

Low-Melting Ionic Solids: Versatile Materials for Ion-Sensing Devices

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ABSTRACT Ionic liquids that melt slightly above room temperature (and may be called low-melting ionic solids, LMISs) were used as sensing materials for the detection of ions in aqueous solutions. A simple procedure based on the consecutive melting and further solidification of the LMISs was applied to prepare solid-contact ion-sensitive electrodes. A potentiometric response toward a number of anions was observed, and the possibility of altering the selectivity by incorporating additional ionophores into the LMIS matrix was demonstrated.

KEYWORDS: ionic liquids • low-melting ionic solids • potentiometric sensors

1. INTRODUCTION

Because the latest advances in the fundamental understanding of the ion-selective-electrode (ISE) response mechanism gave rise to drastic improvements of the sensitivity and selectivity, many efforts have been focused on the development of novel potentiometric sensors for the detection of ions in aqueous solutions (1). Easily fabricated, low-cost, and miniaturizable ISEs favorably compete with more complicated and expensive analytical instruments (2).

The ion-sensing properties of ISEs largely depend on the nature of the employed sensing material. Traditional sensing materials were mainly inorganic ionic solids (3), including glasses and crystals. Nowadays, the most actively pursued materials are, probably, plasticized polymers [typically poly(vinyl chloride) (PVC)] doped with appropriate ionophores (4). In this last approach, a polymeric membrane serves as an inert (with reservation for its inherent solvating ability and the presence of ionic sites in PVC (3)) embedding medium, while a neutral or charged ionophore is responsible for recognition of the target ion.

Current research activity is related to the optimization and rational design of both ionophores and matrixes targeted to particular applications. Along these lines, a number of effective ionophores were synthesized and utilized, thanks to the development of “host–guest” and coordination chemistry (although the simple lipophilic ion exchangers still play an important role, especially in the field of anion-selective electrodes) (4). At the same time, the search for novel matrixes became the subject of increasing interest. For example, some nonconventional polymeric materials have been proposed as a basis for plasticizer-free sensing membranes (5). Perfluorinated polymers have been reported as promising materials for ISE membranes (6).

Herein, we report on the use of novel sensing materials that act as a matrix and ionophore (ion exchanger) at the same time. These are ionic liquids that melt moderately above room temperature; alternatively, they may be called “low-melting ionic solids” (LMISs). While slightly heated and being liquid, they may be conveniently used to modify various surfaces; after cooling, they form a solid ion-sensing layer on the surface.

By the current definition, ionic liquids (ILs) are organic salts that melt below 100 °C (7). Room temperature ILs (RTIL) are ILs that are liquid at room temperature. Because of a unique combination of physical and chemical properties (ionic nature, good extraction ability, ion-exchange properties, low equilibrium vapor pressure, etc.), ILs are considered as advanced multifunctional materials. In particular, a huge advantage of these substances is the possibility of fine-tuning the IL characteristics via variation of the structures of the constituent ions. Although ILs have been employed in different instrumental analytical techniques including sensors (8), only a few examples of the application of ILs in ISE membranes have been presented. Thus, ILs can behave as ionic additives (9) in a polymer plasticized membrane or as binders for graphite paste electrodes (10). Some ILs can act dually as a plasticizer and an ion exchanger in liquid- and solid-contact ISE (11); hydrophilic and hydrophobic ions are detectable (12). It is worth mentioning that the use of ILs in ISEs may be traced to papers, which did not explicitly use the term “ionic liquid”, of the 1990s and even the 1980s (13).

Notably, the above examples are related to ILs that are liquid at room temperature. Using RTILs requires a presence of embedding media (polymeric membrane) to create a stable sensing layer in ISEs (although it is possible to use an all-liquid ISE setup (14), in practice liquid membranes are inconvenient). At the same time, ILs that are not RTILs (that is, are LMISs) were undoubtedly used many times in various ISEs, being dissolved in plasticized membranes as ionogenic components (again, without use of the term “ionic liquid”).

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It is easy to note that LMISs may themselves be solid materials that provide an embedding for their own ion-exchange sites (naturally, these materials should have low solubility in water to be practical). The ion-sensing layers formed from such materials are not only plasticizer-free but also polymer-free. Evidently, they may be considered as close relatives to well-known solid inorganic ionic membranes (to closer make the analogy, one may recall episodic early examples of creating ISE membranes by cooling molten inorganic salts (15)). A huge difference, however, is the ability of LMISs to be liquefied much easier, which gives rise to an extremely simple procedure of fabrication of ion-sensing devices. Finally, it is highly important that LMISs may be easily doped (when liquid) by various external ionophores/additives.

2. EXPERIMENTAL SECTION

Differential scanning calorimetry (DSC) curves were obtained with a Shimadzu DSC-50 differential scanning calorimeter (aluminum seal, heating rate $5.0\text{ }^{\circ}\text{C min}^{-1}$). Thermogravimetric analysis (TGA) was performed with a Shimadzu TGA-50 thermobalance (platinum pan, temperature range $25\text{--}600\text{ }^{\circ}\text{C}$, heating rate $10\text{ }^{\circ}\text{C min}^{-1}$, and air atmosphere); decomposition temperatures were measured at the onset of decomposition (10% mass loss) (16).

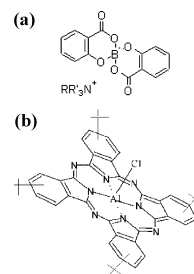
Lithium bis[salicylato(2-)]borate was obtained similarly to the known technique (17). A total of 276.24 g (2.00 mol) of salicylic acid (Riedel-de Haën, puriss.), 41.96 g (1.00 mol) of lithium hydroxide monohydrate (Fluka, puriss. pa), 61.83 g (1.00 mol) of boric acid (Fluka, puriss. pa), and 100 mL of distilled water were transferred into a flask fitted with a reflux condenser. The heterogeneous mixture was heated to boiling, where a homogeneous solution was obtained. The product crystallized after cooling to room temperature. The salt was dried after filtration and recrystallized from acetonitrile. The recrystallized salt was dried in an oven at $150\text{ }^{\circ}\text{C}$ for about 20 h.

Tetraoctylammonium Bis[salicylato(2-)]borate (TOA BSB). A total of 11.01 g (0.038 mol) of lithium bis[salicylato(2-)]borate, 19.73 g (0.036 mol) of tetraoctylammonium bromide (Fluka, purum, $\geq 98.0\%$), and 200 mL of chloroform were transferred into a round-bottomed flask equipped with a reflux condenser and a magnetic stirrer. The heterogeneous mixture was heated to boiling and stirred for 8 h. The mixture was then cooled to room temperature and rinsed with 100 mL of distilled water 10 times. Chloroform was evaporated using a rotary evaporator; the product was dried under vacuum for 4 h. $^1\text{H NMR}$ (500 MHz, CDCl_3 , δ/ppm relative to TMS): 0.87 (t, 12 H), 1.23 (m, 40 H), 1.54 (m, 8 H), 3.10 (m, 8 H), 6.84 (m, 2 H), 6.91 (d, 2 H), 7.36 (m, 2 H), 7.88 (dd, 2 H). Found (calcd) for $\text{C}_{46}\text{H}_{76}\text{BNO}_6$: C, 73.57 (73.67); H, 10.37 (10.22); N, 1.86 (1.87); Br, 0.25 (0.00). NMR spectra were recorded with a DRX500 spectrometer (Bruker, Germany).

Aluminum Tetra-tert-butylphthalocyanine Chloride was synthesized and supplied by Prof. L. G. Tomilova (Department of Chemistry, M. V. Lomonosov Moscow State University), and its purity was proven by means of thin-layer chromatography, Fourier transform IR, NMR, and mass spectrometry.

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, $\geq 99\%$) as the plasticizer were used. Weighed amounts of TOA BSB, PVC, and 2-NPOE 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

Scheme 1. Electrode-Active Components Studied in the Present Work^a



^a (a) $\text{R} = \text{R}' = \text{C}_8\text{H}_{17}$ - Tetraoctylammonium bis(salicylato[2-])borate, TOA BSB; $\text{R} = \text{CH}_3$, $\text{R}' = \text{C}_8\text{H}_{17}$ - trioctylmethylammonium bis(salicylato[2-])borate, TOMA BSB; $\text{R} = \text{R}' = \text{C}_6\text{H}_{13}$ - tetrahexylammonium bis(salicylato[2-])borate, THA BSB. (b) Aluminum tetra-tert-butylphthalocyanine chloride.

Table 1. DSC and TGA Data of Tetraalkylammonium Bis[salicylato(2-)]borates

salt	melting point, $^{\circ}\text{C}$	dec temp, $^{\circ}\text{C}$
THA BSB	100.1	301
TOMA BSB	70.9	301
TOA BSB	43.2	294

10 mm internal diameter. The electrode was filled with an internal solution containing 10^{-3} M potassium chloride and 10^{-3} M sodium salicylate; a silver wire coated with silver chloride was applied as the inner reference electrode.

Screen-printed electrodes (SPEs) of configuration “3 in 1” (graphite paste working, counter, and Ag/AgCl reference electrodes printed on the polyester substrate, $28 \times 10\text{ mm}$) were utilized for solid-contact sensor fabrication. Typically, these electrodes are used for voltammetric measurements. For the present study, SPEs were chosen as convenient substrates for the covering with the solid LMIS-based membranes. Weighed amounts of chosen LMISs were located on the working electrode surface (0.2 cm^2) and heated over the surface of a laboratory hot plate in 30 s. This time was found to be sufficient for melting the appropriate salt, resulting in the formation of a viscous colorless droplet on the electrode surface. After cooling to room temperature, homogeneous solid membranes with extremely strong adhesion properties were produced.

Sodium and potassium anion salts (Reahim, Russia) were of analytical reagent grade. Distilled deionized water ($18\text{ M}\Omega\text{ cm}$) was used in all cases. The activity coefficients were calculated by the Debye–Hückel approximation. Selectivity measurements were performed on the order of a foreign ion lipophilicity increase without any preliminary preconditioning of the electrodes; unbiased selectivity coefficients were calculated using a modified separate solution method (18) with I^- as the primary ion. All potentiometric measurements were performed at $20 \pm 2\text{ }^{\circ}\text{C}$ upon stirring versus Ag/AgCl (Esr-10101, Russia) as the reference electrode. Potentials were monitored with a pH-meter/ionometer Expert-001 (Econiks-Expert, Russia).

3. RESULTS AND DISCUSSION

Three potential LMISs—tetraalkylammonium bis(salicylato[2-])borate salts (see Scheme 1)—were synthesized and characterized by means of DSC and TGA. The melting points and decomposition temperatures of the corresponding compounds are given in Table 1. No water traces were observed in the TGA curves for all compounds. The decomposition temperatures of all of the obtained compounds are typical for ILs (7) and very weakly depend on the cation’s structure.

Table 2. Potentiometric Response of TOA BSB-Based Electrodes

anion	PVC plasticized membrane electrode		solid membrane electrode		solid membrane electrode with 20 wt % Pc^tAlCl	
	slope, mV/dec	linear range, mol dm^{-3}	slope, mV/dec	linear range, mol dm^{-3}	slope, mV/dec	linear range, mol dm^{-3}
F^-	-43.5	10^{-1} - 10^{-2}	-22.2	10^{-1} - 10^{-2}	-43.1	10^{-1} - 10^{-2}
AcO^-^a	-12.2	10^{-1} - 10^{-2}	-21.3	10^{-1} - 10^{-2}	-46.3	10^{-1} - 10^{-2}
Cl^-	-46.6	10^{-1} - 10^{-2}	-48.5	10^{-1} - 10^{-2}	-64.0	10^{-1} - 10^{-2}
NO_3^-	-42.9	10^{-1} - 10^{-2}	-38.6	10^{-1} - 10^{-2}	-62.3	10^{-1} - 10^{-2}
Br^-	-50.1	10^{-1} - 10^{-4}	-34.8	10^{-1} - 10^{-4}	-65.8	10^{-1} - 10^{-4}
Sal^-^a	-59.8	10^{-1} - 10^{-5}	-52.7	10^{-1} - 10^{-4}	-57.9	10^{-1} - 10^{-4}
I^-	-59.2	10^{-1} - 10^{-5}	-49.3	10^{-1} - 10^{-4}	-63.2	10^{-1} - 10^{-4}
SCN^-	-61.8	10^{-1} - 10^{-5}	-59.4	10^{-1} - 10^{-4}	-58.5	10^{-1} - 10^{-4}
ClO_4^-	-49.9	10^{-1} - 10^{-3}	-51.7	10^{-1} - 10^{-4}	-63.3	10^{-1} - 10^{-4}
DDS^-^a	-123.2	10^{-3} - 10^{-5}	-50.5	10^{-3} - 10^{-4}	-58.2	10^{-3} - 10^{-4}

^a AcO^- = acetate, Sal^- = salicylate, and DDS^- = dodecylsulfate.

At the same time, the melting points have been found to strongly depend on the cation's structure. Because of the lowest melting point, TOA BSB can be liquefied in a very simple way, even by short-time heating over the surface of a laboratory hot plate. Being melted and, consequently, cooled to room temperature, TOA BSB produces a homogeneous solid layer on various supports (glass, plastics, metals, etc.). This simple and fast (several minutes) procedure was successfully applied to modify, with a TOA BSB covering, the surface of a miniature SPE. Notably, only 1 mg of TOA BSB was found to be enough to obtain a modified SPE: a solid-contact electrode with good response characteristics.

The potentiometric response and selectivity of solid-contact electrodes were investigated and compared with those of specially prepared liquid-contact electrodes having a plasticized PVC membrane containing TOA BSB (32 wt % PVC, 63 wt % 2-NPOE, and 5 wt % TOA BSB). For both solid- and liquid-contact electrodes, the potentiometric response toward single-charged anions of different lipophilicity was studied (the electrodes exhibit no response toward cations, probably, because of the high hydrophobicity of the LMIS cation tetraoctylammonium).

It was found that LMIS-based electrodes do respond to both hydrophilic (e.g., fluoride or acetate) and much more hydrophobic (perchlorate and dodecylsulfate) anions. Response characteristics of the solid- and liquid-contact electrodes are given in Table 2. As can be seen, the slopes of the electrode functions approach the Nernstian value and the linear range widens with a decrease in the anion hydrophilicity. Thus, the best results were obtained for salicylate, perchlorate, thiocyanate, and iodide anions; typical plots are presented in Figure 1. Dynamic characteristics of LMIS electrodes were estimated as well (see Figure 2). As is seen, the higher the anion concentration, the better is the stability of the potential and the less is the response time.

In some cases (e.g., hydrophilic fluoride or acetate anions), a sub-Nernstian or half-Nernstian response has been observed (Table 2). This fact may be explained by the comparably high hydrophobicity of the BSB^- anion, which is presumably exchanging to a target anion. In order to measure the selectivity coefficients, linear intervals of elec-

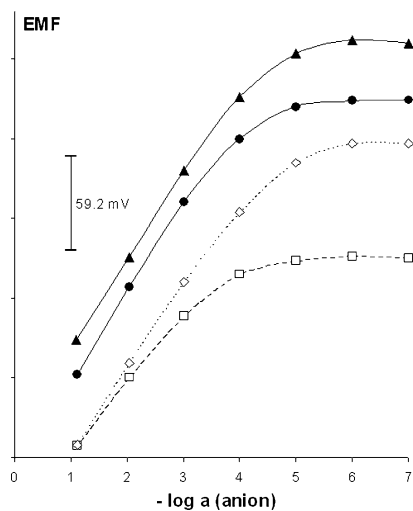


FIGURE 1. Potentiometric response of a bulk TOA BSB-based solid membrane electrode toward different anions (▲, salicylate; ◇, perchlorate; ●, thiocyanate; □, iodide).

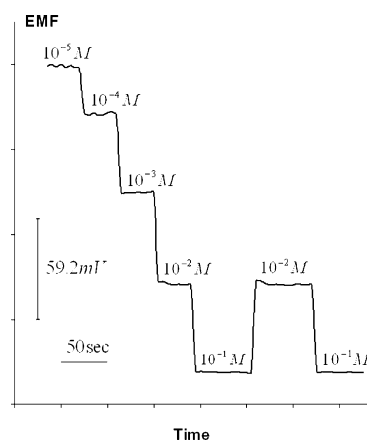


FIGURE 2. Response time of a bulk TOA BSB-based solid membrane electrode in aqueous solutions of sodium salicylate.

trode functions were extrapolated to $a_i = 1$ and corresponding electromotive force values were used for calculation, as recommended elsewhere (18). It is clear that the measured selectivity coefficients are slightly biased because of non-theoretical values of the electrode functions for both target and interfering anions. At the same time, for the estimation

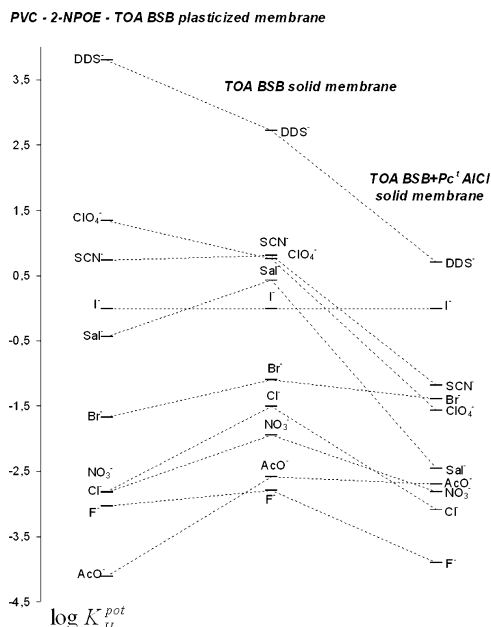


FIGURE 3. Logarithmic values of potentiometric selectivity coefficients (AcO⁻ = acetate, Sal⁻ = salicylate, and DDS⁻ = dodecylsulfate).

of the anions' selectivity order, the obtained selectivity coefficients seem quite correct.

Both liquid- and solid-contact TOA BSB-based electrodes have been found to respond with minor deviations from the Hofmeister series (19); logarithmic values of calculated selectivity coefficients are presented in Figure 3. As can be seen, PVC plasticized membranes (Figure 3, left) containing TOA BSB as only an additive are characterized with the selectivity order of AcO⁻ < F⁻ < Cl⁻ ≈ NO₃⁻ < Br⁻ < Sal⁻ < I⁻ < SCN⁻ < ClO₄⁻ ≪ DDS⁻. For the bulk TOA BSB-based solid membrane (Figure 3, middle), the increase in the anion interference can be represented by the series F⁻ < AcO⁻ < NO₃⁻ < Cl⁻ < Br⁻ < I⁻ < Sal⁻ < ClO₄⁻ ≈ SCN⁻ ≪ DDS⁻. Moreover, in the latter case, the difference in $\log K_{ij}^{pot}$ values is extremely eliminated for both highly hydrophilic and hydrophobic anions, even for DDS⁻, which is well-known as an anionic surfactant and, therefore, is expected to interfere the most. In other words, solid TOA BSB membranes are characterized by the worst selectivity (in comparison with PVC plasticized membranes) in the presence of hydrophilic anions, but, surprisingly, lipophilic anions do not have as much affect, as might have been expected for traditionally used membrane compositions. The elimination of the selectivity difference could likely be explained in terms of an absolute excess (in comparison with traditionally used membrane compositions) of ionic sites in a bulk TOA BSB-based membrane, and it is in good agreement with the previously introduced experimental data of other groups (20).

As is seen, LMIS-based ion-sensitive materials are characterized by diminished selectivity, with respect to that of PVC membranes and, therefore, may be better called ion-sensing rather than ion-selective. It is worth mentioning that this drawback may be turned into an advantage if one has in mind applications, for example, in nonselective detectors.

Interestingly, we found that the ionic selectivity of the LMIS sensor may be increased/alterd by incorporating a proper additive into the ionic solid matrix. Namely, we used aluminum tetra-*tert*-butylphthalocyanine chloride (Pc^tAlCl; Scheme 1) as an additive, which is known to behave as an anion receptor (21). The work surface of SPE was covered with a solid TOA BSB layer additionally containing 20 wt % Pc^tAlCl. Selectivity measurements were carried out in the manner described above; the results are shown in Figure 3 (right). Anti-Hofmeister selectivity order has been observed without any loss of sensitivity (Table 2): F⁻ < Cl⁻ < NO₃⁻ < AcO⁻ < Sal⁻ < ClO₄⁻ < Br⁻ < SCN⁻ < I⁻ < DDS⁻. While the difference in foreign anion interference is still diminished, the selectivity toward iodide anion increased notably. Likely, the careful design of the LMIS-layer composition may result in even better characteristics.

Last but not the least, the potentiometric response of a LMIS electrode is fairly reproducible and reversible. The response time for the TOA BSB membrane does not exceed 10 s even for relatively dilute analyzed solutions.

4. CONCLUSIONS

We have found that organic salts, which are LMISs (or, alternatively, above RTILs), can be successfully employed as ion-sensing materials in analytical devices. A simple and fast procedure of fabrication of LMIS ionic sensors looks very attractive and general (the data on using LMISs of various nature will be reported elsewhere). It is also shown that the incorporation of additional ion-responsive components into the LMIS matrix (again through a simple and fast procedure) allows one to alter the selectivity order, thus enabling a tuning of the sensor's properties.

Some examples of utilization of related materials do occur in the literature. Organic "ionic plastic crystals" were investigated as solid electrolytes by MacFarlane and co-workers (22). In general, solidified ILs have lately drawn notable interest from researchers because of their sometimes unusual applications. Frozen ILs were demonstrated to be applicable substrates for rewritable imaging (23). Ambient stable micro- and nanosized ILs were recently introduced (24). We consider the present study as another advance in the field.

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