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SPECIFIC ADSORPTION OF CARBONATE IONS AT THE ZINC OXIDE/ELECTROLYTE SOLUTION INTERFACE

A study of adsorption of carbonate ions at the interface of ZnO/aqueous solution of $NaClO_4$ is presented. The concentration range of carbonate ions was $1 \cdot 10^{-6}$ to $1 \cdot 10^{-3}$ M. The shape of adsorption of carbonate ions plot vs. pH is characteristic for anions adsorption onto metal oxides and is called the "adsorption envelope". In order to prevent carbon dioxide access to solution, all measurements must have been taken in special chamber in nitrogen atmosphere.

key words: zinc oxide, carbonate ions, adsorption

INTRODUCTION

Practical application is the most important aspect for experimental study of properties of the electrical double layer. Zeta potential measurements give important information concerning the properties of the diffuse part of the edl. Measurements include surface charge, ion adsorption, and zeta potential. Zinc oxide occurs in nature as zincite and is widely used in technology (Bolewski, 1982). Recently, ZnO is considered as a biosensing material. This explains the need for theoretical and experimental studies involving the oxide/electrolyte interface. In order to obtain precise research results the measurements were carried out using ZnO with rigorously defined properties. A higher solubility of this oxide in comparison to either TiO_2 or Fe_2O_3 complicates potentiometric titration because dissolution processes also compete significantly for added acid or base.

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Zinc oxide is a white powder with exceptional and unique properties. Partly due to its various applications in electronic, cosmetics and medicine devices, zinc oxide has been a subject of many studies. ZnO is one of important ceramic materials and has been found to have diversified applications in electronic devices such as gas sensors, varistors and transducers. The adsorption process of ions at the metal oxide/water solution interface and its influence on the electrical double layer structure is well described in literature. However, in real dispersed systems, for instance in many technological processes or aqueous environment, the composition of the solid phase as well as of the solution is rich in many organic and inorganic substances.

EXPERIMENTAL

MATERIALS AND METHODS

All measurements were carried out on commercial (Aldrich) zinc oxide (zincite structure). The specific surface of the powder, determined by the Braunauer Emmet Teller (BET) method (nitrogen adsorption - desorption) was 5.7 m^2/g. BJH (Barret, Joyner, Halenda) cumulative desorption volume of pores between 1.7 and 300 nm was 4.59 cm^3/g, which means that the sample was porous with an average pore diameter of 12.80 nm. Polydispersity coefficient (by PCS method) is equal to 0.02 means that the investigated zinc oxide is monodispersed. X-ay diffraction data revealed the crystalline zincite structure of oxide. XRF data showed that zinc oxide was pure without any contaminations. All reagents (NaOH, sodium carbonate , analytical grade, supplied by Polskie Odczynniki Chemiczne, Gliwice, Poland; $NaClO_4$, analytical grade, supplied by Aldrich) were dissolved in doubly-distilled water. The surface charge of zinc oxide was calculated by comparison of the potentiometric titrations curve of the oxide suspension and the background electrolyte. These titrations of oxide suspensions were carried out in a thermostatic teflon vessel under free of CO_2 nitrogen atmosphere at $25°C$ with $0.1°C$ accuracy (Julabo Refrigerated/Heating Circulator model F10) in a special chamber that isolates titration vessel from the outer environment. During experiments the nitrogen pressure in the chamber was slightly higher than that in the outside chamber.

Measurements were performed using a PHM 240 Radiometer Research pH-meter with a glass electrode and calomel reference electrode. The whole titration procedure (e.g. addition of titrant by Dosimat 665) and data acquisition from pH-meter during measurement was controlled by a computer. Potentiometric titration was carried out with the use of an automatic burette (Dosimat 665. Metrohm). For adsorption and potentiometric titration experiments, sample of ZnO (1.0 g) was added to 50 cm^3 of solution.

The background electrolyte concentrations were $1 \cdot 10^{-1}$, $1 \cdot 10^{-2}$ and $1 \cdot 10^{-3}$ M, respectively. The concentration range of carbonate ions in the system was from $1 \cdot 10^{-6}$ to $1 \cdot 10^{-3}$ M. Adsorption measurements of carbonate ions from the $NaClO_4$ solution were carried out with and ^{14}C isotopes as the radiotracer. The radioactivity of samples was measured with a LS5000 TD Beckman beta counter.

The measurements were limited to narrow pH range (from 10 to 6) because of relatively high solubility of zinc oxide ($1 \cdot 10^{-5}$ M and higher).

The ζ potential measurements were carried out for concentration ranging from $1 \cdot 10^{-6}$ to $1 \cdot 10^{-3}$ M. The ζ potential was measured with Malvern 3000 Standard Zetasizer. Each survey of the ζ potential was repeated five times.

RESULTS AND DISCUSSION

The surface charge is formed on the metal oxide as a result of ionization and complexation reaction of surface hydroxyl groups. Surface charge density as a function of pH is very important characteristic of the surface properties of the metal oxide/electrolyte solution. pH_{pzc} position depends on the alkali-acid character of surface hydroxyl groups. For zinc oxide, the value of this parameter is in a very wide range of 6.9 – 9.8 (Kosmulski, 2001).

In aqueous solution ZnO dissolution takes place according to following reactions:

$$Zn^{2+}_{(aq)} + OH^- \Leftrightarrow Zn(OH)^+_{(aq)} \tag{1}$$

$$Zn(OH)^+_{(aq)} + OH^- \Leftrightarrow Zn(OH)_{2(s)} \tag{2}$$

$$Zn(OH)_{2(s)} \Leftrightarrow Zn(OH)_{2(aq)} \tag{3}$$

$$Zn(OH)_{2(s)} \Leftrightarrow Zn^{2+}_{(aq)} + 2\,OH^- \tag{4}$$

$$Zn(OH)_{2(s)} + OH^- \Leftrightarrow Zn(OH)_3^{-}{}_{(aq)} \tag{5}$$

$$Zn(OH)_{2(s)} + 2\,OH^- \Leftrightarrow Zn(OH)^{2-}_{4\,(aq)} \tag{6}$$

$$ZnO_{(s)} \Leftrightarrow Zn^{2+} + O^{2-} \tag{7}$$

$$ZnO_{(s)} + H_2O \Leftrightarrow Zn^{2+} + 2OH^- \quad pK=16,4 \tag{8}$$

$$ZnO_{(s)} + H_2O \Leftrightarrow ZnOH^+ + OH^- \quad pK=12,0 \tag{9}$$

$$ZnO_{(s)} + H_2O \Leftrightarrow ZnO_2H^- + H^+ \quad pK=17,0 \tag{10}$$

$$ZnO_{(s)} + H_2O \Leftrightarrow ZnO_2^{2-} + 2H^+ \quad pK = 29{,}7 \tag{11}$$
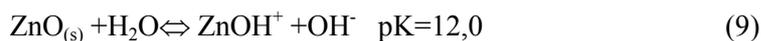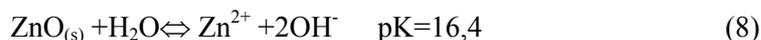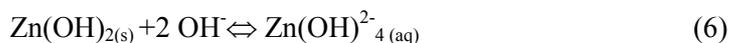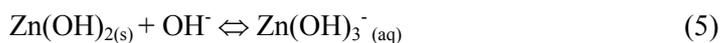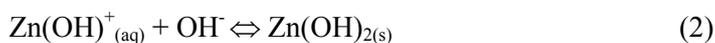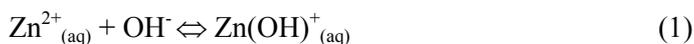
The solubility diagram for zinc oxide in equilibrium with an aqueous solution at varying pH is shown in Fig. 1 (Blok and de Bruyn, 1970). The minimum solubility is at pH=9.9 – 12.3.
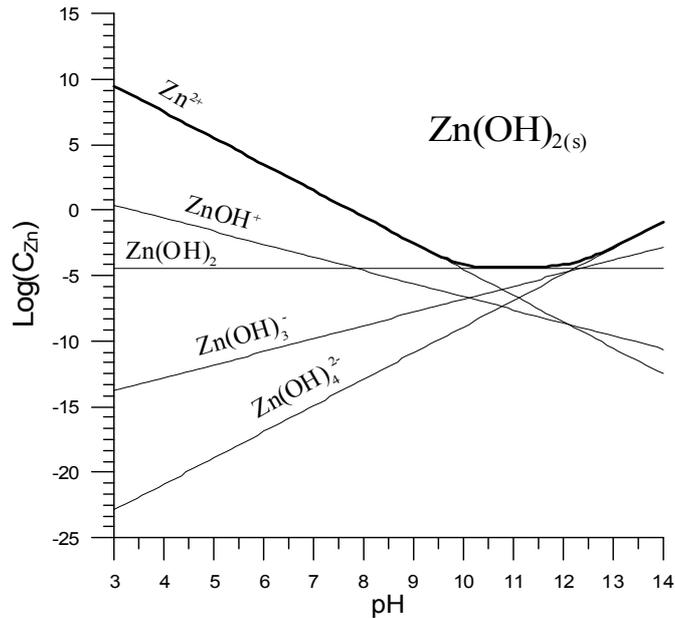
Fig. 1. Solubility diagram for zinc oxide

The surface charge density dependence on pH for ZnO/aqueous solution of the NaClO$_4$ shows that pH$_{pzc}$ is equal to 8.0, however, the ζ potential pH$_{iep}$= 8.7 (Fig. 2). It seems that the difference between these points may arise from particle size of ZnO dispersion that was used in the potentiometric titration and electrophoretic measurements. In the last method, fine particle were used while in potentiometric titrations aggregates of zinc oxide particles were present.

The ζ potential of ZnO as a function of pH in the presence of carbonate ions is shown in Fig. 3. As one can see, the isoelectric point of ZnO is equal to pH=8.7 in the absence of carbonate ions and shifts towards lower pH in presence of carbonate ions with increase of their concentration. At the initial concentration of 0.001M carbonate ions the pH$_{iep}$ is equal to 8.3.
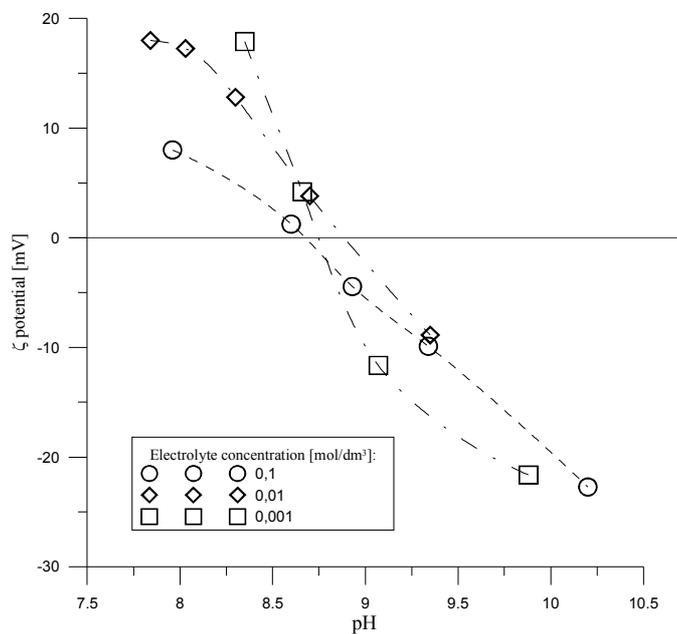
Fig. 2. The ζ potential of ZnO as a function of pH
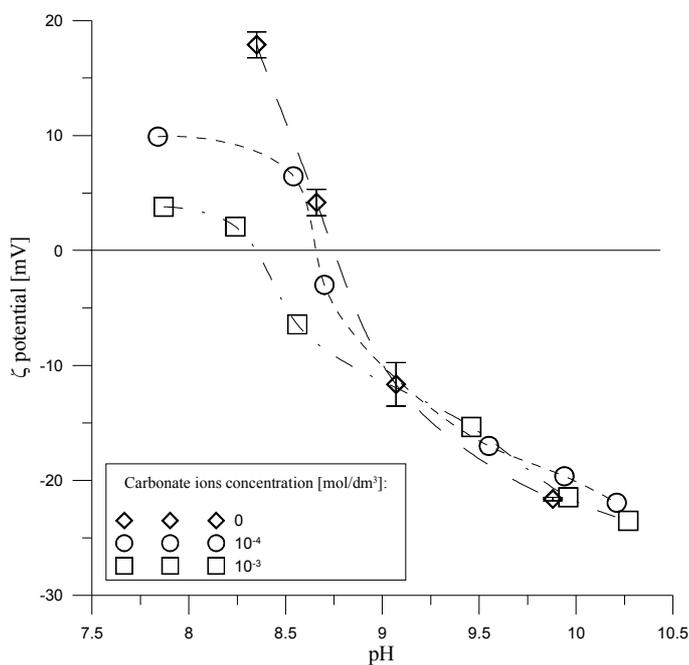
Fig. 3. The ζ potential of ZnO as a function of pH in 0.001 M NaClO$_4$ solution in presence of carbonate ions

Specific adsorption of anions at the metal oxide/electrolyte interface leads to a decrease of pH_{iep} due to the increase of concentration, complexed by anions, positively charged groups at the ZnO/electrolyte interface, eg. $\equiv ZnOH_2^+HCO_3^-$ and simultaneous decrease of concentration of ionized positively charged forms like $\equiv ZnO_2^+$. Because the diffuse layer charge is proportional to algebraic sum of negatively and positively charged groups, the decrease of concentration of positively charged groups leads to the formation of negatively charged ions, and to the decrease of zeta potential and shift of pH_{iep} towards low pH.

The adsorption densities and equilibrium concentrations of carbonate ions as a function of pH are depicted in Figs 4, 5, 6 and 7.
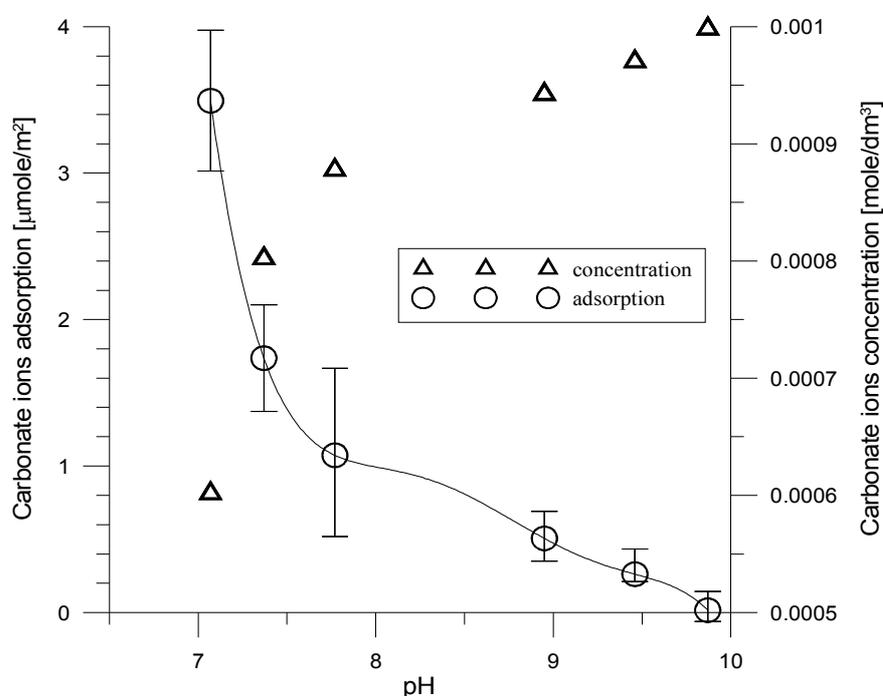
Fig. 4. Adsorption density as a function of pH solution in the Zn/0.001M $NaClO_4$ + 0.001 M HCO_3^- system

The initial concentration of carbonate ions was from $1\cdot10^{-3}$ M to $1\cdot10^{-6}$ M, respectively. The shapes of adsorption of carbonate ions plot vs. pH are characteristic for anions adsorption onto metal oxides and are called "adsorption envelope". One can observe an increase of adsorption and decrease of concentration of carbonate ions with a decrease of pH of the electrolyte. That progress of adsorption is characteristic for specific anion adsorption onto metal oxides.
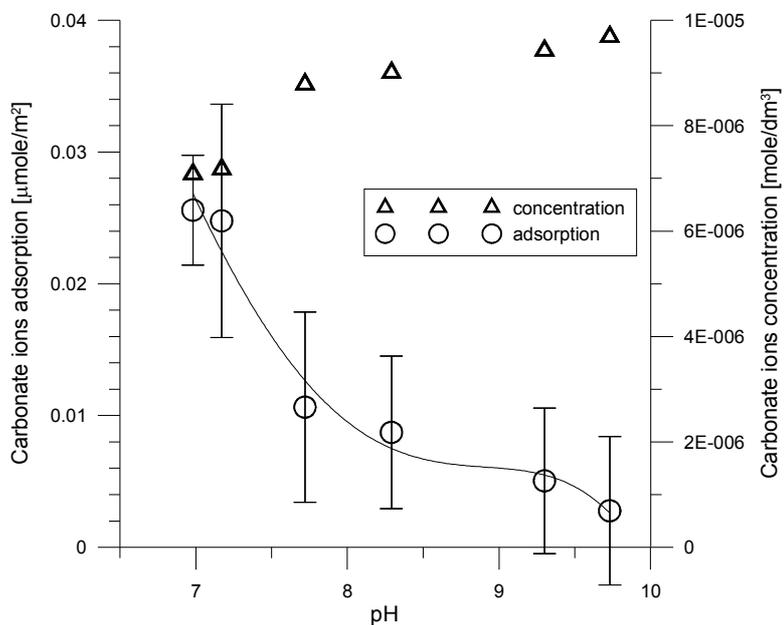
Fig. 6. Adsorption density as a function of pH solution in the Zn/0.001M NaClO$_4$ + 0.0001 M HCO$_3^-$ system
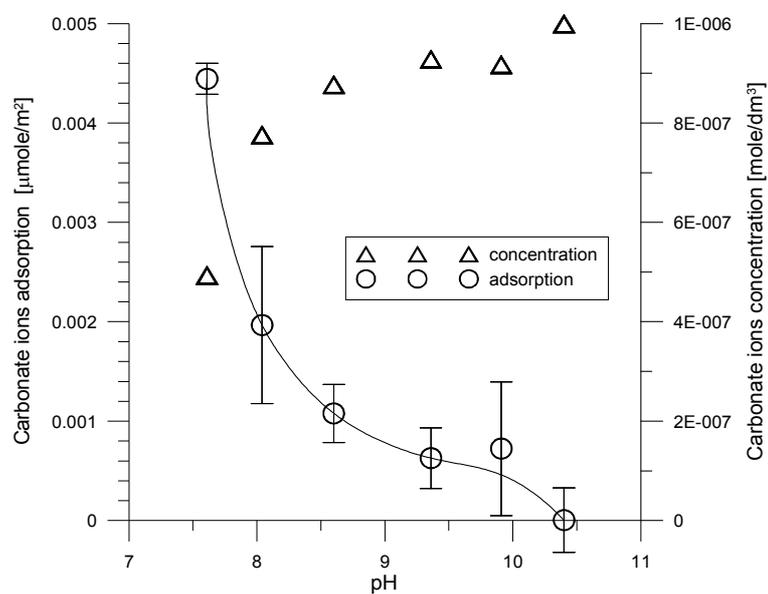
Fig. 7. Adsorption density as a function of pH solution in the Zn/0.001M NaClO$_4$ + 0.000001 M HCO$_3^-$ system

The edge of adsorption moves to acidic environment with the increase of the concentration of the carbonate ions. That means that the carbonate ions adsorption may go through exchange of hydroxyl groups with innersphere complex formation (Eq. 7) or through hydrogen ions consumption with outersphere complex formation (Eq. 8). According to both equations, the increase of pH causes a decrease of carbonate ions adsorption.

$$- ZnOH + HCO_3^- \Leftrightarrow - ZnCOH + OH^- \tag{7}$$

$$2 - ZnOH + H^+ + HCO_3^- \Leftrightarrow \left(- ZnOH_2^+ \right)_2 CO_3^{2-} \tag{8}$$
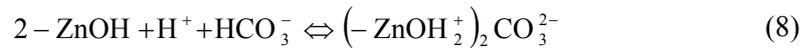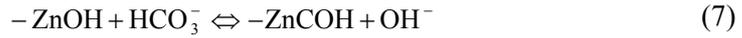
The decrease of adsorption of carbonate ions with increase of pH is result of the following reaction:

$$\equiv ZnOH + H^+ + HCO_3^- \Leftrightarrow \equiv ZnOH_2^+ HCO_3^- \tag{9}$$

As one can conclude from Eq. 9, the decrease of pH will support the formation of carbonate groups at the zinc oxide surface. The concentration of carbonate ions in the solution decreases but even at the end of adsorption process it is still high, and can be a result of a small affinity of carbonate ions towards the surface of zinc oxide.

Table 1. Zinc oxide's surface parameters before and after adsorption of 0.001 M carbonate

Parametr	ZnO	ZnO+0.001M HCO$_3^-$
BET surface area	5.74 m^2/g	6.37 m^2/g
Langmuir surface area	7.89 m^2/g	9.08 m^2/g
BJH cumulative adsorption pore volume of pores 1,7nm<d<300nm	0.014 cm^3/g	0.016 cm^3/g
BJH cumulative desorption pore volume of pores 1,7nm<d<300nm	0.012 cm^3/g	0.014 cm^3/g
Average pore diameter	6.62 nm	8.68 nm
BJH adsorption average pore diameter	12.80 nm	8.83 nm
BJH desorption average pore diameter	12.94 nm	7.57 nm

From Table 1 one can see that the surface area of the zinc oxide increased after adsorption of the carbonate ions. This may be a result of the surface fluffing because the XRD measurements did not showed any formation of new structural phases. In Figs 8 and 9 the results of measurement of the ZnO particle size before and after adsorption of carbonate ions (concentration of carbonates equaled 0.001 M) are shown. The results proved that the average size of particles decreased. It can be explained by disaggregation of the zinc oxide particles.
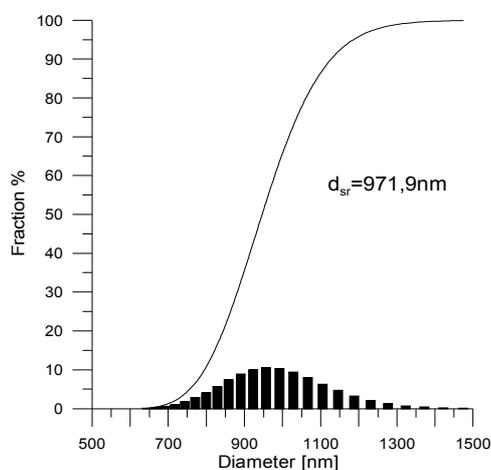
Fig. 8. Particle size of ZnO
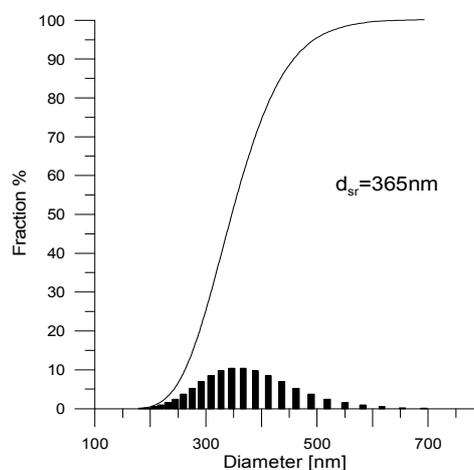
Fig. 9. Particle size of ZnO after adsorption of
0.001M carbonate ions

CONCLUSIONS

Carbonate ions adsorption causes exchange of surface groups with carbonate groups that cause an increase of negatively charged groups on the surface of zinc oxide and in consequence a decrease of ζ. The shapes of adsorption of carbonate ions plot vs. pH are characteristic for anions adsorption onto metal oxides and are called "adsorption envelope". One can observe an increase of adsorption and decrease of concentration of carbonate ions with a decrease of pH of the electrolyte. Adsorption on the zinc oxide is not complete because of small affinity of carbonate ions to the zincite surface.

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Badania nad adsorpcją jonów węglanowych na granicy faz tlenek cynku/wodny roztwór NaClO$_4$ są przedstawione w niniejszej pracy. Zakres stężenia jonów węglanowych, dla których przeprowadzono pomiary wynosi od 10^{-6} do 10^{-3} M. Kształt krzywych adsorpcji względem pH jest charakterystyczny dla adsorpcji anionów na tlenkach metali i jest nazywany „obwiednią" adsorpcji. W celu wyeliminowania dostępu dwutlenku węgla do układu badanego wszystkie pomiary były przeprowadzone w specjalnej komorze.

Słowa kluczowe: telenek cynku, jony węglanowe, adsorbcja