Experiment 1

Complex Formation and Solubility Product

Student Handout

Purposes

1. To study the effect of $S_2O_3^{2-}$ ions on the solubility of AgBr.
2. To determine the stability constant, K_{st}, for $[Ag(S_2O_3)_2]^{3-}$.

Background

An essential step in processing photographic film involves the removal of the AgBr crystals that are not exposed to light. The solubility product, K_{sp}, for AgBr is very small (5.0×10^{-13} mol^2 dm^{-6} at 25.0 °C), making this compound extremely difficult to dissolve in water. However, the solubility of AgBr is greatly enhanced in a reagent called 'fixer'. It contains $S_2O_3^{2-}$ ions, which form the complex ion, $[Ag(S_2O_3)_2]^{3-}$, with Ag^+ ions. A new equilibrium is then established:

$$Ag^+(aq) + 2\ S_2O_3^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq)$$

where the equilibrium constant is given by:

$$K_{st} = \frac{[[Ag(S_2O_3)_2]^{3-}(aq)]}{[Ag^+(aq)][S_2O_3^{2-}(aq)]^2}$$

The equilibrium of a complex formation of this kind usually overwhelmingly favours the product side. The majority of free Ag^+ ions are 'removed' and the position of the equilibrium,

$$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$$

shifts to the right hand side, resulting in increase in the solubility of AgBr.

In a saturated AgBr solution without the presence of $S_2O_3^{2-}$ ion, $[Ag^+(aq)] = [Br^-(aq)]$, $K_{sp} = [Ag^+(aq)][Br^-(aq)] = [Ag^+(aq)]^2$. Hence $[Ag^+(aq)] = [Br^-(aq)] = K_{sp}^{½} = 7.1 \times 10^{-7}$ mol dm^{-3}. On the other hand, if $S_2O_3^{2-}$ is present and its initial concentration is $[S_2O_3^{2-}]_0$, at equilibrium (i.e., when no more AgBr can be dissolved), we have

$$K_{sp} = [Ag^+(aq)][Br^-(aq)]$$

$$K_{st} = \frac{[[Ag(S_2O_3)_2]^{3-}(aq)]}{[Ag^+(aq)][S_2O_3^{2-}(aq)]^2}$$

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$[S_2O_3^{2-}(aq)]_0 = [S_2O_3^{2-}(aq)] + 2[[Ag(S_2O_3)_2]^{3-}(aq)]$
$[Br^-(aq)] = [Ag^+(aq)] + [[Ag(S_2O_3)_2]^{3-}(aq)]$

where the last equation indicates the fact that the total concentration of Ag^+ ion is equal to the concentration of Br^- ion. Assume that almost all $Ag^+(aq)$ is consumed in complex formation (i.e., $[[Ag(S_2O_3)_2]^{3-}(aq)] >> [Ag^+(aq)]$), we may approximate the last equation as:

$$[Br^-(aq)] = [[Ag(S_2O_3)_2]^{3-}(aq)]$$

Solving all these equations, we find that

$$[Br^-(aq)] = [2 + (K_{sp}K_{st})^{-1/2}]^{-1}[S_2O_3^{2-}(aq)]_0$$

After performing this experiment and determining K_{st}, you will find that the solubility of AgBr greatly increases in the presence of $S_2O_3^{2-}$ ion.

Safety

Handle all chemicals with great care. Avoid direct contact of chemicals with skin. Dispose of chemical waste, broken glassware and excess materials according to your teacher's instruction.

Further information on the chemicals used in the experiment can be found in the Material Safety Data Sheet (MSDS). Consult your teacher for details.

EYE PROTECTION
MUST BE WORN

Materials and Apparatus Available

0.01 M KBr solution
0.01 M $AgNO_3$ solution
Test tubes
Test tube rack
0.01 M $Na_2S_2O_3$ solution
Graduate pipette
Droppers

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Experimental Procedure

Photos of the experiment are available at http://www.chem.cuhk.edu.hk/ssc.htm.

1. Pipette 1.00 cm^3 of 0.01 M $AgNO_3$ solution and 1.00 cm^3 of 0.01 M KBr solution to each of five test tubes. Shake the test tubes gently. Record the observations.
2. Pipette 3.00, 2.50, 2.00, 1.50 and 1.00 cm^3 of 0.01 M $Na_2S_2O_3$ solution separately into the test tubes in (1). Shake the test tubes gently. Record the observations.
3. Estimate the minimum volume of $Na_2S_2O_3$ solution needed to dissolve all AgBr. Then work out the value of $[Br^-(aq)]$ (which is equal to the solubility of AgBr in mol dm^{-3}) and $[S_2O_3^{2-}(aq)]_0$. Finally determine the value of K_{st}.

Questions for Further Thought

1. Verify the assumption: $[[Ag(S_2O_3)_2]^{3-}(aq)] >> [Ag^+(aq)]$.
2. Why is $AgNO_3$ solution stored in brown bottle?
3. A large number of complexes are formed between transition metal ions and anions/molecules. A well-known example is the complex between Cu^{2+} and NH_3.
   (a) Write down the formula for this complex.
   (b) Some main-group metal ions also form complexes with anions/molecules. Give an example.

Reference

G. M. Bonder and H. L. Pardue, *Chemistry - An Experimental Science,* 2nd Ed., John Wiley & Sons, New York, 1995, pp. 647 - 677.

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