

G. Horányi

Specific adsorption of anions preceding the dissolution of CuO in acidic solution

Received: 17 September 2001 / Accepted: 14 November 2001 / Published online: 19 December 2001
© Springer-Verlag 2001

Abstract The specific adsorption of sulfate and chloride ions on powdered CuO was studied by radiotracer techniques in acidified of 0.5 mol dm^{-3} NaClO₄ supporting electrolyte. It was found that the pH and concentration dependence of the adsorption of labelled sulfates could be determined over a wide pH range ($2.0 \leq \text{pH} \leq 7.0$), despite the gradual dissolution of the copper oxide. No specific adsorption was found at $\text{pH} \geq 7.0$. It was postulated that the specific adsorption was preceded by the protonation of the CuO surface. No reliable relationships were found for labelled chlorides, owing to the relatively high desorption rate of the surface complexes formed in the sorption process. The apparent adsorbability of sulfate ions was significantly higher than that of the chloride ions, as shown by the results of competitive adsorption of the two species. This observation was in agreement with the postulated lower desorption rate of the surface complex formed with sulfates than that of species formed with chlorides.

Keywords Copper oxide · Sulfate ions · Chloride ions · Adsorption · Radiotracer technique

Introduction

In a previous study [1] it was shown that the specific adsorption of sulfate ions on powdered copper oxide in concentrated strong acid solution (1 mol dm^{-3} HClO₄) can be easily demonstrated by radiotracer techniques despite the continuous dissolution of CuO. The feasibility of this type of study follows from the nature of the radiotracer technique itself, in which isotopes emitting

soft β -radiation are applied and powdered adsorbents are used. These adsorbents are sprinkled on the bottom of a cell to form a layer of a thickness exceeding that of the self-absorption of the radiation used. From the considerations outlined in previous communications [1, 2, 3] it follows that the adsorption equilibrium (or steady state) with respect to some species present in the solution phase can be maintained in the case of slow dissolution for a relatively long time.

Properties of the Cu/Cu(OH)₂/electrolyte interface could be of interest for several branches of chemistry, especially for electrochemistry (corrosion of copper, electrochemical behaviour of an oxide-covered Cu electrode) and colloid chemistry (formation of a double layer following protonation processes). The aim of the present paper is to report the results of SO₄²⁻ and Cl⁻ anion adsorption in acidic solutions carried out by means of the radiotracer technique.

Experimental

The experimental technique and set-up for the radiotracer study of sorption processes are described in previous papers [1, 2, 3, 4, 5, 6, 7]. The main principle of the method [8] used in the present study consists in the measurement of the radiation intensity originating from solution species adsorbed on a powdered oxide layer sprinkled on a thin plastic foil. This foil serves, simultaneously, as the window for radiation measurements. The measurements were carried out at ambient temperature in an argon atmosphere. The argon purge of the solution was directed through the gap between the bottom of the measuring cell and the detector. ³⁵S-labelled H₂SO₄ (Amersham, specific activity: $200 \text{ MBq mmol}^{-1}$) and ³⁶Cl-labelled HCl (Amersham, specific activity 26 MBq mmol^{-1}) were used for study of the sulfate and chloride adsorption, respectively. Generally, the amount of CuO (referred to the geometric surface area of the bottom of the cell) was $20\text{--}30 \text{ mg cm}^{-2}$. This thickness of the CuO layer can be considered as infinite with respect to the depth of propagation of the soft β -radiation of ³⁵S.

In most of the experiments, concentration of the labelled compounds was at least by one order of magnitude lower than that of the supporting electrolyte in order to determine the specific adsorption of these compounds on the oxide surface.

A commercial CuO powder (p.a., Reanal) was used. The particle size distribution of the sample used (determined by laser

G. Horányi
Institute of Chemistry, Chemical Research Center,
Hungarian Academy of Sciences,
P.O. Box 17, 1525 Budapest, Hungary
E-mail: hor34@ludens.elte.hu
Tel.: +36-1-2670820
Fax: +36-1-2663899

particle sizer "analysette 22") is shown in Fig. 1. As the aim of the present study was only to clarify the main trends of behaviour, and not to study the properties of a specific CuO, no effort was undertaken to obtain more physical data characterizing the CuO powder.

Results and discussion

pH and concentration dependence of the adsorption of sulfate ions

Similar to the earlier studies carried out with hematite and γ -Al₂O₃ [2, 3, 4, 5], the first experiments of the present work were aimed at the determination of the pH dependence of the specific adsorption of sulfate ions in order to obtain information on the pH range in which measurable adsorption occurs. These studies were performed for the 0.5 mol dm⁻³ NaClO₄ supporting electrolyte at low sulfate concentration ($c < 10^{-3}$ mol dm⁻³), as required for the determination of specific adsorption without any interference from electrostatic effects.

In a previous communication [1], it was shown that the dissolution rate of a CuO layer of 30 mg cm⁻² does not prevent specific adsorption of sulfate ions, even in the presence of 1 mol dm⁻³ HClO₄ (pH ≈ 0). Figure 2 shows how the radiation detector responds to the sulfate adsorption in a process leading to complete dissolution of the CuO layer in 1 mol dm⁻³ HClO₄. From this figure it may be seen that the maximum value of the count rate due to the sulfate ions adsorbed on the CuO layer thickness, above that of self-absorption of the radiation, remains unaltered for 3–5 minutes. Thus, reliable results can be expected at a larger layer thickness and higher pH values.

Figure 3 shows the pH dependence of the count rate versus pH curve. The shape of this curve is close to those for Fe₂O₃ and Al₂O₃ [2, 3]. This type of behaviour was interpreted in terms of the protonation of the oxide surface, characterized by an equilibrium formulated by the equation:

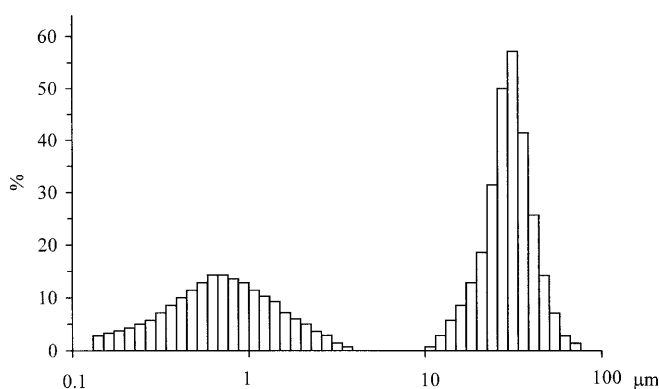


Fig. 1 Particle size distribution of the CuO sample studied

where X is a surface site. The tendency of attaining a limiting value of the surface protonation is also in accordance with the observations made with other oxides.

In the case of equilibrium:

$$k_a c_{H^+} (1 - \theta_{H^+}) - k_d \theta_{H^+} = 0 \quad (2)$$

where k_a and k_d are the rate constants of adsorption and desorption, respectively, and:

$$Kc_{H^+} = \frac{\theta_{H^+}}{(1 - \theta_{H^+})} \quad (3)$$

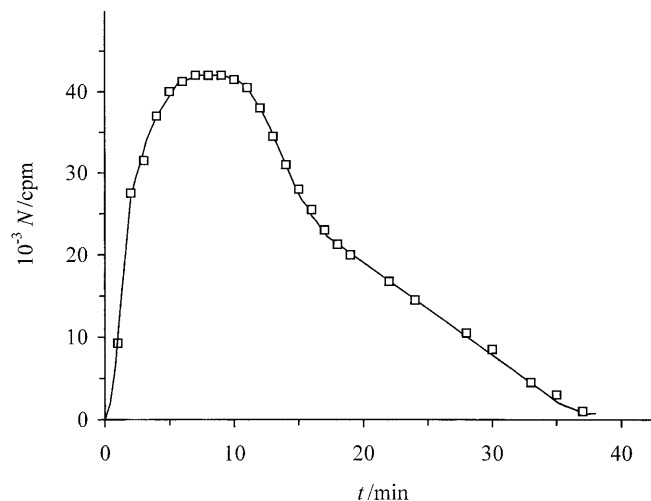


Fig. 2 Count rate (proportional to the extent of the adsorption of labelled sulfate species) versus time curves over the course of the dissolution of CuO in 1 mol dm⁻³ HClO₄. The initial amount of oxide powder referred to the projected surface area is 30 mg cm⁻²; 5×10^{-4} mol dm⁻³ H₂SO₄

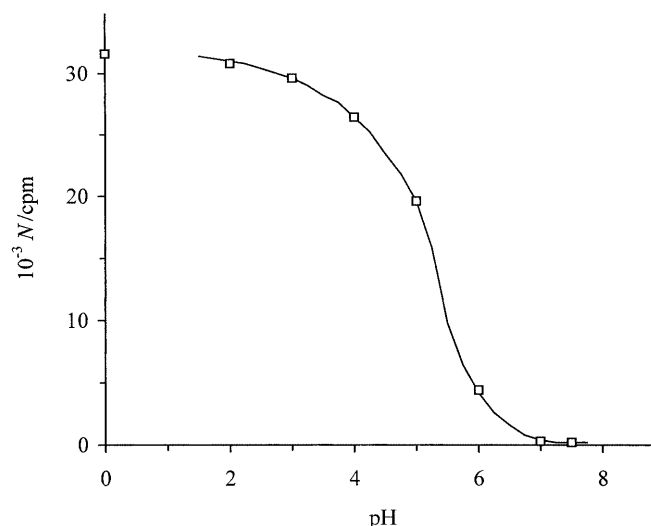


Fig. 3 pH dependence of the adsorption of labelled sulfate ions (expressed in count rate) on a CuO powder (50 mg cm⁻²); 2×10^{-4} mol dm⁻³ H₂SO₄ in 0.5 mol dm⁻³ NaClO₄ supporting electrolyte

where $K = \frac{k_a}{k_d}$ is the proton equilibrium constant and θ_{H^+} is the coverage with respect to the protonated surface sites. For:

$$\frac{\theta_{H^+}}{1 - \theta_{H^+}} = 1 \quad (4)$$

$$\log K = \text{pH} \quad (5)$$

Thus, one can estimate the value of the protonation equilibrium constant from the count rate versus pH curve (see [2, 3]). Taking into consideration the data presented in Fig. 3, one can estimate the $\log K$ value as being ca. 5.5.

The concentration dependence of the adsorption of sulfate ions (expressed in count rate) was determined at pH 5.0 in the presence of the NaClO_4 supporting electrolyte. The results obtained are presented in Fig. 4. A similarity of the behaviour of the studied system to those of other oxides is evident (Langmuir-like adsorption isotherm showing a limiting value at moderate concentrations) [2, 3]. The $1/N$ versus $1/c$ plot gives a linear relationship, advocating the Langmuir-like behaviour.

Study of the reversibility of the adsorption of sulfate ions

The ‘‘mobility’’ of the adsorbed ions is an important issue when describing the adsorption phenomena in terms of isotherms. In order to describe unambiguously the adsorption equilibrium or equilibrium states with respect to the adsorbed species, the investigation of their desorption rates is of primary importance.

The study of the exchange of labelled adsorbed sulfate ions with those non-labelled added, in a large excess, to the solution phase reveals that the adsorbed sulfate ions are loosely bound to the CuO surface. This effect is

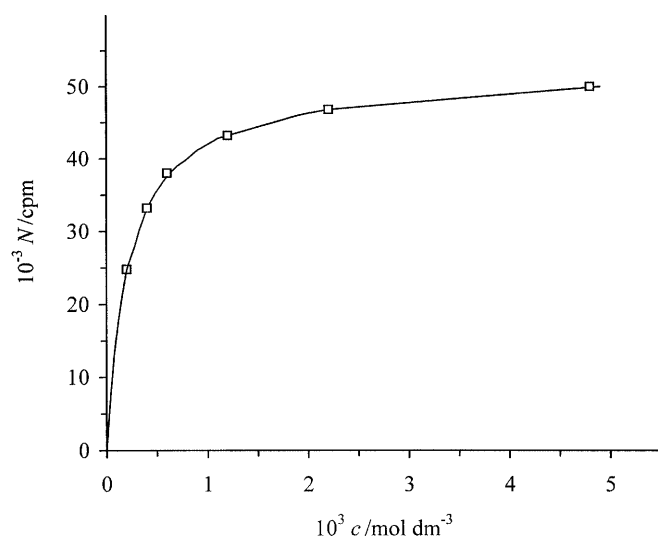


Fig. 4 Concentration dependence of the adsorption of labelled sulfate ions in $0.5 \text{ mol dm}^{-3} \text{ NaClO}_4$ at pH 5.0

demonstrated in Fig. 5. In this figure it may be seen that the addition of non-labelled SO_4^{2-} results in a rapid decrease in the count rate.

In the case of gradual isotope dilution, i.e. stepwise addition of non-labelled sulfate ions to the solution, resulting in, for instance, doubling of the total concentration of sulfate ions (Fig. 6), a new equilibrium is attained also very rapidly after the addition of each new portion of the non-labelled ions.

Studies with labelled Cl^- ions

The behaviour of Cl^- ions differs from that of the SO_4^{2-} ions. Firstly, the count rate versus time transients are ill

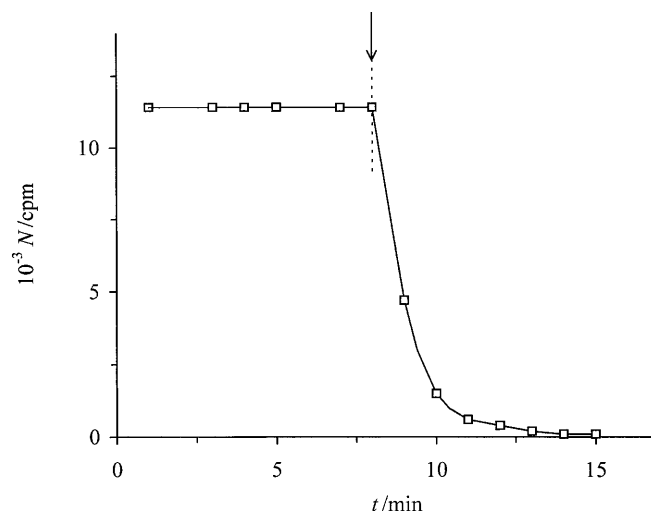


Fig. 5 Exchange of labelled adsorbed sulfate ions with non-labelled ions added to the solution in a large excess at an instant indicated by the arrow; initial and final SO_4^{2-} concentrations were 2×10^{-4} and $4 \times 10^{-2} \text{ mol dm}^{-3}$, respectively

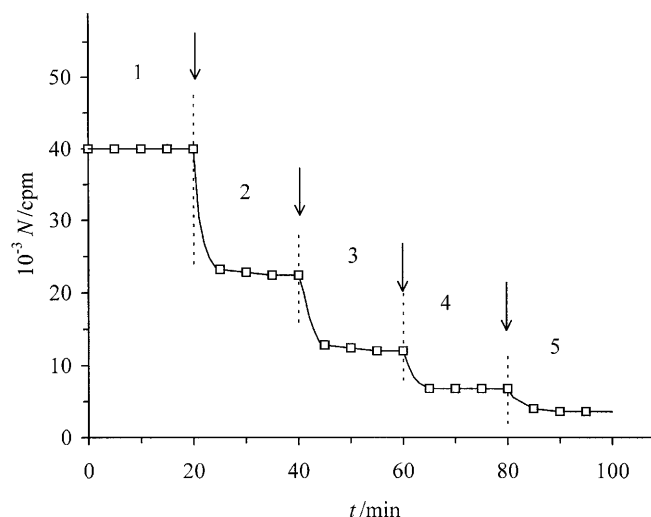


Fig. 6 Effect of isotope dilution on the count rate, starting from $6 \times 10^{-4} \text{ mol dm}^{-3}$ labelled H_2SO_4 in $0.5 \text{ mol dm}^{-3} \text{ NaClO}_4$ at pH 3.0. Sections 1, 2, 3, 4, 5 correspond to stepwise doubling of the sulfate concentration by addition of non-labelled sulfate ions

defined, presumably owing to the higher dissolution rate of CuO caused by the Cl^- ions. This effect is demonstrated in Fig. 7. In this figure it may be seen that the addition of protons (in the form of HClO_4) to a system containing labelled Cl^- ions results in a very rapid increase in the count rate, even in the case of addition of a small amount of HClO_4 (curve 1 in Fig. 7). However, this process is followed by a similarly rapid decrease of the count rate and the pH shifts to 5.0. These phenomena indicate that the specific adsorption of the anion is preceded by protonation also in the case of Cl^- ions. However, the dissolution of the protonated complexes of Cl^- is very rapid and results in a sharp peak on the radiation intensity versus time curve, in contrast to the behaviour of sulfate ions.

In the case of curve 2 in Fig. 7, the amount of HClO_4 added to the system is one order of magnitude larger than that used in the previous case. That is, the initial HClO_4 concentration corresponds to $2 \times 10^{-1} \text{ mol dm}^{-3}$. A quasi steady state is attained at a pH value of about 2.0. Further stirring up of the CuO powder results in the pH increase and, accordingly, the count rate decrease.

Considering the effects presented in Fig. 7, one is unable to determine reliably the pH or concentration dependence of the count rate owing to the adsorption of Cl^- ions on CuO, in contrast to the adsorption of SO_4^{2-} ions. The comparison of the results for these two ions, for instance in an attempt to study the pH dependence of adsorption, makes clear the difference in the behaviour of the two ions, as shown in Fig. 8.

Figure 8a shows the count rate changes due to the stepwise addition of HClO_4 to a system containing labelled sulfate. In this figure it may be seen that the count rate attains a constant value in each section,

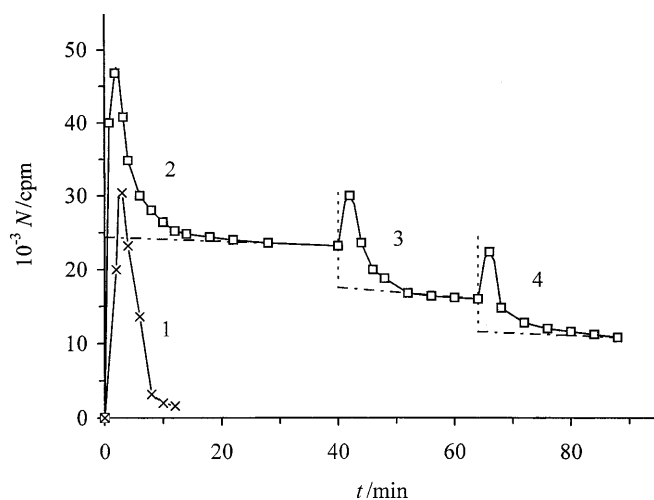


Fig. 7 Radiation intensity versus time curves recorded after addition of HClO_4 to a system which was $1 \times 10^{-4} \text{ mol dm}^{-3}$ in labelled Cl^- ions, 0.5 mol dm^{-3} in NaClO_4 and was in contact with a thick (65 mg cm^{-2}) CuO powder layer. Total volume: 25 ml; total amount of CuO: 10 mmol. (1) Addition of 0.5 ml of 1 mol dm^{-3} HClO_4 (0.5 mmol); initial $\text{pH} \approx 2.0$; final $\text{pH} 5.0$; (2) addition of 0.5 ml of 10 mol dm^{-3} HClO_4 (5 mmol); final $\text{pH} 2.0$; (3) and (4) transients following the stirring up of the powder

indicating that an equilibrium or a quasi-equilibrium (steady) state is attained with respect to the adsorption of sulfate ions.

In contrast to the behaviour of the SO_4^{2-} , Fig. 8b shows that a similar experiment does not lead to unambiguous results in the case of Cl^- ions. The adsorbability (adsorption strength) of sulfate ions is higher than that of Cl^- ions. Thus sulfate ions should exert a significant influence on the adsorption of Cl^- ions in a solution containing both Cl^- and SO_4^{2-} . This effect is shown in Fig. 9. Besides, it may be seen in Fig. 10 that Cl^- ions affect the sulfate adsorption only for high Cl^- to SO_4^{2-} concentration ratios.

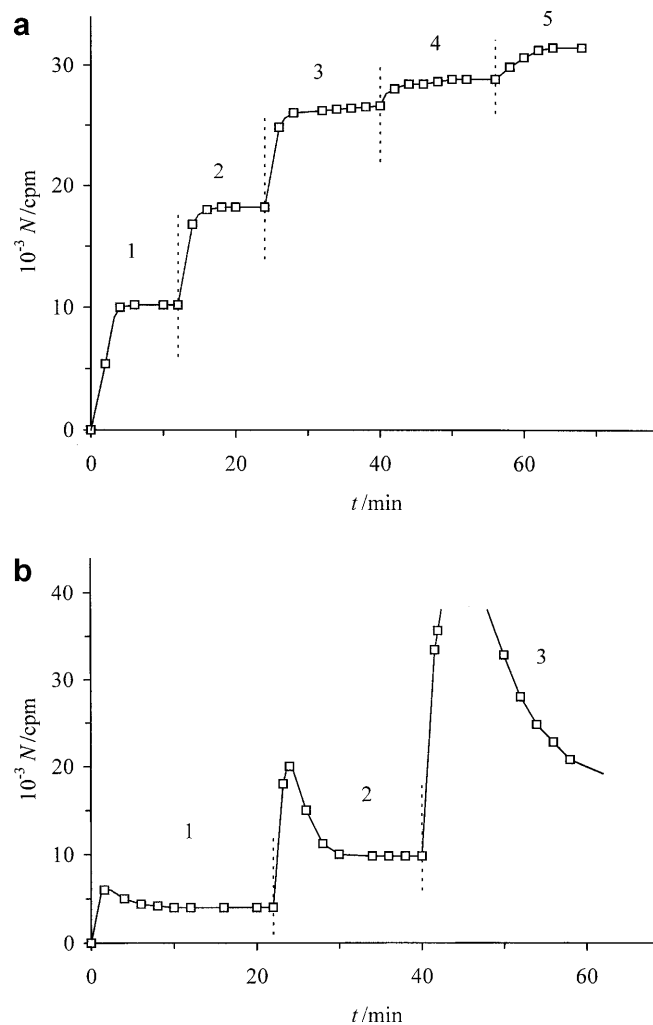


Fig. 8 a Count rate versus time curve recorded after the addition of labelled H_2SO_4 and HClO_4 to a $\text{CuO}/0.5 \text{ mol dm}^{-3} \text{ NaClO}_4$ solution system (volume 25 ml, 5 mg cm^{-2} CuO). Addition of (1) $1 \times 10^{-4} \text{ mol dm}^{-3}$ labelled H_2SO_4 to final $\text{pH} 5.5$; (2) $1 \times 10^{-3} \text{ mol dm}^{-3}$ HClO_4 to final $\text{pH} 5.25$; (3) $4 \times 10^{-3} \text{ mol dm}^{-3}$ HClO_4 to final $\text{pH} 5.0$; (4) $1 \times 10^{-2} \text{ mol dm}^{-3}$ HClO_4 to final $\text{pH} 4.0$; (5) $4 \times 10^{-2} \text{ mol dm}^{-3}$ HClO_4 to final $\text{pH} 2.0$. **b** Count rate versus time curve recorded after addition of HClO_4 to the solution which was 0.5 mol dm^{-3} in NaClO_4 , $1 \times 10^{-4} \text{ mol dm}^{-3}$ in labelled Cl^- ions and was in contact with a CuO powder. Initial $\text{pH} 6.0$. Addition of (1) $1 \times 10^{-3} \text{ mol dm}^{-3}$ HClO_4 to final $\text{pH} 5.0$; (2) $4 \times 10^{-3} \text{ mol dm}^{-3}$ HClO_4 to final $\text{pH} 4.5$; (3) $4 \times 10^{-2} \text{ mol dm}^{-3}$ HClO_4 to final $\text{pH} 1.5$

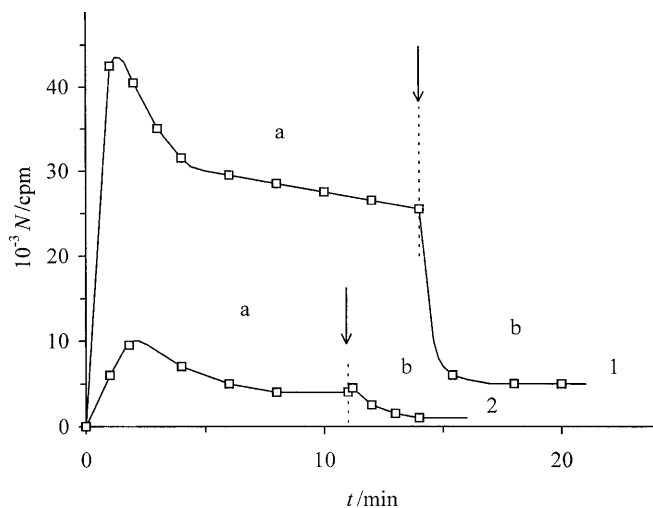


Fig. 9 Effect of sulfate ions on the adsorption of Cl^- ions. *Curve 1.* (a) Count rate versus time curve recorded after addition of $4 \times 10^{-3} \text{ mol dm}^{-3}$ HClO_4 to the solution which was 0.5 mol dm^{-3} in NaClO_4 , $1 \times 10^{-4} \text{ mol dm}^{-3}$ in labelled Cl^- and was in contact with CuO . (b) Addition of $1 \times 10^{-3} \text{ mol dm}^{-3}$ non-labelled H_2SO_4 . *Curve 2.* (a) Same procedure as in the case of (a) of curve 1 but the solution was $1 \times 10^{-3} \text{ mol dm}^{-3}$ in non-labelled sulfate. (b) Addition of $1 \times 10^{-2} \text{ mol dm}^{-3}$ non-labelled sulfate

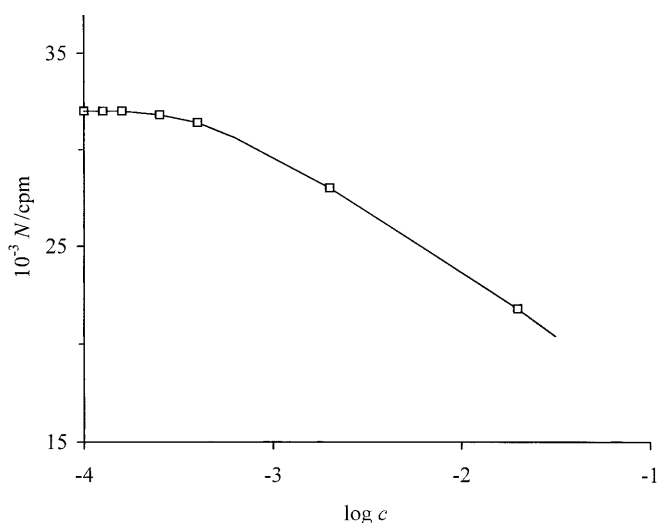


Fig. 10 Effect of the Cl^- ion concentration on the adsorption of labelled sulfate ions ($1 \times 10^{-4} \text{ mol dm}^{-3}$ labelled sulfate in 0.5 mol dm^{-3} NaClO_4 ; pH 4.0)

Conclusions

The dissolution of the CuO powder in acidic solution is influenced by two fundamental processes occurring on the copper oxide surface. The first one is the protonation of the oxide surface, as described by Eq. 1. The second process is the specific adsorption of anions present in the solution. It was postulated that the positive charge of the protonated CuO surface is compensated by the anion involved in a complexation reaction on the oxide surface. These two processes are followed by the desorption of the complex containing both the copper ion and the anion. The shapes of the count rate versus time curves for chloride ions (curves going through a maximum) strongly support this postulate, as the dissolution of CuO is accompanied by a significant decrease of the anion adsorption induced by the protonation.

The pattern of competitive adsorption of Cl^- and SO_4^{2-} is also in agreement with the mechanism proposed above. The smaller adsorbability of Cl^- ions could be due to the higher desorption rate of the surface complexes containing Cl^- . In the presence of sulfate ions, the adsorption of Cl^- ions is partially blocked owing to the significant adsorbability of these ions. Therefore the formation of surface complexes containing Cl^- is inhibited.

Acknowledgements Financial support from the Hungarian Scientific Research Fund is acknowledged (OTKA grants T 023056, T 031703).

References

1. Joó P, Horányi G (2000) *J Colloid Interface Sci* 223:308
2. Horányi G, Joó P (2000) *J Colloid Interface Sci* 227:206
3. Horányi G, Joó P (2000) *J Colloid Interface Sci* 231:373
4. Horányi G, Joó P (2001) *J Colloid Interface Sci* 243:46
5. Horányi G, Joó P (2000) *Russ J Electrochem* 36:1189
6. Horányi G, Joó P (2001) *Prog Colloid Polym Sci* 117:27
7. Kálmán E, Horányi G (2002) *J Solid State Electrochem* (in press) DOI 10.1007/s100080100220
8. Horányi G (1999) In: Wieckowski A (ed) *Interfacial electrochemistry: theory, experiment, and applications*. Dekker, New York, p 477