–297.
[8] N.V. Shvedene, D.V. Chernyshov, I.V. Pletnev, Ross. Khim. Zh. 52 (2008) 80–91.
[9] N.V. Shvedene, D.V. Chernyshov, M.G. Khrenova, A.A. Formanovsky, V.E. Baulin, I.V. Pletnev, Electroanalysis 18 (2006) 1416–1421.
[10] N.V. Shvedene, D.V. Chernyshov, Yu.P. Gromova, Russ. J. Anal. Chem. 65 (2010) 880–884.
[11] D.V. Chernyshov, M.G. Khrenova, I.V. Pletnev, V.E. Baulin, N.V. Shvedene, Vestn. Mosk. Univ. Ser.2: Khim. 48 (2007) 56–59.
[12] V.V. Sviridov, O.A. Avramenko, A.A. Raeva, I.V. Pletnev, V.E. Baulin, N.V. Shvedene, Vestn. Mosk.Univ. Ser.2: Khim. 48 (2007) 245–249.
[13] R. Gourishety, A.M. Crabtree, W.M. Sanderson, R.D. Johnson, Anal. Bioanal. Chem. 400 (2011) 3025–3033.

[14] C. Coll, R.H. Labrador, R.M. Manez, J. Soto, F. Sancenon, M.-J. Segui, E. Sanchez, Chem. Commun. (2005) 3033–3035.
[15] D.V. Chernyshov, V.M. Egorov, N.V. Shvedene, I.V. Pletnev, ACS Appl. Mater. Interfaces 1 (2009) 2055–2059.
[16] N.V. Shvedene, O.A. Avramenko, V.E. Baulin, L.G. Tomilova, I.V. Pletnev, Electroanalysis 23 (2011) 1067–1072.
[17] B.P. Nikolskii, E.A. Materova, Ion-Sel. Electrode Rev. 7 (1985) 3–39.
[18] J. Bobacka, Anal. Chem. 71 (1999) 4932–4937.
[19] J.M. Crosthwaite, S. Aki, E.J. Maginn, J.F. Brennecke, J.Phys. Chem. B. 108 (2004) 5113–5119.
[20] E. Baker, E. Malinowska, R.D. Shiller, M.E. Meyerhoff, Talanta 41 (1994) 881–890.