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Measurement of surface potential at silver chloride aqueous interface with single-crystal AgCl electrode

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ABSTRACT

The surface potential at the silver chloride aqueous interface was measured by means of a single-crystal silver chloride electrode (SCr-AgCl). The measurements were conducted by titration of the KCl solution with $AgNO_3$, and vice versa. The SCr-AgCl electrode potentials were converted to surface potentials ψ_0 by setting zero at the point of zero charge at pCl = 5.2. The ψ_0(pCl) function was linear, with a slope 12% lower with respect to the Nernst equation. It was demonstrated that the surface potential at the silver halide aqueous interface could be interpreted by means of the surface complexation model, originally developed for metal oxides.

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1. Introduction

The surface potential at the silver halide aqueous interface is believed to obey the Nernst equation with respect to the activities of the potential-determining halide and silver ions [1], at least in the zero charge region [2]. For a metal oxide aqueous interface the potential-determining ions are hydronium and hydroxide ions. According to the common surface complexation model (SCM) [3–6], surface potentials for metal oxides are lower than the Nernstian potentials [2,7–9]. Metal electrodes covered with sparingly soluble crystalline particles exhibit Nernstian behavior. Owing to a porous crystalline layer, their potential is determined by the redox equilibrium at the metal surface and is influenced by the solubility of the salt [10]. To avoid a direct contact of the electrolyte solution with the metal surface, and to measure the surface potential, ion-sensitive field-effect transistors (ISFET) [11–14] and single-crystal electrodes [15–20] have been introduced. The measurements with metal oxides [16–20], and also with ice [15], have shown the surface potential to be lower than the Nernstian potential, thus supporting the predictions based on the SCM [3–6]. With a single crystal of silver chloride available, one can construct a single-crystal silver chloride electrode (SCr-AgCl) and examine experimentally the dependence of the surface potential at the silver chloride aqueous interface on the composition of the solution. This work aims at presenting the construction of a SCr-AgCl electrode, examining its equilibration and reproducibility, and assessing surface potentials from electrode potentials. It also aims at demonstrating the dependence of the surface potential on the activities of chloride and silver ions.

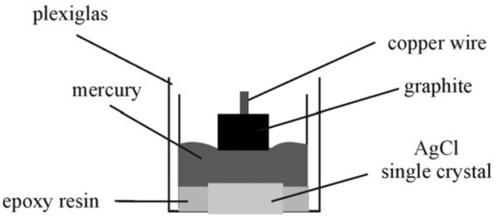

Fig. 1. Single-crystal AgCl electrode.

2. Single-crystal silver chloride electrode

The SCr-AgCl electrode (Fig. 1) consisted of a Plexiglas body with a single crystal of silver chloride mounted at its end and sealed with epoxy resin. The crystal was almost rectangular 10 × 10 mm, with a thickness of 4 mm. Internal electric contact was ensured by mercury into which a graphite rod was immersed. A copper wire was connected to the graphite rod. Fig. 1 is a schematic presentation of the SCr-AgCl electrode.

In order to examine a possible effect of epoxy resin a separate “epoxy resin electrode” was constructed, and as no response was obtained, the electric resistance of the resin was taken to be sufficiently high.

The electric resistance of silver chloride was measured directly. Contacts on both sides were ensured by mercury. The resistance of the SCr-AgCl electrode in this work was approximately 20 MΩ and was markedly lower than that of the glass electrode ($\sim 10^{12}\,\Omega$). The internal resistance of the pH-meter was therefore sufficiently

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high to ensure a reversible condition, i.e., absence of drop in the potential due to the passage of the current through the electrode.

3. Surface potential

There are several potential differences in the measuring circuit. In addition to the potentials at the reference electrode, there are contact potentials at the copper/graphite, graphite/mercury, and mercury/silver chloride interfaces, as well as at the potential difference at the silver chloride aqueous interface. The last one is due to the adsorption (binding) of chloride and silver ions on the silver chloride surface. This is the (inner) surface potential, Ψ_0. According to the general model of electrical interfacial layer, Ψ_0 is defined as the difference in the electrostatic potential of the solid surface and the bulk of the solution [21,22]. The first potential drop within the interfacial layer is from Ψ_0 to Ψ_β, i.e., from the surface 0-plane to the β-plane where the associated counterions are located. From that plane the potential gradually decreases as described by the Gouy–Chapman theory [1].

The measured value of the electrode potential E is the sum of all potential differences in the circuit. As the only potential difference that depends on the activity of the potential-determining ions is the surface potential Ψ_0, and since all other potential differences E_T are constant, one can calculate Ψ_0 from

$$\Psi_0 = E - E_T. \tag{1}$$

The value of E_T being constant it suffices to perform calibration under one condition only. For that purpose the value of the electrode potential at the point of zero potential E_{pzp}, where $\Psi_0 = 0$, can be used. Accordingly,

$$\Psi_0 = E - E_{\text{pzp}}. \tag{2}$$

In the absence of specific adsorption, at low neutral electrolyte concentration, the point of zero potential (p.z.p.) corresponds to the point of zero charge (p.z.c.) and to the isoelectric point (i.e.p.) [20,23,24]. At higher electrolyte concentrations, if cations and anions exhibit different affinities for association with the oppositely charged surface groups, the i.e.p. and p.z.c. do not coincide. The analysis [20] based on the SCM has shown that in that case the point of zero potential lies between the two points, but is close to the point of zero charge. Therefore, the p.z.c. data may be used for evaluating the surface potential from the measured values of the single-crystal electrode potentials. A possible error would affect the value of the surface potential, but not the slope of the function, e.g., $\Psi_0(\text{pCl})$ in the case of silver chloride.

4. Method

Potassium chloride aqueous solution was titrated with silver nitrate aqueous solution, and vice versa. The temperature was 25.0 °C. The ionic strength was controlled by sodium nitrate. Surface potentials were measured by means of a SCr-AgCl electrode, whereas the activities of silver and chloride ions were determined with an Ag/AgCl electrode, i.e., a silver wire covered with silver chloride microcrystals. A pH-meter (Metrohm 713) was used with the former, and a multimeter (HP3457A) with the latter electrode. In both cases the reference electrode was an Ag/AgCl/Cl$^-$ electrode filled with 3 $\text{mol}\,\text{dm}^{-3}$ KCl solution and equipped with a salt bridge (Metrohm, 6.0729.100) filled with the same electrolyte solution as the measuring system.

The SCr-AgCl electrode was tested in the solution containing 10^{-3} $\text{mol}\,\text{dm}^{-3}$ KCl and 10^{-2} $\text{mol}\,\text{dm}^{-3}$ $NaNO_3$ in the following manner. At first, the electrode potential of the SCr-AgCl electrode (vs reference electrode) was measured as 108.8 mV. Then, an additional source of potential was introduced (serial connection), so that the measuring circuit was SCr-AgCl electrode–external source of the potential difference–pH-meter–reference electrode–electrolyte solution. Then, the potential difference of the introduced source of potential difference was changed. The introduction of an additional 246.0 mV into the circuit resulted in a reading of pH-meter of 354.7 mV. A subsequent change of polarity and introduction of −402.7 mV gave a potential value of −294.0 mV. In this experiment the current was increased and also reversed. With all introduced potential differences taken into account, the SCr-AgCl electrode potential always turned out to have an almost identical value (108.8 ± 0.1 mV). The measurements suggested that the surface reactions were reversible and that the interfacial equilibrium condition was satisfied.

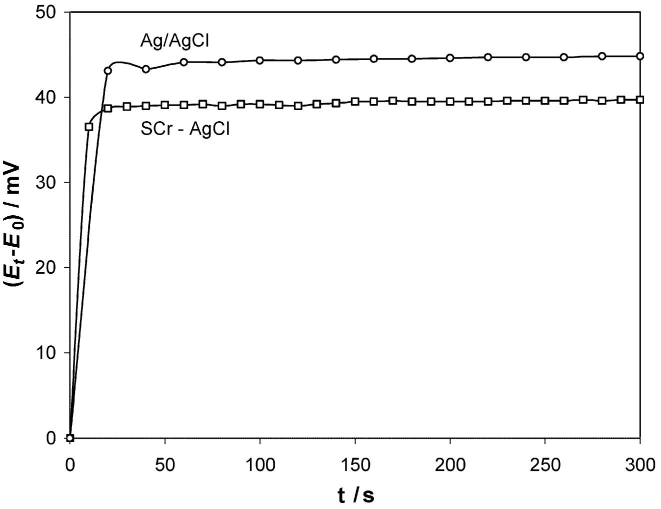

Fig. 2. Response of SCr-AgCl electrode (□) and Ag/AgCl electrode (○) vs Ag/AgCl reference electrode, after addition of $AgNO_3$ into KCl solution, as a function of time at 25.0 °C.

The electrode response was tested by addition of a certain amount of $AgNO_3$ to the KCl solution, so that the concentration of chloride ions decreased, and that of silver ions increased. The change of the potential of the SCr-AgCl and Ag/AgCl electrodes with time is presented in Fig. 2.

Evidently, the equilibration rate of the SCr-AgCl electrode was high and comparable to that of the Ag/AgCl electrode. It was concluded that the equilibration time of the system was 2 min after the addition of the reactant. Fig. 2 also shows that the potential change of the SCr-AgCl electrode was 12% lower than the one for the Ag/AgCl electrode. Since a commonly prepared Ag/AgCl electrode follows the Nernst equation, and the SCr-AgCl electrode exhibited a lower response, one may conclude that the surface potential at the silver chloride aqueous interface did not obey the Nernst equation.

5. Results

Fig. 3 shows the dependence of the SCr-AgCl and Ag/AgCl electrode potentials on the activity of chloride ions in the solution calculated from their concentrations, using the Debye–Hückel activity coefficient γ and the equilibrium constant of AgCl dissolution [25] $\lg K_s^\circ = -9.75$. As expected, the slope of the Ag/AgCl electrode potential was almost Nernstian, i.e., 59.2 mV. However, the slope of the SCr-AgCl electrode potential was significantly lower, i.e., 52.3 mV. The reversibility was tested by backtitration, and as seen from Fig. 3, an appreciable agreement was obtained.

The measured Ag/AgCl electrode potentials were used for calibration and thus for determining the chloride-ion activities. Fig. 4 shows the measured dependence of the surface potential Ψ_0 on the activity of chloride ions as determined by the Ag/AgCl electrode; $\text{pCl} = -\lg a(\text{Cl}^-)$. Surface potentials of silver chloride were calcu-

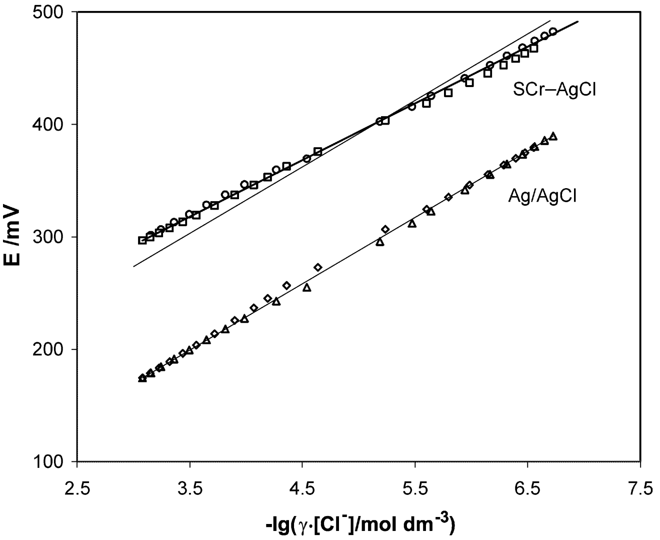

Fig. 3. Electrode potential of a single-crystal AgCl electrode (○, □) and Ag/AgCl electrode (△, ◇) vs Ag/AgCl reference electrode as a function of the chloride ion activity at 25.0 °C. Titration with KCl (○, △), and backtitration with $AgNO_3$ (□, ◇) are shown, $c(\mathrm{NaNO_3}) = 10^{-2}\ \mathrm{mol\,dm^{-3}}$. Dashed lines mark the Nernstian slope. Equilibration time: ~2 min.

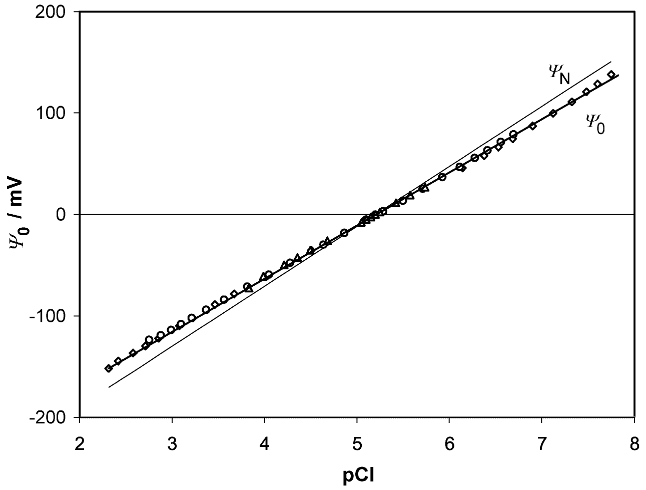

Fig. 4. Surface potential at the silver chloride aqueous interface as a function of the chloride ion activity at 25.0 °C. The ionic strength was controlled with $NaNO_3$; $c/\mathrm{mol\,dm^{-3}} = 10^{-3}$ (△), 10^{-2} (○), and 10^{-1} (◇). Full line of the slope of 52.3 mV was drawn through the experimental points, while dashed line marks the Nernstian slope (ψ_N).

lated from the SCr-AgCl electrode potentials by means of Eq. (2) using the literature data [26,27] for the point of zero charge $\mathrm{pCl_{pzc}} = 5.2$. The experiments were performed at ionic strengths of 10^{-3}, 10^{-2}, and 10^{-1} $\mathrm{mol\,dm^{-3}}$. The results obtained by titrating KCl with $AgNO_3$ agreed with those of backtitrations with KCl. The surface potential of silver chloride was a linear function of the logarithm of the activity of the potential-determining ions with a slope of 52.3 mV, which was 12% lower than the one predicted by the Nernst equation. It should be noted that the slope did not depend on the ionic strength.

6. Discussion

To understand the results of the study, i.e., the finding that the surface potential is lower than the Nernstian potential we shall analyze surface equilibrium by using the surface complexation model [6] and also applying a thermodynamic approach based on the exchange of potential-determining ions between interfacial layer and the bulk of the solution.

The surface complexation model may be adapted for the silver chloride aqueous interface as follows. It is known [28] that silver and chloride ions form several complexes in the bulk of the solution, such as $\mathrm{AgCl_4^{3-}}$, $\mathrm{AgCl_3^{2-}}$, $\mathrm{AgCl_2^{-}}$, AgCl, $\mathrm{Ag_2Cl^{+}}$, and $\mathrm{Ag_3Cl^{2+}}$, so that one may expect that at the silver chloride aqueous interface chloride ions bind to the silver sites incorporated in the crystal lattice (≡Ag), while silver ions are bound to the surface chloride sites (≡Cl)

$$\equiv\mathrm{Ag} + \mathrm{Cl}^- \rightarrow \equiv\mathrm{AgCl}^-;\quad K_n^\circ, \tag{3}$$

$$\equiv\mathrm{Cl} + \mathrm{Ag}^+ \rightarrow \equiv\mathrm{ClAg}^+;\quad K_p^\circ. \tag{4}$$

The extent of the reactions and the net surface charge depend on the activities of the chloride and silver ions present in the bulk of the solution. According to the SCM, the corresponding thermodynamic equilibrium constants are defined as

$$K_n^\circ = \exp(-F\psi_0/RT)\frac{\{\equiv\mathrm{AgCl}^-\}}{\{\equiv\mathrm{Ag}\}a_{\mathrm{Cl}^-}}, \tag{5}$$

$$\begin{aligned} K_p^\circ &= \exp(F\psi_0/RT)\frac{\{\equiv\mathrm{ClAg}^+\}}{\{\equiv\mathrm{Cl}\}a_{\mathrm{Ag}^+}} \\ &= \exp(F\psi_0/RT)\frac{\{\equiv\mathrm{ClAg}^+\}a_{\mathrm{Cl}^-}}{\{\equiv\mathrm{Cl}\}K_s^\circ}, \end{aligned} \tag{6}$$

where curly braces denote surface concentrations of relevant species. According to Eqs. (5) and (6), the surface potential is equal to

$$\psi_0 = \frac{RT}{2F}\ln\frac{K_p^\circ K_s^\circ}{K_n^\circ} + \frac{RT}{2F}\ln\frac{\{\equiv\mathrm{AgCl}^-\}\{\equiv\mathrm{Cl}\}}{\{\equiv\mathrm{ClAg}^+\}\{\equiv\mathrm{Ag}\}} - \frac{RT}{F}\ln a_{\mathrm{Cl}^-}. \tag{7}$$

By introducing the point of zero potential one obtains

$$\psi_0 = \frac{RT}{2F}\ln\frac{\{\equiv\mathrm{AgCl}^-\}\{\equiv\mathrm{Cl}\}}{\{\equiv\mathrm{ClAg}^+\}\{\equiv\mathrm{Ag}\}} + \frac{RT\ln 10}{F}(\mathrm{pCl} - \mathrm{pCl_{pzp}}). \tag{8}$$

The last term in the r.h.s. of Eq. (8) is Nernstian, while the first is responsible for deviation from the Nernst equation.

For example, as the activity of Cl^- ions increases (pCl value decreases) more Cl^- ions and less Ag^+ ions are adsorbed (activity of Ag^+ ions decreases). Consequently, the surface concentration of $\equiv\mathrm{AgCl}^-$ sites increases and of $\equiv\mathrm{ClAg}^+$ decreases so that the value of the first term in the r.h.s. of Eq. (8) becomes more positive (or less negative) reducing the negative value due to the second Nernstian term. According to the results presented in Fig. 4, the surface potential was found to be (approximately) a linear function of pCl with the slope lower with respect to the Nernst equation. The linearity of the surface potential function suggests that the first term in Eq. (8) varies linearly with pCl. This is a useful finding which may be helpful in elucidation of the interfacial equilibrium at the AgCl aqueous interface. According to results presented in Fig. 4, the slope of the surface potential function is approximately the same for the ionic strengths of 10^{-3}, 10^{-2}, and 10^{-1} $\mathrm{mol\,dm^{-3}}$. To explain this finding one should perform complete interpretation of the interfacial equilibrium. The association of counterions with the oppositely charged surface groups should also be considered. It affects the surface potential indirectly through occupation of active surface sites. The degree of association depends on the counterion affinity for association and is higher at higher ionic strengths. The analysis based on the surface complexation model shows that the interfacial counterion association could affect the surface potential, but the opposite was also found to be possible [16], depending on the interfacial equilibrium parameters.

Accumulation of the potential-determining ions at interface may also be considered in terms of their distribution between two phases. For example, if one considers the distribution of chloride ions between the interface (int) and in the bulk of the solution, equating of corresponding chemical potentials μ will lead to

$$\mu^{\circ}_{\mathrm{int}}(\mathrm{Cl}^-) - F\Psi_0 + RT\ln x_{\mathrm{int}}(\mathrm{Cl}^-) = \mu^{\circ}_{\mathrm{aq}}(\mathrm{Cl}^-) + RT\ln a(\mathrm{Cl}^-). \qquad (9)$$

At approximately a constant amount (mole) fraction of Cl^- ions at the surface, $x_{\mathrm{int}}(\mathrm{Cl}^-)$, Eq. (9) leads to the surface potential equivalent to the Nernst potential. However, since $x_{\mathrm{int}}(\mathrm{Cl}^-)$ increases with $a(\mathrm{Cl}^-)$, the slope will be reduced, which may be in principle negligible. Such an approach requires consideration of the simultaneous process, i.e., the distribution of silver ions, and the definition of the equilibrium state based on the minimum of the Gibbs function.

7. Conclusion

As expected on the basis of the surface complexation model, the measured surface potential at the silver chloride aqueous interface is lower than the one predicted by the Nernst equation. The slope reduction of 12% is significant. It may be concluded that the measurements of surface potential with the single-crystal electrode provide useful data for better understanding the equilibria at silver halide aqueous interfaces.

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