ELECTROCHEMICAL FORMATION OF MICROLAYERS OF IONIC LIQUIDS. NEW TYPE OF VOLTAMMETRIC OSCILLATIONS AND RAMAN SPECTROSCOPY STUDIES

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Pure organic solvents like simple aliphatic alcohols or nitroalkanes are reported to give well-defined, stable and reproducible voltammetric oxidation or reduction waves at platinum microelectrodes in the presence of small amounts of supporting electrolyte. Since the medium acts as an electroactive species at the same time, it can be described as an undiluted redox liquid.

The electrode process of undiluted solvents leads to the generation of a diffusive layer with unique physicochemical properties. Within this layer such quantities as density, viscosity and conductivity are significantly altered in comparison to the solvent in the bulk, which is predicted by the theory. We have managed to confirm these theoretical expectations performing the temperature and gravitational voltammetric experiments. The temperature measurements allow one to judge on the viscosity of the generated ionic microlayers, whereas the gravitational studies provide information on their density.[1, 2]

Reflective Raman spectroscopy appeared to be a useful tool for further investigation of undiluted redox liquids. The redistribution of ionic species and their accumulation in the microelectrode vicinity under steady-state conditions was clearly reflected in the recorded spectra. This is illustrated in Figure 1. The more positive potential the more advanced is the process, and the higher are the perchlorate peaks.

The stability of generated ionic liquid at the microelectrode surface may be disturbed within a particular potential range. Surprisingly stable and reproducible current and potential oscillations can appear. These oscillations are probably due to consecutive increase and fall of the local resistance, as a consequence of the displacement (reduction) and re-incorporation of the supporting electrolyte counterion present in the ionic layer. Typical oscillations are presented in Figure 2.

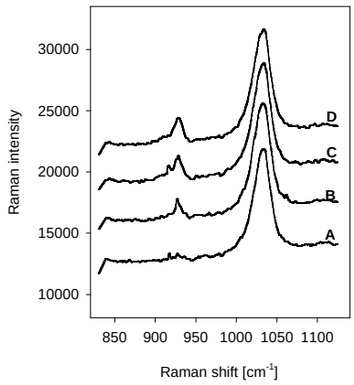

Figure 1
Reflective Raman spectra of undiluted methanol during its oxidation at: 2.9 (**A**), 3.1 (**B**), 3.2 (**C**) and 3.35 V (**D**). Supporting electrolyte: 0.02M $LiClO_4$; WE-platinum microelectrode of r_{el}= 10 μm; distance from the electrode surface: 150μm.

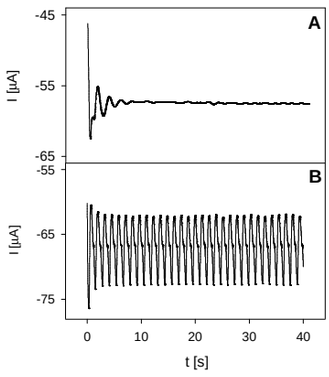

Figure 2
Chronoamperometric responses of 25.4-μm-radius Pt microelectrode in undiluted nitromethane at various potentials applied: -6V (**A**) and -7V (**B**). Supporting electrolyte: THABr ($5x10^{-3}$M), T = 21^0C

[1] W.Hyk, K.Caban, M.Donten, Z.Stojek, *J.Phys.Chem.B*, 105 (2001) 6943-9.
[2] K.Caban, M.Donten, W.Hyk, Z.Stojek, *Chem.Anal.(Warsaw)*, 46 (2001) 813-22.