



Correlation between the standard Gibbs energies of an anion transfer from water to highly hydrophobic ionic liquids and to 1,2-dichloroethane



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ABSTRACT

Cyclic voltammetry is used to investigate the transfer of several semihydrophobic and hydrophilic anions (F^- , Cl^- , Br^- , I^- , NO_3^- , NO_2^- , SCN^- , BF_4^- , ClO_4^- , PF_6^-) across the polarized interface between an aqueous electrolyte solution and a highly hydrophobic ionic liquid (IL) membrane. Three ILs are examined being composed of the trioctadecylmethylammonium (TOMA⁺), tridodecylmethylammonium (TDMA⁺) or tetradodecylammonium (TDA⁺) cation and the tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB⁻) anion. The standard Gibbs energies of the anion transfer from water to IL, $\Delta G_{tr,i}^{0,w-IL}$, are evaluated from the voltammetric measurements by applying the classical tetraphenylarsonium-tetraphenylborate hypothesis. Comparison of data for various ILs points to a small systematic effect of the cationic IL component, which is manifested by somewhat lower values of $\Delta G_{tr,i}^{0,w-IL}$ for most anions in the presence of TDMA⁺ or TDA⁺, indicating their stronger association with the anions. The capillary electrophoresis measurements suggest that the degree of interaction of anions with the IL cations in water could follow the order TDMA⁺ > TOMA⁺ > TDA⁺. It is shown that a linear correlation with the nearly unity slope between $\Delta G_{tr,i}^{0,w-IL}$ and the standard Gibbs energy of anion transfer from water to 1,2-dichloroethane (DCE), $\Delta G_{tr,i}^{0,w-DCE}$, can be established for all three ILs studied. An extended correlation including both the present and the literature values of $\Delta G_{tr,i}^{0,w-IL}$ for the ion transfer from water to TDMATFPB reveals the consistency of data for the semihydrophobic cations and anions, and the presence of a weak solvation effect favoring the transfer of hydrophilic anions (F^- , Cl^- , Br^- , I^-) and disfavoring the transfer of hydrophilic cations (H^+ , Li^+ , Na^+ , K^+ , Rb^+ , Cs^+).

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1. Introduction

Room temperature ionic liquids (ILs) are chemicals that are composed entirely of ions, which exist in the liquid state at ambient temperature ($\sim 25^\circ C$) [1]. IL composed of the tetrahexylammonium cation and the bis[(n-fluoroalkyl) sulfonyl]imide anion has been used for the first time to form an electrochemically polarizable interface between water and IL [2], which has many properties similar to those of an interface between two immiscible electrolyte solutions (ITIES) [3], cf. [4,5] for a review. The introduction of the highly hydrophobic ILs, such as N-octadecylisoquinolinium tetrakis[3,5-bis(trifluoromethyl) phenyl]borate ($C_{18}IqTFPB$) [6], tridodecylmethylammonium tetrakis(pentafluorophenyl) borate (TDMATFPB) [7], or tridodecylmethylammonium tetrakis[3,5-bis(trifluoromethyl) phenyl]borate (TDMATFPB) [8], has lead to a significant extension of the polarized potential window

(ppw) up to about ca. 0.8 V, which has enabled to investigate the transfer of a broad range of the semi-hydrophobic ions [4,5].

The standard Gibbs energy of ion transfer from water to IL, $\Delta G_{tr,i}^{0,w-IL}$, is the key thermodynamic parameter characterizing the ion transfer having relevance to extraction behavior of ILs and to the ion selectivity of the polarized water|IL interfaces [4,5]. The correlation between $\Delta G_{tr,i}^{0,w-IL}$ and the analogous quantity for the ion transfer to an organic solvent (o), $\Delta G_{tr,i}^{0,w-o}$, could help to understand the uniqueness of the solvation environment of ILs, and to predict their values from known thermodynamic data.

The existence of linear Gibbs energy relationships for the ion transfer from water to an ionic liquid (IL) has been demonstrated first by the linear plots between the half-wave potentials for the transfer of the tetraalkylammonium cations from water to a hydrophobic IL, $C_{18}IqTFPB$, and the standard ion transfer potentials for the ion transfer from water to 1,2-dichloroethane (DCE) or nitrobenzene (NB) [6]. Greater than unity slopes of the linear regression lines were explained by a lower polarity of $C_{18}IqTFPB$ compared with the polarity of 1,2-DCE or NB [6]. More recently, the half-wave

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potentials for the transfer of several anions from water to the moderately hydrophobic 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($C_8mimC_1C_1N$) have been also found to exhibit a linear correlation with the standard ion transfer potentials for the ion transfer from water to DCE or NB [9]. However, the linear regression lines were characterized by much smaller slopes of about 0.5, which conversely were attributed to a higher polarity of $C_8mimC_1C_1N$ [9].

Linear correlation with the practically unity slope between the standard Gibbs energy of transfer of the tetraalkylammonium cations from water to an IL and to DCE or *o*-dichlorobenzene (DCB) have been found for highly hydrophobic ILs including TDMATFPB [7], TDMATFPB [8], (ferrocenyl-methyl)dodecyldimethylammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (FcMDDATFPB) [10], and tridodecylmethylammonium dicarbollycobaltate (TDMADCC) [11]. The evaluation of the standard Gibbs energy of ion transfer from water to IL, $\Delta G_{tr,i}^{0,w-IL}$, was based on the classical tetraphenylarsonium-tetraphenylborate hypothesis postulating that the tetraphenylarsonium cation (TPAs⁺) and the tetraphenylborate anion (TPB⁻) have equal standard Gibbs energies of ion transfer between any pair of solvents [12]. The same hypothesis has been previously used in the evaluations of the standard Gibbs energy of ion transfer from water to an organic solvent, $\Delta G_{tr,i}^{0,w-o}$ [3]. A comparison of data for various ILs has indicated that the structure of the cationic and anionic component of IL has a small effect on the value of $\Delta G_{tr,i}^{0,w-IL}$ for a particular tetraalkylammonium cation [8,10,11]. The calculations of the standard Gibbs energies of ion transfer from water to the studied ILs and to DCE, which was based on the Born-Uhlig expression, suggested that the observed correlation between the standard Gibbs energies of ion transfer to IL and to DCE has the origin in the similar solvophobic contributions rather than in the comparable polarity of ILs [11].

The main aim of this work was to extend the linear Gibbs relationships found previously for the transfer of the tetraalkylammonium cations from water to TDMATFPB [8] by including the data for the semihydrophobic and hydrophilic anions (F^- , Cl^- , Br^- , I^- , NO_3^- , NO_2^- , SCN^- , BF_4^- , ClO_4^- , PF_6^-), which were inferred from the present voltammetric measurements, as well as the literature data for the hydrophilic cations (H^+ , Li^+ , Na^+ , K^+ , Rb^+ , Cs^+) [13]. The absence of a significant effect of the IL structure on the value of $\Delta G_{tr,i}^{0,w-IL}$ for the tetraalkylammonium cations [8,10,11] has motivated us to examine also the effect of the cationic IL component on the anion transfer. The voltammetric measurements of the anion transfer were performed using three ILs composed of the tridodecylmethylammonium (TDMA⁺), trioctadecylmethylammonium (TOMA⁺), or tetradodecylammonium (TDA⁺) cation and the TFPB⁻ anion. The standard Gibbs energies of the anion transfer from water to IL were evaluated from the voltammetric half-wave potentials measured in the single-interface polarized membrane (SIPM) and two-interface polarized membrane (TIPM) configurations [7] by using the theory of cyclic voltammetry of TIPMs, which has been reported earlier [14]. The interaction between an anion and the cationic IL component in water was inspected by the capillary electrophoresis measurements.

2. Experimental

Sodium salts of the ClO_4^- , BF_4^- , CNS^- , I^- , Br^- , Cl^- , F^- , NO_3^- , NO_2^- and $HCOO^-$, anions, trioctadecylmethylammonium bromide (TOMABr), tridodecylmethylammonium chloride (TDMACl), tetradodecylammonium chloride and bromide (TDACl, TDABr), sodium tetraphenylborate (NaTPB), tetraphenylarsonium chloride (TPAsCl), potassium hexafluorophosphate (KPF₆), were purchased

as analytical grade chemicals from Fluka. Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate dihydrate (NaTFPB) (Kobayashi reagent) was purchased from Dojindo Laboratories. All salts were used as received. TOMATFPB, TDMATFPB and DATFPB were prepared by metathesis from the corresponding salts in acetone. The resulting solution was filtered and purified using a column filled with aluminum oxide (Fluka for chromatography), and acetone was evaporated. The obtained ILs were thoroughly washed several times with deionized water and completely dried out in a laboratory oven at a temperature not exceeding 70 °C. Lithium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (LiTFPB) was prepared following a two-step procedure. In the first step, the acid HTFPB was prepared by metathesis from gaseous HCl and NaTFPB in diethylether. The precipitated NaCl was removed by filtration, and diethylether was evaporated at a temperature not exceeding 60 °C. In the second step, the preparation of LiTFPB was completed by a titration of HTFPB with the aqueous solution of LiOH. Aqueous electrolyte solutions were prepared from highly purified water with resistivity of 18.2 MW (Millipore). The supported membrane was prepared by impregnating a polyvinylidene fluoride microporous filter (Millipore, type GVHP 1300, pore size of 0.22 μm, thickness of ~112 μm) with the corresponding IL [7]. The membrane disk with the diameter of 0.9 cm was cut off the impregnated filter and mounted in a four-electrode cell [15]. The area of the membrane exposed to the aqueous electrolyte solution was 0.071 cm².

Voltammetric measurements were performed at the ambient temperature of 25 ± 2 °C using the cells with a two-interface polarized membrane (TIPM) or a single interface polarized membrane (SIPM), which are described by the schemes (I) and (II), respectively,



or



where IL = TOMATFPB, TDMATFPB or DATFPB, A⁻ = F⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, NO₂⁻, SCN⁻, BF₄⁻ or ClO₄⁻, RX = TEACl or KPF₆, y = 1, 10 or 100 and x = 0 or 1. The reference electrodes RE' = Ag|AgCl|0.1 M LiCl and RE = Ag|AgCl|0.1 M LiCl were connected to the aqueous phases w' and w by means of the Luggin capillary, the tip of which was filled with the aqueous agar gel containing 0.1 M LiCl. In the SIPM cell, the potential difference across the w'|m interface is controlled by the equilibrium partition of the TFPB⁻ anion, i.e. when applying the external voltage to the cell, only the w|m interface is polarized. The cell potential E,

$$E = \phi^{Ag} - \phi^{Ag'} = \Delta_m^w \phi - \Delta_m^{w'} \phi - E_{ref} \quad (1)$$

was controlled with the help of a four electrode potentiostat Solartron ModuLab System (Solartron Analytical, Ametek) equipped with the automatic compensation of the ohmic potential drop. This instrument was also used to measure the complex impedance of the cell enabling to estimate the solution resistance for the adjustment of the ohmic potential drop compensation.

The capillary electrophoresis (CE) measurements were carried out using the HP^{3D}CCE system (Agilent Technologies, Germany) equipped with a contactless conductivity detector [16], which was placed in the electrophoretic cassette kept at a constant temperature of 25 °C. A fused-silica capillary (Composite Metal Services, UK) with 25 μm inner diameter, 363 μm outer diameter, 70 cm in total length and 55 cm distance to the detector, was used as a separation device.

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