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Electrooxidation of undiluted organic liquids swelling *N*-isopropylacrylamide-based copolymers

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Abstract Polyacrylate gels such as: *N*-isopropylacrylamide (NIPA), ionic copolymer NIPA-co-sodium acrylate (NIPA-co-SA) and ionic copolymer NIPA-co-[2-(acryloyloxy)ethyl]trimethylammonium chloride (NIPA-co-XCl) were swollen by methanol, ethanol and *N,N*-dimethylformamide. These solvents were oxidized voltammetrically in the gels at platinum microelectrodes. The blocking coefficients, defined as the ratio of the currents observed in the presence and absence of the polymeric chains, were different for the solvents in the charged and uncharged polymers and did not differ for the electroactive probe, ferrocene, present in the solvents at millimolar level. This may mean that the micro ionic layer that is formed at microelectrodes at the plateau of the voltammetric solvent waves leads to a kind of collapse/phase transition of the polymer in the depletion layer. For methanol, the gel structure was found to prevent occasionally the formation of large gas bubbles at the potentials positive versus the first wave and then three one-electron waves could be obtained. Experiments done with a capillary cell and an optical microscope indicated that before formation of large bubbles at the Pt microelectrode a very dynamic, dense stream of microbubbles leaves the electrode surface.

Keywords Undiluted redox liquids · Poly(*N*-isopropylacrylamide) gels · Voltammetry · Blocking coefficient

Introduction

It has been found that several organic liquid compounds, including popular solvents, give well-defined

voltammetric waves at microelectrodes at their undiluted state. These compounds/solvents are the following: acetonitrile [1], *N,N*-dimethylformamide (DMF) [2], dimethylsulfoxide [3], simple aliphatic alcohols [4, 5], nitrobenzene and benzonitrile [6], nitromethane and its homologs [7], aniline and pyrrole [8], 4-cyanopyridine [9], and acetophenone [10]. A small amount of supporting electrolyte is needed in the medium to get reasonable conductivity in the cell and to know which ion is the major counterion to the ionic product formed. The concentration of supporting electrolyte can be as small as the millimolar level. The existence of a plateau at the voltammetric waves of an undiluted solvent means that the substrate concentration at the electrode surface drops to zero. It also indicates that in the thin reaction layer at the electrode surface, there exists an ionic liquid consisting of the ionic product and the appropriate counterion. The properties of the ionic microlayers, such as viscosity and density, differ substantially from those of undiluted substrates and can be examined by doing voltammetry at various temperatures and in a rotated cell [5]. A recent paper provides experimental evidence for the accumulation of ions at the microelectrode surface when the electrode process of undiluted methanol takes place [11].

Copolymeric gels based on *N*-isopropylacrylamide (NIPA) and other monomers have been extensively studied in recent years. They are commonly defined as three-dimensional polymeric networks swollen by water or another solvent. The attention of scientists was especially focused on the analysis of the structure and properties of hydrogels. These gels were found useful in such applications as batteries and sensors [12, 13, 14, 15, 16, 17, 18]. The measurements were done to study the phase transition (from the swollen state to the shrunken state) of these gels. The research on influence of pH [19, 20, 21], temperature [22], pressure [23], solvent composition [19], supporting electrolyte [24] and electromagnetic radiation [25] on this transition helped to develop applications of stimuli-responsive polymeric gels [26]. The phase transition of polymeric gels was predicted

Dedicated to Zbigniew Galus on the occasion of his 70th birthday

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theoretically in 1968 by Dusek and Patterson [27], while the experimental evidence was provided several years later. Knowledge of the transport properties of the reagents in the polymeric gels became of great importance for developing further applications. Several experimental techniques were used to study the transport of various species in the polymeric gels: NMR spectroscopy [28], scanning electrochemical microscopy [29], conductivity measurements [30] and steady-state voltammetry [31, 32, 33]. Recently, a simple electrochemical method has been developed to measure the efficiency of solute release from thermoresponsive poly(*NIPA*) hydrogels [34].

Alcohols have already been considered as the solvents for swelling the isopropylacrylamide gels [32, 33]. Voltammetry of methanol in the gels was done to characterize the transport properties of the gels [32]. The aim of this paper was to extend the examination of the electrooxidation process of undiluted redox liquids. Methanol, ethanol and DMF were selected as such substrates/solvents. Special attention was paid to the electrooxidation of these compounds present in the *NIPA* various copolymers swollen by them. It was of interest to determine how the parameters of the total waves, including the blocking coefficient, are affected by the compositions and amounts of the polymers in the gels.

Materials and methods

Voltammetry was done in the three-electrode mode using an EG&G PARC, model 283, potentiostat that was controlled via personal computer. The cell was enclosed in a Faraday cage to minimize the electrical noise. Platinum disk microelectrodes (nLab, Warsaw) of sizes 5, 10 and 25 μm in radius served as the working electrodes. Two pieces of platinum foil (of surface area ca 1 cm^2) were used as the counter and the quasi-reference electrodes to eliminate a possible leak of ions from the bridge. Before each experiment the working electrode was polished with aluminum oxide powders of various particle size (down to 0.05 μm) on a wet pad and then rinsed with a direct stream of ultrapure water (Milli-Q, Millipore, conductivity of 0.056 mS/cm). After polishing, the electrodes were dried using ethyl alcohol. Occasionally the electrode surface was inspected optically with an inverted metallurgical microscope (Olympus, model PME 3).

A special experimental arrangement with an optical microscope equipped with a digital camera (Nikon) and a capillary cell parallel to the microscope stand was made to observe the evolution of gaseous products at the tip of the microelectrode and their movement in the depletion layer. Another capillary cell with a micro reservoir located above the microelectrode tip was made to allow the collection of microliter samples of evolved gas for further mass spectrometric analysis.

Spectral experiments with the gels were done using an UV-VIS spectrometer (Lambda 20, Perkin Elmer). To get UV-VIS spectra in the range 700–290 nm, a quartz cuvette was used. The collected gaseous samples were analyzed using a Shimadzu GC 17A chromatograph with a QP 5000 mass spectrometry detector. The chromatograph was equipped with a SPB 1 (Supelco, PA, USA) capillary column of 60 m in length, 0.32 mm I.D. and of 1 mm film thickness. The carrier gas was pure helium (< 1.6 ppm H_2O , < 1.2 ppm O_2).

Lithium perchlorate (LiClO_4 , 99%) was purchased from Fluka and was used as supporting electrolyte. Ferrocene [$\text{Fe}(\text{C}_5\text{H}_5)_2$, 98%] was purchased from Aldrich. Regarding solvents: acetonitrile (Fluka) was of p.a. grade, DMF ($\text{C}_3\text{H}_7\text{NO}$, Aldrich) was of 99.9% purity, methanol (CH_3OH) and ethanol ($\text{C}_2\text{H}_5\text{OH}$) were purchased from POCh, Gliwice and were spectral pure. All experiments were performed at room temperature.

The polyacrylate gels such as: *NIPA*, ionic copolymer *NIPA-co-sodium acrylate* (*NIPA-co-SA*) and ionic copolymer *NIPA-co-[2-(acryloyloxy)ethyl]trimethylammonium chloride* (*NIPA-co-XCl*) were synthesized according to the slightly modified procedure given in [35]. *N,N'*-methylenebisacrylamide was used as the crosslinker. Dried gel powders were swollen with solvents and ferrocene solutions at least 1 day before experiments.

Ferrocene was added to the cells to construct the potential scale versus the Fc/Fc^+ couple.

Results and discussion

In preliminary experiments, total voltammetric waves of oxidation of methanol, ethanol and DMF in the polymer gels were obtained for three different concentrations of supporting electrolyte: 0.001, 0.01 and 0.1 M LiClO_4 . These waves were compared with the voltammetric curves obtained in the pure solvent without polymeric network. Figure 1 presents typical total waves of oxidation of methanol with 4% *NIPA*. The voltammograms were very well reproducible. The coefficient of variation calculated for the wave height ($n=5$) was smaller than 1.2%. In particular, no substantial changes in the plateau current were observed with the increase in the concentration of supporting electrolyte in the gel from 10 to 100 mM. Only the half-wave potential of the total wave shifted to a less positive potential and the slope of the semi-logarithmic plot diminished as the concentration of LiClO_4 increased, which was apparently a result of diminishing the ohmic potential drop in the system.

The electrode process, run at a potential belonging to the plateau of the first methanol wave quickly reaches the steady state, and the current is stable for hundreds of seconds. This was shown earlier for undiluted methanol without polymeric net [5]. The current is also stable for ethanol and DMF swelling the gels; however, for DMF a potential range exists on the wave plateau where the

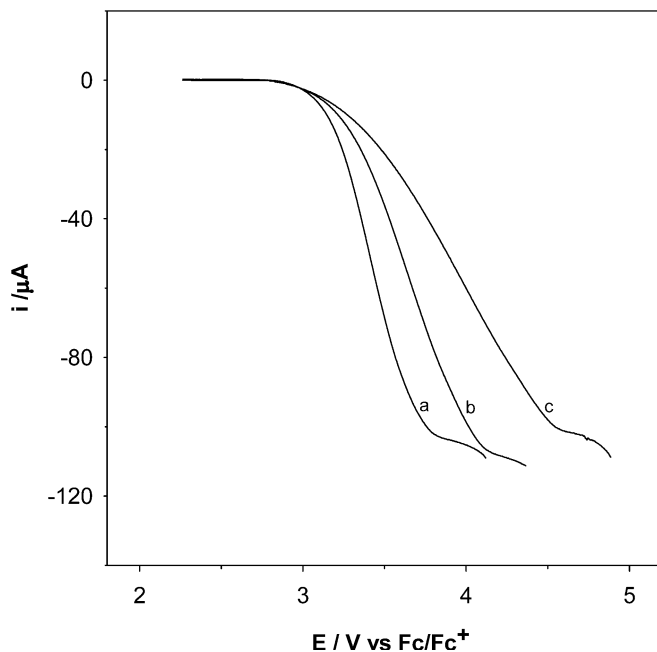


Fig. 1 Voltammograms of oxidation of methanol present in 4% swollen *N*-isopropylacrylamide (NIPA) gel. Concentration of supporting electrolyte, LiClO_4 : 0.1 M (a), 0.01 M (b), 0.001 M (c). Pt microdisk electrode 10 μm in radius; $\nu = 20$ mV/s, $T = 25$ °C. *Fc* Ferrocene

current drops. Typical chronoamperometric curves for all three solvents present in 4% NIPA gel are shown in Fig. 2. In fact, the stability of the current of oxidation of a solvent in the polymeric gel is something of a surprise, since the possible oxidation of the surface-present polymeric net could lead to the faulting of the electrode surface.

The wave heights of methanol, ethanol and DMF present in the polymeric gels were always smaller, by circa 15%, in comparison to those obtained for appropriate undiluted liquids. This is understandable, as not only does the polymer network occupy a part of the electrode surface, but the existence of the channels in the gels should also restrict the diffusion to some extent. To measure quantitatively the wave-height drop due to the existence of the polymeric network, we use in this paper a coefficient named the blocking coefficient and defined as the ratio of the currents in the gels and those in the appropriate undiluted liquid. The blocking coefficients obtained for the waves of the solvents were compared with those obtained for a reference compound, ferrocene, present in the systems at 2 mM concentration. A comparison of several parameters of the voltammetric waves of the solvents and the ferrocene probe for two different gels is given in Table 1. The total waves obtained in the polyacrylamide gels have semi-logarithmic slopes bigger than those for undiluted solvents, which indicates that the resistance of the solutions present in the swollen polymers is smaller and the presence of polymeric chains contribute to the conduction in the system.

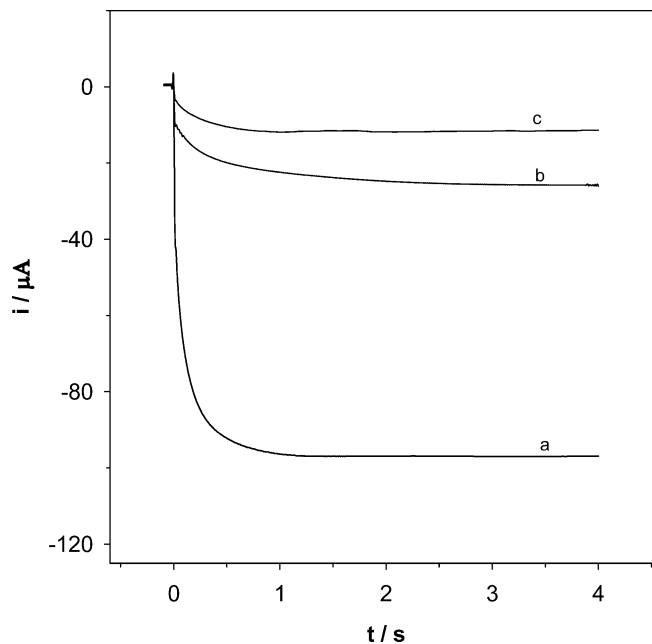


Fig. 2 Chronoamperograms obtained at Pt microelectrode for oxidation of solvents swelling 4% NIPA gel: methanol (a), ethanol (b), *N,N*-dimethylformamide (c). Electrode potential versus Pt quasi reference electrode: 4.1 (a), 3.5 (b), 3.0 V (c). Concentration of LiClO_4 : 0.1 M (a, b), 0.01 M (c). $T = 24$ °C

The steady-state current (I_{SS}) ratio $I_{SS \text{ gel}}/I_{SS \text{ solv}}$ for ferrocene is similar to the blocking coefficients for the solvents; however, some significant differences exist. For example, in the 4% NIPA medium the blocking coefficients are a little higher for methanol and DMF compared to ferrocene, while in 4% NIPA-co-XCl (positively charged chains), the blocking coefficients for methanol and ethanol are lower. Also, for all solvents examined, the blocking coefficients are lower in 4% NIPA-co-XCl compared to in 4% NIPA. Interestingly, the blocking coefficients for ferrocene are practically identical in methanol and ethanol, lower in DMF and not affected by the type of polymer. The larger differences between the blocking coefficients for the waves of the solvents must be a result of the formation, at the electrode surface, of a microlayer of ionic liquid. These liquids differ substantially in viscosity and density [5]. We want to stress here that the above-reported decrease in the voltammetric wave heights is a good indication for the correct measurements, since the absence of such a difference would mean that a solvent pool is formed between the electrode surface and the gel net.

The voltammetric wave height for a microdisk electrode under steady-state conditions is given by:

$$I_{ss} = 4nFDCr_e \quad (1)$$

where C is the bulk concentration of the reactant, r_e is the electrode radius, F is Faraday's constant, n is the number of electrons transferred per molecule and D is the diffusion coefficient of the reactant. In the case of voltammetry of an undiluted liquid substance, D for this

Table 1 Electrochemical parameters of oxidation of undiluted solvents in polyacrylate gels

Solvent	Undiluted solvent		Undiluted solvent with gel							
			4% NIPA			4% NIPA-co-XCl				
	I_{SS} (μA)	$E_{1/2}^a$ (V)	I_{SS} (μA)	$E_{1/2}^a$ (V)	Blocking coefficient	I_{SS} (μA)	$E_{1/2}^a$ (V)	Blocking coefficient		
				$\frac{I_{SS, \text{gel}}}{I_{SS, \text{solv}}}$		$\frac{I_{SS, \text{Fc, gel}}}{I_{SS, \text{Fc, solv}}}$			$\frac{I_{SS, \text{gel}}}{I_{SS, \text{solv}}}$	$\frac{I_{SS, \text{Fc, gel}}}{I_{SS, \text{Fc, solv}}}$
Methanol ^b	126	3.39	114	3.51	0.90	0.86	103	3.62	0.82	0.86
Ethanol ^c	33.4	2.78	29.1	2.81	0.87	0.86	27.1	2.92	0.81	0.86
DMF ^b	11.2	2.25	9.93	2.29	0.88	0.80	9.29	2.31	0.83	0.81

^aPotential measured vs Fc/Fc⁺

^bConcentration of supporting electrolyte, $C=0.01$ M (LiClO₄)

^cConcentration of supporting electrolyte, $C=0.1$ M (LiClO₄)

compound is determined by the viscosity of the ionic microlayer formed at the microelectrode surface. As we can see from Eq. 1, the steady-state current is proportional to the radius of microelectrode. Therefore the ratio I_{ss}/r_e should be constant for the processes with diffusional transport. An examination of this ratio was done for all three studied solvents, and indeed the ratio was found to be constant, and therefore the wave heights obtained are determined by the diffusion rate. For example, for DMF in 4% NIPA, for 5, 10 and 25 μm in radius platinum microelectrodes, the ratio I_{ss}/r_e was found to be 1.09, 1.12 and 1.12 $\mu\text{A}/\mu\text{m}$, respectively. Equation 1 has been used in papers [32, 33] to determine the diffusion coefficients of electroactive probes and the apparent diffusion coefficients for methanol in the diffusion layer in the poly(NIPA) gels.

An increase in the percentage of the NIPA polymer in the gel medium leads to a further decrease in the current. This is illustrated in Fig. 3. The current decreases more slowly than linearly with the percentage of the gel, which is somewhat surprising; a linear relationship was expected.

Doing some experiments with the negatively charged chains (NIPA-co-SA) has extended the data on the voltammetric differences between positively charged and neutral polymeric chains presented in Table 1. A comparison of the voltammetric waves of methanol obtained for three types of polymers is presented in Fig. 4. It is clear that both negatively and positively charged polymeric chains (NIPA-co-SA and NIPA-co-XCl) restrict diffusion to the same extent, by circa 11%, compared to the NIPA polymer. For ethanol and DMF the behavior is very similar. Formally, since all three solvents consist of uncharged molecules, the corresponding total voltammetric waves should not differ in the above polymers. The difference seen in Fig. 4 for methanol must appear owing to the formation, at a potential belonging to the wave plateau, of the ionic liquid layer, where the interactions with the charge polymeric chains and the ionic products should be significant. The corresponding drop in the wave height means that the charged polymeric nets shrink and perhaps collapse and undergo the phase transition within the ionic liquid microlayer.

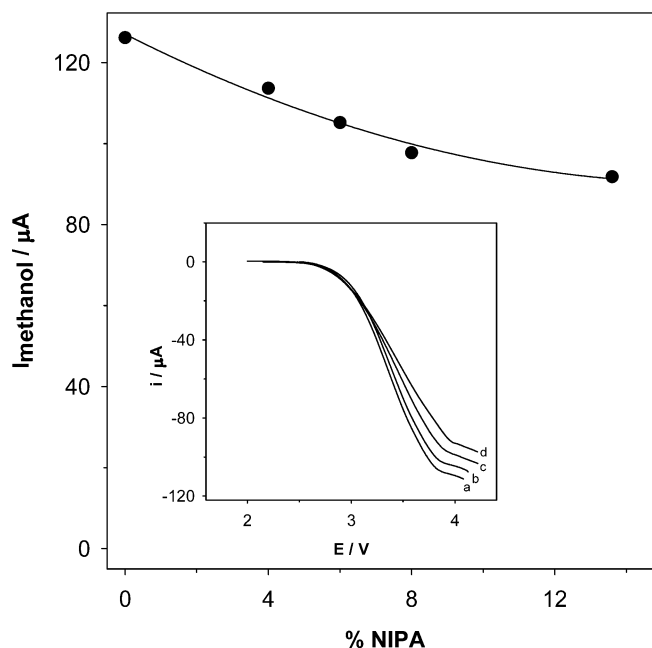


Fig. 3 Dependence of wave height of oxidation of methanol containing 0.01 M LiClO₄ on percentage of NIPA. Inset: Voltammograms obtained for: 4 (a), 6 (b), 8 (c), and 14% NIPA (d). $T=23$ °C

Ferrocene solutions in the gel matrices were pretty stable. The corresponding spectra of ferrocene and ferrocene cation obtained in a 4% NIPA gel soaked with methanol and of ferrocene in pure methanol are presented in Fig. 5. The absorbance of the gels without electroactive probe in the region from 800 nm to 300 nm was negligible. Two absorption bands appear at 430 and 326 nm after introduction of ferrocene to the gel. They are shifted by circa 10 and 1 nm, respectively, towards shorter wavelengths, in comparison to the pure undiluted methanol medium. This is a hypochromic shift and the decrease in the sensitivity may indicate the hypochromic effect in the Fc absorbance in the gel matrix. For the gel solutions older than 2 weeks a new small broad band appears at 386 nm and the band at 326 nm starts to disappear. This new band cannot be assigned to

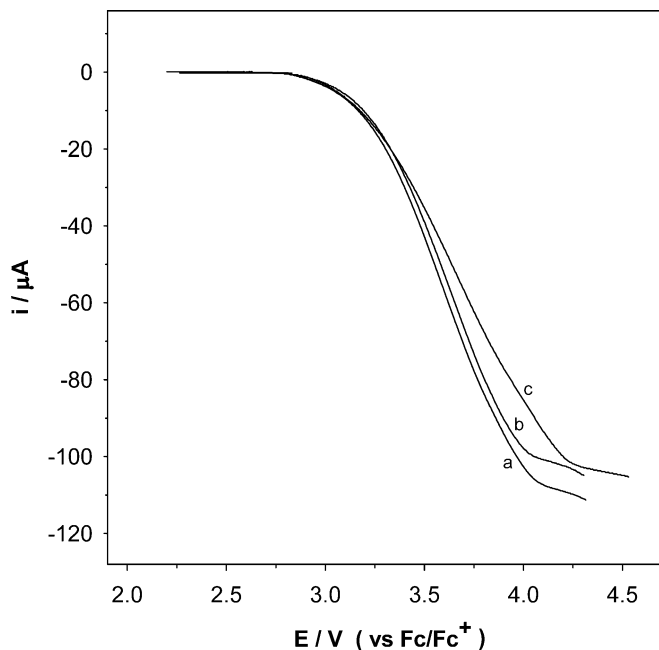


Fig. 4 Voltammograms of oxidation of methanol swelling various gels: 4% NIPA (*a*), 4% NIPA-co-sodium acrylate (NIPA-co-SA) (*b*), 4% NIPA-co-[2-(acryloyloxy)ethyl]trimethylammonium chloride (NIPA-co-XCl) (*c*). $T = 22\text{ }^{\circ}\text{C}$; other conditions as in Fig. 1

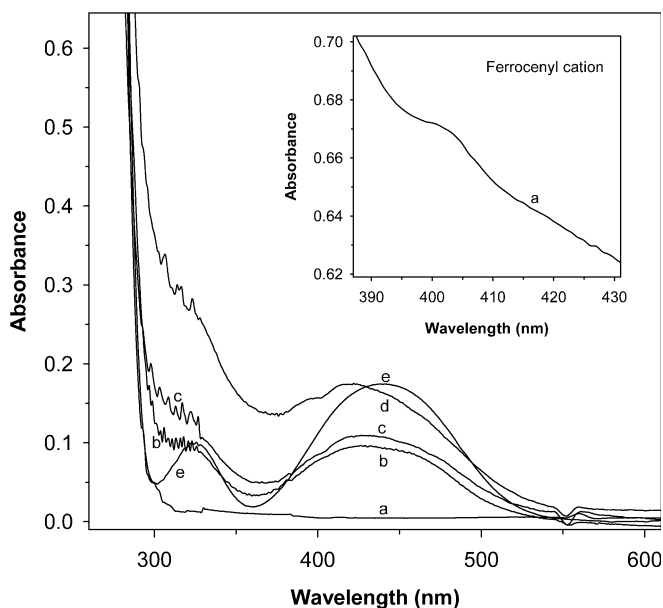


Fig. 5 UV-VIS spectra of ferrocene (*b*, *c*, *d*) and ferrocenyl cation (inset, *a*) in 4% NIPA gel. Time of aging of ferrocene solution: 1 (*b*), 14 (*c*), 28 days (*d*); spectrum obtained for ferrocene in pure methanol (*e*). Concentration of ferrocene and LiClO_4 : 2 mM and 0.01 M, respectively. $T = 25\text{ }^{\circ}\text{C}$

the formation of ferrocene cation, since this ion gives an adsorption band near 400 nm. Also, the voltammograms of ferrocene did not change even 1 month after the preparation of the ferrocene gel solutions. All this indicates that ferrocene could not be partially oxidized

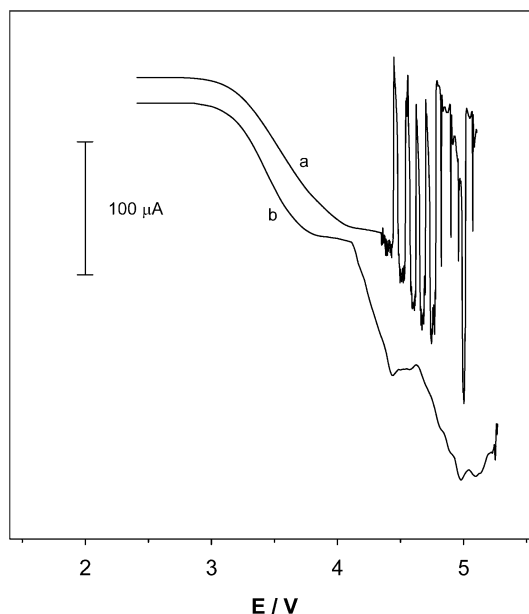


Fig. 6 Voltammograms of oxidation of pure methanol (*a*) and methanol present in 4% NIPA swollen gel (*b*). Concentration of LiClO_4 : 0.1 M. $T = 23\text{ }^{\circ}\text{C}$; other conditions as in Fig. 1

or broken up. It rather means that ferrocene may be partially incorporated into the gel structure. For the pure 2 mM ferrocene solutions in methanol the above adsorption effects were not seen and the spectrum recorded on the day of preparation had exactly the same shape as that obtained 1 month later.

We have also tried to obtain and examine the total waves of acetonitrile in the polyacrylate gels; however, the gelling process in this solvent did not proceed.

Further steps of oxidation of undiluted methanol

Following the well-defined first oxidation wave of undiluted methanol, the oxidation current first fluctuates very little (the amplitude of fluctuations is relatively small) and next it is strongly disturbed. This is illustrated by curve *a* in Fig. 6. We investigated those disturbances using a special capillary cell and an optical microscope. It appeared that small fluctuations are caused by a very dynamic stream of microscopic gas bubbles. A typical situation in the solution is presented in Fig. 7. The very dynamic movement of the microbubbles is little affected by the gravitational field. At more positive potentials, large bubbles are formed and this leads to the disturbances of large amplitude; the oxidation current occasionally drops to the zero level.

In a separate experiment with the capillary cell/optical microscope arrangement some methyl orange was added to methanol and, as a result, the colorless neighborhood of the Pt microdisk became intensively pink in the potential region of the wave. This means that the methanol cations that are formed within the first voltammetric wave are strongly acidic. The thickness of



Fig. 7 Evolution of microbubbles of gas during electrooxidation of undiluted methanol at Pt microelectrode. The picture was taken as the voltammogram entered the region of current oscillations (circa 4.3 V vs Pt quasi reference electrode). Radius of Pt microdisk: 10 μm ; $T=22\text{ }^\circ\text{C}$

the pink region was found to be relatively large: circa 0.3 mm. We think that this number well represents the thickness of the diffusion layer at the microdisk electrode.

We made an effort to analyze the contents of the gas bubbles. Using a gas chromatograph connected to a mass spectrometer several species were detected. Two major peaks were located at masses of 28 (N_2/CO) and 32 (O_2), and their ratio was higher than 4:1; it is therefore possible that CO is one of the products. The minor products were identified as dimethoxymethane, methyl formate and ethyl alcohol. Most probably they are the products of the follow-up chemical reactions. NMR experiments confirmed the presence of methoxy groups in the collected samples of the final solution. The rigorous determination of the major gas products requires an improvement in the handling of gaseous microsamples. Such experiments are in progress.

The existence of the polymeric net at the electrode surface may help in preventing the formation of large bubbles. Indeed, it does; however, rarely. An example is given in Fig. 6 (curve b). We believe curve b presents three one-electron waves of oxidation of undiluted methanol.

Conclusions

All three polymers based on NIPA and containing one of negative, positive or no charge at the chains can be easily swollen by methanol, ethanol and DMF. These solvents give well-defined voltammetric total waves at Pt microelectrodes at extreme positive potentials in the presence of all polymeric nets examined. The microelectrode surface does not get polluted and only the formation of large bubbles at the electrode surface (at

potentials positive vs. the first wave plateau) requires an action of limited moving of the microelectrode in the solution to reestablish the initial state of the surface.

An interesting difference appears for the wave heights of the solvents obtained in the uncharged and the charged polymers. For the same percentage of the polymer in the gel, the wave height of methanol obtained in the presence of charged copolymers is always smaller compared to the NIPA polymer. This must be interpreted in terms of the polymeric net getting denser, and consecutively by a local collapse or phase transition of the gel. Since such an effect does not appear for the voltammograms of ferrocene, we conclude that it must be related to the formation of a microlayer of the ionic liquid at the electrode surface.

One thing needs further investigation. This is the problem of very dynamic evolution of microbubbles of a gas at the potential belonging to the plateau of the first methanol wave. This gas could not be identified beyond any doubt. The formation of CO within the second wave is possible, however, then, the second oxidation wave of methanol would require at least four electrons per molecule. This would be in contradiction with the well-established fact, that the number of electrons transferred within the first oxidation wave is one and the three waves of oxidation of methanol obtained in the gel are of equal height.

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