**Introduction**

Interaction of physical fields of different origin can cause sufficient increase in rate of electrode processes, influence physical-chemical properties of solution [1–7]. It is suggested, in particular, that under the action of electromagnetic fields the processes of water and aqueous solution structure transformation take place [5–7]. However, possible changes in phase boundary construction when applying external electromagnetic field have not been investigated yet, while changes in component state exposed to radiation in solution is to affect their state in the surface layer and result in transformation of structure of double electric layer (DEL) and adsorptivity of surface-active organic substances (SAS) at their presence in solution. Investigations in this field allow us to extend the concepts on influence of external actions on electrochemical system.

Our study have permitted us to state that at interaction of low-intensive (power is less than 1 W) high-frequency electromagnetic field (in the frequency range from 30 to 200 MHz) partial desorption of surface-active cations (ammonia tetrabutyl and pyridinium cetyl) [8, 9] and anions (sulphate lauryl) [10] from the surface of mercury-film electrode is observed, it revealing itself in partial and complete regeneration of analytical signal in the method of inversion voltamperometry (IVA).

The purpose of the given work is to study desorption of butyl alcohol from the surface of indicator electrode by means of its activation with HF field and removing inhibitory effect of SAS on the rate of electrode reaction.

The choice of butanol as a SAS is conditioned by the fact that its adsorption on mercury surface has been well examined: concentrations at which there is a sufficient change of DEL parameters were determined, area of adsorption potentials of the given organic substance was found, influence of different factors (origin and concentrations of base electrolyte, temperature etc) on capacitive characteristics of DEL was stated [11–15].

Investigation of adsorption-desorptive processes was carried out by the IVA method. The value of butanol adsorption was judged by decrease in current of anode peak Zn(II), Cd(II) and Pb(II), conventionally determined voltamperometrically. The choice of the method was conditioned by the fact that the presence of SAS in the object analysed decreases sufficiently sensitivity of analytical determination and affects its accuracy [16, 17], therefore, search for the ways of removing SAS influence on metrological properties is an actual task. Thus, the performed research can find practical application.

**Experimental part**

Investigation has been carried out with the help of polarograph PU-1. Mercury-film electrode (RFE) was used as an indicator electrode. The comparison electrode was silver chloride. Standard solutions Cd(II), Pb(II) and Zn (II) (C=10^{-4} \text{ mol/l}) were prepared by the method of subsequent dilution from GSО. As base electrolytes 0,1 М of KF , K_{2}SO_{4}, KClO_{4}, KCl, KBr and KI solutions, anions of which are distinguished by surface activity were used. Butanol was purified by the standard technique. Alcohol purity was controlled by the boiling temperature and refraction index. Butanol solution of 0,4 mol/l concentration was prepared using deionised water.

Application of HF field was made by means of high-frequency generator G3-19А in the noncontact way. The cell for HF analysis was a Teflon glass of 20 ml volume, fig. 1. One of HF electrodes was placed in the central part of the cell and represented a brass rod located in Teflon tube. The second HF electrode was copper foil, intimately mating of external cell part. HF electrode lead was made through the cell bottom. HF electrodes were connected with HF cable of 10 sm long, ending with joint which was connected with generator. Indicator and auxiliary electrodes were placed in the gap between HF electrodes.

**Fig. 1.** Flow-chart of installation: 1) indicator electrode; 2) comparison electrode (c.s.e.); 3) external HF electrode; 4) internal HF electrode
The cell was placed in platform and provided with Teflon cover to isolate from the environment. In the cover holes for electrodes and gaseous nitrogen tube were made.

Technique of voltamperometric measurements consisted in the following. Potential difference was applied to the electrodes, and during 60 sec electrical reduction of the investigated elements was performed while mixed the solution with gaseous nitrogen, preliminary being treated. 5 sec before electrolysis end the feed of nitrogen was stopped for the solution quieting. The curve of anode dissolution was registered at linearly changed potential with the rate $W=60$ mV/s in the potential range from $-1.4$ V to 0.1 V. After obtaining regenerated voltamperograms butanol admixture was introduced into the solution involved and voltamperogram, on which there was a decrease in signal of the mentioned elements, was registered. After stating stationary value of signals the next addition of alcohol was made. The data on anode peak current dependence of Cd(II), Pb(II) and Zn(II) on butanol concentration were presented in relative coordinates $I_0-I_{rel}=\Delta I/I_0=(I_0-I_{rel})/I_0$ ($I_0$ is the current peak without SAS, $I_{rel}$ is the current peak with SAS addition). According to the determination $0<\Delta I/I_0<1$, $\Delta I/I_0=0$ in the absence of SAS, but at $\Delta I/I_0=1$ a complete signal suppression was observed.

Study of HF field influence was carried out at butanol concentration corresponding to the limiting degree of filling electrode surface when registered currents had the minimal value.

**Results and discussion**

First of all, polarization curves of mercury-film electrode in base solutions containing butanol addition were obtained. It was shown that the degree of change in curve position depends on initial potential and grows as alcohol concentration increases. The maximum difference in curve position was observed at $C_{SAS}=44$ mmol/l and the value of initial potential equal to $-1.4$ V (fig. 2).

Decrease of base current in the range of potentials $(-1.4)\ldots(-1.0)$ B is conditioned mainly by inhibiting the reduction process of hydrogen ions with electrode. In the area of less negative potentials, where current is determined mostly by DEL charging current, displacement of polarization curve is explained by butanol adsorption in the surface of indicator electrode leading to, according to [14], decrease of differential electrode capacity. Thus, one can point out that adsorption of butanol is well expressed in the potential area corresponding to peak potentials of the elements involved. All further investigation were performed at electrolysis potential $-1.4$ V, i.e. under the conditions when current of hydrogen reduction is minimal, but in fact, all quantity of electricity is spent for reduction of high-density metal ions.

Then the dependence curves of current suppression degree of anode peaks of Cd(II), Pb(II) and Zn(II) on butanol concentration were obtained. The performed investigation showed that suppression degree depends on origin of electrically active particle and anion of base electrolyte, which is explained by the change in form of ion presence in the solution when using complex-forming bases as well as by the attraction action of SAS molecules and base ions in DEL. The curves produced are described by the equation

$$I_{rel}=I_0+a e^{-\frac{b}{c}}$$

where $I_0$ is the peak current in the absence of SAS, $a$, $b$, $c$ are the constants depending on element origin and base anion.

In table 1 the data on maximum degree of blocking-out of the determined elements by butyl alcohol $\Delta I/I_0$ observed at $C_{SAS}=44$ mmol/l, using different base electrolytes are presented.

<table>
<thead>
<tr>
<th>Base (C=0.1M)</th>
<th>Pb</th>
<th>Cd</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>KClO$_4$</td>
<td>0.39±0.02</td>
<td>0.35±0.02</td>
<td>0.73±0.06</td>
</tr>
<tr>
<td>KCl</td>
<td>0.65±0.05</td>
<td>0.26±0.02</td>
<td>0.50±0.03</td>
</tr>
<tr>
<td>KF</td>
<td>0.70±0.06</td>
<td>0.49±0.04</td>
<td>0.55±0.02</td>
</tr>
<tr>
<td>KCl</td>
<td>0.46±0.03</td>
<td>0.42±0.04</td>
<td>0.73±0.05</td>
</tr>
<tr>
<td>KBr</td>
<td>0.74±0.07</td>
<td>0.16±0.01</td>
<td>0.64±0.06</td>
</tr>
<tr>
<td>KI</td>
<td>0.67±0.06</td>
<td>0.36±0.02</td>
<td>0.85±0.07</td>
</tr>
</tbody>
</table>

When studying the influence of ion origin of base electrolyte on value of butanol adsorption on the surface of mercury dripping electrode (MDE) definite regul-
larities consisting in growth of the number of adsorbed butanol as surface activity of base anion were revealed [12, 13], which is an effect of decreasing repelling interaction between the positive ends of butanol dipoles. If similar regularities were maintained at MDE, the degree of signal blocking-out of the elements involved in transition from KF to KI would be expected to increase. Nevertheless, even for electrode processes with zinc ions not forming stable complexes with anions used in base electrolytes the revealed regularity are not realized. Obviously, differences in literature data and our experiment are explained by different structure of electrode processes in traditional polarography and IVA method. Besides, the role of indicator electrode origin is apparent. Without dwelling in details on the analysis of dependence of electrode process rate with butanol on the origin of base anion it should be noted that in all investigated solutions a strong blocking-out of analytical signals of the elements involved is observed, which indicates high adsorptivity of butanol on the surface of MDE and significant decrease in its active surface.

As showed the previous investigations [1–3] under the influence of HF field growth of analytical signals without SAS takes place due to acceleration in delivery of electrical active particles to the electrode surface, the influence of HF field on value of lead, cadmium and zinc signals without SAS has been studied. It is shown that HF action results in increase of maximum currents of volt-ampere curves of the elements involved, moreover, the degree of their increase depends essentially on frequency of the applied field, origin of electrically active particle and base electrolyte. In table 2 the values of maximum current increase of anode peak of the elements involved at mentioned frequencies of HF field corresponding to maximum efficiency of affect are presented. The values of I/I₀ (I₀ is the current of anode peak at frequency of applied field f, I is the current of anode peak without field) varies in the range from 1,1 to 3,3.

**Table 2.** Maximum degree of signal increasing of lead, cadmium and zinc at exposure of solution to HF field, not containing SAS: Е₀=–1,4 V, tₑ=60 s, W=60 mV/s, С₀=2,5·10⁻⁷ M, С₀=2,5·10⁻⁷ M, С₀=5·10⁻⁷ M, С₀=0,1 M

<table>
<thead>
<tr>
<th>Base</th>
<th>Pb</th>
<th>Cd</th>
<th>Zn</th>
<th>Pb₁⁺</th>
<th>Cd²⁺</th>
<th>Zn²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>KClO₄</td>
<td>1,5±0,2</td>
<td>50</td>
<td>17±0,2</td>
<td>200</td>
<td>1,5±0,2</td>
<td>120</td>
</tr>
<tr>
<td>KCl</td>
<td>1,5±0,2</td>
<td>90</td>
<td>33,3±0,4</td>
<td>90</td>
<td>1,2±0,1</td>
<td>120</td>
</tr>
<tr>
<td>KF</td>
<td>1,1±0,1</td>
<td>40</td>
<td>1,6±0,2</td>
<td>200</td>
<td>1,4±0,3</td>
<td>40</td>
</tr>
<tr>
<td>KCl</td>
<td>2,1±0,3</td>
<td>130</td>
<td>2,3±0,5</td>
<td>160</td>
<td>2,2±0,2</td>
<td>160</td>
</tr>
<tr>
<td>KBr</td>
<td>1,5±0,2</td>
<td>90</td>
<td>1,8±0,2</td>
<td>160</td>
<td>2,1±0,2</td>
<td>200</td>
</tr>
<tr>
<td>KI</td>
<td>1,3±0,2</td>
<td>180</td>
<td>1,3±0,1</td>
<td>110</td>
<td>1,2±0,2</td>
<td>180</td>
</tr>
</tbody>
</table>

When introducing butyl alcohol into the investigated solution the character of frequency dependence of anode peak current changes sufficiently. The investigations performed showed that under the influence of electrochemical cell of high-frequency field the growth of signals suppressed by butanol takes place. Peak current of the element is either regenerated to its initial value, or more often it exceeds the value of peak current observed before introduction of SAS into the solution. The experiments have been carried out at butanol concentration corresponding to limit degree of signal suppression of the elements involved. Degree of signal regeneration depends on origin of element and base (Table 3).

**Table 3.** Maximum degree of signal regeneration of Pb, Cd, Zn with butanol using different base electrolytes: С₀=0,1 М, Е₀=–1,4 V, W=60 mV/s, tₑ=60 s, С₀=2,5·10⁻⁷ M, С₀=2,5·10⁻⁷ M, С₀=5·10⁻⁷ M, С₀=44 mmol/l

<table>
<thead>
<tr>
<th>Base</th>
<th>Pb</th>
<th>Cd</th>
<th>Zn</th>
<th>Pb₁⁺</th>
<th>Cd²⁺</th>
<th>Zn²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>KClO₄</td>
<td>1,5±0,2</td>
<td>50</td>
<td>2,1±0,2</td>
<td>200</td>
<td>2,5±0,2</td>
<td>30</td>
</tr>
<tr>
<td>KClO₄</td>
<td>1,5±0,1</td>
<td>130</td>
<td>1,5±0,1</td>
<td>40</td>
<td>1,1±0,1</td>
<td>30</td>
</tr>
<tr>
<td>KF</td>
<td>1,1±0,1</td>
<td>190</td>
<td>1,8±0,2</td>
<td>200</td>
<td>2,1±0,2</td>
<td>70,110</td>
</tr>
<tr>
<td>KCl</td>
<td>1,0±0,1</td>
<td>50,60</td>
<td>1,5±0,2</td>
<td>40</td>
<td>1,7±0,2</td>
<td>30</td>
</tr>
<tr>
<td>KBr</td>
<td>1,4±0,2</td>
<td>150</td>
<td>1,1±0,1</td>
<td>100</td>
<td>1,9±0,1</td>
<td>40,50</td>
</tr>
<tr>
<td>KI</td>
<td>1,6±0,2</td>
<td>200</td>
<td>1,3±0,0</td>
<td>70</td>
<td>1,3±0,1</td>
<td>70</td>
</tr>
</tbody>
</table>

In fig. 3 dependence of relative increase in peak current of lead, cadmium and zinc on frequency of HF field in presence of butanol: base 0,1 М KI (a); 0,1 М KClO₄ (b). Е₀=–1,4 В, tₑ=60 s, W=60 mV/s, С₀=44 mmol/l, С₀=2,5·10⁻⁷ M, С₀=5·10⁻⁷ M, С₀=5·10⁻⁷ M, С₀=5·10⁻⁷ M, С₀=5·10⁻⁷ M, С₀=5·10⁻⁷ M

In fig. 3 dependence of relative increase in peak current of lead, cadmium and zinc on frequency of HF field applied against the background of 0,1 М of KI (a) and 0,1 М KClO₄ (b) solutions is shown. Initial points
on the curves correspond to the degree of signal suppression by butanol. When increasing the value of $I/I_0$ to 1 one could speak of removing inhibition of electrode process due to butanol desorption from the surface of indicator electrode under the action on the electrode-electrolyte system of electromagnetic field. However, the values of $I/I_0>1$ indicate the fact that increase in signal is conditioned by both processes in the solution and processes connected with changes of DEL structure.

To answer the question uniquely whether increase in signals of the elements involved is connected with butanol adsorption from the surface of indicator electrode, the method of experiment was changed. The solution without butanol was exposed to HF field of definite frequency until stationary value of anode peak current of the element involved increasing its initial value to this or that degree was established. Only then butanol was added to solution under study. The influence of field did not cease. As a result, the dependence curves of peak current on butanol concentration at the given frequency until stationary value of anode peak current of lead without butanol was exposed to HF field of definite frequency were obtained and they were compared to similar dependences obtained without field.

![Graph](image)

**Fig. 4.** Dependence of relative value of peak current of Pb on butanol concentration at its introduction of into irradiated solution; base 0,1 M KF (a); 0,1 M KCl (b). $E_0=–1,4$ V, $t_0=60$ s, $W=60$ mV/s, $C_{PE}=2,5\cdot10^{-3}$ M

Against the background of 0,1 M of KF butanol was added at 60 and 180 MHz. Dependence of relative value of lead peak current on butanol concentration is presented in fig. 4, a. It was shown that at addition of SAS into irradiated solution the signals decrease to some extent, but their suppression degree is significantly lower than that without field, that indicates the creation of conditions preventing from SAS adsorption on the electrode surface. It develops to more extent at 180 MHz frequency. At alcohol concentration of 20 mmol/l the lead signal decreased just by 8 %, while without field at the same alcohol concentration the signal was suppressed by more than 60 %. At 60 MHz frequency the lead signal did not practically change its value to butanol concentration of 10 mmol/l. Increasing concentration to 20 mmol/l signal decreases by 20 %. Similar investigation was performed for lead against the background of 0,1 M of KCl at $f=140$ MHz (fig. 4, b). In this case when adding butanol lead peak current not only increased, but also exceeded the initial signal nearly 1,2 times. Obviously, in the given case the continuing action of HF field led to more essential reconstruction of DEL connected with not only SAS desorption, but also with change in the number of base electrolyte ions. Thus, the given experiment permits us to state that electromagnetic field influencing the electrode-solution boundary change adsorption characteristics of butanol.

It should be noted that stating stationary value of signal at HF influence on system (with or without SAS) took place gradually during 4...5 min. After switching off generator a gradual decrease to initial value occurred, i.e. resorption processes of butanol molecules on the electrode surface were observed. Time of relaxation was 10...15 min. Thus, in all the cases system relaxation processes proceeded slower than those of stationary state corresponding to maximum efficiency of HF influence.

To determine the degree of filling electrode surface with butanol molecules the values of differential electrode capacity at different SAS concentration in the solution in potential area of volt-ampere curve registration were defined. For this purpose the method of alternating current voltamperometry giving great possibilities for research of double electric layer and investigation dealing with adsorption of different substances on electrode surface was used [18, 19]. Such possibilities exist since due to high voltage frequency large currents conditioned by charging and charge of double electric layer flow through the circuit (DEL):

$$I_z = C_d \frac{dE}{dt},$$

where $I_z$ is the charging current, $C_d$ is the differential capacity of DEL.

Since the magnitude $\frac{dE}{dt}$ is constant at potential linear sweep, the current registered without Faraday’s process is proportional to differential capacity of double layer. Having determined electrode capacity at different potentials we calculated the degree of its surface filling with adsorbent molecules $\Theta$ according to the well-known method [13], as well as found the degree of filling of potential of indicator electrode. In table 4 the dependence of filling degree of mercury-film electrode with butanol molecules in 0,1 M KF solution is presented in absence of and under the influence of HF.
field 200 MHz frequency. The results obtained indicate essential decrease in filling degree of electrode potential in the range involved. Similar picture was observed on the bases of all the rest studied electrolytes under the HF field influence of different frequency. However, in the presence of surface-active base anions (Br– and I–) HF action efficiency was significantly lower — the value of $\Theta_a - \Theta_d$ did not exceed 0.2...0.3.

On the basis of $\Theta$ values constant isotherm equations of the Frumkin’s adsorption including interaction of SAS molecules and ions in DEL with solution components were calculated. It is often used for description of adsorption processes with electrodes.

$$Bc = \frac{\theta}{1 - \theta} \exp(-2a\theta),$$

where $B$ is the adsorption equilibrium constant, $a$ is the attraction constant [13].

### Table 5.

Values of attraction constant and adsorption equilibrium constant of the Frumkin’s isotherm without HF field and at $f=50$ MHz ($C_{SAS}=44$ mmol/l, $E=(0,4)...(0,8)$ V, t=20° C)

<table>
<thead>
<tr>
<th>Base</th>
<th>$f=0$ MHz</th>
<th>$f=50$ MHz</th>
<th>$f=0$ MHz</th>
<th>$f=50$ MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>KClO$_4$</td>
<td>0.14</td>
<td>0.43</td>
<td>4.54</td>
<td>2.13</td>
</tr>
<tr>
<td>KF</td>
<td>0.15</td>
<td>0.45</td>
<td>4.47</td>
<td>2.06</td>
</tr>
<tr>
<td>KCl</td>
<td>0.20</td>
<td>0.42</td>
<td>5.12</td>
<td>2.21</td>
</tr>
<tr>
<td>KBr</td>
<td>0.52</td>
<td>0.28</td>
<td>77.2</td>
<td>27.2</td>
</tr>
<tr>
<td>KI</td>
<td>0.57</td>
<td>0.31</td>
<td>73.3</td>
<td>33.8</td>
</tr>
</tbody>
</table>

The results of experiment are presented in table 5. The highest positive values of attraction constant without field indicate the presence of attraction forces among butanol molecules in DEL when using surface-inactive base electrolytes. In transfer to the bases containing surface active anions (Br– and I–), attraction interaction increases because of the specific anion adsorption, weakening repulsive force between positive ends of butanol dipoles. Under the action of HF field the attraction constant changes its sign in the presence of surface-inactive bases, which can be due to increase in cation concentration of DEL base resulting in growth of electrostatic repulsion between adsorbed cations and positive ends of SAS molecule dipoles. In the presence of surface-active base anions there is no change in the sign of attraction constant, however, its value decreases. Under the influence of electromagnetic field the constant of adsorption equilibrium $B$ decreases, that indicates adsorption shift of equilibrium towards desorption process.

Being based on the literature data [4, 5, 7, 20–22] and our own studies [2, 3, 8–10], one can assume on the qualitative level about nature of processes occurring under the influence of electromagnetic field on electrode-electrolyte system.

Aqueous solution absorbs field energy that leads to gradual change in structure of solutions. The water part bonded in clusters increases owing to appearance of new hydrogen bonds and strengthening those existed before. Intensification of cohesive interaction in water clusters weakens ion-dipole interaction that results in raising ion mobility and growing the rate of their delivery to the electrode surface (increase in conductivity of aqueous electrolyte solutions has been stated by us experimentally). Besides, the process of electro-active ion reduction accelerates, since activation barrier for a particle without hydration sheath is significantly lower.

Based on the hypothesis suggested, the hydration degree in polar group of butanol difilline molecule also has to decrease, which leads to growth in alcohol surface activity. However, since solution adsorption takes place as a competitive adsorption, one can suppose that as a result of HF influence, equilibrium at the electrode-solution boundary is displaced towards base ion adsorption, partially devoid of hydration sheath and water molecules. Increase in base cation adsorption and squeezing diffusive part of DEL enables to increase volume charge density that prevents from SAS dipole orientation in the direction of electrode by its positive end. It appears as weak dependence of peak current of the investigated elements on butanol concentration after its introduction into irradiated solution (fig. 4).

In case when SAS is introduced into radiation-free solution, and then HF field is applied, it is likely to enable particles of adsorbed substance to be squeezed from DEL owing to increase in attraction interaction of water molecules on the electrode surface and rise of base cation concentration in the dense part of DEL, that contributes to strengthening in repulsion interaction between the base ions and SAS dipoles.

The evidence for adsorption-desorption equilibrium displacement at HF action is the stated decrease in filling degree of electrode surface (table 4) and reduction of adsorption equilibrium constant (table 5). Dependence of signal regeneration degree of defined element and position of base line on time of HF influence indicates the gradual change of solution structure and DEL construction connected with it due to HF energy accumulation by the system, but relaxation of the listed parameter to the initial value shows gradual conversion of field energy into heat energy after stopping the influence on the system.
REFERENCES


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