ACTA UNIVERSITATIS LODZIENSIS
FOLIA CHIMICA 9, 1991

Maria Turowska*, Jerzy Sokołowski*

THE pH EFFECT ON THE POTENTIAL OF ZERO CHARGE OF GOLD ELECTRODES**

Potential of zero charge (pzc) of gold in solutions with constant mole concentration of ions in the range pH 1,5-11 was measured. Measurements were carried out by the inversion immersion method with application of an automatic measuring equipment. Empirical formula of linear reciprocality of pzc of gold in the pH function was given.

Values of the zero charge potential of polycrystalline gold electrodes in non-adsorbing salt solutions found experimentally by various authors differ considerably [1-12, 23, 24]. The differences result from applied measuring methods, of electrode surface preparation as well as electrode material. Examinations of the electrodes made of monocrystals of gold dependance of pzc on crystalographic orientation of gold [13-17, 22]. The most positive pzc values display crystals with orientation (111), next with (100) and the most negative with the orientation (110). In accordance with the paper [22, 25] pzc values of polycrystalline gold electrodes are close to pzc values for mono-crystalline gold electrodes of orientation (110).

It appears purposeful to study the pH effect on pzc of a gold electrode by means of measuring that value using identical methods of preparing electrodes and the application of the same measuring method. In the present paper, influence of hydrogen ion concentration upon pzc value of polycrystalline gold in 0.01 mole/dm^3 sodium sulphate was measured by means of the inversion immersion method.

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[*] Institute of Chemistry, University of Łódź, Poland.

[**] This work was financially supported by CPBP 01.15 research programm.

Similar experiments were carried out by the scrape method of pzc measurement of gold electrode [7, 18, 20, 25].

EXPERIMENTAL

Measurements of the potential of zero charge were taken by an inversion immersion method by means of an apparatus constructed in the Department of General and Inorganic Chemistry of the Lodziensis University allowing an automatic measurements and recording of data by this method [1].

In this method surface of the metal is prepared by an induction heating of the electrodes for several hours in the atmosphere of electrolitically obtained hydrogen.

Examined electrodes of a cylindrical shape were produced from a gold foil of 99,9% purity. As reference a silver electrode in solution 0.01 mole/dm^3 was used.

Measurement were carried out in Na_2SO_4 solution as the weak-adsorbing electrolyte. To prepare solutions of a required pH the solutions of Na_2SO_4, H_2SO_4 and NaOH were used with application of a constant ion concentrations (SO_4^{2-}) equalling 0,01 mole/dm^3.

pH of the solutions was checked with a Mera-Elwro pH-meter of N-512 type calibrated for seven buffer solutions with known pH values.

Solutions of used electrolytes were prepared of weigh portions of high purity salts dissolved in tripple distilled water. For degreasing of the electrodes methanol was used.

Each measuring cycle of pzc of an electrode consisted of:

a) flushing of an electrode with tripple distilled water - 5 min,

b) induction heating of an electrode at a temp. 1073-1093 K for 10 min,

c) cooling down of an electrode - 5 min,

d) measurement.

All operations were carried out in the hydrogen stream at the rate of flow 2,5-3,5 cm^3/sec.

Given above conditions of electrode preparation and measuring apparatus were established experimentally and allowed obtaining the most repeatable results in shortest possible time of cycle duration to prepare the electrode for measurements.

RESULTS AND DISCUSSION

Obtained results consist of 8 measuring series. One series covers 10 measurements of pzc values of the gold electrode in solution of Na_2SO_4 of an established pH value.

Obtained values of immersion impulse were scaled on the values releted to a normal hydrogen electrode. The error was determined statistically, making use of Student's distribution of 9 degrees of freedom and of 0,95 confidence level. In calculations no mistakes connected with defining of the silver-silver chloride electrode potential and liquid potential were taken into account, but as it was experimentally proven they were much smaller than a statistical measurement error.

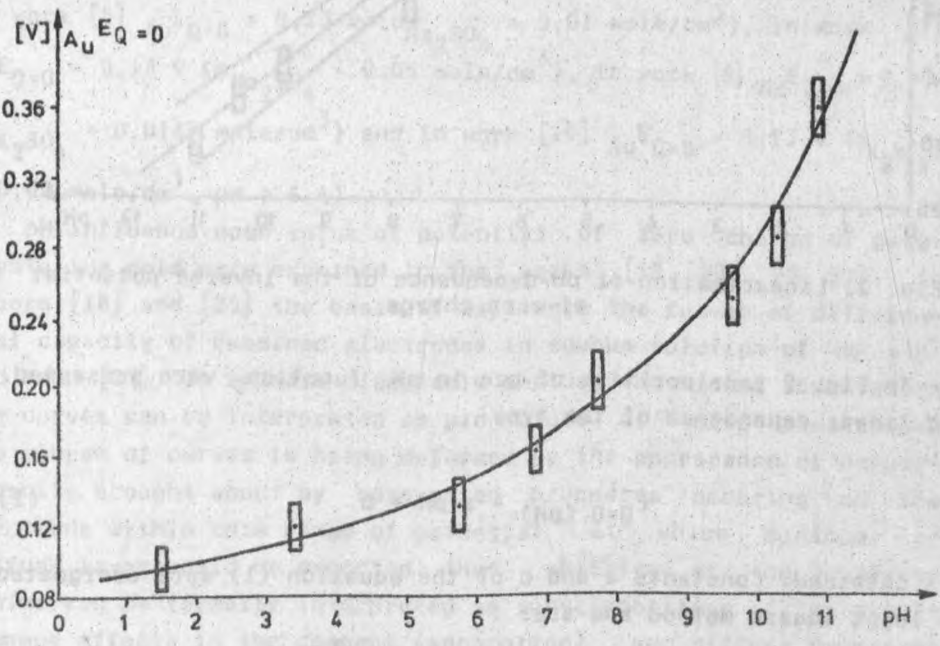

Fig. 1. Dependence of the potential of zero charge on the pH of solution

Obtained results are shown in Fig. 1. On the diagram (Fig. 1) calculated statistical errors of pzc were plotted and errors of pH measurement values estimated. Obtained pzc values of the gold electrode are positive and increase accordingly with the growth of pH of solution. At pH < 7 changes reaching several times milivolts are observed, above that values of pH are more distinct.

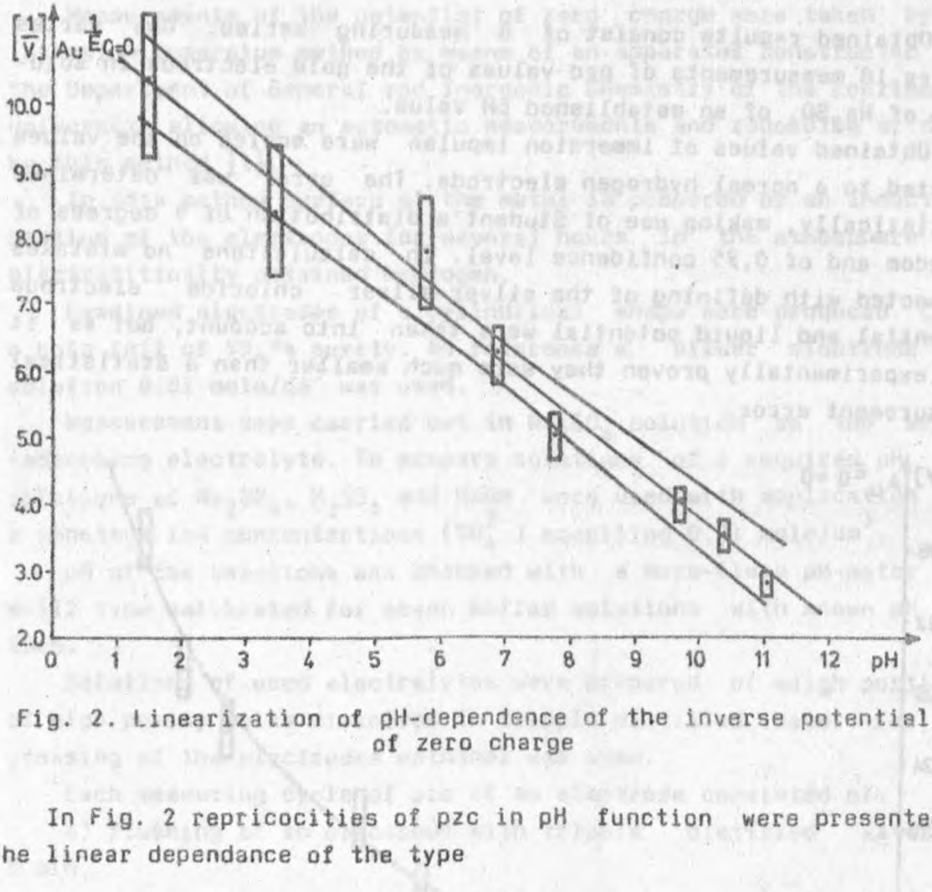

Fig. 2. Linearization of pH-dependence of the inverse potential of zero charge

In Fig. 2 repricocities of pzc in pH function were presented. The linear dependance of the type

$$E^{-1}_{Q=0\ (pH)} = a\,pH + b \qquad (1)$$

was obtained. Constants a and b of the equation (1) were designated by least square method and are:

$$a = (-0{,}77 \pm 0{,}10)\ V^{-1}$$
$$b = (11{,}5 \pm 0{,}7)\ V^{-1}$$

The errors a and b were determinated for confidence level $\alpha = 0,95$.

In Fig. 2 confidence level curve designating confidence region were marked, in which the probability of finding measurement points p_i $(pH_i; E_{Q=0_i})$ amounts 0,95.

Basing on carried out calculations the dependence of potential of zero charge of polycrystalline gold electrode in described conditions may be presented by the following empirical eqution:

$$_{Au}E^{-1}_{Q=0}\ (pH) = (-0,77\ pH + 11,5)V^{-1} \qquad (2)$$

Obtained results correlate rather well with literature data. Obtained in this work pzc values of gold for values of pH = 7 amount $_{Au}E_{Q=0} = 0,17$ V whereas recommended by Trasatti [11], after analysis of experimental data obtained by a number of authors amounts $_{Au}E_{Q=0} = 0,18$ V, and by Khruszczev and Kazarinov [12] $_{Au}E_{Q=0} = 0,19$ V. Potential of zero charge of gold obtained from capacity minimum in solutions of sulphates amount: in work [5] $_{Au}E_{Q=0} = 0,23$ V $(c_{Na_2SO_4} = 0,01\ mole/dm^3)$, in work [7] $_{Au}E_{Q=0} = 0,13$ V $(c_{Na_2SO_4} = 0,05\ mole/dm^3)$, in work [8] $_{Au}E_{Q=0} = 0,1$ V $(c_{K_2SO_4} = 0,0167\ mole/dm^3)$ and in work [18] $_{Au}E_{Q=0} = 0,13$ V $(c_{K_2SO_4} = 0,02\ mole/dm^3$, pH = 6,4).

pH influence upon value of potential of zero charge of polycrystaline gold were examined in the works [18, 20, 25, 27]. In papers [18] and [25] the basis of data were the curves of differential capacity of examined electrodes in aquous solution of NaF [18] and NaOH [25]. It appears disputable whether the minima observed on the curves can be interpreted as pzc values of these electrodes. The course of curves is being deformed by the appearance of pseudocapacity brought about by adsorption processes occuring on the electrode within this range of potential at which minimum of diffuse layer could be expected. Thus shifting of the observed minima can be formally interpreted as superimposition of two simultaneous effects in the compact (adsorption) and diffuse (minimum) layers. Formally similar proces was analyzed in the paper [26]. View of the above it is difficult to compare obtained by us results with the data of above authors. The values of pzc of gold measured by the scrape method are more negative than obtained by another methods.

As can be seen from carried studies gold displays increased sensitivity to changes of the solution acidity compared to copper [19] and silver [21]. It is comendable, therefore, that measurement of the potential of zero charge of gold electrode be carried out at a controlled pH of the solution. For measurement in sulphate solutions it is purposeful to use a buffer consisting of sodium sulphate and sodium hydrosulphate [27].

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Maria Turowska, Jerzy Sokołowski

WPŁYW pH NA WARTOŚĆ POTENCJAŁU ŁADUNKU ZEROWEGO ELEKTROD ZŁOTYCH

Zmierzono potencjał ładunku zerowego (płz) złota w roztworach o stałym stężeniu molowym jonów siarczanowych ($c_{SO_4^{2-}} = 0,01$ mol/dm^3) w granicach pH 1,5-11. Pomiary prowadzono inwersyjną metodą zanurzeniową stosując automatyczną aparaturę pomiarową. Stwierdzono, że wartość płz elektrody złotej wzrasta wraz ze wzrostem pH roztworu. Podano empiryczny wzór liniowej odwrotności wartości potencjału płz złota w funkcji pH roztworu.