Thin Liquid Films Voltammetry For The Thermodynamics Of Interfacial Ions Transfer

M.Yu. Vagin[1], S.Zh. Ozkan[2], G.P. Karpachova[2],
A.A. Karyakin[1]
[1] Faculty of Chemistry, M.V. Lomonosov Moscow State University, 119992, Moscow, Russia;
MYV@enzyme.chem.msu.ru
[2] A.V. Topchiev Institute of Petrochemical Synthesis RAS, Leninskii prospect 29, 117912, Moscow, Russia

The interface between two immiscible liquids attracts a particular interest for physical and analytical chemistry. The structure of the interface, which is considered as a model of a half of biological membrane, is highly important for life sciences. The conventional four-electrode setup is used for the electrochemical studies of thermodynamics and kinetics of charge transfer. This approach gives the opportunity for the direct amperometric detection of non-electroactive ions, which is of high importance for analytical chemistry.

However, the classical four-electrode setup has certain limits for the studies of biomolecular transfer. The latter is highly perspective for the applications in analytical biotechnology.

Recently, the alternative approach for the studies of charge transfer across liquid|liquid interface in common three-electrode electrochemical cell were proposed by F.C. Anson and C. Shi [1]. The thin liquid film of organic solvent shielded the surface of carbon electrode, which was immersed into the aqueous electrolyte solution. Organic phase contained water-insoluble redox mediator. Its oxidation-reduction on the electrode surface has to be accomplished with charge transfer through water-organic interface for the electroneutrality keeping. However the approach application is limited by the possibility of redox material loss from organic phase in charged state and nonreproductivity of electrode surface hydrophobized in flame.

We propose the improved setup for the charge transfer studies by means of thin liquid film voltammetry. The use of hydrophobic graphite material (graphite cloth LSG) allowed achieving high reproducibility of the system. The specially synthesized redox polymer polyphenothiazine (PPTA) totally insoluble in water even in oxidized state was used. The cyclovoltammetry was carried out in different supporting electrolytes (Fig. 1). The dependence of formal potential on the nature of supporting electrolyte anion was observed (Fig. 2). When the polarity of organic solvent is decreased, the slope of the plot is also decreased. However the difference in Gibbs free energy transfer for hydrophilic ions is increased as the polarity of the organic solvent is decreased [3]. The explanation of the effect was proposed. As the polarity of organic phase is decreased, the impact of enthalpy is also decreased, but the impact of entropy term is increased [2]. As a driving force of ion transfer across thin liquid film interface the entropy can be considered. And the very weak temperature dependence of observed potential (Fig. 3) proves this idea. Thus, the new approach provide the simple thermodynamic studies of ions transfer across liquid|liquid interface by means of thin liquid film voltammetry

[1] C. Shi, F.C. Anson. Anal. Chem., 70, (1998), 3114.
[2] Y. Marcus. Ion Properties, Marcel Dekker: New York, 1997.

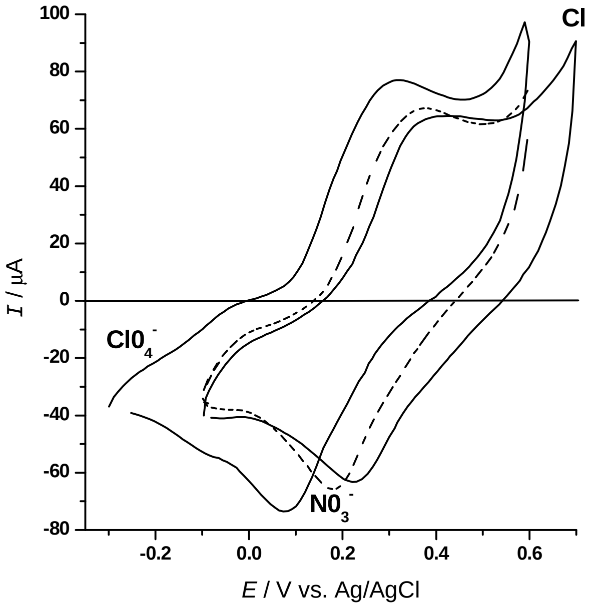

Fig. 1. Shift of the PPTA redox activity potential within thin liquid film of chloroform on the graphite surface with the counterion hydrophobicity increase.

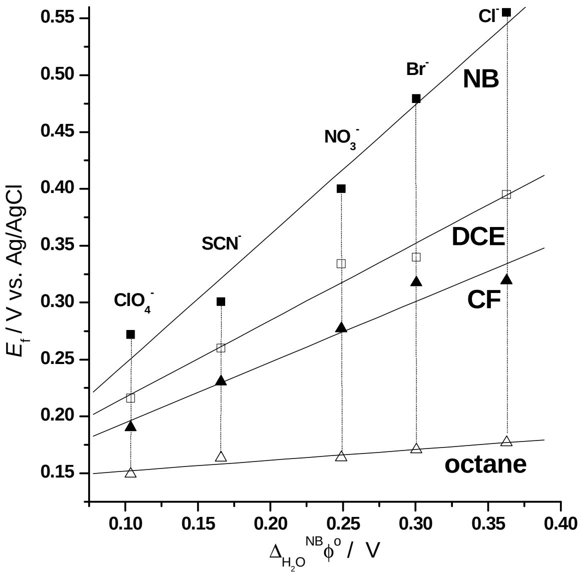

Fig. 2. The dependence of the potential of PPTA redox activity within thin liquid film of different organic solvents (nitrobenzene, 12dichloroethane, chloroform and n-octane) on the standard potential of ion transfer across water|nitrobenzene interface.

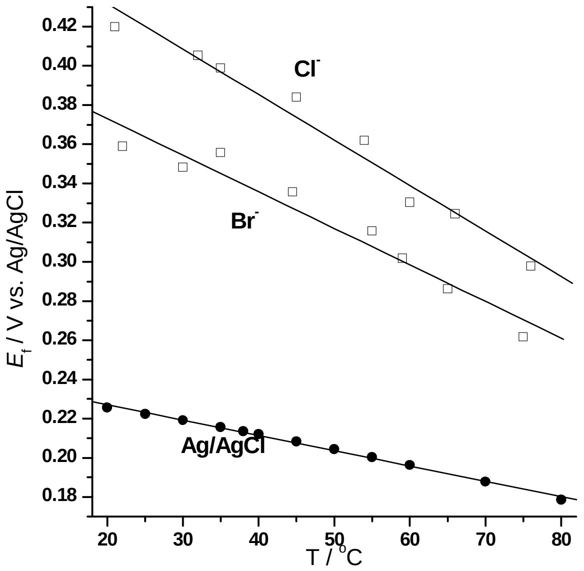

Fig. 3. The temperature dependencies of potential of PPTA redox activity within thin liquid film of 1,2-dichloroethane on the graphite surface.