FACULTY RESEARCH EDITION

of

The Savannah State College Bulletin

Published by

The Savannah State College

Volume 27, No. 2 Savannah, Georgia December, 1973

PRINCE A. JACKSON, JR. *President*

Editorial Committee

Articles are presented on the authority of their writers, and neither the Editorial Committee nor Savannah State College assumes responsibility for the views expressed by contributors.

TABLE OF CONTENTS

MEASUREMENT OF THE SOLUBILITY AND SOLUBILITY PRODUCT OF ZINC CHROMATE BY THE RADIOTRACER METHOD*

Levone Kornegay and M. P. Menon
Savannah State College, Savannah, Georgia

Saturated solution of a slightly soluble salt contains very low concentration of the dissolved solute which may be difficult to determine by most of the conventional methods. If the dissolved substance is radioactive its concentration can, however, be measured with good precision using raditracer techniques. The method has the advantage over the frequently used conductivity method, because it measures the total amount of the tagged element in solution regardless of whether the dissolved substance exists as ions or undissociated molecules (1). The sensitivity of the radiotracer method and the ease with which the radioactivity of the solution samples is measured make this analytical technique a valuable tool to determine the solubility of slightly soluble substances. Radiotracer methods have been employed, in the past, to measure the solubility of slightly soluble compounds such as PbS, $PbCrO_4$, AgBr etc., with much success (2, 3).

Physical data on the solubility and solubility product of the sparingly soluble zinc chromate are not available in literature (4). In this work the solubilities of zinc chromate at various temperatures have been determined using 243d ^{65}Zn + 2 tracer. The solubility data have also been used to measure the standard enthalpy change ($\Delta H°$) for the solution process of this salt.

EXPERIMENTAL

Reagents and Apparatus: Approximately 0.1 M reagent grade zinc sulfate solution, 0.1 M potassium chromate solution, zinc-65 tracer solution containing about 1 mC of activity and dil. hydrochloric acid solution were used. The apparatus consists of a thermostat keeping constant temperature and a gamma-ray spectrometer.

a) Measurement of the Specific Activity of the Labeled Zinc Chromate:

About twenty milliliters of the zinc sulfate solution was mixed thoroughly with an aliquot of ^{65}Zn tracer solution (about 0.075 mC) and treated with an excess of potassium chromate solution at a pH of about 7. The mixture was heated in a water bath, centrifuged and washed several times until the excess of chromate is completely removed. The residue was then washed with 95% ethanol and dried. A portion of the dried solid, Zn^*CrO_4, (~15 mg) was weighed in a counting tube as accurately as possible, dissolved in 5 ml of dil. HCl and counted in a NaI(Tl)

*This paper was presented at the Southeast ACS student Affiliate Regional conference held at Georgia Institute of Technology, April 5-7, 1973

well type gamma-ray spectrometer. The gamma-ray activity resulting from the annihilation gamma-rays and 1.12 Mev gamma-rays of the positron emitting ^{65}Zn above a cut off energy of about 0.3 Mev was measured. This was used to determine the specific activity of the standard solid sample (Zn*CrO).

b) Procedure for the Determination of the Solubility:

The rest of the labeled solid sample was mixed with deionized water taken in a large tube which was kept in the thermostat. With continuous stirring the solution was made saturated with Zn*CrO at the desired temperature. At each temperature the solution was kept in contact with the solid for about 15 minutes to ensure that equilibrium was reached. Five milliliters of the supernatent solution was withdrawn and transferred to a counting tube with a pipette, the nozzle of which was covered with glass wool to prevent the entrance of any solid particles into the pipette. This process was repeated at other temperatures. The gamma-ray activity of each aliquot of the saturated solution was measured under identical conditions. The background of the gamma-ray counter was also determined.

RESULTS AND DISCUSSION

The solubility of zinc chromate at any given temperature was calculated from the measured activity of 5 ml of the saturated solution and the specific activity of the solid sample using the relation:

$$C_{sat.}\ (M/l) = \frac{R_{sample}\ (cpm)}{R_{standard}\ (cpm)} \times \frac{1000}{5} \times \frac{W}{M} \quad \ldots\ (1)$$

where $R_{standard}$ is the activity of W g of the solid sample and M the molecular weight of $ZnCrO_4$. The values for Rsample and the solubility of $ZnCrO_4$ at different temperatures are listed in Table L.

The temperature dependence of the solubility of $ZnCrO_4$ may be represented by Van't Hoff's equation:

$$\log C_{sat.} = -\frac{\Delta H^\circ}{2.303R} \cdot \frac{1}{T} + \text{constant} \quad \ldots\ (2)$$

where ΔH° is the standard enthalpy change for the solution process. Figure 1 shows a plot of log $C_{sat.}$ versus 1/T the slope of which equals $-\Delta H^\circ/2.303R$. The standard enthalpy change for the solution of $ZnCrO_4$ calculated from the slope is 2.250 kcal/mole.

The solubility product of $ZnCrO_4$ may be expressed by the relation:

$$K_{sp} = (a_{Zn++})(a_{CrO_4--}) = C^2_{ZnCrO_4} \cdot (\partial_{\pm})^2 \quad \ldots(3)$$

where a and $\partial \pm$ represent the activity and the mean activity coefficient of the ions, respectively and C the concentration of zinc chromate in the saturated solution.

The mean activity coefficient for the ions in water solution at 25°C may be evaluated from the following equation:

$$-\log(\partial_{\pm}) = 0.509\, Z_{+} Z_{-} \sqrt{\tfrac{1}{2}\Sigma C_i Z_i^2} \quad \text{.....(4)}$$

where Z_+ and Z_- are the charges carried by cation and anion, respectively, of the electrolyte under study and C_i and Z_i are the respective concentration and charge of any ion present in the solution. The numerical constant, 0.509, is not, however, the same at different temperatures. The following expression for the numerical constant, $N'_{const.}$, can, nevertheless, be derived from Debye-Huckel's limiting law (5):

$$N'_{const.} = \frac{0.509 \times 3.71 \times 10^6}{(\epsilon' T')^{3/2}} \quad \text{.....(5)}$$

where ϵ' is the dialectric constant of water at temperature T' on Kelvin scale.

Values of ϵ', $N'_{const.}$, $\partial_{\pm}$ and Ksp at different temperatures (T') are given in Table II. It is obvious from this table that, in spite of a decrease in the mean activity coefficient, the solubility product of $ZnCrO_4$ also increases with temperature as does the solubility.

REFERENCES

1. Paneth, F., "Radioelements as Indicators", McGraw-Hill Book Co., New York, 1928
2. Hevesy G. and Paneth, F., Z. anog. Chem. *82*, 322 (1913)
3. Ruka, R. and Willard, J., J. Phys & Colloid Chem. *53*, 351 (1949)
4. "Handbook of Chemistry and Physics", Chemical Rubber Company, 48th edition, CRC, Cleveland, Ohio, 1967-68, page B-240
5. Hamill, W. H., Williams, Jr. R. R. and MacKay C., "Principles of Physical Chemistry" Prentice-Hall, Inc., 1966, N. J., page 262

Table I

Solubility of $ZnCrO_4$ at Various Temperatures Obtained from Activity Measurements

Specific Activity of the Standard (solid sample) = 9.5×10^9 cpm/M

Samples	Temperature (°C)	*Net activity in 5 ml sample (cpm)	Solubility ($\times 10^4$ M/l)
1	27.5	5478 ± 317	1.15 ± 0.07
2	36.0	5320 ± 633	1.12 ± 0.13
3	45.5	5164 ± 969	1.09 ± 0.20
4	55.0	4365 ± 429	0.92 ± 0.09
5	63.0	4450 ± 292	0.93 ± 0.06
6	72.0	4102 ± 109	0.86 ± 0.02

*Average of two values

Table II

Solubility Product of $ZnCrO_4$ as a Function of Temperature

Temp.(°K)	$*\epsilon'$	$N'_{const.}$	$\partial \pm$	K_{sp}
300.5	76.86	0.550	0.895	1.06×10^{-8}
309.0	74.09	0.555	0.891	0.994×10^{-8}
318.5	70.76	0.558	0.898	0.962×10^{-8}
328.0	67.90	0.565	0.905	0.696×10^{-8}
336.0	65.46	0.568	0.904	0.713×10^{-8}
345.0	62.82	0.590	0.905	0.607×10^{-8}

*Taken from the Handbook of Chemistry and Physics, CRC

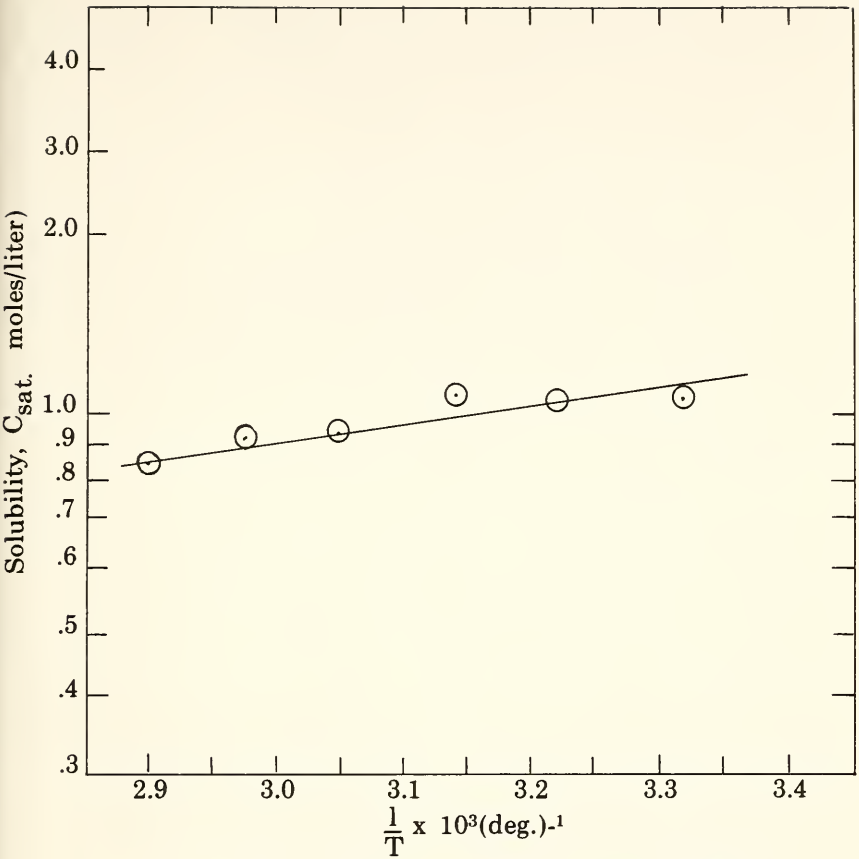

Fig. 1 Plot of log $C_{sat.}$ as a function of 1/T