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Charging of water at inert and hydrophobic surfaces. Effect on interfacial properties of silver halides

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Abstract Isoelectric point of silver halides depends on pH due to charging of interfacial water layer. The isoelectric point of water at inert and hydrophobic surfaces lies at $\mathrm{pH} \approx 3$ so that water at surfaces is negatively charged in the pH region above 4. Consequently the electroneutrality point of silver halides $\mathrm{pAg}_{\mathrm{eln}}$ in aqueous environment, with respect to adsorption of silver and halide ions, does not correspond to the isoelectric point $\mathrm{pAg}_{\mathrm{iep}}$ measured at $\mathrm{pH} \approx 6$, as previously assumed. The effect of assumed value of $\mathrm{pAg}_{\mathrm{iep}}$ was examined. The equilibrium constants for adsorption of silver and halide ions on silver chloride and silver bromide were calculated for the range of assumed $\mathrm{pAg}_{\mathrm{iep}}$ values ranging from isoelectric points measured at $\mathrm{pH} = 6$ to $\mathrm{pH} = 3$. The values of $\mathrm{pAg}_{\mathrm{iep}}$ obtained at $\mathrm{pH} = 3$ was taken as $\mathrm{pAg}_{\mathrm{eln}}$ and the corresponding equilibrium constants of interfacial reactions were obtained.

Keywords Single crystal electrode · Silver chloride · Silver bromide · Surface potential · Electrical interfacial layer · Equilibrium parameters · Interfacial water layer

1 Introduction

Electrokinetic measurements of gas bubbles (argon or nitrogen) in aqueous electrolyte solution show negative surface charge (charge of electrokinetic stagnant interfacial water layer) in the broad pH region above 4, and positive charge in the pH region below 3 (Takahashi 2005; Yang et al. 2001; Najafi et al. 2007). This finding was interpreted as preferential accumulation of OH^- ions at the surface, with respect to H^+ ions (Lützenkirchen et al. 2008). Similar findings were observed with other inert (hydrophobic) materials, such as hydrocarbon oils (Beattie and Djerdjev 2004; Marinova et al. 1996), Teflon (Preočanin et al. 2011), ice (Kallay et al. 2003), diamond (Härtl et al. 2007; Horinek et al. 2007), *etc*. Electrokinetic potentials of gas bubbles and other "inert" surfaces were recently reviewed by Healy and Fuerstenau (2007) and by Kosmulski (2012). Summary of electrokinetic literature data are presented in Fig. 1.

According to results obtained for inert aqueous interfaces, one may assume that water layer at any, especially inert hydrophobic surfaces, exhibits special structure and properties being charged depending on pH. Properties of hydrophobic silver halides were examined by measuring surface potential by means of single crystal electrodes and the interfacial equilibrium parameters were evaluated (Kallay et al. 2008; Preočanin et al. 2009, 2010a, 2010b, 2011). Recently, it was observed that interfacial water influences interfacial equilibrium of hydrophobic silver halides, directly (hydration of ionic species and permittivity) but also trough additional pH dependent electric field (Kallay et al. 2012). Electrokinetic behavior is result of a net charge of particle surface and of the thin water layer (stagnant layer). In electrophoresis the stagnant water layer moves together with particles. Consequently, the electrokinetics (charge, mobility and potential) is a measure of both surface charge and the charge of the interfacial water layer. Thus, electrokinetic experiments are suitable tool to study effect of charging of the interfacial water layer on interfacial properties of colloids (Hunter 1981). In the case of metal oxides, metal hydroxides, and most of the organic materials, potential determining ions are H^+ and OH^- ions so that surface charge depends on pH (Stumm et al. 1970;

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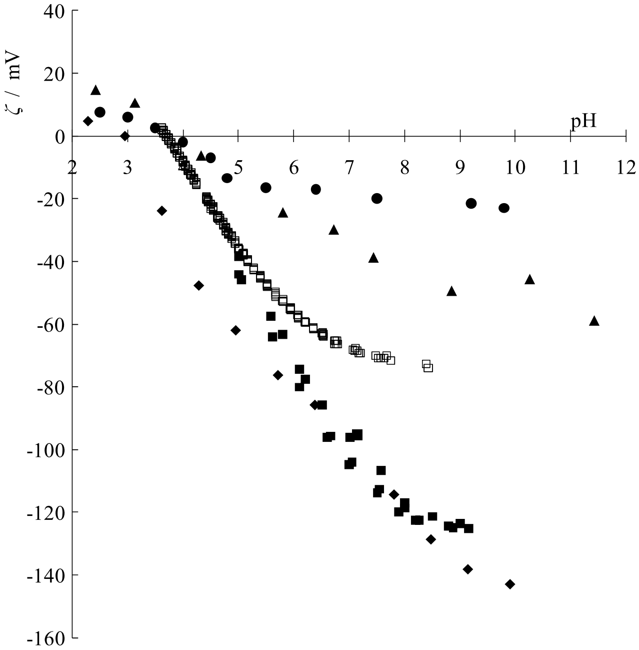

Fig. 1 Electrokinetic data for different aqueous systems: air (▲, $c(\mathrm{NaCl}) = 10^{-3}$ mol dm^{-3}, Yang et al. 2001), ice (●, $c(\mathrm{NaNO_3}) = 10^{-3}$ mol dm^{-3}, Kallay et al. 2003), diamond (◆, $c(\mathrm{KCl}) = 10^{-3}$ mol dm^{-3}, Härtl et al. 2007), oil (■, $c(\mathrm{NaCl}) = 4 \times 10^{-4}$ mol dm^{-3}, Beattie and Djerdjev 2004), Teflon (□, $c(\mathrm{KCl}) = 10^{-3}$ mol dm^{-3}, Preočanin et al. 2011)

Yates et al. 1974). The charge of interfacial water is also pH dependent so that one cannot simply separate these processes, *i.e.* binding or release of $\mathrm{H^+}$ and $\mathrm{OH^-}$ ions on/from active surface sites from accumulation of these ions within thin layer of water at the surface. For metal oxides both electrokinetic data and surface charge data, as measured by pH titration of colloids or mass titration, will show cumulative effect (Lützenkirchen et al. 2010). To distinguish between surface reactions and accumulation of $\mathrm{H^+}$ and/or $\mathrm{OH^-}$ ions within the interfacial water layer one would need to examine systems for which potential determining ions, being involved in surface reactions, are not $\mathrm{H^+}$ and $\mathrm{OH^-}$ ions. For this purpose suitable systems are silver halides. For example, silver chloride is charged due to interactions of the surface sites with $\mathrm{Ag^+}$ and $\mathrm{Cl^-}$ ions, while interfacial water is charged due to unsymmetrical distribution of $\mathrm{H^+}$ and $\mathrm{OH^-}$ ions between interfacial layer and bulk of the solution (Kallay et al. 2008). Silver halides are considered as hydrophobic systems (Lyklema 1995) which means that water is not bound to the surface so that it probably behaves similar as in contact with inert surfaces. The only restriction in experiments involving silver halides is that one should avoid pH region in which $\mathrm{Ag^+}$ ions undergo hydrolysis, *i.e.* basic pH region. As expected, surface potential measured by single crystal silver halide electrodes (Kallay et al. 2012) does not depend on pH, since according to the Surface Complexation Model (SCM) surface potential, *i.e.* electrostatic potential at the solid surface, should be determined by activities of potential determining silver and halide ions (Kallay et al. 2008; Preočanin et al. 2009, 2010a, 2010b, 2011). The situation with electrokinetic properties is somehow different since it involves both surface and the interfacial water. Electrokinetic potential is determined by activities of silver and halide ions, but also by activities of $\mathrm{H^+}$ and $\mathrm{OH^-}$ ions. For example, at $\mathrm{pH} = 6$ interfacial water is negatively charged which means that electrokinetic potential is more negative (or less positive) with respect to the electrokinetic potential of the system with uncharged interfacial water (*i.e.* at $\mathrm{pH} \approx 3$). This effect would result in the shift of isoelectric point to higher $\mathrm{pAg_{iep}}$ values in the acidic region. The shift, expressed as $\Delta\mathrm{pAg_{iep}} = \mathrm{pAg_{iep}(pH3)} - \mathrm{pAg_{iep}(pH6)}$, was found to lie between 0.5 and 1, depending on the type of silver halide and the ionic strength (Kallay et al. 2012). According to the above hypothesis, the mass titration, performed by addition of solid powder to aqueous electrolyte initially at *e.g.* $\mathrm{pH} = 6$, should show decrease in pH due to preferential accumulation of $\mathrm{OH^-}$ ions at the interface, as indeed observed (Kallay et al. 2012).

In the previous articles (Preočanin et al. 2009, 2010a, 2010b, 2011) equilibrium constants for binding of silver and halide ions to corresponding silver halides were calculated by assuming the electroneutrality point being equal to the isoelectric point measured in the neutral aqueous environment, i.e. at $\mathrm{pH} = 6 \cdots 7$. According to above discussion, these isoelectric points do not correspond to the surface electroneutrality. Therefore, the isoelectric points as measured in acidic environment should be taken into account. The aim of this article is recalculate equilibrium constants assuming different values of the electroneutrality point, ranging from iep measured in neutral to that measured in the acidic region.

2 Theoretical

The accumulation of $\mathrm{H^+}$ ions at the interface could be represented by

$$\mathrm{H^+_{(bulk)}} \rightleftarrows \mathrm{H^+_{(int)}}$$

$$K^\circ_{\mathrm{H^+}} = \frac{\{\mathrm{H^+}\}}{a_{\mathrm{H^+}}} \cdot \exp\left(\frac{\Psi_{\mathrm{int}} \cdot F}{RT}\right) \tag{1}$$

while for $\mathrm{OH^-}$ ions the following relationships are representative

$$\mathrm{OH^-_{(bulk)}} \rightleftarrows \mathrm{OH^-_{(int)}}$$

$$\begin{aligned} K^\circ_{\mathrm{OH^-}} &= \frac{\{\mathrm{OH^-}\}}{a_{\mathrm{OH^-}}} \cdot \exp\left(\frac{-\Psi_{\mathrm{int}} \cdot F}{RT}\right) \\ &= \frac{\{\mathrm{OH^-}\} \cdot a_{\mathrm{H^+}}}{K^\circ_{\mathrm{w}}} \cdot \exp\left(\frac{-\Psi_{\mathrm{int}} \cdot F}{RT}\right) \end{aligned} \tag{2}$$

In above equations curly brace denotes surface concentration, *i.e.* amount (number of moles) of relevant species per surface area, expressed in $\mathrm{mol\,m^{-2}}$, K°_w is thermodynamic equilibrium constant for dissociation of bulk water, while $K^\circ_{\mathrm{H}^+}$ and $K^\circ_{\mathrm{OH}^-}$ are thermodynamic equilibrium constants for distribution of H^+ and OH^- ions between bulk and the interface, corrected for electrostatic effects (also known as distribution coefficients). Electrostatic potential Ψ_int is affecting state of H^+ and OH^- ions at the interface. Isoelectric point, *i.e.* $\mathrm{pH_{iep}}$ at which interfacial water layer is uncharged, is determined by the values of $K^\circ_{\mathrm{H}^+}$ and $K^\circ_{\mathrm{OH}^-}$ and slightly influenced by the nature and concentration of the electrolyte.

Charging process at a silver halide surface could be described by the Surface Complexation Model (Stumm et al. 1970; Yates et al. 1974; Preočanin et al. 2009, 2010a, 2010b, 2011). For example, charging processes at silver chloride surface is assumed as binding of potential determining Ag^+ and Cl^- ions. Binding of silver ions with chloride being part of the surface structure (≡Cl) results in positive surface complex denoted as $\equiv\mathrm{Cl\ Ag}^+$ or more simply by $\equiv\mathrm{Ag}^+$

$$\equiv\mathrm{Cl} + \mathrm{Ag}^+_{(\mathrm{bulk})} \rightleftarrows \equiv\mathrm{Cl\ Ag}^+$$

$$K^\circ_{\mathrm{Ag}^+} = \frac{\{\equiv\mathrm{Ag}^+\}}{a_{\mathrm{Ag}^+}} \cdot \exp\left(\frac{\Psi_0 \cdot F}{RT}\right) = \frac{\{\equiv\mathrm{Ag}^+\} \cdot a_{\mathrm{Cl}^-}}{K^\circ_\mathrm{AgCl}} \cdot \exp\left(\frac{\Psi_0 \cdot F}{RT}\right) \tag{3}$$

the equilibrium constant of AgCl dissolution (Owen and Brinkley 1938) at 25 °C is $\lg K^\circ_\mathrm{AgCl} = -9.75$.

Binding of chloride ions with silver being part of the surface structure (≡Ag) results in negative surface complex denoted as $\equiv\mathrm{Ag\ Cl}^-$ or more simply by $\equiv\mathrm{Cl}^-$

$$\equiv\mathrm{Ag} + \mathrm{Cl}^-_{(\mathrm{bulk})} \rightleftarrows \equiv\mathrm{AgCl}^-$$

$$K^\circ_{\mathrm{Cl}^-} = \frac{\{\equiv\mathrm{Cl}^-\}}{a_{\mathrm{Cl}^-}} \cdot \exp\left(\frac{-\Psi_0 \cdot F}{RT}\right) = \frac{\{\equiv\mathrm{Cl}^-\} \cdot a_{\mathrm{Ag}^+}}{K^\circ_\mathrm{AgCl}} \cdot \exp\left(\frac{-\Psi_0 \cdot F}{RT}\right) \tag{4}$$

Counterions, such as *e.g.* nitrate or potassium ions, associates with charged surface groups thus partially reducing surface charge producing surface ion pairs denoted by $\equiv\mathrm{ClAg}^+ \cdot \mathrm{NO}_3^-$ (more simply by $\equiv\mathrm{Ag}^+ \cdot \mathrm{NO}_3^-$) and/or $\equiv\mathrm{AgCl}^- \cdot \mathrm{K}^+$ (more simply by $\equiv\mathrm{Cl}^- \cdot \mathrm{K}^+$). Association of counterions is represented by Eqs. (5, 6):

Association of anions

$$\equiv\mathrm{ClAg}^+ + \mathrm{NO}^-_{3(\mathrm{bulk})} \rightleftarrows \equiv\mathrm{ClAg}^+ \cdot \mathrm{NO}_3^-$$

$$K^\circ_{\mathrm{NO}_3^-} = \frac{\{\equiv\mathrm{Ag}^+ \cdot \mathrm{NO}_3^-\}}{a_{\mathrm{NO}_3^-}} \cdot \exp\left(\frac{-\Psi_\beta \cdot F}{RT}\right) \tag{5}$$

Association of cations

$$\equiv\mathrm{AgCl}^- + \mathrm{K}^+_{(\mathrm{bulk})} \rightleftarrows \equiv\mathrm{AgCl}^- \cdot \mathrm{K}^+$$

$$K^\circ_{\mathrm{K}^+} = \frac{\{\equiv\mathrm{Cl}^- \cdot \mathrm{K}^+\}}{a_{\mathrm{K}^+}} \cdot \exp\left(\frac{\Psi_\beta \cdot F}{RT}\right) \tag{6}$$

In Eqs. (3–6) the following symbolism is used. Species being part of the solid surface are denoted by ≡. The corresponding thermodynamic equilibrium constants (traditionally called "intrinsic constants"), $K^\circ_{\mathrm{Ag}^+}$, $K^\circ_{\mathrm{Cl}^-}$, $K^\circ_{\mathrm{NO}_3^-}$, and $K^\circ_{\mathrm{K}^+}$, are corrected for electrostatic effects. Surface potential Ψ_0, is defined as electrostatic potential affecting state of surface species $\equiv\mathrm{ClAg}^+$ and $\equiv\mathrm{AgCl}^-$, while associated counterions (K^+ and NO_3^-) are exposed to potential Ψ_β. K°_AgCl is the thermodynamic equilibrium constant of dissolution of silver chloride ("solubility product").

Thermodynamic surface equilibrium constants $K^\circ_{\mathrm{Ag}^+}$, $K^\circ_{\mathrm{Cl}^-}$, $K^\circ_{\mathrm{NO}_3^-}$, and $K^\circ_{\mathrm{K}^+}$ determine adsorption equilibrium at solid/liquid interface. They could be evaluated by interpreting different kinds of experimental data. Commonly, one would use surface charge data obtained by potentiometric titration of dispersions (Lützenkirchen et al. 2012). More recently surface potential data, obtained by means of single crystal electrode, were used for that purpose (Zarzycki 2007; Preočanin et al. 2007, 2009, 2010a, 2010b).

3 Evaluation of equilibrium parameters from surface potential data

Measurements of the surface potential Ψ_0 that affects state of ionic species bound to the surface could be performed by using single crystal electrodes (SCrE) (Kallay et al. 2005, 2011; Preočanin et al. 2009, 2010a, 2010b). By electrochemists, this kind of measurements would be considered as "open circuit measurements" (Yanina and Rosso 2008; Boily et al. 2011; Shimizu et al. 2012). In the experiment one measures potential of SCrE with respect to the reference electrode as a function of the activity of potential determining ions. To obtain absolute value of surface potential Ψ_0 one would need to know the point of zero potential (pzp) which is not always a simple task. In the case of silver halides Ψ_0 is found to be a linear function of pAg with a slope lower in magnitude than the Nernstian slope (Kallay et al. 2008; Preočanin et al. 2009, 2010a, 2010b, 2011). The deviation from the Nernstian slope is represented by coefficient α defined as

$$\frac{\mathrm{d}\psi}{\mathrm{dpAg}} = -\alpha \frac{RT \ln 10}{F} \tag{7}$$

Determination of α coefficient does not require knowledge of pzp and is therefore liberated of any assumption or choice regarding the pAg_{pzp} value. Since α coefficient depends on the values of the equilibrium parameters determining the surface charge one could in principle obtain these values from the surface potential measurements (Kallay et al. 2008; Preočanin et al. 2009, 2010a, 2010b, 2011). However, experimental α coefficients do not yield separate values of equilibrium constants of *e.g.* $K^{\circ}_{Ag^+}$ and $K^{\circ}_{Cl^-}$, but rather their product. The problems could be solved by knowing their ratio, *i.e.* the electroneutrality point pAg_{eln} being equal to

$$pAg_{eln} = \frac{1}{2} \cdot \log \frac{K^{\circ}_{Ag^+}}{K^{\circ}_{Cl^-} \cdot K^{\circ}_{AgCl}} \tag{8}$$

By knowing the product and the ratio of $K^{\circ}_{Ag^+}$ and $K^{\circ}_{Cl^-}$ one directly obtains their individual values. In the simple case when electrokinetic charge is determined solely by adsorbed potential determining ions, *e.g.* by Ag^+ and Cl^- ions, one may take electrokinetic isoelectric point pAg_{iep} as the electroneutrality point pAg_{eln}. However, if electrokinetics is influenced by the pH dependent charge of water layer at the surface such a procedure is in principle incorrect. The effect of the pH on the electrokinetic properties of silver halides was only recently observed (Kallay et al. 2012), so that the isoelectric points obtained in neutral aqueous environment ($pH \approx 7$) were used in the interpretation of interfacial equilibrium of silver halides (Kallay et al. 2008; Preočanin et al. 2009, 2010a, 2010b, 2011). At $pH \approx 7$ the interfacial water is negatively charged, thus at iep the surface is positively charged but not uncharged as assumed in the mentioned articles. Therefore, the isoelectric point measured in acidic region, *e.g.* at $pH = 3$, when the interfacial water layer is uncharged should be taken into account. Consequently, previous results of surface potential measurements and corresponding interpretation of interfacial equilibrium at silver halide aqueous interface were recalculated, and presented in this article, for different assumed pAg_{eln} values.

4 Results and discussion

Figure 2 displays thermodynamic equilibrium constants of interfacial reactions for silver chloride obtained at 25 °C and ionic strength of 10^{-3} mol dm^{-3} controlled by KNO_3. The calculation procedure was described previously (Preočanin et al. 2009). The whole pH range of interest was examined. For that purpose the dependency of isoelectric point on pH should be known. For example, isoelectric points of silver chloride were found to be at $pAg_{iep} = 4.6$ at $pH = 6$, but at $pH = 3$ isoelectric point shifts to $pAg_{iep} = 5.3$. Due to the pH dependent charge of interfacial water layer, the isoelectric point is not necessarily equal to the electroneutrality point, so that assumption that $pAg_{eln} = pAg_{iep}$ could lead to the incorrectly obtained thermodynamic equilibrium constants of interfacial reaction. Accordingly, in calculations a broad range of assumed pAg_{eln} values, from 4.6 to 5.6, was covered. As shown in Fig. 2, equilibrium constant for binding of Ag^+ ions to surface sites $K^{\circ}_{Ag^+}$ increases with the increase of assumed pAg_{eln} values. The opposite trend was obtained for binding of Cl^- ions. The value of $K^{\circ}_{Cl^-}$ decreases. and value of $K^{\circ}_{Ag^+}$ increases with pAg_{eln} in such a way that their product remains practically constant. As expected, the values of thermodynamic equilibrium constant for association of counterions at the surface was not found to be sensitive on the choice of the electroneutrality point pAg_{eln}.

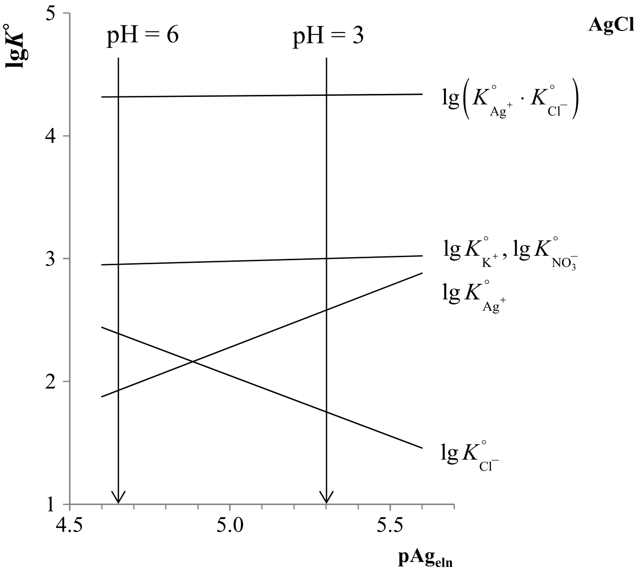

Fig. 2 The effect of assumed electroneutrality point pAg_{eln} on evaluated thermodynamic equilibrium constants of interfacial reaction at silver chloride aqueous interface at 25 °C: binding of silver ions ($\lg K^{\circ}_{Ag^+}$), binding of chloride ions ($\lg K^{\circ}_{Cl^-}$), and association of counterions ($\lg K^{\circ}_{K^+} = \lg K^{\circ}_{NO_3^-}$). The product of equilibrium constants for binding of silver and of chloride ions to corresponding sites, $\lg(K^{\circ}_{Ag^+} \cdot K^{\circ}_{Cl^-})$, corresponding to incorporation of adsorbed ions into the crystal structure, is also represented

The same procedure was applied to silver bromide and the results are presented in Fig. 3. The isoelectric point of silver bromide was found to be at $pAg_{iep} = 4.5$ at $pH = 6$, but at $pH = 3$ isoelectric point of silver bromide shifts to $pAg_{iep} = 5.7$. Accordingly, in order to obtain representative values of interfacial equilibrium constants for silver bromide aqueous interface, the pAg_{eln} region from 4.5 to 5.9 was covered in calculations. Again, the increase of $K^{\circ}_{Ag^+}$ and decrease of $K^{\circ}_{Br^-}$ with the increase of assumed pAg_{eln} value was observed, while their product remained practically constant.

It is interesting to analyze incorporation of adsorbed potential determining ions into the solid structure. The fact that incorporation of adsorbed silver and halide ions into crystal lattice do not depend on pH additionally supports the results of this study, since one can hardly imagine that the charge of

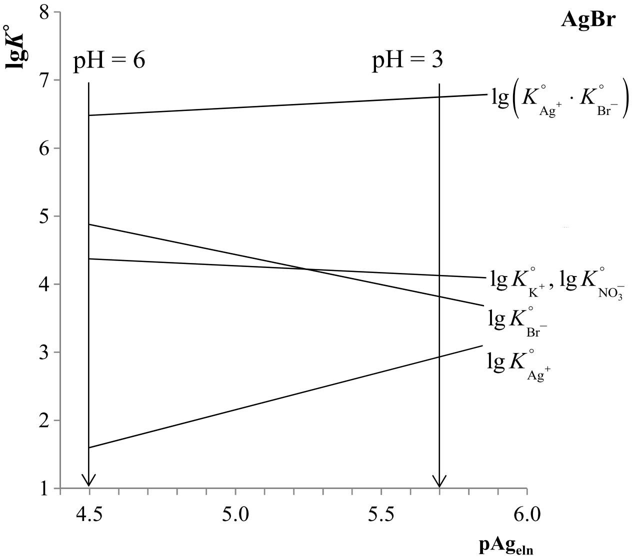

Fig. 3 The effect of assumed electroneutrality point $\mathrm{pAg_{eln}}$ on evaluated thermodynamic equilibrium constants of interfacial reaction at silver bromide aqueous interface at 25 °C: binding of silver ions ($\lg K^{\circ}_{\mathrm{Ag}^+}$), binding of bromide ions ($\lg K^{\circ}_{\mathrm{Br}^-}$), and association of counterions ($\lg K^{\circ}_{\mathrm{K}^+} = \lg K^{\circ}_{\mathrm{NO}_3^-}$). The product of equilibrium constants for binding of silver and of bromide ions to corresponding sites, $\lg(K^{\circ}_{\mathrm{Ag}^+} \cdot K^{\circ}_{\mathrm{Br}^-})$, corresponding to incorporation of adsorbed ions into the crystal structure, is also represented

surrounded water layer affects the process of incorporation of adsorbed constituent ions int the crystal lattice.

The incorporation of silver and halide ion (X^-) bound to corresponding surface sites into the surface lattice is represented by

$$\equiv\mathrm{XAg}^+ + \equiv\mathrm{AgX}^- \rightarrow 2\mathrm{AgX(s)};\ \ K^{\circ}_{\mathrm{trs}};\ \ \Delta_{\mathrm{trs}}G^{\circ} \qquad (9)$$

The equilibrium constant of transformation and corresponding change in standard Gibbs energy are given by

$$\begin{aligned} &\lg K^{\circ}_{\mathrm{trs}} = -\lg\left(K^{\circ}_{\mathrm{Ag}^+} \cdot K^{\circ}_{\mathrm{X}^-} \cdot K^{\circ}_{\mathrm{AgX}}\right); \\ &\Delta_{\mathrm{trs}}G^{\circ} = -RT \ln K^{\circ}_{\mathrm{trs}} \end{aligned} \qquad (10)$$

As shown in Figs. 2 and 3 the product of equilibrium constants for charging the surfaces of silver chloride and silver bromide was found to be practically independent on assumed $\mathrm{pAg_{eln}}$ value. Accordingly, for silver chloride

$$\lg K^{\circ}_{\mathrm{AgCl}} = -9.75; \qquad \lg\left(K^{\circ}_{\mathrm{Ag}^+} \cdot K^{\circ}_{\mathrm{Cl}^-}\right) = 4.34;$$

$$\lg K^{\circ}_{\mathrm{trs}} = 5.43; \qquad \Delta_{\mathrm{trs}}G^{\circ} = -31.0\ \mathrm{kJ\,mol^{-1}}$$

and for silver bromide

$$\lg K^{\circ}_{\mathrm{AgBr}} = -12.28; \qquad \lg\left(K^{\circ}_{\mathrm{Ag}^+} \cdot K^{\circ}_{\mathrm{Br}^-}\right) = 6.73;$$

$$\lg K^{\circ}_{\mathrm{trs}} = 5.55; \qquad \Delta_{\mathrm{trs}}G^{\circ} = -31.7\ \mathrm{kJ\,mol^{-1}}$$

5 Conclusion

Since interfacial water is uncharged in the pH region around pH = 3, the above analysis results in the correct values of the interfacial equilibrium constants.

For silver chloride: $\mathrm{pAg_{eln}} = 5.3$, $\lg K^{\circ}_{\mathrm{Ag}^+} = 2.6$; $\lg K^{\circ}_{\mathrm{Cl}^-} = 1.8$ and $\lg K^{\circ}_{\mathrm{K}^+} = \lg K^{\circ}_{\mathrm{NO}_3^-} = 3.0$. For silver bromide: $\mathrm{pAg_{eln}} = 5.7$, $\lg K^{\circ}_{\mathrm{Ag}^+} = 2.9$; $\lg K^{\circ}_{\mathrm{Br}^-} = 3.8$ and $\lg K^{\circ}_{\mathrm{K}^+} = \lg K^{\circ}_{\mathrm{NO}_3^-} = 4.2$.

References

Beattie, J.K., Djerdjev, A.M.: The pristine oil/water interface: surfactant-free hydroxide-charged emulsions. Angew. Chem., Int. Ed. Engl. **43**, 3568–3571 (2004)

Boily, J.F., Chatman, S., Rosso, K.M.: Inner-Helmholtz potential development at the hematite (alpha-$\mathrm{Fe_2O_3}$) (001) surface. Geochim. Cosmochim. Acta **75**, 4113–4124 (2011)

Härtl, A., Garrido, J.A., Nowy, S., Zimmermann, R., Werner, C., Healy, T.W., Fuerstenau, D.W.: The isoelectric point/point-of zero-charge of interfaces formed by aqueous solutions and nonpolar solids, liquids, and gases. J. Colloid Interface Sci. **309**, 183–188 (2007)

Horinek, D., Netz, R., Stutzmann, M.: The ion sensitivity of surface conductive single crystalline diamond. J. Am. Chem. Soc. **129**, 1287–1292 (2007)

Hunter, R.J.: Zeta Potentials in Colloid Science. Academic Press, London (1981)

Kallay, N., Čop, A., Chibowski, E., Holysz, L.: Reversible charging of the ice–water interface: II. estimation of equilibrium parameters. J. Colloid Interface Sci. **259**, 89–96 (2003)

Kallay, N., Dojnović, Z., Čop, A.: Surface potential at the hematite–water interface. J. Colloid Interface Sci. **286**, 610–614 (2005)

Kallay, N., Šupljika, F., Preočanin, T.: Measurement of the surface potential at silver chloride aqueous interface by means of the single crystal electrode. J. Colloid Interface Sci. **327**, 384–387 (2008)

Kallay, N., Preočanin, T., Kovačević, D., Lützenkirchen, J., Villalobos, M.: Thermodynamics of the reactions at solid/liquid interfaces. Croat. Chem. Acta **84**, 1–10 (2011)

Kallay, N., Preočanin, T., Šupljika, F., Lützenkirchen, J., Lovković, M.: Influence of interfacial water layer on surface properties of silver halides: effect of pH on isoelectric point. J. Colloid Interface Sci. **375**, 167–171 (2012)

Kosmulski, M.: IEP as a parameter characterizing the pH-dependent surface charging of materials other than metal oxides. Adv. Colloid Interface Sci. **171–172**, 77–86 (2012)

Lützenkirchen, J., Preočanin, T., Kallay, N.: A macroscopic, water structure based model for describing charging phenomena at hydrophobic surfaces in electrolyte solutions. Phys. Chem. Chem. Phys. **10**, 4946–4955 (2008)

Lützenkirchen, J., Zimmermann, R., Preočanin, T., Filby, A., Kupcik, T., Küttner, D., Abdelmonem, A., Schild, D., Rabung, T., Plaschke, M., Werner, C., Geckeis, H.: The sapphire c-plane electrolyte interface—an attempt to explain contradictory observations. Adv. Colloid Interface Sci. **157**, 61–74 (2010)

Lützenkirchen, J., Preočanin, T., Kovačević, D., Tomišić, V., Lövgren, L., Kallay, N.: Potentiometric titrations as a tool for surface charge determination. Croat. Chem. Acta (2012). doi:10.5562/cca2062

Lyklema, J.: Fundamentals of Interface and Colloid Science, Volume II: Solid-Liquid Interface. Academic Press, London (1995)

Marinova, K.G., Alargova, R.G., Denkov, N.D., Velev, O.D., Petsev, D.N., Ivanov, I.B., Borwankar, R.P.: Charging of oil–water interfaces due to spontaneous adsorption of hydroxyl ions. Langmuir **12**, 2045–2051 (1996)

Najafi, A.S., Drelich, J., Yeung, A., Xu, Z., Masliyah, J.: A novel method of measuring electrophoretic mobility of gas bubbles. J. Colloid Interface Sci. **308**, 344–350 (2007)

Owen, B.B., Brinkley, S.R.: The elimination of liquid junction potentials. II. The standard electrode potential of silver from 5 to 45°, and related thermodynamic quantities. J. Am. Chem. Soc. **60**, 2233–2239 (1938)

Preočanin, T., Janusz, W., Kallay, N.: Evaluation of equilibrium parameters of the anatase/aqueous electrolyte solution interface by introducing surface potential data. Colloids Surf. A **297**, 30–37 (2007)

Preočanin, T., Šupljika, F., Kallay, N.: Evaluation of interfacial equilibrium constants from surface potential data: silver chloride aqueous interface. J. Colloid Interface Sci. **337**, 501–507 (2009)

Preočanin, T., Šupljika, F., Kallay, N.: Charging of silver bromide aqueous interface: evaluation of equilibrium constants from surface potential data. J. Colloid Interface Sci. **346**, 222–225 (2010a)

Preočanin, T., Šupljika, F., Kallay, N.: Evaluation of interfacial equilibrium constants from surface potential data: silver bromide aqueous interface. J. Colloid Interface Sci. **346**, 222–225 (2010b)

Preočanin, T., Šupljika, F., Kallay, N.: Charging of silver bromide aqueous interface: evaluation of enthalpies and entropies of interfacial reactions from surface potential data. J. Colloid Interface Sci. **354**, 318–321 (2011)

Shimizu, K., Lasia, A., Boily, J.-F.: Langmuir **28**, 7914–7920 (2012)

Stumm, W., Huang, C.P., Jenkins, S.R.: Specific chemical interaction affecting the stability of dispersed systems. Croat. Chem. Acta **42**, 223–245 (1970)

Takahashi, M.: ζ potential of microbubbles in aqueous solutions: electrical properties of the gas–water interface. J. Phys. Chem. B **109**, 21858–21864 (2005)

Yang, C., Dabros, T., Li, D., Czarnecki, J., Masliyah, J.H.: Measurement of the zeta potential of gas bubbles in aqueous solutions by microelectrophoresis method. J. Colloid Interface Sci. **243**, 128–135 (2001)

Yanina, S.V., Rosso, K.M.: Linked reactivity at mineral-water interfaces through bulk crystal conduction. Science **320**, 218–222 (2008)

Yates, D.E., Levine, S., Healy, T.W.: Site-binding model of the electrical double layer at the oxide/water interface. J. Chem. Soc. Faraday Trans. I **70**, 1807–1818 (1974)

Zarzycki, P.: Comparison of the Monte Carlo estimation of surface electrostatic potential at the hematite (0001)/electrolyte interface with the experiment. App. Surf. Sci. **253**, 7604–7612 (2007)