POLAROGRAPHIC STUDY OF Mo(V) IN METHANOL IN THE PRESENCE OF PHOSPHATIDYL CHOLINE

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In a nitrogen-fixing system containing a complex of Mo(III) with Mg(II) (catalyst) and an amalgam of Na (reducing agent) in alkaline methanol solution, the rate of formation of hydrazine increases by tens of times when phosphatidyl choline (PC, where R^1CO and R^2CO are residues of oleic and stearic acids) or dipalmitoyl phosphatidyl choline (DPC, where R^1CO-R^2CO are palmitic acid residues) are added to this system [1]

\[ \text{PC} : \text{Me(O)CH}_2\text{CH}_2\text{PO(}\text{H}_2\text{NMes})\text{O}_2\text{CH}R^1\text{COOCH}R^2\text{COOCH}_2 \]

We found that in oxidation of Mo(III) in methanol solutions of MeOLi or MeONa in concentrations not exceeding 0.1 M, particles of Mo(V) are formed and their electrochemical properties are identical to the properties of particles obtained on addition of a methanol solution of MoCl_5 to these solutions. Since Mo(V) is more stable in these solutions than Mo(III), the study was conducted in solutions containing Mo(V). We studied the electrolytic reduction of Mo(V) on a mercury drop electrode (MDE) in methanol solutions of MeOLi and MeONa with additives of PC, DPC, and glycerophosphatidyl choline (GPC, whose molecule contains no fatty acid residues), and palmitic acid (PA) to determine the cause of the strong effect of the phospholipids. In addition, it was interesting to follow the effect of addition of PC and DPC on electrolytic reduction of Mo(V) in guanidine buffer solution (pK_a 13.6). This would permit predicting the effect of addition of these phospholipids on the electrochemical behavior of the Mo(III) catalyst in a nitrogen-fixing system containing Mo(III), Ti(III), and guanidine hydrochloride [2-4].

EXPERIMENTAL

The study was conducted with methods of classic and alternating current polarography on MDE in methanol solutions of MeOLi and MeONa using a PU-1 universal polarograph equipped with a device for force rupture of the mercury drops. MDE characteristics: m = 4.18 mg/sec, τ = 2.5 sec, and m = 0.48 mg/sec, τ = 25 sec in 0.07 M MeOLi. The alternating current curves were recorded in 2.1 sec at a frequency of 25 z and an alternating voltage amplitude of 20 mV. The capacitance component of the current was separated with a phase-sensitive detector in which the reference signal was phase-shifted 90° with respect to the alternating voltage on the cell. To separate the capacitance component, the alternating current curves were made with a phase shift of the sinusoidal alternating voltage reference pulses of 90°. An aqueous normal calomel electrode separated from the cell by a transition bridge filled with the background electrolyte was used as the reference electrode. The potentials were given with a precision of ±5 mV. The alternating current curves were converted to capacitance curves for C with the E curve of LiCl in MeOH [5]. All measurements were made in an atmosphere of Ar (high purity). All solutions were prepared under Ar in MeOH dehydrated according to [6] and distilled twice under argon. The solutions of MeOLi and MeONa were prepared by dissolving the corresponding metals in MeOH and 1 M MoCl₅ was prepared by dissolving a weighed portion in MeOH. The solutions were subsequently used for preparing a 0.05 M solution of MoCl₅, and aliquots were added to the solutions studied.

RESULTS AND DISCUSSION

The presence of a bipolar "head" and long hydrocarbon "tails" in PC favor their adsorption both with positive and with negative surface charges and consequently affects the course of electrode reactions. Adsorption of PC and DPC was studied in a wide range of MDE potentials (from -0.1 to -2.0 V). The capacitance curves of PC are shown in Fig. 1; they are identical to the curves for DPC, also obtained in 0.07 M MeOLi. The capacitance curves obtained here are similar to the curves obtained for DPC [7, 8]. Adsorption of PC and DPC is observed from -0.1 to -2.0 V. There are two adsorption regions: the molecules of PC and DPC which lie flat on the surface of the MDE are adsorbed in the region of -0.1 to -0.9 V. A reorientation peak then follows, after which the region of adsorption of molecules of PC and DPC in the vertical position from -1.5 to -2.0 V is located. However, we did not observe the sharp decrease in the capacitance with high negative MDE potentials when C(PC) > 5·10⁻⁴ M due to the formation of a condensed adsorption layer, since the methanol solutions of PC and DPC studied here, in contrast to [7, 8], contained no water, which causes formation of micelles.

The electrolytic reduction of Mo(V) on MDE in methanol alkaline and guanidine buffer solutions in the absence of PC and DPC was studied previously [9]. The electrochemical process in these systems takes place irreversibly with the participation of two electrons. The saturation currents I_d are diffusion currents.

A wave (WA) of reduction of Mo(V) +2e⁻ Mo(III) with E₁/₂ = -1.61 V and a one-electron wave of oxidation Mo(V) -2e⁻ Mo(VI) with E₁/₂ = -0.36 V are observed in alkaline methanol solutions. In solutions of 5·10⁻⁵ M PC or 7.5·10⁻⁵ M DPC containing 10⁻³ M Mo(V) and 0.07 M MeOLi, a new cathode wave (WB) with E₁/₂ = -1.4 V appears in the polarograms with more positive potentials. When the concentration of phospholipid C_L is increased to 8·10⁻³ M, WB is monotonically shifted to the cathode region (Fig. 2). E₁/₂ of WA changes weakly. With an increase in C_L, the saturation current of WA decreases, and the I_d of WB increases, which indicates an increase in the number of electroactive particles formed in the reaction of Mo(V) with PC or DPC. With a 7.5·10⁻⁴ M concentration of the lipid, only WB is observed, while WA disappears. With C_L of 7.5·10⁻⁴ M, I_d for WB is a diffusion wave proportional to [Mo(V)] in the range of concentrations from 5·10⁻⁴ to 1.5·10⁻³ M and the square root of the height of the mercury column. We note that substitution of Li⁺ by Na⁺ in the background electrolyte does not alter the overall character of the polarograms and E₁/₂ in the presence of these ions almost coincide. The capacitance curves show that the Mo(V) reduction wave lies in the region of molecules of PC and DPC vertically adsorbed on the MDE. It is suggested in [7, 8] that binding of the background Li⁺ cations with the phospholipid gives the lipid layer an additional positive charge. The particles of Mo(V) bear a negative charge in alkaline methanol solutions [10]. For this reason, binding of Mo(V) with the polar head of the phospholipid in the pores of the positively charged adsorption layer will facilitate discharge of Mo(V) on the negatively charged surface of the MDE. The appearance of WB at -1.4 V confirms this hypothesis. According to [11], facilitation of the reduction of complexes of metals with an adsorbed ligand, catalyst, can be due both the appearance of a "bridge effect" and to the significant effect of the electric field.