Voltammetric and chemical behaviour of tetraazamacrocyclic complex Cu(TAAB)²⁺ adsorbed on the surface of the graphite electrode

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The redox properties of copper(II) complex with tetrabenzo[b,f,j,n]-[1,5,9,13]tetraazacyclohexadecine attached to the surface of the graphite electrode have been investigated. The adsorption of the complex is characterized by the Langmuir isotherm. The quasi-reversible character of redox process ($a = 0.42$, $k_s = 5\,\text{s}^{-1}$) was confirmed by the cyclic voltammetry. The catalysis of oxygen cathodic reduction as well as the inhibition of anodic oxidation of ascorbic acid were found. The influence of redox reactions with persulfate and ascorbic acid on the origin of catalytic currents was studied.

Изучались окислительно-восстановительные свойства комплекса меди(II) с тетрабензо[b,f,j,n][1,5,9,13]тетраазациклогексадеценом фиксированного на поверхности графитового электрода. Адсорбцию комплекса характеризует изотерма Ленгмюра. Циклическая вольтамперометрия подтвердила квазиобратимый характер окислительно--восстановительного процесса ($a = 0,42$, $k_s = 5$ с⁻¹). Обнаружен катализ катодного восстановления кислорода и ингибирование анодного окисления аскорбиновой кислоты на химически модифицированном электроде. Изучено влияние реакции комплекса с надсернокислым калия и аскорбиновой кислотой на образование каталитических токов.

Macrocyclic complexes are studied intensively as structural and functional analogues of several natural species. Besides the type of central atom the polydentate ligand is the decisive factor of their reactivity. Complex reactivity may be essentially changed through immobilization. The comparison of redox properties of attached complexes with their behaviour in the solution is the classic theme of study of chemically modified electrodes (CME).

The copper bond with tetrabenzo[b,f,j,n][1,5,9,13]tetraazacyclohexadecine ligand (TAAB) results in the characteristic redox (as well as catalytic) properties. With respect to other complexes with N_4 donor set the Cu(TAAB)²⁺ with 16-membered macrocycle and with high electron delocalization on the ligand is reduced easily to Cu(TAAB)⁺, the latter being reoxidized by superoxide in catalytic reactions [1]. The Cu(TAAB)²⁺ complex is the structural analogue of the active centre of superoxide dismutase [2].

Reagents that have extended π-bond systems are effectively chemisorbed on carbon electrodes. This paper deals with voltamme⸱ and chemical behaviour of the Cu(TAAB)$^{2+/+}$ complex attached on the surface of graphite electrode by the spontaneous adsorption. Characterization of the Cu(TAAB)$^{2+/+}$ redox pair in the immobilized state and its catalytic effects were the aim of the study.

Experimental

Cu(TAAB)(NO$_3$)$_2$ was synthesized as described previously [3]. The L-ascorbic acid was a commercial preparation (Spofa, Prague), all other reagents were of anal. grade (Lachema, Brno) and were used without further purification. The solutions were prepared in redistilled water and had the constant temperature 25 °C. Ionic strength of buffer solutions was kept at 0.1 mol dm^{-3} by the KNO$_3$ addition. Argon was employed as inert gas.

Voltammetric measurements were performed by the help of Polarographic Analyzer PA 2 (Laboratorní přístroje, Prague). The conventional electrochemical vessel was used. The indicating electrode was constructed from spectral graphite of cylindrical shape (Elektrokarbon, Topoľčany). The electrode was impregnated at the reduced pressure by paraffin at 100 °C. The cylindrical part was paraffined from time to time and the basal plane of this was freshly cleaned prior to each use by abrasive paper and polished on the filter paper. The exposed area of the electrode determined chronoamperometrically through the o-dianidizine oxidation made $A = 0.185$ cm^2. The electrode was modified by dipping to 1×10^{-3} M-Cu(TAAB)(NO$_3$)$_2$ solution for two minutes after which the electrode was rinsed with redistilled water and kept in 0.1 M-KNO$_3$ for 10 min. The potential was measured against the saturated calomel electrode (SCE). The large-surface platinum electrode served as an auxiliary one. The constant scan rate 0.1 V s^{-1} was used.

Results and discussion

The cyclic voltammetry

Fig. 1 shows the cyclic voltammetry of Cu(TAAB)$^{2+}$ adsorbed to basal plane of the graphite electrode. In the solution without Cu(TAAB)$^{2+}$ at first it comes to the desorption of the complex due to which the Cu(TAAB)$^{2+}$ peak current decreases during approximately 15 min to 25—20 % of the initial value, further on this is not changed substantially anymore. The voltammogram in Fig. 1 shows such a steady state.

It is difficult to evaluate the charge linked with the voltammetric peak since the correction to the background current is not negligible. The charge was estimated on the basis of the area between the peak line and that of background and represents the value 2.3×10^{-7} C. Under the assumption that all im-

mobilized particles are electroactive in voltammetric time scale the superficial concentration Γ of the adsorbed substance takes 1.3×10^{-11} mol cm^{-2}. The reproducibility of the Cu(TAAB)$^{2+}$ superficial concentration determined from five repetitions of preparation and from keeping the CME in the supporting electrolyte for 15 min is characterized by the relative standard deviation 15 %.
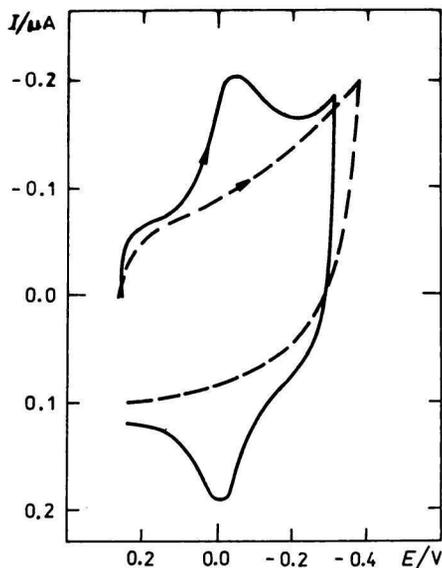

Fig. 1. Cyclic voltammogram of adsorbed Cu(TAAB)$^{2+}$ (——) and background current on a bare electrode at the same conditions (---); 0.1 M-KNO$_3$, pH = 6.0.

The dependences of superficial concentration Γ after keeping the CME in 0.1 M-KNO$_3$ on adsorption time and on Cu(TAAB)$^{2+}$ concentration in parent solution at 25.0 °C are shown in Fig. 2. Due to the limited solubility of the complex reaching the higher concentration of parent solution was impossible. To the greatest adsorption it comes during the first 2 min. Assuming that the Cu(TAAB)$^{2+}$ ions lie flat on the surface of the electrode and that one ion takes the area *ca.* 0.93 nm^2 ($r = 545$ pm [4]) the $\Gamma = 1.3 \times 10^{-11}$ mol cm^{-2} represents the electrode covering approximately 0.07 of the monolayer. It will thus not come to the interactions between the adsorbed molecules and the isotherm is the case of the Langmuir one.

The difference of potentials of cathodic and anodic peaks of the complex $\Delta E_p = 0.050$ V (Fig. 1) shows quasi-reversibility of the redox process like in the solution [4]. The change of polarization rate v within the range 0.050 up to 0.500 V s^{-1} caused the linear increase of Cu(TAAB)$^{2+}$ peak current (totally
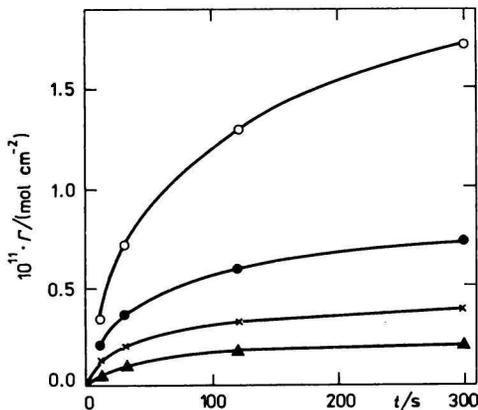
Fig. 2. Cu(TAAB)$^{2+}$ superficial concentration dependence on adsorption time and complex concentration in parent solution
(O 1×10^{-3} mol dm^{-3}; ● 1×10^{-4} mol dm^{-3}; x 1×10^{-5} mol dm^{-3}; ▲ 1×10^{-6} mol dm^{-3}).

9.7 times) in dependence vs. v (the correlation coefficient $r = 0.9955$) which is in good agreement with the diffusionless voltammetry theory [5]. The given relatively small change of v was, however, not sufficient for the change of ΔE_p value. Using the relationships and graphs for the case of quasi-reversible process going on the surface of the electrode [6] the value of charge transfer coefficient $a = 0.42$ as well as rate constant of electrochemical reaction $k_s = (5 \pm 4)$ s^{-1} was obtained. The same value a was offered also by calculation coming from the relationship for maximum peak current in the case of totally irreversible reaction [5].

Electrocatalytic behaviour

To the systems which are often used to evaluate the catalytic properties of metals or of their complexes attached to the electrode surface there belong the oxygen reduction and ascorbic acid oxidation, as well. These systems were used to characterize the CME also in our case.

It is known that the electrocatalytic effect as well as the voltammetric response of the substance itself depends on the quality of carbon electrode surface. There was published e.g. the potential shift of oxygen reduction by $+0.20$ V after preceding carbon anodization [7]. In our case, for modification we used the original graphite adjusted as described in Experimental and new electrode properties are the result of the adsorption of the complex.

The voltammogram of oxygen reduction on the freshly prepared CME recorded in the neutral 0.1 M-KNO$_3$ and in the phosphate buffer solution of pH 5.0 and 8.0. respectively, contained one cathodic peak already at $E_p = -0.60$ V and the next one, with approximately the same maximum current, at $E_p = -1.10$ V. The sum of both peak currents was somewhat higher than the peak current of oxygen reduction of bare graphite electrode ($E_p = -1.10$ V).

The next voltammograms registered by the given CME always after a short mixing of solution contained already only one peak taking broader potential range with the maximum at -0.9 V and with maximum current like on the bare electrode. The potential shift of oxygen peak was less marked in acidic solutions (in 1 M-HClO$_4$ from -0.90 to -0.75 V, in the Britton—Robinson buffer solution of pH = 4.5 from -1.10 to -1.05 V).

With respect to the change of chemical reactivity of the complex in neutral and weak alkaline medium (faster reduction and difficult reoxidation compared to weak acidic solution) [8] the catalytic effect of CME prepared by the adsorption of complex from the weak alkaline solution (pH = 8.0) was also verified. On this electrode the lasting shift of oxygen cathodic peak to $E_p = -0.70$ V (Fig. 3) was found.

The electroreduction of oxygen is in aqueous solutions a complex multielectron reaction [9]. The two-electron character of this reduction ($O_2 \rightarrow H_2O_2$) typical for carbon (as well as mercury and gold) electrode, was not changed as a whole by the pursued chemical modification. It is, however, separated into two steps according to reaction site of the electrode (graphite or mediator).

With respect to the considerably negative potential of oxygen reduction compared to that of Cu(TAAB)$^{2+}$ it can be said that the reduced form of the complex shows catalytic effect. From similar electrocatalytic studies it is known

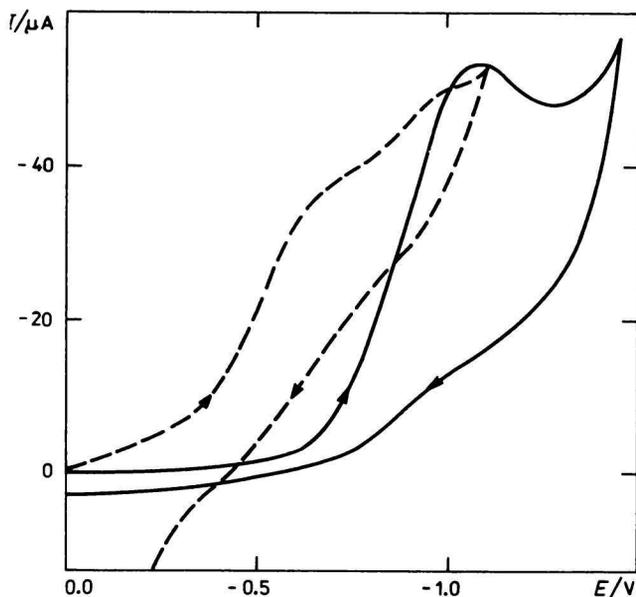Fig. 3. Cyclic voltammogram of oxygen reduction in 0.1 M-KNO$_3$, graphite electrode (——) and CME prepared through complex adsorption at pH = 8.0 (–––).

that if the reoxidation of macrocyclic complex by oxygen is rapid the potential of oxygen reduction is determined by that of the reduction of the complex. In the opposite case the potential of the reduction is determined by intermediate formed between the reduced complex and oxygen [10]. The $Cu(TAAB)^+$ is known not to react with oxygen in the solution but to act as Lewis acid against the superoxide radical $HO_2^{\cdot}$ and to reduce the latter to H_2O_2 in the weak acidic medium [1]. The reduced complex herewith does not react with the anionradical $^{\cdot}O_2^-$ ($pK_a(HO_2^{\cdot}) = 4.7$) under the conditions of the solution [8]. $Cu(TAAB)^+$ inertia to molecular oxygen does not change through its immobilization. Overall reduction of oxygen can be expressed by eqn (A)

$$Cu(TAAB)^+ + O_2 \rightarrow Cu(TAAB) \cdot O_2^+ \xrightarrow[2H^+]{2e^-} Cu(TAAB)^+ + H_2O_2 \quad (A)$$
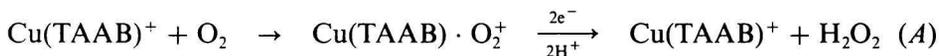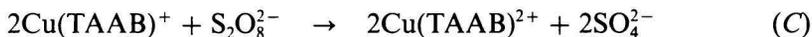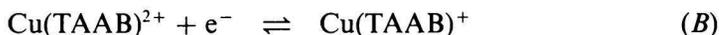
The loss of catalytic activity of the complex after the first voltammogram is obviously linked with the lasting change of the mediator caused *e.g.* by the changed coordinating environment of copper atom. This can be a matter of coordination of the oxygen attached to graphite. In contrast to the report [11] in our case the superoxide radical does not disturb the adsorption layer of the complex. The complex adsorbed from the weak alkaline medium is chemically changed already [8] and the catalytic activity of this is not lost in this way.

The electrocatalytic activity of complexes against oxygen reduction is also linked with the nature of the central atom. The copper complexes use to be worse catalysts because their d_{z^2} orbital necessary for the activation of the oxygen molecule is occupied [11]. In phthalocyanines the order of activity is $a(Fe) > a(Co) > a(Ni) > a(Cu)$ [12], in porphyrines and tetraazaanulenes, respectively, this is $a(Co) > a(Fe) > a(Ni) \approx a(Cu)$ [13]. The increase in dimensions of delocalized system of π-bonds of the ligand increases the electrocatalytic effect [13, 14]. In this way also the observed effect of $Cu(TAAB)^+$ is explained.

The next catalysis connected with the $Cu(TAAB)^{2+}$ reaction is the reduction of persulfate. The cathodic peak current of the adsorbed complex is in the 1×10^{-3} M-$S_2O_8^{2-}$ several times higher than in absence of this oxidizing agent. The same phenomenon was observed in the case of the dissolved $Cu(TAAB)^{2+}$ when the platinum indicating electrode was used. Herewith the $S_2O_8^{2-}$ itself was reduced on the graphite electrode up to $E = -1.4$ V and on the platinum one at $E = -0.6$ V *vs.* SCE.

The mechanism of the observed catalysis can be expressed by the equations

$$Cu(TAAB)^{2+} + e^- \rightleftharpoons Cu(TAAB)^+ \qquad (B)$$

$$2Cu(TAAB)^+ + S_2O_8^{2-} \rightarrow 2Cu(TAAB)^{2+} + 2SO_4^{2-} \qquad (C)$$

The decrease in catalytic current during the repetition of the voltammogram with CME indicates the gradual disturbing of the adsorption layer through the

effect of $S_2O_8^{2-}$. In the solution the decrease in Cu(TAAB)$^{2+}$ cathodic current was not observed, thus the complex itself is not disturbed by $S_2O_8^{2-}$ at laboratory temperature.

Fig. 4 shows the voltammograms of ascorbic acid oxidation on the bare graphite electrode and on CME. In both cases the oxidation is extremely irreversible, obviously due to the use of unactivated graphite electrode. It is namely known that polishing, esterification or thermal working of carbon electrodes, respectively, lead to the shift of the potential of anodic peak of ascorbic acid by -0.15 up to -0.20 V and to its narrowing (to the decrease in $E_p - E_{p/2}$ difference) since the superficial activation of the electrode removes impediments of electron transfer (thus this is not catalysis) [15—17].

The chemical modification of the electrode through the complex Cu-(TAAB)$^{2+}$ had negative effect on the electrochemical oxidation of ascorbic acid. Its peak potential shift towards more positive values of the potential represents in 0.1 M-KNO$_3$ of pH = 5 the value $\Delta E_p = 0.35$ V, in the Britton—Robinson buffer solutions of pH = 3.5—6.0 $\Delta E_p = 0.20$ V and in 1M-HClO$_4$ $\Delta E_p = 0.07$ V (where $E_p - E_{p/2} = 0.10$ V). Peak current is on the CME lower by 5—10 % in comparison with that on the bare electrode.

From the literature, on the contrary, strong catalytic influence of several adsorbed metals is known. Thus *e.g.* bismuth and lead caught on the platinum electrode shift the E_p of ascorbic acid by -0.4 V [18]. However, the copper effect is small (slight increase in peak current of ascorbic acid at the practically unchanged E_p) [18] although the copper ions represent the most effective catalyst of the autooxidation of ascorbic acid in the solution. The Cu(TAAB)$^{2+}$ is thus equally bad or still worse mediator of the electrochemical oxidation of ascorbic acid than Cu. The oxidation of ascorbic acid or that of its anion, respectively,
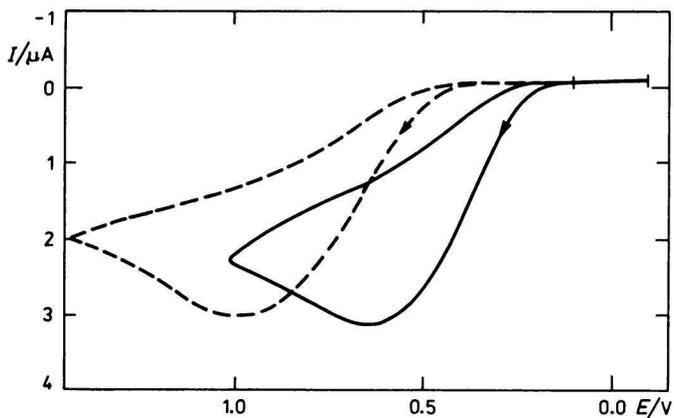

Fig. 4. Cyclic voltammogram of ascorbic acid oxidation in 0.1 M-KNO$_3$, pH = 5.0, graphite electrode (———) and CME (– – –).

is linked with the proton transfer. The proton acceptor attached to the surface of the electrode could thus be more effective catalyst of ascorbic acid oxidation [9].

The analysis of voltammogram of the adsorbed complex in the ascorbic acid solution ($c = 1 \times 10^{-4}$ up to 1×10^{-3} mol dm^{-3}, the Britton—Robinson buffer solution of pH 6.0 up to 8.0) has shown that chemical reduction of the complex occurs

$$Cu(TAAB)^{2+} + HA^- \rightarrow Cu(TAAB)^+ + {}^\cdot A^- + H^+ \qquad (D)$$

This reduction is much faster in neutral as well as in weak basic media than in acidic solution. Reaction rate of the chemical reduction, however, is not sufficient for the origin of $Cu(TAAB)^+$ catalytic anodic current and by this way for catalysis of ascorbic acid oxidation.

Conclusion

Preparation of CME with sub-monolayer quantity of the attached reactant secures that no interactions of the complex molecules occur and at the same time it gives possibility for some contact (and activation) of reactants with bare electrode surface. Study of the adsorbed $Cu(TAAB)^{2+}$ has shown the correspondence between electrochemistry of immobilized and dissolved complex.

Surface-immobilized macrocyclic complex acts as an electron transfer mediator in molecular oxygen reduction. Electron transport properties of the complex can be connected with the specific ligand structure as well as with changes of copper oxidation state.

Immobilization of the complex does not increase substantially its chemical redox reactivity. In the case of coupling of $Cu(TAAB)^{2+}$ redox change with fast chemical reaction (reoxidation by $S_2O_8^{2-}$) the electrocatalysis takes place. Application of CME based on heterogeneous catalysis of the oxidase-type reaction [1] which proceeds in the reaction layer at the electrode and on the reactant concentration electrochemical monitoring (as it is in the case of enzyme electrodes) would need evidently higher superficial concentration of the copper complex.

References

1. Labuda, J., Mocák, J., Hlavačková, E., and Yatsimirskii, K. B., *Chem. Papers 38*, 739 (1984).
2. Tainer, J. A., Getroff, E. D., Beem, K. M., Richardson, J. S., and Richardson, D. C., *J. Mol. Biol. 160*, 181 (1982).
3. Melson, G. A. and Busch, D. H., *J. Am. Chem. Soc. 86*, 4834 (1964).
4. Labuda, J. and Šima, J., *Inorg. Chim. Acta 112*, 59 (1986).

5. Hubbard, A. T. and Anson, F. C., in *Electroanalytical Chemistry*. Vol. *4*. (Bard, A. J., Editor.) P. 129. M. Dekker, New York, 1970.
6. Laviron, E., *J. Electroanal. Chem. 101*, 19 (1979).
7. Nagaoka, T. and Yoshino, T., *Anal. Chem. 58*, 1037 (1986).
8. Labuda, J. and Plaskoň, V., *Inorg. Chim. Acta 146*, 13 (1988).
9. Zurilla, R. W., Sen, R. K., and Jeager, E., *J. Electroanal. Soc. 125*, 1103 (1978).
10. Chan, R. J. H., Su, Y. O., and Kuwana, T., *Inorg. Chem. 24*, 3777 (1985).
11. Zagal, J., Sen, R. K., and Jeager, E., *J. Electroanal. Chem. 83*, 207 (1977).
12. Savy, M., Andro, P., Bernard, C., and Magner, G., *Electrochim. Acta 18*, 191 (1973).
13. Alt, H., Binder, H., and Sandstede, G., *J. Catal. 28*, 8 (1973).
14. Tarasevich, M. P. and Radyushkina, K. A., *Usp. Khim. 49*, 1498 (1980).
15. Koman, G. N., Willis, W. S., and Rusling, V. F., *Anal. Chem. 57*, 545 (1985).
16. Fagan, D. T., Hu, I., and Kuwana, T., *Anal. Chem. 57*, 2759 (1985).
17. Deakin, M. R., Koval, P. M., Stutss, K. J., and Wightman, R. M., *Anal. Chem. 58*, 1474 (1986).
18. Takamura, K. and Sakamoto, M., *Chem. Pharm. Bull. 27*, 254 (1979).

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