Experiment 14

THE SOLUBILITY PRODUCT CONSTANT OF SILVER ACETATE

Objective

The purpose of this experiment is to determine the solubility product constant of silver acetate (CH_3COOAg) at different temperatures.

Lab techniques

- Operating graduated pipet, stirrer/hot plate, gravity filtration, and titration

Introduction

When excess slightly soluble salt A_mB_n is added to water, an equilibrium is established between the solid and its dissociated ions in solution (14-1). Such a solution is said to be saturated. The solubility product constant, K_{sp}, of this reaction is given by equation 14-2. The K_{sp} value depends on the temperature. At a given temperature, K_{sp} is a constant for a given salt.

$$A_mB_n(s) \rightleftharpoons m\,A^{n+}(aq) + n\,B^{m-}(aq) \quad (14\text{-}1)$$

$$K_{sp} = [A^{n+}]^m\,[B^{m-}]^n \quad (14\text{-}2)$$

When two ionic solutions with large enough concentrations that the ion product Q ($Q = [A^{n+}]_0^m[B^{m-}]_0^n$) exceeds K_{sp} are mixed, the cations and anions will combine and precipitate. Occasionally, the salt does not precipitate even if the ion product exceeds K_{sp}. In this case, the solution is said to be supersaturated. In a supersaturated solution, precipitation can be induced by stirring the solution or scraping the walls of its container with a glass rod.

There are many ways to determine K_{sp} including potentiometry, conductivity measurement, and quantitative spectral analysis. In this experiment, we will determine the K_{sp} value of silver acetate (CH_3COOAg, abbreviated as AgOAc) by precipitation titration. The solubility equilibrium and the solubility product constant expression of silver acetate are given by equations 14-3 and 14-4:

$$AgOAc(s) \rightleftharpoons Ag^+(aq) + OAc^-(aq) \quad (14\text{-}3)$$

$$K_{sp} = [Ag^+][OAc^-] \quad (14\text{-}4)$$

If the concentrations of Ag^+ and OAc^- in a saturated solution are measured, the K_{sp} value can be determined. Hence, we measure a fixed volume of silver nitrate ($AgNO_3$) and sodium acetate (CH_3COONa) solutions of known concentrations, which satisfy the condition $Q > K_{sp}$. Then the two solutions are mixed to precipitate AgOAc(s) and obtain a saturated AgOAc solution. After filtering out the precipitate, the

equilibrium concentration of Ag^+ in the solution is determined by titration with SCN^- using Fe^{3+} as an indicator. The Ag^+ ions reacts completely with SCN^- ions to form a white AgSCN precipitate as shown in equation 14-5. Beyond the equivalence point, a small excess of SCN^- will react with Fe^{3+} to form red $FeSCN^{2+}$ complex ions (14-6), signaling the titration end-point. This titration gives the concentration of Ag^+, while the concentration of acetate ions can be determined by stoichiometric calculations.

$$Ag^+(aq) + SCN^-(aq) \rightarrow AgSCN(s) \quad (14\text{-}5)$$

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq) \quad (14\text{-}6)$$

In general, K_{sp} is independent of the concentration of ions or pH value. However, K_{sp} changes with temperature. The K_{sp} values of most substances increase with increasing temperature. Since higher temperatures supply more energy to break the crystal lattice of the precipitate, the solubility is increased. For example, $PbCl_2$ and Ag_2SO_4 are insoluble in cold water but soluble in hot water. In this experiment, we will determine and compare the K_{sp} values of silver acetate at different temperatures.

Apparatus

Stirrer/hot plate, stir bar, buret (25 mL), graduated pipet (10 mL), pipet filler, Erlenmeyer flask (125 mL, 4), beaker (100 mL, 5), thermometer, Styrofoam bowl (for ice-water bath), funnel (3), filter paper, iron ring, and NBR gloves.

Chemicals

0.020 *M* Potassium thiocyanate, KSCN

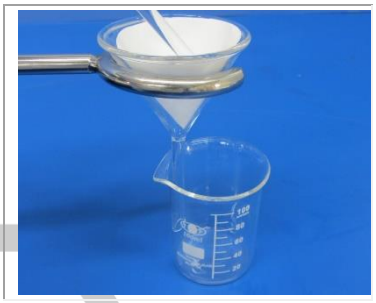
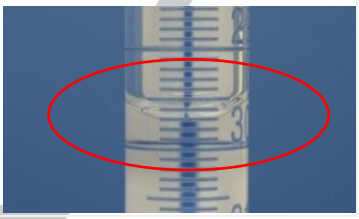
0.10 *M* Silver nitrate, $AgNO_3$

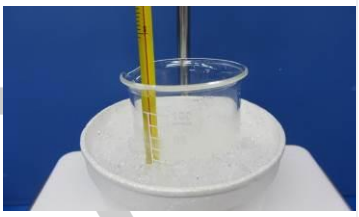
0.30 *M* Sodium acetate, abbreviated as NaOAc, $CH_3COONa{\cdot}3\,H_2O$

0.17 *M* Fe(III) indicator: ammonium ferric sulfate dodecahydrate, $NH_4Fe(SO_4)_2{\cdot}12\,H_2O$, dissolved in 6 *M* HNO_3

Procedure

Procedure		Illustration
I. K_{sp} of silver acetate at room temperature		
1.	Wash clean and oven-dry four 100 mL beakers and two funnels in advance.	

2.	Measure accurately 10.0 mL of 0.10 *M* $AgNO_3$ and 15.0 mL of 0.30 *M* NaOAc to a 100 mL beaker. Mix and stir for 15 min. Record the temperature of the solution.	
3.	Filter out AgOAc precipitate by gravity filtration. The filtrate is a saturated AgOAc solution. Note: Do not wet the filter paper used in this step to avoid affecting the concentration of saturated solution.	
4.	Use a 10 mL graduated pipet and a pipet filler to transfer accurately 5.0 mL of saturated AgOAc solution to an Erlenmeyer flask. Add 1 mL of Fe^{3+} indicator and perform a preliminary "rough" titration.	
5.	Wash a 25 mL buret clean and rinse it twice with *ca.* 5 mL of 0.020 *M* KSCN standard solution each time. Fill the buret with 0.020 *M* KSCN and record the initial volume (V_i) to 0.01 mL. Note 1: Use a clean and dry 100 mL beaker to take *ca.* 30 mL 0.020 *M* KSCN. Note 2: Expel air from the buret tip.	 
6.	Perform titration with 0.020 *M* KSCN (a white AgSCN precipitate is formed) until the solution turns orange-red (formation of $FeSCN^{2+}$). The end point is reached when the color persists for 15 s of swirling. Read and record the final volume (V_f) to 0.01 mL. Use the result of this "rough" titration to estimate the volume needed for the precise titration of the silver acetate solution in the following procedure.	 Left: before end-point Middle: the end-point Right: over titration

7.	Measure accurately 10.0 mL of saturated AgOAc solution and transfer it to another Erlenmeyer flask. Add 1 mL of Fe^{3+} indicator and perform a precise titration.	
II. K_{sp} of silver acetate at low temperature		
8.	Repeat steps 2~3 but place the beaker with the solution in an ice-water bath and stir it for 15 min. until the equilibrium is reached. Measure and record the equilibrium temperature, and then filter the solution immediately. Note 1: Continually add ice to the ice-water bath to maintain the constant low temperature. Note 2: During the filtration, the remaining solution in the beaker should be kept in the ice-water bath to prevent the dissolution of the AgOAc(s) caused by the temperature change, which will change the concentration of Ag^+ ions.	 
9.	Repeat steps 4~7 using the filtrate obtained in step 8 to determine the titration volume of 0.020 *M* KSCN.	
10.	(1) Both the liquid waste and the precipitate of this experiment contain the noble metal Ag. Recycle them in the indicated silver-containing waste container. (2) Brush clean the beakers and flasks with cleanser and tap water.	

References

1. Skoog, D. A.; West, D. M. *Fundamentals of Analytical Chemistry*; 3rd ed., Holt, Rinehart & Winston, Inc.: New York, **1976**; pp180-181.
2. Harris, D. C. *Quantitative Chemical Analysis*, 5th ed.; W. H. Freeman and Company: New York, **1999**; p 164.