

Władysław JANUSZ, Anna GAŁGAN, Marek RESZKA *

ELECTRICAL DOUBLE LAYER AT THE Cu_2O /AQUEOUS SOLUTION OF ALKALI METAL CHLORIDES INTERFACE

Received March 15, 2006; reviewed; accepted May 15, 2006

Cuprite, copper oxide (I), is commonly found as an oxidation product of copper sulphides in the upper zones of copper deposits. This oxide in a dispersion form has found wide application. The structure of its double layer at copper oxide/electrolyte solution interface was not described yet because of its relatively high solubility and redox reactions. Experiments, presented in the paper, were performed on the copper oxide sample obtained by reduction of alkaline solution of copper(II) acetate by glucose. Surface charge density measurements were taken by potentiometric titrations taking into account solubility of the oxide. Zeta potential versus pH was calculated from electrophoretic measurements of the Cu_2O in 1:1 electrolyte solutions of alkali metal chlorides. Adsorption density of the background electrolyte was measured as a function of pH. To avoid CuCl precipitation all measurements were taken at concentrations lower than 0.001M of Cl^- . Basing on surface charge density versus pH dependence the ionization and complexation reaction constants were calculated.

Key words: electrical double layer, copper oxides/electrolyte interface, pzc, iep

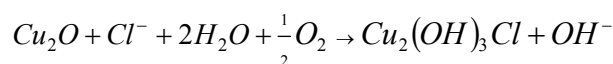
INTRODUCTION

Studies of electrical double layer (edl) at metal oxide/electrolyte solution have been performed for many years. Usually, they concern simple model systems of high thermodynamic stability and very low solubility that do not produce problems during experiments. Complex studies of surface properties of electrical double layer, comprising surface charge, zeta potential and adsorption of background electrolyte ions, were made for a few oxides such as silica, alumina, titania and iron oxides. The same properties for other oxides (mainly transition metals) are hardly known. It is also true for copper oxide. The oxide is used as a catalyst of partial oxidation of some alkenes. Being better catalyst of carbon monoxide oxidation than copper it may be

* Uniwersytet Marii Curie-Skłodowskiej, Wydział Chemii, Pl. M.C. Skłodowskiej 3, 20-031 Lublin

used in car combustion gas controlling devices. Moreover, Cu_2O is applied for protective paints for sea vessels, and pigment for glass and china. Its semi conductive properties may found application in solar cells. Cuprite (copper (I) oxide) is one of the most important copper minerals. Deposits of this mineral contain often Se, I, Pb, and sometimes also In, V, Cd, Sn, and Bi as admixtures (Surowce Mineralne Swiata 1977).

Cuprite is also presented in all patinas - that is copper or bronze covered objects, outdoor exposed for a long time. Usually, patinas formed on the objects exposed to atmosphere are brightly green. Surfaces, screened from atmospheric precipitation are dark. They are formed by copper hydroxychloride ($\text{Cu}_2(\text{OH})_4\text{Cl}$) and atacamite (Nassau et al. 1987, Selwyn et al. 1996). Copper hydroxychloride is also formed in reaction with cuprite (Strandberg 1998):



This reaction may take place on copper, bronze or brass covered surfaces at the sea coast as a result of interaction with salt water. Besides, the high concentration of chloride ions is produced by application of some salts as de-icers.

Depending on redox potential and pH, copper (I) ions in aqueous solutions containing chloride and hydroxide ions may form several insoluble compounds such as copper oxide (I), copper chloride (I) and copper oxide (II) (Pourbaix 1965, 1978). Figure 1. presents equilibrium diagram for three components system Cu-Cl-H₂O.

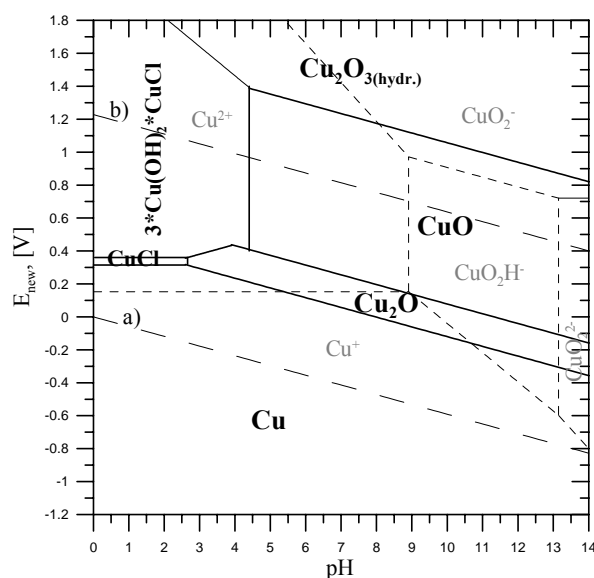
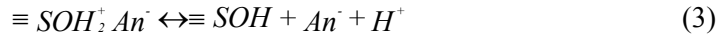


Fig. 1 Potential - pH equilibrium diagram for the system $\text{Cu}+0,001\text{M Cl}^-+\text{H}_2\text{O}$ at 25°C

It may be noticed that CuCl (nancotite) is not stable and in neutral environment hydrolyzes to Cu₂O. In oxidizing, acid environment a stable form is 3Cu(OH)₂·CuCl₂ (paratacamite).

The study of the electrical double layer (edl) structure at the solid/solution interface is useful in the explanation of the flotation reagents that adsorbs by electrostatic interaction as well as the interaction between particles and between particles and air bubbles. The formation of edl is due to presence of charge at mineral surface. The surface charge at the metal oxides /electrolyte solution interface, according to the site binding theory is created by of ionization (reactions 1 and 2) and complexation (reactions 1 and 2):



Above reactions (1-4) are described by thermodynamic constants:

$$K_{a_1} = \frac{[\text{H}^+][\equiv \text{SOH}]}{[\equiv \text{SOH}_2^+]} \cdot \frac{\gamma_H \gamma_0}{\gamma_+} \cdot \exp\left(\frac{-e\Psi_0}{kT}\right) \quad (5)$$

$$K_{a_2} = \frac{[\text{H}^+][\equiv \text{SO}^-]}{[\equiv \text{SOH}]} \cdot \frac{\gamma_H \gamma_-}{\gamma_0} \cdot \exp\left(\frac{-e\Psi_0}{kT}\right) \quad (6)$$

$$K_{An} = \frac{[\text{H}^+][\text{An}^-][\equiv \text{SOH}]}{[\equiv \text{SOH}_2^+ \text{An}^-]} \cdot \frac{\gamma_H \gamma_{An} \gamma_0}{\gamma_{\pm}} \cdot \exp\left(\frac{-e(\Psi_0 - \Psi_{\beta})}{kT}\right) \quad (7)$$

$$K_{Ct} = \frac{[\text{H}^+][\equiv \text{SO}^- \text{Ct}^+]}{[\equiv \text{SOH}][\text{Ct}^+]} \cdot \frac{\gamma_H \gamma_{\mp}}{\gamma_0 \gamma_{Ct}} \cdot \exp\left(\frac{-e(\Psi_0 - \Psi_{\beta})}{kT}\right) \quad (8)$$

where:

K_{a_1} - dissociation constant of surface group $\equiv \text{SOH}_2^+$; K_{a_2} - dissociation constant of surface group $\equiv \text{SO}^-$; K_{An} - anion complexation constant; K_{Ct} - cation complexation constant; [.] - concentrations of specific surface forms or ions in the solution; Ψ_0 - surface potential; Ψ_{β} - potential of Inner Helmholtz Plane (IHP); T- temperature; k-Boltzman constant ($1.38 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1}$), e- electron charge, γ_H - activity coefficient of H^+ ions, γ_0 - activity coefficient of $\equiv \text{SOH}$ groups, γ_+ - activity coefficient of $\equiv \text{SOH}_2^+$ groups, γ_- - activity coefficient of $\equiv \text{SO}^-$ groups, γ_{An} activity coefficient of

anions, γ_{Ct} - activity coefficient of cations, γ_{\pm} - activity coefficient of $\equiv\text{SOH}_2^+\text{An}^-$ groups, γ_{\mp} - activity coefficient of $\equiv\text{SO}^-\text{Ct}^+$ groups.

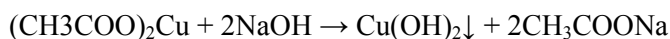
In the paper, some studies on electrical double layer at copper oxide (I)/electrolyte solution are presented. Measurements comprise surface charge, zeta potential and electrolyte ion adsorption. Alkali metal chlorides LiCl, NaCl, KCl, CsCl were used as background electrolytes to study influence of their cations on the electrical double layer properties. Experimental data were used to theoretical calculations of the ionization and complexation constants of reactions of the surface hydroxyl groups. The results of these calculations allowed estimate the shares of respective surface groups in the surface charge at the copper oxide (I)/electrolyte solution interface.

For calculations of ionization and complexation constants of surface hydroxyl groups the numerical optimization (Janusz 1994), Davies et al. 1978, modified Schwarzenbach's (Janusz 1991) and Sprycha (Sprycha and Szczypta 1984) methods were adopted.

EXPERIMENTAL

CU₂O PREPARATION

Copper (II) oxide, Cu₂O, may be precipitated from alkaline solutions of copper ions using reducing compounds such as hydrazine, hydroxylamine or saccharides with aldehyde groups. This method, widely applied for detection and quantitative determination of saccharides, was used in present research. Copper (II) acetate - 0.1M and glucose solutions were used as substrates. The procedure was as follows: 23 ml of NaOH solution was added to 250 ml of the copper (II) acetate solution to obtain blue precipitate of copper (II) hydroxide.



The sediment was ultrasonicated and obtained dispersion was heated to 30°C. Then, 500 ml of the glucose solution (180.1g/l) was added and reactor was heated to 98°C to reduce copper ions from Cu(II) to Cu(I). Obtained Cu₂O was quickly cooled with icy water then ultrasonicated again and left for a few hours to settle. Sedimented Cu₂O was washed with double distilled water till supernatant conductivity was below 2 μS/cm. Simultaneously, the fine particles were removed. Finally, the sediment was dried at 60°C. Applied concentration of the glucose was higher than calculated for side reactions of sugar molecules in alkaline environment as was noticed by Stanek et al. (1963).

METHODS

Potentiometric titration was performed in a Teflon thermostated vessel, in nitrogen atmosphere, free from CO₂, at 25°C. The pH of the solution was measured using PHM240 Research pH-meter (G202C and K401 electrodes). The whole titration

procedure (e.g. the addition of the titrant via Dosimat 6655 (Methrom) and data acquisition from the pHmeter was controlled by a computer. The surface charge density was calculated from the potentiometric titration data for blank (background) electrolyte solution and Cu₂O suspension. Copper (I) oxide is sparingly soluble oxide, so beside the charge formation reactions, the oxide dissolution reactions should also be considered in the hydrogen ion balance. The method of the Block and de Bruyn of surface charge determination, regarding the reaction of dissolution was used for investigated system (Block and de Bruyn 1970).

Adsorption densities of Na⁺, Cs⁺ and Cl⁻ ions were measured using a radiotracer technique with ²²Na, ¹³⁷Cs and ³⁶Cl radioisotopes supplied by Polatom (Świerk, Poland). The radioactive sources of respective isotopes, prepared from electrolyte solution before and after adsorption were measured using LS 5000 counter made by Beckman, USA. Adsorption of Li⁺ and K⁺ ions was calculated from uptake of concentration of these ions that was determined by ASA method.

Electrokinetic potential was measured using Zetasizer 3000, manufactured by Malvern (United Kingdom). Diluted Cu₂O suspensions containing 20 mg of solids in 200 cm³ of electrolyte solution were used. Before measurement the suspension were dispersed using Sonicator XL2020 made by Misonix.

OXIDE CHARACTERISTICS

Crystal structure of synthesized Cu₂O was determined by XRD analysis (X-ray diffraction). Made soon after sedimentation, it revealed minimal oxidation of copper oxide (I) to (II) as may be proved by peak at 2θ=38.65°. The oxidation took place mainly during drying that was manifested by darkening of the oxide surface. To avoid this reaction the oxide sample was washed with acetone immediately before drying. Such modification allowed obtains the oxide without CuO phase. Morphology and size of oxide particles was measured by electron microscopy (see Fig. 2.) One can see uniform (polydispersity equal 0.09), almost spherical particles of the mean diameter 296 nm determined by PCS method (Fig. 3.).

Table 1. Porosity and specific surface characteristic of Cu₂O sample.

Specific surface from BET isotherm [m ² /g]	6.15
Specific surface from Langmuir isotherm [m ² /g]	8.7
Summary pore volume from adsorption 1.7nm<d<300nm BJH method [cm ³ /g]	0.014198
Summary pore volume from desorption 1.7nm<d<300nm BJH method [cm ³ /g]	0.01778
Average pore radius from BET method [nm]	8.6
Average pore radius from adsorption - BJH method [nm]	8.3
Average pore radius from desorption - BJH method [nm]	8.8

Specific surface and porosity of the copper (I) oxide was determined by BET method. Obtained results are listed in Table 1.

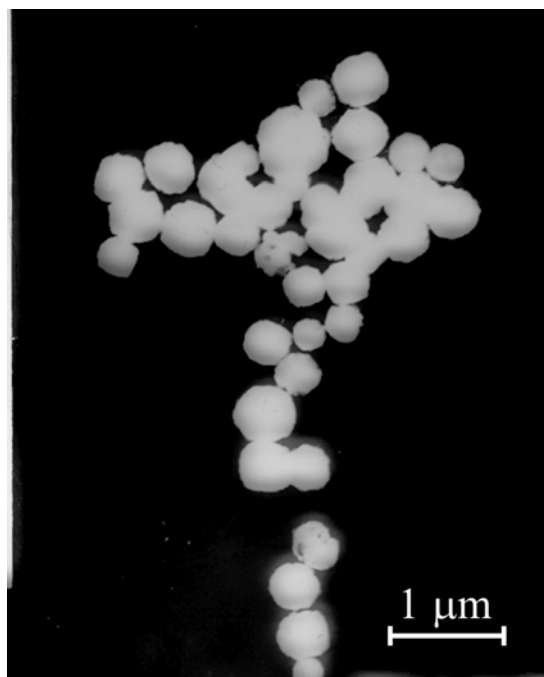


Fig 2. Transmission electron microscopy image of particles of Cu₂O sample

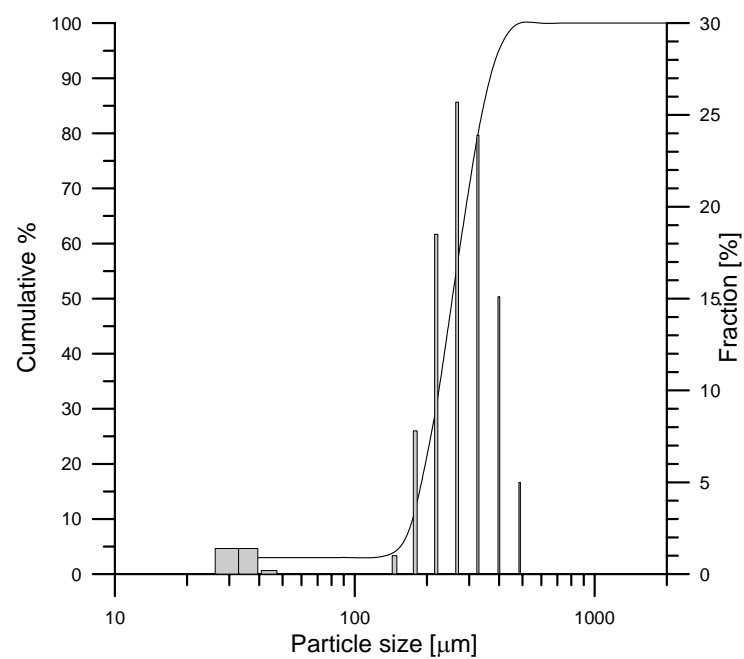


Fig. 3. Particle size distribution of Cu₂O sample

The very small volume of pores proves low porosity of the studied sample. The surface charge density calculations were carried out using BET specific surface area values.

ELECTRICAL DOUBLE LAYER AT $\text{Cu}_2\text{O}/1:1$ ELECTROLYTE SOLUTION INTERFACE

Electrical double layer at metal oxides/1:1 electrolyte solutions interface is in the *site binding* model characterized by following physicochemical properties: ionization and complexation constants, compact and diffuse layer capacity, pH_{pzc} and pH_{iep} . To calculate above values the surface density and zeta potential measurements were taken for $\text{Cu}_2\text{O}/1:1$ electrolyte solution (LiCl, NaCl, KCl, CsCl) systems. Basing on the relation the surface charge density versus pH the ionization and complexation reaction constants were calculated according to Davies et al. (1978) modified Schwarzenbach (Janusz 1991), and numerical optimization (Janusz 1994) methods. The ionization constants of surface hydroxyl groups were calculated from zeta potential versus pH dependence according to Sprycha (Sprycha and Szczypa 1984). To avoid $\text{CuCl}_{(\text{s})}$ formation (Fig. 1), all measurements were taken in chloride ion solutions of concentration below solubility product of CuCl i.e. $< 0.01 \text{ mole/dm}^3$

SURFACE CHARGE AND pH_{pzc}

Surface charge density as a function of pH and ionic strength of background electrolyte for $\text{Cu}_2\text{O}/\text{LiCl}$, $\text{Cu}_2\text{O}/\text{NaCl}$, $\text{Cu}_2\text{O}/\text{KCl}$, $\text{Cu}_2\text{O}/\text{CsCl}$ systems is presented on Fig. 4a, 4b, 4c and 4d respectively.

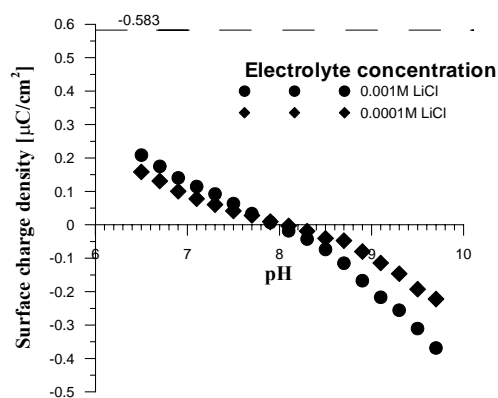


Fig. 4a. Surface charge density as a function of pH for Cu_2O /aqueous solution of LiCl

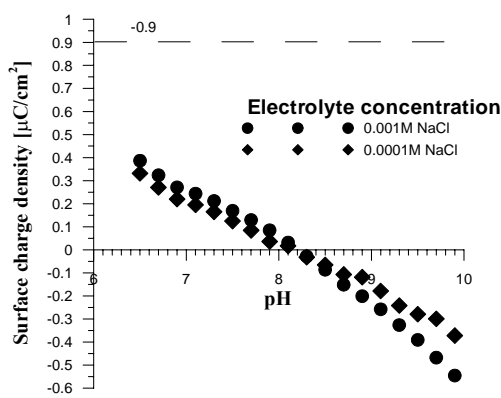


Fig. 4b. Surface charge density as a function of pH for Cu_2O /aqueous solution of NaCl

Relatively small values of surface charge density (below $2 \mu\text{C}/\text{m}^2$) in the whole studied pH range (6-10) may be observed for all systems. It is connected with substantial consumption of H^+ ions in Cu_2O dissolution reactions that take place

beside adsorption of H^+ ions at the surface of the oxide. The original surface charge was negative in the whole pH range and the position of CIP (*common intersection point*) of surface charge density curves versus pH for various ionic strengths is close to pH_{iep} . For system with LiCl (Fig. 4a) CIP is at $pH=8.0$, for NaCl (Fig. 4b) at 8.3, for KCl (Fig. 4c) 8.15 and for CsCl (Fig. 4d) 8.2.

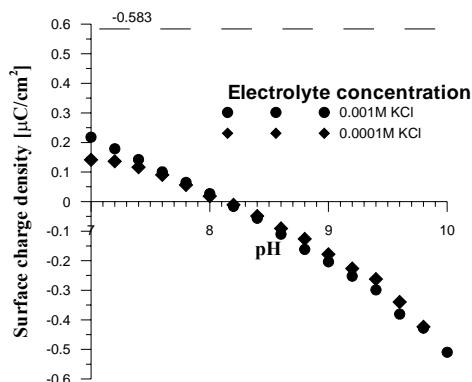


Fig. 4c. Surface charge density as a function of pH for Cu_2O /aqueous solution of KCl

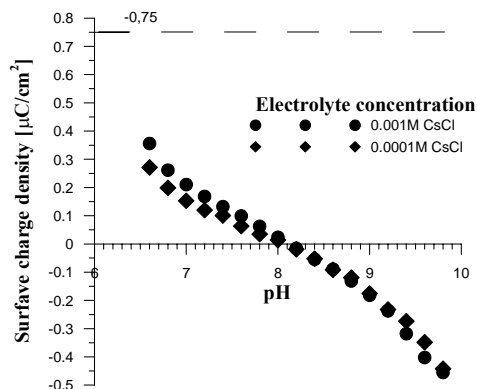


Fig. 4d. Surface charge density as a function of pH for Cu_2O /aqueous solution of CsCl

The position of CIP below pH axis may suggest presence of synthesis residues in the system as alkaline contaminations that are firmly bound to the Cu_2O surface. Considering above surface charge values were corrected for CIP value. The position of x-axis without correction is marked as dashed line. In all cases the influence of the ionic strength of the background electrolyte on the surface charge value is small. It is caused by previously mentioned compulsion - measurements at low concentration of electrolytes which gives low shares of complexation reactions in the surface charge. Basing on the surface charge values as functions of pH and concentration of the background electrolyte the ionization and complexation constants of surface hydroxyl groups on Cu_2O in solutions of alkali metal halides were calculated by Davie's et al. (Davis 1978) and modified by Schwarzenbach (Janusz 1991) methods. Obtained values of the constants are collected in Table 2.

As can be see from optimized data of Table 2 the most stable, positively charged groups are in CsCl solution and the least ones in LiCl. Stability of negatively charged groups, except LiCl, is almost the same for all solutions.

Surprising is the influence of the cation on the ionization and complexation reaction constants that leads to formation of positively charged groups. It may results from neglecting the activity coefficient of the surface groups and disregarding by *site binding* model some reactions at the interface. There is no accepted method of the above coefficient calculation till now. Ionization constants of both, negatively and positively charged groups, calculated by Davies method are comparable to these ones

obtained by Schwarzenbach. Analyzing complexation reaction constants of cations one may state the caesium cations as the most firmly adsorbed whereas lithium ions form the weakest bonding that is in agreement with Hoffmeister lyotropic series.

Table 2. Ionization and complexation reactions constants of surface hydroxyl groups for $\text{Cu}_2\text{O}/\text{Ct}(\text{Ct}=\text{Li, Na, K, Cs})\text{Cl}$ systems

Constant	Method		
	Optimization	Davis et al.	Schwarzenbach
$\text{Cu}_2\text{O}/\text{LiCl}$			
pK_{a1}	4.64	4.20	4.38
pK_{a2}	11.16	12.04	11.82
pK_A	5.50	5.73	7.25
pK_K	10.48	10.39	8.66
$\text{Cu}_2\text{O}/\text{NaCl}$			
pK_{a1}	4.72	4.9	5.2
pK_{a2}	11.69	11.45	11.4
pK_A	7.92	6.29	7.87
pK_K	8.12	10.99	8.71
$\text{Cu}_2\text{O}/\text{KCl}$			
pK_{a1}	4.69	5.19	5.16
pK_{a2}	11.63	11.49	11.49
pK_A	7.72	4.32	-
pK_K	8.33	10.48	8.62
$\text{Cu}_2\text{O}/\text{CsCl}$			
pK_{a1}	4.77	4.29	4.24
pK_{a2}	11.89	11.47	11.30
pK_A	7.23	6.23	7.87
pK_K	8.15	11.42	-

ZETA POTENTIAL AND pH_{iep}

Zeta potential versus pH and ionic strength of background electrolyte dependences for $\text{Cu}_2\text{O}/\text{LiCl}$, $\text{Cu}_2\text{O}/\text{NaCl}$, $\text{Cu}_2\text{O}/\text{KCl}$, $\text{Cu}_2\text{O}/\text{CsCl}$ systems are presented in Figs: 5a, 5b, 5c, and 5d.

In all cases, small differences (0.1-0.2 pH unit) may be observed for respective ionic strengths of background electrolytes. For LiCl solutions (Fig. 5a) pH_{iep} is 7.9 at concentration 0.001M and 8.0 for 0.0001M and 0.00001M. For systems with NaCl (Fig. 5b) 0.001M solution gives $\text{pH}_{\text{iep}}= 8.2$ whereas for 0.0001 and 0.00001M it reaches 8.0. In the case of KCl (Fig. 5c) pH_{iep} is equal to 8.2 for 0.001 and 0.0001M

solutions and 8.1 for concentration 0.00001M. The system with CsCl (Fig. 5d) pH_{iep} = 8.1 for 0.001M, 8.0 for 0.0001M and 8.2 for 0.00001M respectively. Shift of pH_{iep} connected with increase of the background electrolyte concentration is caused by specific adsorption of chloride ions on hydroxyl groups for all systems.

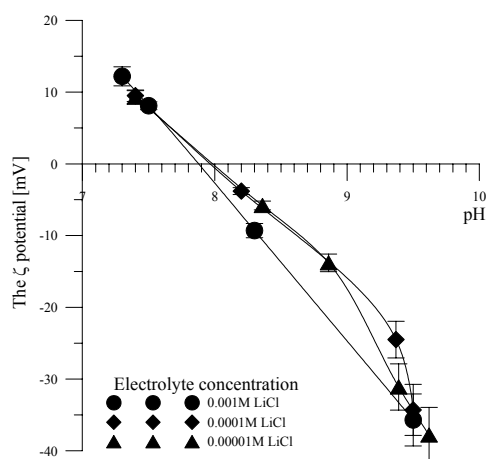


Fig. 5a. The ζ potential as a function of pH for Cu_2O in LiCl solutions

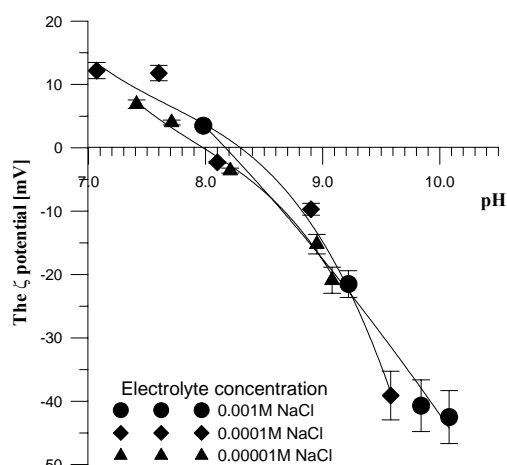


Fig. 5b. The ζ potential as a function of pH for Cu_2O in NaCl solutions

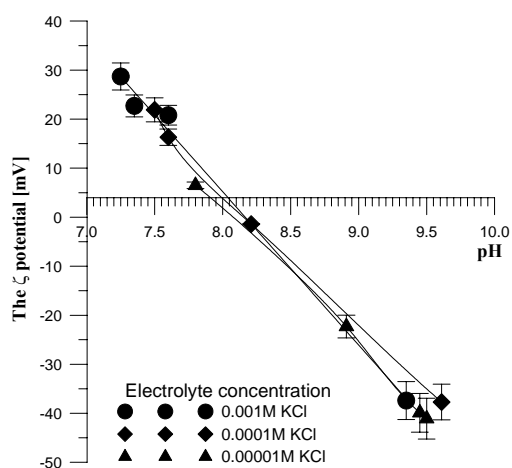


Fig. 5c. The ζ potential as a function of pH for Cu_2O in KCl solutions

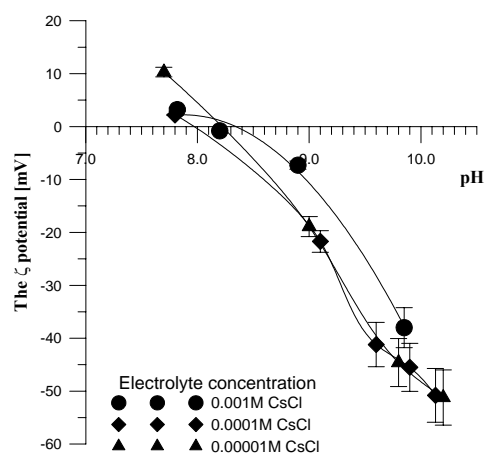


Fig. 5d. The ζ potential as a function of pH for Cu_2O in CsCl solutions

Increase of the concentration of the groups complexed by chlorides on copper oxide surface lowers concentration of ionized groups with positive charge that usually is manifested by small shift of pH_{iep} towards lower pH values. Because the

measurements were taken at low concentration of background electrolyte (to avoid CuCl formation) the lowering ζ potential value, accompanying the increase of the electrolyte concentration was not observed.

From potential zeta versus pH and background electrolyte concentration data the values of ionization constants of surface hydroxyl groups, on the surface of Cu_2O in alkali metal halides solutions were calculated following method proposed by Sprycha (Sprycha and Szczypa 1984). Obtained results are presented in Table 3.

Table. 3. Ionization constants of surface hydroxyl groups calculated according to Sprycha (Sprycha and Szczypa 1984)

Constant	Background electrolyte			
	LiCl	NaCl	KCl	CsCl
pK_{a1}	2.8	3.3	4.3	3.4
pK_{a2}	12.8	12.8	12.4	12.5

One may notice similar values for all constants connected with negatively charged group formation. Some unexpected differences, observed for the constants of positively charged groups may be connected with dissolution of the oxide and produced inaccuracy of pH measurements below pH_{iep} . Ionization constants, calculated from surface charge may differ from the ones obtained by Sprycha's method even by unit of pH.

Such big difference may arise from an error in determination of ionization and complexation constants from the surface charge and small dependence of σ_0 versus background electrolyte concentration. This weak dependence makes problems in determination of ionization and complexation constants by extrapolation acidity (complexation) quotients to electrolyte concentration.

BACKGROUND ELECTROLYTE ION ADSORPTION

Adsorption density of background electrolyte ions Li^+ , Na^+ , Cs^+ , and Cl^- is presented on Figures 6a, 6b, 6c, respectively. The adsorption of studied cations increases with pH rise that is in agreement with reaction of site binding model (Davis et al., 1978). Noticeable drop of adsorption at pH_{pzc} ($\text{pH}=8.0$) suggests that up to this value ionic exchange takes place. Li^+ adsorption (Fig. 6a) is nearly five-fold higher than Na^+ and Cs^+ ions adsorption. These last cations, as may be seen from Fig. 6b reveal the same adsorption (within error). Adsorption of Cl^- (Fig. 6c) decreases with growth of pH that is in agreement with reaction of site binding model (Davis et al. 1978). However, above pH_{iep} the adsorption of Cl^- ions do not decrease asymptotically to zero that proves specific adsorption of the anion as mentioned earlier.

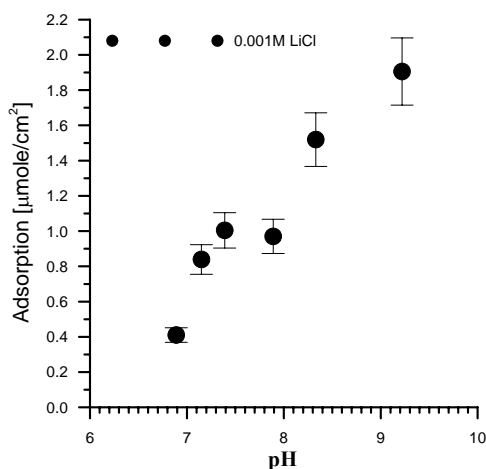


Fig. 6a. Li^+ ion adsorption as a function of pH at the $\text{Cu}_2\text{O}/0.001\text{M LiCl}$ interface

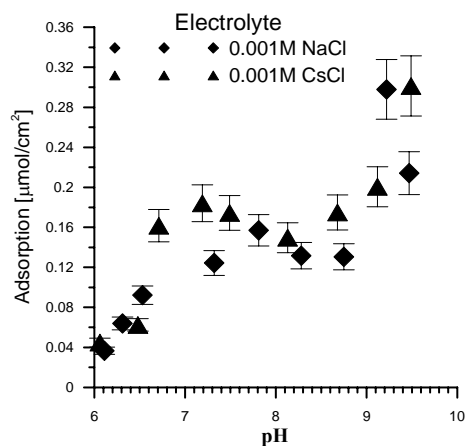


Fig. 6b. Na^+ (Cs^+) ion adsorption as a function of pH at the $\text{Cu}_2\text{O}/0.001\text{M NaCl}$ (CsCl) interface

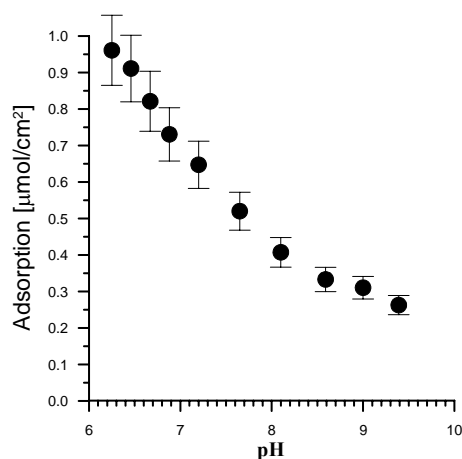


Fig. 6c. Cl^- ion adsorption as a function of pH at the $\text{Cu}_2\text{O}/0.001\text{M NaCl}$ interface

CONCLUSIONS

The study of electrical double layer structure at copper(I) oxide/aqueous solution interface of alkaline metal chlorides presented in this paper may be summarized as follows:

1. Density of the surface charge for Cu_2O in alkali metal chloride solutions changes by about $2 \mu\text{C}/\text{m}^2$ in pH 6-10 range due to dissolution of the oxide.
2. CIP was found in pH 8-8.2 range, depending on the system and agree with pH_{iep} for the same electrolyte. Position of CPI below x-axis suggests alkaline type

contamination, firmly bound to the surface that might remain after synthesis of the oxide.

3. According to calculated constants of electrolyte ions and adsorption measurements the studied cations may be arranged as follows: $\text{Li}^+ < \text{Na}^+ \approx \text{Cs}^+$ that is in agreement with Hofmeister lyotropic order.
4. In all studied systems pH_{iep} was found in pH 7.9 - 8.2 range.
5. Increase of adsorption of: Li^+ , Na^+ and Cs^+ cations below pH_{pzc} proves ion exchange in this range.
6. Adsorption density of Cl^- anions in pH_{pzc} is much higher than the adsorption density for studied cations that shifts insignificantly pH_{iep} with background electrolyte concentration change.

REFERENCES

- BLOK L., DE BRUYN P. L., (1970), *The ionic double layer at the ZnO/solution interface*, J. Colloid Interface Sci., 32, 527.
- DAVIS J. A., JAMES R.O., LECKIE J.O., (1978), *Surface Ionization and Complexation at the Oxide/Water Interface. I. Computation of Electrical Double Layer Properties in Simple Electrolytes*. J. Colloid Interface Sci., 63, 480.
- JANUSZ, W., *Electrical Double Layer in the System $\text{TiO}_2(\text{Anatase})/\text{Aqueous Solution of NaCl}$* , (1994), Polish J. Chem., 68, 1871.
- NASSAU K., GALLAGHER P.K., MILLER A.E., GRAEDEL T.E., (1987), *The characterization of patina components by X-ray diffraction and evolved gas analysis*, Corrosion Sci. 27, 669.
- POURBAIX H., (1965), *Atlas of Electrochemical Equilibria in Aqueous Solutions*, CEBELOR, Brussels, pp.385-392.
- POURBAIX M.; *Wykłady z korozji elektrochemicznej*; (1978), PWN; Warszawa.
- SELWYN L., BINNIE N.E., POITRAS J., LAVER M.E., DOWNHAM D.A, (1996), *Studies in Conservation* 1, pp. 2050-228.
- SPRYCHA R., SZCZYPA J., (1984), *Estimation of surface ionization constants from electrokinetic data*, J. Colloid Interface Sci., 102, 288.
- STANEK J., CERNY M., KOCOUREK J., PACAK J., (1963), *The Monosaccharides*, pp.180-181, Academic Press, New York.
- STRANDBERG H., *Reactions of copper patina compounds--II. Influence of sodium chloride in the presence of some air pollutants*, (1998), Atmospheric Environment, vol. 32, No.20, pp.3521-3526.
- SUROWCE MINERALNE ŚWIATA, *Miedź-Cu*, (1977), Wydawnictwa Geologiczne Warszawa

Janusz W., Galgan A., Reszka M., *Podwójna warstwa elektryczna na granicy faz tlenek miedzi(I)/wodny roztwór chlorków metali alkalicznych*, Physicochemical Problems of Mineral Processing, 40 (2006), 161-174 (w jęz. ang.).

Kupryt czyli tlenek miedzi (I) jest jednym z głównych minerałów miedzi. Występuje on również w tzw. strefie utleniania złóż zasobnych w siarczkowe minerały miedzi. Tlenek ten stosowany jest jako katalizator częściowego utlenienia niektórych alkenów, a także jest on lepszym od miedzi katalizatorem utleniania CO w związku z czym może być użyty do kontroli spalin samochodowych. Ponadto Cu_2O jest składnikiem farb do pokrywania dna statków, stosowany jest barwienia szkła i porcelany. Jako półprzewodnik, Cu_2O , jest także od kilkadziesiąt lat przedmiotem badań mających na celu wykorzystanie go w ogniwach słonecznych.

Badania przedstawione w pracy prowadzono na próbce otrzymanej przez redukcję glukoza zasadowego roztworu octanu miedzi (II). Przeprowadzono pomiary gęstości ładunku powierzchniowego metodą miareczkowania potencjometrycznego z uwzględnieniem rozpuszczalności tlenku. Metodą elektroforetyczną wyznaczono zależność potencjału zeta na granicy faz Cu_2O / roztwór elektrolitu 1:1 chlorków metali alkalicznych. Wyznaczono zależność adsorpcji jonów elektrolitu nośnego w funkcji pH. W celu uniknięcia wytrącania się CuCl pomiary prowadzono w roztworach o stężeniu nie wyższym niż 0,001M. W oparciu o zależność gęstości ładunku powierzchniowego od pH obliczono wartości stałych równowag reakcji jonizacji i kompleksowania.