Thermodynamics of Ion Transfer Across the Liquid|Liquid Interface at a Solid Electrode Shielded with a Thin Layer of Organic Solvent

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Thermodynamics of ion transfer across the liquid|liquid interface at a solid electrode shielded with a thin layer of water-immiscible organic solvent is investigated. The shielded electrode has been made by using a commercial hydrophobic carbon filament material (LSG) as an electrode support and a specially synthesized water-insoluble electroactive polymer (polyphenotiazine, PPTA) as a mediator. Oxidation of PPTA dissolved in the organic layer is accomplished with anion transfer from the aqueous phase to compensate for the positive charge of the mediator. The formal potential of the electrode shielded with PPTA solution in nitrobenzene (NB) is proportional to the Gibbs free energy of anion transfer across the liquid|liquid interface. An enhanced potential window as compared to a "classic" four-electrode setup allowed direct determination of Gibbs free energy for fluoride ion transfer from water to NB. For less polar organic solvents the formal potential of a shielded electrode is mainly determined by the enthalpy of anion transfer across the liquid|liquid interface, whereas the entropy term of Gibbs free energy causes only a minor effect.

Introduction

Since a pioneer publication by Koryta and coauthors,[1] an interface of immiscible liquids has a particular interest for physical and analytical chemistry. The structure of the water|organic interface, which is considered as a model of half a biological membrane, is highly important for life sciences.

A simple four-electrode setup with two auxiliary and two reference electrodes, the latter enclosing the interface, allows the direct investigation of thermodynamics and kinetics of charge transfer. Transfer of ions through the interface results in an increase of current similar to that of the Faradaic processes at the metal−solution interface. This allows amperometric detection of nonelectroactive ions, which is of great importance in analytical chemistry.

After the mentioned pioneered article, a number of publications on the investigation of structure and properties of liquid|liquid interface,[2] as well as on its analytical applications,[3] appeared. However, a classical four-electrode setup has certain limits. First, it requires ionic conductivity of both phases, and thus, nonpolar liquids cannot be investigated. Second, the surface of an interface (shape of a meniscus) is not reproducible enough. Third, micelles forming surfactants, which may be used to facilitate polyion transfer, the latter of which are of biological nature, cause a breakdown of the interface.[4] The latter property makes the classic four-electrode setup inapplicable for investigation of protein transfer through the liquid|liquid interface, which is of great importance in analytical chemistry for allowing detection of hormones, toxins, and certain pathology precursors without immunochemistry methods and in physical chemistry for investigation of trans-membrane processes during protein synthesis and refolding.

Recently, an alternative approach for the study of charge transfer across the liquid|liquid interface was proposed. Cyclic voltammetry was performed on the systems in which a thin layer of organic liquid, containing a dissolved electroactive solute, is placed on a working electrode surface and submerged in an aqueous electrolyte solution with common reference and counter electrodes.[5−10] Oxidation of electoactive material within the organic phase has to be associated with the counterion transfer from water, so as to keep the electrical neutrality within the organic phase. Ion transfer across the liquid|liquid interface was successfully studied in such systems.[5c,8−10] Also electron transfer between reactants located on opposite sides of the liquid|liquid interfaces was studied in thin liquid film systems by voltammetry.[5a,b,6,7]

Another approach is based on the systems that are similar except that there is also a direct contact between the working electrode and the aqueous phase, so that a three-phase junction exists.[11−13] The case of low ionic conductivity of organic phase electrode reactions occurring near the three-phase junction[12a] leads to the appearance of proportionality of the oxidation peak current with the radius of the circular drop|electrode interface in high scan rates.[14]

The disadvantages of the known shielded electrodes are their poor reproducibility and stability. The former concerns a pretreatment (hydrophobization) step of common carbon materials used as electrode supports. Industrial hydrophobization is carried out at 3000 °C over several hours. This procedure is inconvenient, and never has been reported as a pretreatment step for shielded electrodes. Poor stability is a result of using a low molecular weight mediator, which can leak from the organic layer.[13]

We investigated the applicability of the electrodes shielded with a thin later of organic solvent for studying the thermodynamics of ion transfer across the liquid|liquid interface. To improve the reproducibility of the known shielded electrodes[5,11]

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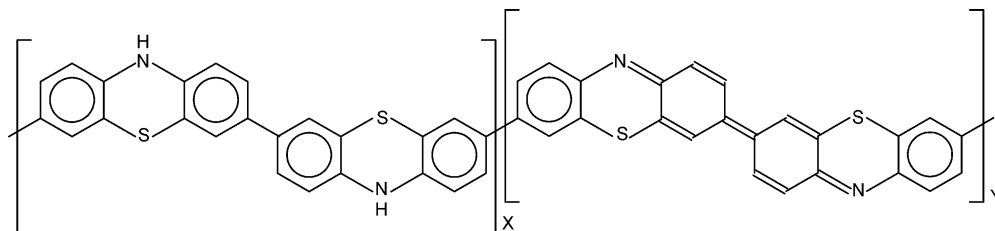† A.V. Topchiev Institute of Petrochemical Synthesis.

Figure 1. Structure of PPTA.

we propose to use a commercial hydrophobic carbon filament material (LSG) as an electrode support. This allows the use of a completely reproducible graphite surface. In addition, to avoid diffusion limitation of the charge transfer through the organic layer by a low molecular weight mediator and to reduce the possibility of the redox material leaking from the organic phase, we use a specially synthesized water-insoluble polymer (polyphenotiazine) instead.

Experimental Section

1. Chemicals. Dichloroethane (DCE), nitrobenzene (NB), chloroform, *n*-octane, methanol, 2-propanol, toluene, and organic and inorganic salts were reagent grade (Reachim, Russia). Phenotiazine ($C_6H_4SNHC_6H_4$) (Fluka) was of high purity and was used as received.

Laboratory distilled water was further purified by passage through a purification train MilliQ Plus (Millipore).

2. Materials. Hydrated cellulose fibers were used for hydrophobic graphite filament material (LSG) preparation. LSG with an apportioned surface of about 10 m^2/g was prepared by a technique developed in Electrougli NIPT of Carbon Wares (Russia).[15] The hydrate cellulose fibers were transformed into fibrous material with textile structure. Heating at 900 °C in an argon atmosphere for 3 h was followed by activation in CO_2 flow at 950 °C for 3 h. After that material samples were treated at 3000 °C in a reductive atmosphere for 2 h.[15] The specific resistance of LSG was about 0.04 Ω cm. The pyrographite overweight was about 10%.

3. Procedures. Tetrabutylammonium tetraphenylborate (TBATPB) was made by addition of 0.5 M tetrabutylammonium bromide (TBABr) (Reachim, Russia) water solution in a surplus of 0.5 M sodium tetraphenylborate (NaTPB) (Merck) in water. The precipitate was recrystallized from acetone.

Redox polymer polyphenotiazine (PPTA) was synthesized by interfacial polymerization on an interface of monomer solution in organic solvent (0.1 M phenotiazine in toluene:2-propanol (1.5:1 v/v)) with aqueous oxidant solution (($NH_4)_2S_2O_8$ in 1 M HCl, [monomer]:[oxidant] = 1:1.25; [monomer]:[HCl] = 1:3). Reaction occurred over 1.5 h with stirring, $t = 15/18$ °C. Then the reaction mixture was poured into methanol for polymer precipitation. After this the product was washed with an aqueous solution of NH$_4$OH for neutralization. The yield of the product was 54%. The degree of polymerization was approximately 10. The obtained polymer was completely insoluble in water, but soluble in various organic solvents.

The chemical structure of PPTA, investigated by electronic, IR, NMR, and X-ray photoelectron spectroscopy methods, is presented in Figure 1. The estimated degree of oxidation (the quantity *Y* of units containing quinoimine groups) was not more than 0.2. The polymer possesses a high degree of crystallinity (~70%). PPTA is thermostable. According to gravimetric analysis intensive decomposition in air occurs at 490−590 °C in the base form and at 390−540 °C in the doped form.

The following procedure was used to deposit a thin layer of organic solvent on the top of the graphite filament material surface. First, a piece of hydrophobic graphite filament material LSG (0.03 × 0.5 × 1 cm^3) was immersed in a solution of PPTA (0.3 mg mL^{-1} for DCE, NB, and chloroform; 0.03 mg mL^{-1} for *n*-octane) in organic solvent. Because of its filament structure LSG sucked organic solvent, and the latter spreads uniformly over filament material surface. Afterward, the LSG piece covered with organic solvent was immediately hung by a platinum hook and immersed in aqueous supporting electrolyte. Upon voltammetric investigations the platinum hook was kept in air, and the visible graphite area immersed in supporting electrolyte was approximately 0.5 × 0.5 cm^2. Graphite cloth with a thin liquid film was used as a disposable working electrode.

A surface of unmodified dry LSG is moderately hydrophobic: when gently put onto the water surface the material does not sink despite its obviously higher density. Hydrophylization of LSG for recording of its electrochemistry without the organic layer was carried out by immersion in concentrated sulfuric acid and subsequent thorough washing with distilled water.

The aqueous supporting electrolyte was 0.1 M KX (X = F, Cl, Br, NO$_3$, SCN, and ClO$_4$), 1 mM KH$_2$PO$_4$, pH 7.4. The PPTA content in organic solvents was 0.3 mg/mL. To improve the redox cyclic voltammograms of PPTA in NB and DCE, 0.1 mM of TBATPB was added to the organic layer.

Cyclic voltammetry was carried out in a conventional three-electrode cell with separated compartments of all electrodes with Solartron 1286 (UK) electrochemical interface. The Ag|AgCl|1 M KCl electrode was used as a reference, and platinum mesh was taken as a counter electrode. To study the temperature dependencies (20/80 °C) the whole cell was put into the water thermostat (MLW U10).

Results and Discussion

1. Voltammetry of the Shielded Electrode. Among the main disadvantages of the known electrodes shielded with the thin layer of organic solvent is their irreproducibility because of a surface pretreatment step to achieve hydrophobic properties. To overcome this problem we decided to use commercial hydrophobic electrode materials. We chose carbon filament material LSG specially designed for fuel cell electrodes. The technology involves hydrophobization of the LSG. As a result this material is apparently not wetted with water.

On the contrary, when exposed to various organic solvents (nitrobenzene, dichloroethane, chloroform, octane) LSG shows high wetting ability. Because of its filament structure LSG sucked organic solvent, even when only partially immersed. The amount of organic solvent consumed by a material is rather reproducible, which was determined by weighing the material before and after wetting. An average thickness of the organic layer was approximately 50 μm.

It was important to check whether the layer of sucked organic solvent was able to shield the electrode surface. For this cyclic

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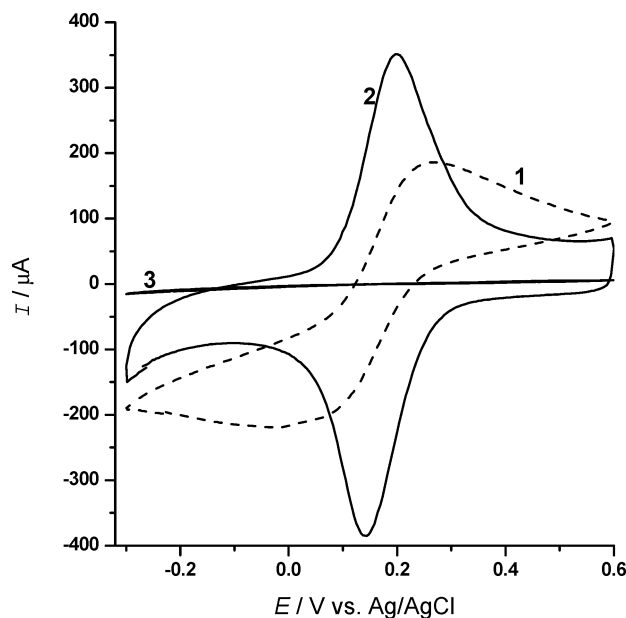
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Figure 2. Cyclic voltammograms of unmodified LSG (1), hydrophilized LSG (2), and unmodified LSG shielded with an *n*-octane layer (3) recorded in aqueous supporting electrolyte (0.1 M KCl, 10 mM KH_2PO_4, pH 7.4) in the presence of ferricyanide (10 mM). Scan rate is 40 mV s^{-1}.

Figure 3. Cyclic voltammograms of PPTA redox activity in chloroform-shielded electrodes in different supporting electrolytes: (1) −0.1 M KF, (2) −0.1 M KNO_3, (3) −0.1 M $KClO_4$ (1 mM KH_2PO_4, pH 7.4). Scan rate is 80 mV s^{-1}.

voltammogram was recorded in an aqueous solution of potassium ferricyanide after covering the LSG working electrode with organic solvent (Figure 2). It is seen that the LSG electrode with a layer of organic solvent does not show any response to the redox mediator. Moreover, capacitive current (half thickness of the voltammogram) is dramatically lower than that in the case of the hydrophylized LSG electrode without the organic layer (Figure 2). The latter exhibits a reversible voltammogram of ferricyanide (Figure 2). To prove that the difference of the shielded and hydrophylized electrodes is not only due to hydrophylization of LSG we forced an unmodified LSG to sink in aqueous solution and afterward recorded the ferricyanide electrochemistry. Despite the ferricyanide cyclic voltammogram on unmodified LSG not being reversible (Figure 2), it still contained the ferricyanide set of peaks, and current values are dramatically higher as compared to those of the shielded electrode. Thus, the organic layer consumed by hydrophobic LSG completely shields the electrode surface.

Besides the mentioned irreproducibility of the thickness of the organic layer, the known shielded electrodes are inconvenient because of the use of low molecular weight mediators. First, a small mediator may cause diffusion limitation of the charge transfer through the organic layer. Second, a low molecular weight molecule may partially cross the liquid|liquid interface. Indeed, leaking of a mediator from shielded electrodes was observed.[13]

We decided to use the redox polymer instead of the small mediator. PPTA (Figure 1) which was completely insoluble in water had been specially synthesized for this purpose. Among the advantages of this polymer are the following: (i) solubility in various organic solvents and (ii) stability of the resulting solutions in contact with water. The latter is highly important, because, for example, processible polyaniline precipitates from its solution in chloroform, when put in contact with water.

Cyclic voltammograms of the LSG electrode shielded with a thin layer of PPTA in chloroform are shown in Figure 3. Despite chloroform having low polarity, which makes it inapplicable for the "classic" four-electrode setup, voltammo-
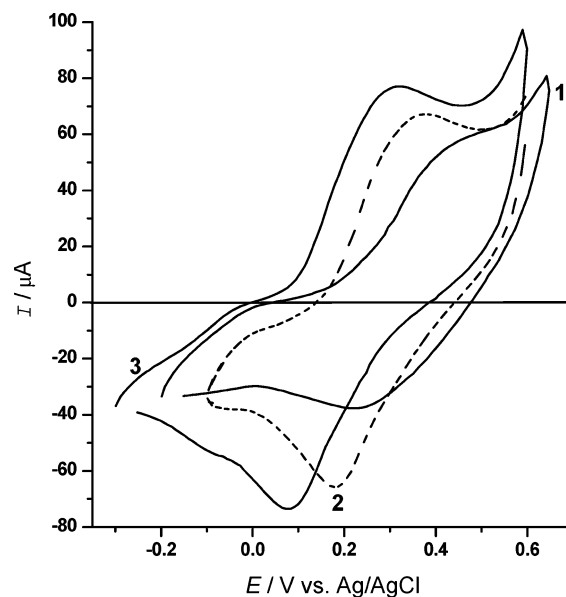
grams of shielded electrodes display recognizable sets of peaks (Figure 3). It is seen that the standard potential of the system (half sum of peak potentials) is dependent on the nature of the counteranion in the water phase. As the hydrophobicity of the anion is increased, the standard potential is shifted in the negative direction.

The use of commercial hydrophobic electrode material and redox polymer as a mediator improves the reproducibility of the shielded electrodes. Cyclic voltammograms of the latter became as reproducible as those of reversible Faradaic electrochemistry.

Shielded electrodes are stable upon continuous cycling: the 15th cyclic voltammogram exactly coincides with the 2nd one presented in Figure 3. This indicates there is no leaking of the electroactive material. Further cycling results in an increase of peak current (5−10%) probably due to slow solubilization of organic solvent in the aqueous phase.

2. Thermodynamics of Ion Transfer across the Liquid|Liquid Interface. Figure 4 illustrates the dependence of the standard potential of the shielded LSG electrode found from cyclic voltammograms on the standard potential of ion transfer from water to nitrobenzene. The latter data were taken from ref 16. Standard deviations for the redox potential values were always less than 10 mV. It is seen that the dependencies are apparently linear.

When nitrobenzene is used for shielding the LSG electrode, a slope of the plot in Figure 4 is equal to 1.1 ± 0.1. Hence, in the case of nitrobenzene the standard potential of the LSG electrode shielded with a thin layer of PPTA in the organic solvent is directly proportional to the Gibbs free energy of ion transfer from water to the organic phase. Similar results with decamethylferrocene as the redox mediator in nitrobenzene were observed by Scholz et al.[12a]

We believe the proposed shielded electrode is suitable for direct measurement of the Gibbs free energy of ion transfer from water to nitrobenzene. In particular, the value reported for fluoride anion (70 kJ mol^{-1} [16]) seems to be too high as it is twice that of chloride ion transfer. Indeed, the redox activity of PPTA in nitrobenzene with the use of KF as supporting electrolyte was observed, and the shape of the cyclic voltam-
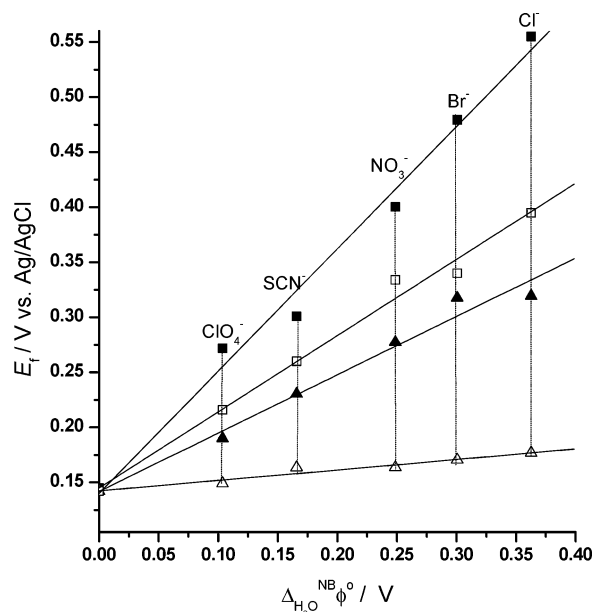
Figure 4. Standard potential of the LSG electrode shielded with PPTA solution in NB (■), DCE (□), chloroform (▲), and *n*-octane (△) versus the standard potential of ion transfer from water to nitrobenzene.
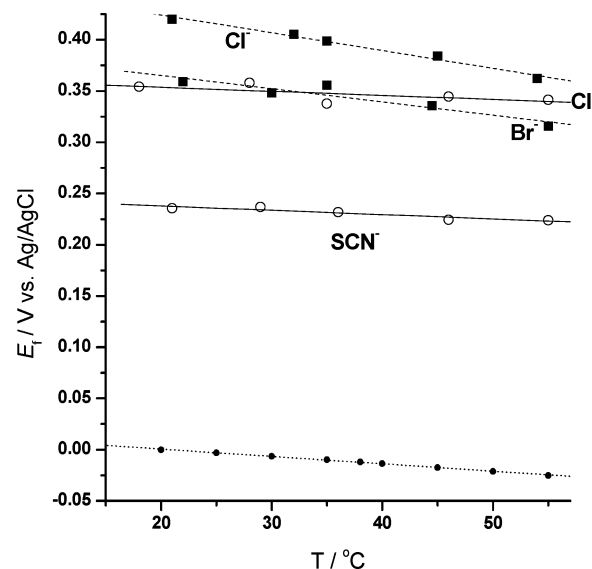

Figure 5. The temperature dependencies of PPTA redox activity in the thin liquid films of DCE (■) and chloroform (○) in different supporting electrolytes and the temperature shift of the Ag/AgCl potential (vs Ag/AgCl at 20 °C[22]) (●).

TABLE 1: Thermodynamic Quantities for the Transfer of Ions from Water to Different Solvents Miscible with Water[20]

ion	solvent	$\Delta G_{tr}^{w \to o}$, kJ mol^{-1}	$\Delta H_{tr}^{w \to o}$, kJ mol^{-1}	$T\Delta S_{tr}^{w \to o}$, kJ mol^{-1}	$(\lvert T\Delta S_{tr}^{w \to o}\rvert)/(\lvert\Delta H_{tr}^{w \to o}\rvert)$
Cl$^-$	MeOH	13.2	8.5	−4.7	0.6
	EtOH	20.1	10.2	−9.9	1.0
	PrOH	25.5	8.3	−17.2	2.1
Br$^-$	MeOH	11	4.6	−6.4	1.4
	EtOH	17.2	5.5	−11.7	2.1
	PrOH	21.9	2.4	−19.5	8.1

mogram was similar to those shown in Figure 3. Thus, we are able to determine both standard potential and Gibbs free energy for fluoride ion transfer from water to nitrobenzene: 0.39 ± 0.01 V and 38 ± 1 kJ mol^{-1}, respectively. The possibility of investigating ions with extreme values of standard transfer potential is obviously provided by an enhanced potential window of the shielded electrodes as compared to the "classic" four-electrode setup.

As seen in Figure 4, when the polarity of the organic solvent is decreased, the slope of the plot is also decreased. The plots of all organic solvents under study have nearly the same intercept at the ordinate axis. The slope for a completely nonpolar octane is low (<0.1) and the potential dependence of the corresponding shielded electrode on the anion hydrophobicity is very close to that of the PPTA redox activity. The latter indicates the ability of anions to shield the positive charge in the polymer.

The decreased slope in Figure 4 in the case of low polar organic solvents is quite unusual, because the Gibbs free energy of ion transfer from water to the organic phase is increased as the polarity of the organic solvent is decreased.[16] To explain this unique behavior of the standard potential of the shielded LSG electrode we investigated its temperature dependence. Standard potentials of the electrodes shielded with low polar organic solvents were found to be almost independent of temperature in different supporting electrolyte solutions (Figure 5). The only electrodes shielded with nitrobenzene are expected to possess minor temperature dependence. Thus, in contrast to polar solvents, in the case of low polar solvents the standard potential of the shielded electrode is mainly determined by the enthalpy of ion transfer across the liquid|liquid interface.

To confirm this conclusion let us consider thermodynamics of ion solvation. Shannon's crystal ionic radii increase as follows: Cl$^-$ < Br$^-$ < NO$_3^-$ < SCN$^-$ < ClO$_4^-$.[17] A smaller ion generates a higher electric field, and as a result Stoke's radii of hydrated ions decrease in the same way as follows: Cl$^-$ > Br$^-$ > NO$_3^-$ > SCN$^-$ > ClO$_4^-$.[18] When the hydrophilic ion is transferred from water to an organic solvent even of high polarity, its hydration shell partially remains.[18,19]

Whereas the Gibbs free energy of ion transfer from water to an organic solvent of high polarity may be determined by the

enthalpy of re-solvation, the opposite case is the nonpolar organic solvent unable to scatter the electric field of the ion charge. Being transferred from water, ions have to remain almost completely in their hydration shell. Organic molecules have to be structured around the immiscible solvent, which causes a decrease of entropy. In this case the standard potential of ion transfer is determined by the entropy term of the Gibbs free energy. The larger the solvated ion is the deeper the decrease of the entropy is expected.

According to the above consideration, the impact of the enthalpy term in the Gibbs free energy of ion transfer from water to the organic phase is smaller for less polar organic solvents. On the contrary, the entropy term in low-polar organics seems to determine the Gibbs free energy of ion transfer. This assumption is confirmed by the data available in the literature. Table 1 presents thermodynamic values for transfer of chloride and bromide ions from water to aliphatic alcohols.[20] As seen for both anions, the Gibbs free energy is increased as the solvent polarity is decreased. The same raw enthalpy term remains unchanged and even is decreased from ethanol to propanol. The main impact from a raise of the Gibbs free energy is provided by the entropy term, which is remarkably increased as the solvent polarity is decreased (Table 1).

Concerning organic solvents used in the present investigation, we were able to find the detailed thermodynamic data only for the bromide ion (Table 2). Unfortunately, the data for nitrobenzene and dichloroethane are from different sources and were obtained by different methods.[16,21] However, Table 2 confirms our general assumption: whereas the Gibbs free energy is higher for ion transfer from water to the less polar organic solvent,

TABLE 2: Thermodynamic Quantities for the Transfer of Ions from Water to Different Solvents Immiscible with Water

ion	solvent	$\Delta G_{tr}^{w \rightarrow o}$, kJ mol^{-1}	$\Delta H_{tr}^{w \rightarrow o}$, kJ mol^{-1}	$T\Delta S_{tr}^{w \rightarrow o}$, kJ mol^{-1}	$(|T\Delta S_{tr}^{w \rightarrow o}|)/(|\Delta H_{tr}^{w \rightarrow o}|)$
Br$^-$	NB[a]	27.8	38.3	10.5	0.3
	DCE[b]	38	1	-39	39.0

[a] Reference 21. [b] Reference 16.

the enthalpy term can be decreased as the solvent polarity is increased.

We now have to consider why the standard potential of the electrode shielded by a thin layer of organic solvent is mainly determined by the enthalpy of ion transfer especially in case of low-polar organics. As mentioned, in such system the anion penetrates the organic phase to compensate for the charge of the oxidized mediator. The uncompensated charge obviously structures the organic solvent. Thus, maintaining entropy at its high level can be considered as a driving force for ion transfer across the water|organic interface at such shielded electrodes.

Conclusions

We conclude that the hydrophobic electrode shielded with the redox polymer in the organic solvent is applicable for investigation of thermodynamics of ion transfer across the liquid|liquid interface. The standard potential of the electrode shielded with highly polar organic solvent is proportional to the Gibbs free energy of anion transfer across the interface. An enhanced potential window as compared to a "classic" four-electrode setup allows the determination of the Gibbs free energy for a wider range of ions.

For less polar organic solvents the formal potential of the shielded electrode is mainly determined by the enthalpy of the anion transfer across the liquid|liquid interface, whereas the entropy term of the Gibbs free energy causes only a minor effect.

Among the advantages of the shielded electrode compared to a "classic" four-electrode setup are (i) the higher reproducibility of the interface, (ii) an enhanced potential window, and (iii) the possibility of investigating the interface with organic solvents of low and zero polarity.

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