

EXPERIMENT G

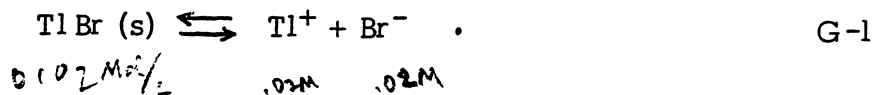
The Determination of the Solubility Product Constant of Tl Br*

The purpose of this experiment is to demonstrate the use of radiotracers in studying chemical phenomena where small quantities of material are involved, such as the solubility of sparingly soluble salts. A second aspect of this experiment involves the study of various physical chemical features of dilute solutions and in particular, the Debye-Huckel limiting law.

A. SURVEY OF PROBLEM.

The use of radiotracers in experiments designed to measure the solubility of sparingly soluble salts represents one of the oldest applications of radiotracers to chemistry. The basic idea of the experiment is simple, i.e., prepare a sample of labeled compound, measure its specific activity, let what little of the compound will dissolve enter solution, and measure the activity of the solution. In this experiment we shall also carefully deal with the effect of the ionic strength of the solution upon the solubility.

Let us now describe the experiment in formal terms. Consider a sparingly soluble salt such as Tl Br. In aqueous solution, the following equilibrium is established



*Some of the basic ideas used in this experiment have been outlined by J. C. Sheppard and R. C. Jensen, J. Chem Ed. 40, 34 (1963).

The solubility product constant is given by

$$K_{sp} = (A_{Tl^+})(A_{Br^-}) \quad G-2$$

where A_{Tl^+} and A_{Br^-} are the activities of the thallium and bromide ions, respectively. This can also be written as

$$K_{sp} = \gamma_{Tl^+} [Tl^+] \gamma_{Br^-} [Br^-] \quad G-3$$

where $[X]$ and γ_X are the concentration and activity coefficient of ion X.

This equation can be rewritten as

$$K_{sp} = \gamma_{\pm}^2 [Tl^+] [Br^-] \quad G-4$$

where the mean activity coefficient, γ_{\pm} , replaces the individual activity coefficients.

The Debye-Huckel limiting law furnishes a way of calculating the mean activity coefficient, γ_{\pm} , i.e.,

$$\log \gamma_{\pm} = 0.5091 Z_+ Z_- \sqrt{\mu} \quad G-5$$

where Z_+ is the positive ion charge, Z_- is the negative ion charge (expressed as a negative number) and μ is the ionic strength of the solution. The ionic strength μ is given as

$$\mu = \frac{1}{2} \sum_i C_i Z_i^2 \quad G-6$$

where C_i is the concentration of the i^{th} ion, Z_i its charge, and the summation extends over all the ions in solution. As will be shown, the Debye-Huckel

limiting law applies to dilute solutions ($<0.01M$) at $25^{\circ}C$. Once one has calculated γ_{\pm} using the Debye-Huckel limiting law, the measurement of the solubility of a compound will allow calculation of the apparent K_{sp} at some finite ionic strength using equation G-4.

Furthermore, if the Debye-Huckel theory is valid, a plot of the calculated value of $\log K_{sp}$ vs $\sqrt{\mu}$ for various values of μ will give a straight line with intercept at zero ionic strength corresponding to the true K_{sp} , i.e., the K_{sp} at zero ionic strength ($\mu = 0, \gamma_{\pm} = 1$). In this experiment, therefore, we shall measure the solubility of TlBr at various ionic strengths, test for linearity in the plot of $\log K_{sp}$ vs $\sqrt{\mu}$ (thus testing the Debye-Huckel limiting law), extrapolate the plot to $\mu = 0$ and report the true value of K_{sp} .

B. EXPERIMENTAL PROCEDURE.

1. Weigh out six samples, each containing 15 mg of dry thallium (I) nitrate. Dissolve each sample in a few ml of water in a 50 ml beaker and add 50 λ of ^{204}Tl tracer (containing $\sim 5 \mu Ci$) to each solution. Then add 0.1M sodium bromide to each solution until all the thallium has precipitated. Transfer each solution to a centrifuge cone, centrifuge and discard the supernatant. Wash each precipitate with 0.01 M sodium bromide, centrifuge and discard the washings.

2. Add 10.0 ml of distilled water to each centrifuge tube and heat to $80^{\circ}C$ for a few minutes to dissolve some of the precipitate. To the first five tubes, add 1.0 ml of a KNO_3 solution (0.01, 0.05, 0.10, 0.50 and 1.0 M in that order) and 1.0 ml of distilled water to the last tube.

3. Place the centrifuge tubes in a constant temperature bath at 25°C. After allowing 30 minutes for equilibration of the tubes, each centrifuge tube is removed from the bath, centrifuged and an aliquot of 0.5 ml is withdrawn from the solution.

4. Evaporate each aliquot to dryness on a planchet and count with a G-M counter to determine its activity. Record data in Table G-1.

5. To determine the activity of the original tracer solution, evaporate 50 λ of the solution on a planchet and count. Record the result in Table G-1.

6. The solubility of Tl Br can be calculated for each Tl Br sample using the following equations.

$$S = \frac{a}{q} \times 2000 \quad \text{G-7}$$

where S is the solubility of Tl Br in g/l ($S = [\text{Tl}^+] = [\text{Br}^-]$), a is the activity of the 0.5 ml aliquot taken from the equilibrated sample and q is the specific activity of Tl in the labeled precipitate. The specific activity, q, can be calculated from

$$q = \frac{\text{(activity per 50}\lambda \text{ aliquot of } ^{204}\text{Tl tracer)}}{\text{weight Tl in the Tl Br ppt. in g.}} \quad \text{G-8}$$

Calculate the solubility S of Tl Br for each sample and record it in Table G-1.

7. Use equations G-4, G-5, and G-6 to calculate the value of the apparent solubility product constant, K_{sp}' , for each solution, recording your results in Table G-1. Plot $\log K_{sp}'$ vs $\sqrt{\mu}$ on a piece of semilog paper. Extrapolate to $\mu = 0$ to get a true value for K_{sp} .

$$K_{sp} \text{ (true)} = \underline{\hspace{10em}}$$

$$K_{sp} \text{ (literature)} = 2.7 \times 10^{-6}$$

Comment upon any disagreement of your value of K_{sp} and the literature value. Also comment upon the range of validity of the Debye-Huckel limiting law as measured in your experiment.

Table G-1

Sample Number	Ionic Strength, μ	Precipitate Weight	Specific Activity of Tl in Precipitate	Activity of 0.5 ml aliquot of solution	Solubility (g/l)	K_{sp}	μ

50 λ of ^{204}Tl tracer contains _____.