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Mechanism of Copper and *tert*-Butyl Alcohol Adsorption on Carbon Materials at Various Open-Circuit Potentials

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The problem of creating new carbon-based hemisorbents is an important one at the present time [1]. When analyzing factors that influence the interaction of carbon-based sorbents with biological media, most authors, such as [1], focus on the reactivity and composition of the functional groups on the surface, as well as defects in the carbon structure (sharp edges, dislocations, and surface heterogeneity). However, as shown in [2], the interaction of activated carbons with blood cells in the sorbent/blood system is due to the electrochemical properties of both the carbon and the blood cells. The adsorption of proteins on various materials also depends on the electrode potential [3].

The use of carbon-based hemisorbents requires them to be indifferent towards blood. Thus, it is important to minimize any Faradaic processes in the course of hemisorption, as they cause trauma to blood cells. According to the electrochemical model of hemisorption [2], it was suggested in the present work that the occurrence of Faradaic processes in the sorbent/blood system depends on the open-circuit potential (OCP) of activated carbon. The goal of the present work was to verify this hypothesis. The concept of the effective number of electrons in the process of adsorption developed by Grafov [4] was used as the key criterion to help elucidate the mechanism of adsorption of Cu^{2+} ions and *tert*-butyl alcohol (TB), carried out on the AG-3 brand activated carbon.

In considering electrochemical reactions at the electrode, it should be noted that the formation of the electrode/electrolyte interface (or, in the case of hemisorption, the sorbent/blood interface) may not necessarily be caused by external electrode polarization; on the contrary, the charge of the electrical double layer can change due to electron transport from the electrode onto adsorbed particles [4] (e.g., toxicant molecules or blood cells in the case of hemisorption). The effective numbers of electrons can be calculated according to [4] by using the formula:

$$n = -C(\Delta E/\Gamma F)_q$$

1. M.V. Bel'kov, I.V. Skorniyakov, G.B. Tolstorozhev, A.V. Tuchkovskaya and V.A. Shablovski. *Journal of Applied Spectroscopy*, **76** (5) 656-659, 2009
2. Mark M. Goldin, A.G. Volkov, Yu.S. Goldfarb, Mikhail M. Goldin. *Journal of Electrochem. Soc.*, **153** (8), J91-J99, 2006
3. Xie Q, Xiang C, Yuan Y, Zhang Y, Nie L, Yao S. *Journal of Colloid and Interface Sci.* **262** (1) 107-115, 2003
4. B.M. Grafov, Ye.A. Ukshe. *Alternating-Current Electrochemical Circuits* Moscow: Nauka, 1973, p.128

where n is the effective number of electrons, C (F) is the electrode differential capacity, ΔE (V) is the change in OCP of the electrode, Γ (mol) is adsorption, and $F = 96500$ C/mol is the Faraday constant.

TB concentration in solution was measured by gas chromatography on an SRI Instruments 310C gas chromatograph, while the Cu^{2+} ion concentration was measured on a Genesys 10uv scanning spectrophotometer at $\lambda_{\text{max}} = 808$ nm.

Changes in the OCP of AG-3 activated carbon in the course of adsorption of TB and Cu^{2+} were measured for 130 min. Carbon samples were pre-polarized to constant potentials in the range of -775 to $+475$ mV by cathodic or anodic treatment according to [2].

Calculations of the effective number of electrons, based on the data shown in Fig.1, showed a near absence of Faradaic processes in the course of TB adsorption on AG-3 carbon (as the calculated n values lie between 0.026 - 0.068); however, carbon potential shifts do take place, indicating an electrochemical mechanism.

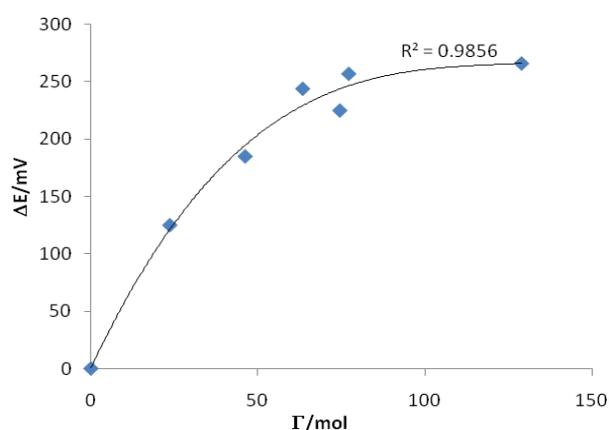


Fig. 1. Shifts of OCP of AG-3 carbon depending on TB adsorption

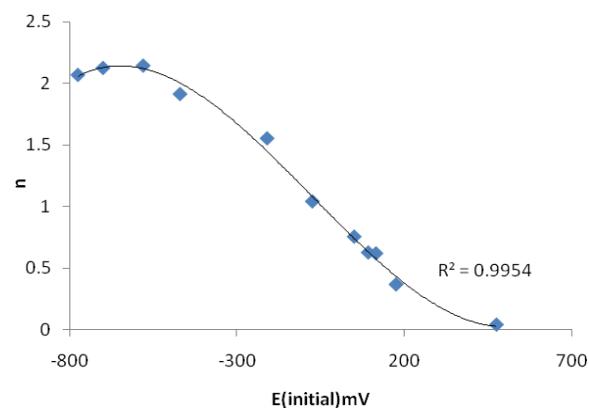


Fig. 2. The effective number of electrons depending on OCP in the course of Cu^{2+} adsorption on AG-3 carbon

It was also observed (Fig. 2) that in the potential range between -775 and $+475$ mV, the following processes took place: Faradaic reactions $\text{Cu}^{2+} + 2e \rightarrow \text{Cu}^0$ (below -200 mV) and $\text{Cu}^{2+} + 1e \rightarrow \text{Cu}^{+1}$ (-200 to -100 mV), as well as a mixed process (copper adsorption as both Cu^{+} and Cu^{2+}) between -100 and $+475$ mV, with the Faradaic processes diminishing and primarily the Cu^{2+} ion being adsorbed as higher positive potentials were reached.

Thus, it was shown that adsorption on activated carbon has an electrochemical mechanism. The presence or absence of Faradaic processes depends on the carbon OCP value and the potential of oxidation or reduction of the adsorbate on the carbon.