Dissolution Potentials of Silver Bromide & Iodide in Aqueous Solutions of Corresponding Halates

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Dissolution potential of the order of 100-300 mV is developed when AgBr or AgI dissolves in aqueous solution of KBr0₃ or KIO₃. Dissolution process in the former case has been studied spectrophotometrically by monitoring Br₂ produced in the reaction. The sign and magnitude of the potentials are in accord with the theory of Rastogi and Khan [J electrochem Soc, 127 (1980) 1929].

In view of the importance of monitoring bromide ions concentration in oscillatory reactions such as Belousov—Zhabotinskii (B-Z) reaction¹ and in view of the fact that AgBr and AgI have Frenkel defects, it was planned to study the dissolution potentials of AgBr and AgI in aqueous BrO₃⁻ and IO₃⁻ solutions. Nisticzisz² has suggested that monitoring of bromide ion concentration in such solutions would be dubious by silver-silver bromide electrode. Noyes and coworkers³ have also observed that stability of such electrodes is attained only after some time. It is known that potentials are developed during the dissolution of electrolytes⁴. Quantitative experiments on dissolution of AgBr in BrO₃⁻ are reported in this connection. It is found that dissolution potential is generated and a steady potential is developed after some time. Results have been interpreted in the light of the theory of Rastogi and Khan⁵.

Materials and Methods
All the chemicals (BDH, AR) were used as such. Solutions were prepared in deionized water.

Solubility of silver bromide in acidic bromate
Preliminary experiments suggested that silver bromide dissolved in acidic bromate liberating molecular bromine which was tested qualitatively and spectrophotometrically on a Toshniwal spectrophotometer (model RLO₂). The absorbance of the filtrate exhibited absorption maxima at 410 nm, corresponding to the maximum of Br₂ (obtained from bromide-bromate mixture) in CCl₄. This confirmed the presence of bromine. The absorption maximum of bromine vapour has been shown⁶ to occur at 420 nm. It was found that solutions of Br₂ in CCl₄ obeyed Beer’s law in the range of concentration studied. The partition coefficient of Br₂ in aqueous/CCl₄ layer was also determined.

Quantitative experiments were also performed to estimate the extent of dissolution in the following manner. Silver bromide was prepared by mixing solutions of silver nitrate and potassium bromide. The resulting precipitate was washed free of ions and dried. AgBr (0.05 g) was added to a 0.0273 M solution of KBrO₃ in 3NH₂SO₄, extracted with CCl₄ and the organic extract analyzed spectrophotometrically at different intervals of time by measuring the absorbance at 410 nm.

Dissolution potential measurements
The procedure for the determination of dissolution, diffusion and phase potentials of silver halide in halate salt was similar to that adopted by Rastogi and coworkers⁷. However, a modified procedure of deposition of halide crystals on the platinum electrode was employed.

Platinum electrodes fused in pyrex glass tubes were welded to copper wire in order to avoid electrical contacts through mercury which might form secondary cells. Coaxial cables were used to eliminate the influence of stray electrical fields. Potentials were recorded with the help of a electrometer (impedance ~ 10⁴).

The electrodes were cleaned with boiling nitric acid, washed with conductivity water, kept for some time in halate solution (KBrO₃ or KIO₃ solution) and short circuited in order to minimize the asymmetry potential. The asymmetry potential was determined before hand for each run with the help of a digital electrometer. One of the platinum electrodes was dipped in molten silver bromide or silver iodide kept in a crucible in a furnace. The melt was allowed to cool gradually. Crystallisation of salt resulted in the deposition of smooth and uniform layer of crystals on the electrode. The electrode was then taken out and allowed to cool.

The dissolution potential was measured using the above electrode in potassium halate solution (KBrO₃ or KIO₃ in conductivity water as the case may be) in an air thermostat maintained at 30 ± 0.05°C.
potential was recorded as a function of time using another bright platinum electrode as the reference electrode. The potential increased initially, then attained a maximum value and subsequently started decreasing. In course of time it attained a steady value which corresponded to phase potential. The procedure for the measurement of diffusion potential was similar to that followed earlier. The actual dissolution potential was estimated by taking the asymmetry, phase and diffusion potentials into account.

\[(\Delta \phi)_{\text{true diss. pot.}} = (\Delta \phi)_{\text{obs. diss. pot.}} - (\Delta \phi)_{\text{diff. pot.}} - (\Delta \phi)_{\text{phase pot.}}\]

In order to stimulate continuous bromine removal by organic substrate in B-Z reaction, experiments were repeated by bubbling air through bromate solution to remove bromine.

Results

The observed dissolution, phase, diffusion and true dissolution potentials of silver halides in 1m aqueous halate solutions, in the presence and absence of air and of silver/silver halide electrodes in 1m aqueous halate solutions and water, in the presence and absence of air are recorded in Table 1. Spectrophotometric results on dissolution of AgBr in KBrO₃ solutions are plotted in Fig. 1. The build-up and decay of observed dissolution potential are shown in Figs. 2-5. The points represent the mean value of several runs and uncertainty is represented by length of vertical bars.

Discussion

On account of interaction of BrO₃⁻ with Br⁻ produced on dissociation of AgBr, one would expect that Br₂ would be produced in the system. Spectrophotometric analysis of the reaction system shows that 4.50 \times 10^{-3} g of Br₂ is produced which is approximately 10% of the theoretically expected (4.25 \times 10^{-2} g) molecular bromine which would be produced on complete reaction (step 3). It is easy to visualise that the reaction would proceed as follows:

\[5\text{AgBr} \rightleftharpoons 5\text{Ag}^+ + 5\text{Br}^-; K_1 = 10^{-13} \quad (1)\]
\[6\text{H}^+ + \text{BrO}_3^- + 5\text{Br}^- \rightleftharpoons 3\text{Br}_2 + 3\text{H}_2\text{O}; K_2 = 10^{33} \quad (2)\]

The Br₂ produced would be partitioned between aqueous layer and CCl₄ layer. K₁ and K₂ are the equilibrium constants. The equilibrium constant of the net reaction (3), obtained by adding (1) and (2), would be thus \(10^{20}\).

\[6\text{H}^+ + 5\text{AgBr} + \text{BrO}_3^- \rightleftharpoons 5\text{Ag}^+ + 3\text{Br}_2 + 3\text{H}_2\text{O} \quad (3)\]

It implies that the reaction proceeds largely in forward direction and AgBr dissolves in excess of BrO₃⁻.

However, our experimental results show that AgBr does not completely dissolve and that equilibrium is established after sometime. The plots in Figs. 2-5 show that as soon as the dissolution starts, the electrodes on

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Fig. 1—Formation of Br₂ at different intervals of time [AgBr = 0.0500 g, KBrO₃ = 0.0273 M, CCl₄ = 30 ml]

Fig. 2—Dissolution potential of silver halides in aqueous solutions of potassium halate (○—○) and water (●—●) [(1) silver bromide/KBrO₃ system; (2) silver bromide/water system; (3) silver iodide/KIO₃ system; (4) silver iodide/water system]

Fig. 3—Influence of bubbling of air on dissolution potential of silver halides in aqueous solutions of potassium halates (○—○) and water (●—●) [(1) silver bromide/KBrO₃ system; (2) silver bromide/water system; (3) silver iodide/KIO₃ system; and (4) silver iodide/water system]

Fig. 4—Dissolution potential of silver halides in aqueous solutions of potassium halates (○—○) and water (●—●) using silver/silver halide electrode [(1) Ag-AgBr electrode/KBrO₃ system; (2) Ag-AgBr electrode/water system; (3) Ag-AgI electrode/KBrO₃ system; and (4) Ag-AgI electrode/water system]

Fig. 5—Influence of bubbling of air on dissolution potential of silver halides in aqueous solution of potassium halates (○—○) and water (●—●) using silver/silver halide electrode [(1) Ag-AgBr electrode/KBrO₃ system; (2) Ag-AgBr electrode/water system; (3) Ag-AgI electrode/KIO₃ system; and (4) Ag-AgI electrode/water system]
which dissolution takes place becomes negative and the electrode potential increases and attains the value corresponding to phase potential at the crystal-solution interface. When air is bubbled through the solution to drive out bromine, both the dissolution potential and the time for attainment of steady state are enhanced. This is expected since dissolution potential depends on rate of dissolution which is enhanced on account of stirring by air. Janicke and coworkers\(^9\) have earlier reported potential changes when AgBr dissolves in solvents where complex formation can occur.

The present experimental results show that steady potentials are obtained after longer time for halate solution as compared to water. Similarly, when air is bubbled through the solvent, attainment of steady state takes still longer time. It is obvious that steady potentials would only be attained when series of equilibria have been established.

Noyes and coworkers\(^3\) have also reported unsteady potential for some time in a similar situation: the potential becomes steady within about 9 min. In the present experiments on the dissolution of AgBr in KBrO\(_3\) solution in the presence of CCl\(_4\), the steady state is reached after 190 min which is much larger. The longer time needed to attain equilibrium state is due to the interference between distribution equilibria and the dissolution equilibria.

Potential response of silver halide membrane electrodes to the corrosive bromous, iodosus and iodic acids in sulphuric acid (typical media for B-Z oscillatory reaction) has been investigated by Noszticzius and coworkers\(^2\). Results have been interpreted in the light of kinetic buffer theory and the corrosion potential theory\(^11\), which is not satisfactory. According to the thermodynamic theory due to Rastogi and Khan\(^5\), the dissolution potential \((\Delta \Phi)_{\text{diss}}\) is given by

\[
(\Delta \Phi)_{\text{diss}} = \frac{RT}{F} \ln \frac{a^{\theta}}{a^{\text{sat}}} \quad \ldots \quad (1)
\]

where \(R\) is the gas constant, \(T\) is the temperature in K, \(F\) is the Faraday, \(U^+\) and \(U^-\) are the mobilities of the corresponding ions leaving the crystal lattice at the crystal solution interface. Further \(a^{\theta}\) is the activity of the solute in the vicinity of the electrode on which dissolution takes place and \(a^{\text{sat}}\) is the activity of the electrolyte in the saturated layer. In general, when dissolution occurs \(a^{\theta} < a^{\text{sat}}\) and hence \((\Delta \Phi)_{\text{diss}}\) is positive when \(U^- > U^+\). Similarly \((\Delta \Phi)_{\text{diss}}\) is negative when \(U^- < U^+\). The effective mobility of Ag\(^+\) at the crystal solution would be greater than that for Br\(^-\) or I\(^-\) in view of its higher tendency for hydration and the fact that the current would be carried by positively charged Ag\(^+\) and negatively charged Br\(^-\) and BrO\(_3^-\) ions. Hence, the electrodes at which dissolution takes place would be negative as is the case for dissolution potentials of alkali halides in water\(^8\).

The above investigation shows that the response time of silver/silver halide electrodes in aqueous halate solutions would be enhanced and the initial response would also include dissolution potential.

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References