



## Solidified ionic liquid as crystalline sensing element of the bromide selective electrode



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### ABSTRACT

We report on the use of solidified ionic liquid (low-melting ionic solid, m.p. 78 °C) 1,3-dihexadecylimidazolium bromide,  $[(C_{16})_2Im]Br$ , as a sensing layer in solid-state ion-selective electrode for bromide. This crystalline material demonstrates high selectivity to the target ion: both too small (strongly hydrated) and too large anions are discriminated. This pattern is in sharp contrast with usual Hofmeister-like series obtained for the sensor based on conventional plasticized PVC membrane containing the same compound,  $[(C_{16})_2Im]Br$ .

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### 1. Introduction

As the name suggests, the most remarkable feature of ion-selective electrodes (ISEs) is the selectivity of their response towards external ions. Given the availability of cheap and simple equipment for direct potentiometric analyses, this provides a strong support for long-term and wide-spread use of ISEs as analytical tool [1]. However, the ISE selectivity is typically far from absolute, and this is especially true for the sensors toward anions. While cation (especially, metal ion) selective ionophores are well known and ubiquitously used in practice [2,3], the selective reagents for anions are much less abundant, and conventional anion-exchangers are still widely employed. For the most common plasticized polyvinyl chloride (PVC) membrane electrodes containing dissolved anion-exchangers, the selectivity typically follows the so-called Hofmeister series. Hofmeister, more than 100 years ago, noticed the specific order in which an anion's (more strictly, salt's) ability to precipitate proteins (and some other materials as well) decreases [4,5]. The very similar order is observed for the increase of efficiency of solvent extraction of anions into non-polar solvents; for univalent ions, the series [6] is  $Cl^- < Br^- < NO_3^- < SCN^- < I^- < ClO_4^-$ . It is well known that this order may be correlated with the decrease in free hydration energy and increase of anion's size/inverse charge density, see Table 1 for selected reference data. This

order is typically preserved for selectivity of ion-exchanger based ISEs. Recent publication [7] listed the potentiometric selectivity coefficients bromide/other anion  $X^-$ ,  $\log k_{Br,X}^{pot}$ , measured for 21 ISEs (based on various quaternary ammonium, phosphonium, dialkylimidazolium and other azaheterocyclic cations) with respect to 17 anions  $X^-$ . Despite large variation of cation's structure as well as variation in pair-wise coefficient differences, the order  $F^- < Cl^- < Br^- < NO_3^- < Sal^- < SCN^- < ClO_4^- < Pic^-$  is invariably observed for univalent anions. Again, this series completely parallels the ion hydration data, Table 1 (which evidently means that no specific cation-anion interactions are operative in non-aqueous phase).

The ability to alter the hydration-driven selectivity pattern would be highly beneficial for the design of ion sensors tuned to various practical applications. Currently, such ability is most often associated with use of ligands able of specific interaction with selected anions through host-guest complexation [2,9], especially with use of metallated compounds [10–12]. Another well-known, and historically older, approach is the use of low-soluble inorganic salts as sensing materials; their affinity to anions correlates with the inverse solubility product. Well known examples are highly specific  $LaF_3$  based fluoride-selective electrode [13] and silver salt electrodes for determination of halides and sulfide [14]. Both approaches have their advantages and drawbacks (e.g., specific hosts are not easy to design and synthesize; the choice of inorganic solids suitable for sensor application is limited, etc.). Any additional general approach to altering selectivity of anion-sensitive materials—ideally, providing a peak selectivity—would be highly valuable for ion sensing and ion separations.

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**Table 1**  
Potentiometric selectivity coefficients of  $[(C_{16})_2Im]Br$  electrodes studied in this work and free energy of hydration  $\Delta G_h(X^-)$  and size of representative anions. Thermochemical radii  $R$  and hydration data are from Moyer et al. [6]; if not available, the hydration energies estimated by Mezhev et al. [8] by solvent extraction data are used (marked with asterisk).

Anion $X^-$	IOS-ISE	PVC-ISE	$\Delta G_h(X^-)$ , (kJ mol $^{-1}$ )	$R(X^-)$ , (Å)
$S^{2-}$	-0.87	-0.68	-1315	1.91
$SO_3^{2-}$	-2.54	-1.04	-1295	2.00
$SO_4^{2-}$	-2.82	-1.43	-1080	2.30
$F^-$	-1.32	-1.12	-465	1.26
$Cl^-$	-0.85	-0.69	-340	1.72
Benzoate, $Bzo^-$	-0.78	1.9	-320*	-
$Br^-$	0	0	-315	1.88
$NO_3^-$	-0.17	0.16	-300	1.96
Salicylate, $Sal^-$	0.08	1.28	-282*	-
$SCN^-$	0.36	1.65	-280	2.13
$I^-$	0.33	1.38	-275	2.10
$ClO_4^-$	-0.08	2.93	-205	2.4
Picrate, $Pic^-$	0.34	4.72	-190	3.29
Dodecylsulfate, $DDS^-$	-0.7	4.19	-165*	-
Bis(2-ethylhexyl) sulfosuccinate), $BEHSS^-$	-0.64	5.01	-131*	-
Tetraphenylborate, $BPh_4^-$	-2	7.28	50	4.21
<i>N</i> -Lauroylsarcosinate, $LS^-$	-1.42	1.87	-	-

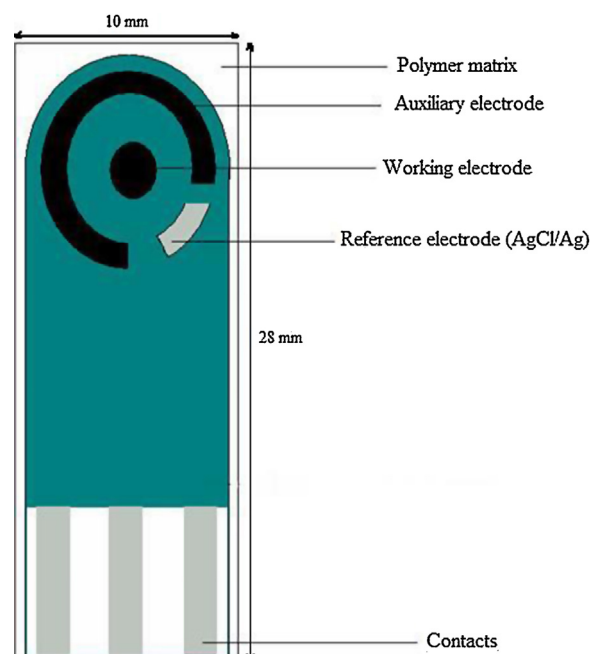
One of the promising recent approaches in ISE field is the use of ionic liquids (ILs) [15,16], fluidic organic salts which may serve as media, ion-exchangers and even plasticizers [17–19] of polymeric membranes. However, from the selectivity's viewpoint ionic liquids typically exhibit conventional ion-exchanger Hofmeister-like behaviour, unless additional specific ionophore is introduced. Recently, we suggested to use, as ion-sensing element of selective electrode, the low-melting organic ionic solids [20] formed by solidification of ionic liquids which melt slightly above ambient temperature (by popular current definition, ILs are compounds which are liquid at or below 100 °C [21]). Using of such ionic organic solids (IOS) makes preparation of all-solid-state sensors straightforward: the procedure involves melting of material followed by a subsequent cooling directly at the surface of appropriate support. As organic ionic solids are close relatives to inorganic solids, one may hope that at least some of them would exhibit high and non-Hofmeister selectivity resembling that of inorganic crystal ISEs. Of course, such a behaviour is not guaranteed as selectivity depends on the details of IOS structure. Indeed, our first studies [20] produced nothing but Hofmeister-like selectivity patterns. However, as is described below, ionic solid 1,3-dihexadecylimidazolium bromide does match original expectations: the corresponding bromide-selective sensor exhibits much higher selectivity than PVC membrane analog, and the selectivity series does substantially differ from Hofmeister's one.

## 2. Experimental details

The compound 1,3-dihexadecylimidazolium bromide ( $[(C_{16})_2Im]Br$ , m.p. 78 °C) was synthesized by Dr. V. Baulin, Institute of Physiologically Active Compounds RAS, Chernogolovka. Its synthesis described in [26] as the first step in synthesis of nitrate salt of the same cation. The ISEs with IOS sensing layer (IOS-ISE) were produced by modification of commercially available SPE, screen-printed electrodes (Elcom, Russia). The SPE have layered design with silver, graphite and insulator ink layers printed at the polyester substrate; electrode dimensions are  $10 \times 28 \times 0.035$  mm (Fig. 1). Electrode work surface (not more than  $0.2 \text{ cm}^2$ ) is free of insulator. Modification of SPE was performed by putting a piece of solid IL to the electrode's surface and heating for a few seconds so IL melts and flows over the surface; after removing a heat, IL is quickly solidified forming a layer on the surface. The whole procedure of preparation of solid-state IOS-ISE is quite simple and takes only 5–10 min.

For comparison purposes, we also prepared the conventional plasticized membrane ISE (PVC-ISE further) containing the same electrode-active compound,  $[(C_{16})_2Im]Br$ . A powdered high molecular weight poly(vinyl chloride) (PVC; Fluka) was used as the polymer matrix and 2-nitrophenyloctyl ether (2-NPOE; Fluka,  $\geq 99\%$ ) as the plasticizer. Weighed amounts of DHDImBr, PVC, and 2-NPOE (weight ratio 5:32:63) were dissolved in freshly distilled tetrahydrofuran, 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  $10^{-4}$  M potassium bromide.

All aqueous solutions for potentiometric measurements were prepared with distilled/deionized water. The silver chloride electrode Esr-10101 (Russia) was used as reference electrode. pH was monitored with combined glass electrode ESK-10601/7



**Fig. 1.** Construction of screen-printed electrode.

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