

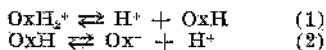
APPLICATION OF THE TYNDALL EFFECT TO THE EVALUATION OF THE SOLUBILITY PRODUCT FOR ALUMINUM TRIS-(8-HYDROXYQUINOLATE)

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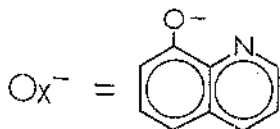
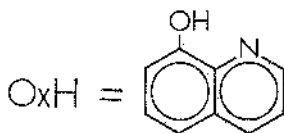
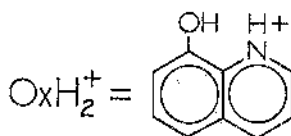
ABSTRACT.—The use of the Tyndall effect as an end-point detection technique for determining the pH of incipient precipitation yields experimental values for the solubility product for aluminum tris-(8-hydroxyquinolate) in excellent agreement with literature values. The determination is much simpler than classical potentiometric techniques and requires no special apparatus other than an ordinary electronic pH meter and a concentrated beam of light, such as that from a pencil flashlight; it is well-suited for high school or college student performance.

Certain metals, e.g., aluminum, iron, copper, zinc, cadmium, nickel, cobalt, and manganese, yield well-defined crystalline precipitates with the reagent 8-hydroxyquinoline (also called oxine, hydroxine, or 8-quinolinol), under certain specific conditions of pH of the precipitation medium. In general, these precipitates have the formula $M(C_9H_6ON)_n$, where n is one-half the coordination number of the metallic ion, M . Such compounds are conveniently designated by the common name *oximates*.

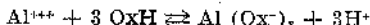
The reagent oxine is an amphoteric electrolyte, capable of functioning either as a weak base or as a weak acid, according to the reactions:



where



In precipitation reactions with the previously mentioned metals, oxine functions as a weak monoprotic acid; the metallic ion undergoing complex formation replaces the acidic proton. Hence, for aluminum ion, the reaction in an acidic medium may be represented as

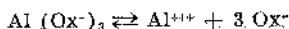


The formation of metal-oxine complexes is dependent upon the pH of the medium in which they are formed; the complex between aluminum and oxine begins initial precipitation at approximately pH 3 (precipitation is essentially complete in the range pH 4-10).

FUNDAMENTAL THEORY

In precipitation analyses, the chemist generally deals with very slightly solu-

ble salts behaving as strong electrolytes in solution. According to the classical definition of strong electrolytes, saturated solutions of such slightly soluble salts contain the complex species completely ionized into its component parts. In the case of aluminum oxinate, the equilibrium is



The reaction is reversible; at equilibrium, the rate of formation of aluminum oxinate is equal to the rate of its dissolution. The law of mass action yields the relationship

$$K = \frac{[\text{Al}^{+++}] [\text{Ox}^-]^3}{[\text{Al}(\text{Ox}^-)_3]}$$

where $[\text{Al}^{+++}]$ and $[\text{Ox}^-]$ represent the molar concentrations of Al^{+++} and Ox^- ions, respectively, and $[\text{Al}(\text{Ox}^-)_3]$ is the "active mass" of the solid salt. As long as undissociated $\text{Al}(\text{Ox}^-)_3$ is present, its active mass in the solution is constant and independent of the amount present. Therefore, the expression becomes

$$K_{sp} = [\text{Al}^{+++}] [\text{Ox}^-]^3 \quad (3)$$

where K_{sp} is the solubility product constant at the temperature of measurement.

The solubility product constant expression for aluminum oxinate may be written in terms of the various species involved in the reagent equilibria. From equations 1 and 2:

$$K_1 = \frac{[\text{OxH}] [\text{H}^+]}{[\text{OxH}_2^+]} \quad \text{and}$$

$$K_2 = \frac{[\text{Ox}^-] [\text{H}^+]}{[\text{OxH}]}$$

from which

$$[\text{OxH}] = \frac{K_1 [\text{OxH}_2^+]}{[\text{H}^+]} \quad \text{and}$$

$$[\text{Ox}^-] = \frac{K_2 [\text{OxH}]}{[\text{H}^+]}$$

Substitution of the expression for $[\text{OxH}]$ into that for $[\text{Ox}^-]$ yields

$$[\text{Ox}^-] = \frac{K_1 K_2 [\text{OxH}_2^+]}{[\text{H}^+]^2}$$

Further substitution of the latter expression for $[\text{Ox}^-]$ into the expression for

the solubility product constant for aluminum oxinate (equation 3) gives the relationship

$$K_{sp} = \frac{[\text{Al}^{+++}] K_1^3 K_2^3 [\text{OxH}_2^+]^3}{[\text{H}^+]^6}$$

which may be rewritten in exponential form as

$$pK_{sp} = -\log [\text{Al}^{+++}] + 3 pK_1 + 3 pK_2 - 3 \log [\text{OxH}_2^+] - 6 p\text{H} \quad (4)$$

The relationship in equation 4 is valid whenever the oxinate is precipitated in an acidic medium, in which the oxine is present almost completely in the form OxH_2^+ (equation 1). The experimental evaluation of the K_{sp} for aluminum oxinate therefore depends on the values of K_1 and K_2 for the reagent oxine, the molar concentrations of Al^{+++} and oxine reagent selected, and the pH at which the precipitation begins (incipient precipitation).

The values of the constants pK_1 and pK_2 have been determined potentiometrically by Lacroix (1947, p. 282) and reported to be 5.09 and 9.82, respectively. Since the concentrations of aluminum ion and the reagent oxine may be fixed, the experimental evaluation of the solubility product constant becomes dependent only upon the measurement of the pH at incipient precipitation.

EXPERIMENTAL

End-Point Detection Techniques.—The precise detection of end-points involving the observation of the first slight turbidity in precipitation titrations is relatively accurate, but tedious in inexperienced hands (Vogel, 1961, pp. 81-3). Application of the Tyndall effect (Skog and West, 1963, p. 164) as a means of detecting the first slight traces of suspended solid in the precipitation medium greatly increases the precision of this type of end-point detection. An ordinary spotlight, e.g., a simple pencil flashlight with the light beam passing through the precipitation medium in a direction perpendicular to the direction of observation, is quite satisfactory for this purpose. Prior to the end-point of the titration, the light beam is invisible through the solution but, as precipitation begins, the beam appears rather dramatically as a result of the Tyndall effect.

Reagents and Solutions.—The oxine reagent solution was prepared by dissolving the requisite weight of A. R. grade 8-hydroxyquinoline in about 50

ml. of M/5 HCl in a 100-ml. volumetric flask, followed by dilution to the mark with the acid. The stock solution of Al^{+++} was prepared by dissolving the requisite weight of A. R. reagent $Al_2(SO_4)_3 \cdot 18H_2O$ in distilled water containing a few drops of concentrated sulfuric acid to retard hydrolysis, followed by dilution to the desired volume. The N/10 NaOH solution was prepared by dissolving A. R. reagent in distilled water, followed by appropriate dilution. Standard pH 4.10 buffer solution was prepared from Coleman Certified buffer tablets, as directed by the manufacturer.

Apparatus.—Any commercial electronic pH meter equipped with glass indicator and saturated calomel reference electrodes is suitable for pH measurements at incipient precipitation; in this study, Coleman Model 18-A and Beckman Zeromatic instruments were used, standardized immediately prior to titrations against the standard pH 4.10 buffer. A variable aperture spotlight lamp, arranged so that the light beam passed through the titration beaker at right angles to the direction of observation, was used as an end-point detector; no significant difference was observed when an ordinary pencil flashlight was substituted for the lamp. Black construction paper placed behind the titration beaker was found to enhance end-point observation. Low-speed magnetic or manual stirring was found to be satisfactory.

Procedure.—After preliminary standardization of the pH meter, appropriate volumes of Al^{+++} and oxine reagent stock solutions were pipetted into the titration beaker. An accurately measured volume of distilled water was then added to increase the volume of the solution to a convenient level, if necessary. The titrations were accomplished by the addition of the NaOH solution from a buret—end-points of separate titrations were detected by normal and Tyndall effect observations of incipient precipitation. The pH value of the sample solutions at the end-points were recorded, as were the volumes of NaOH added; the total volume of solution at the end-point was obtained by simple arithmetical addition (to the nearest 0.5 ml) of all reagent and water volumes contributing to the final mixture. The temperatures of the titration mixtures at the end-points were observed and found to be $27 \pm 2^\circ C$ (room temperature) in all instances. Each titration required 15-30 minutes for completion.

RESULTS AND DISCUSSION

The results of pK_{sp} evaluations for aluminum oxinate at room temperature for normal and Tyndall effect end-point observations are shown in TABLES 1 and 2, respectively. End-points detected by normal visual observation were characterized by the initial appearance of a faint opalescence throughout the solution. The appearance of the Tyndall effect end-point was not only relatively sharp, but also somewhat earlier than normally observed end-points. In all instances, the pK_{sp} values were calculated by substitution of the experimental data into equation 4, along with the literature values for pK_1 and pK_2 previously given.

The pK_{sp} values shown in TABLES 1 and 2 correspond to K_{sp} values of 4.1×10^{-30} and 3.5×10^{-31} , respectively, for normal and Tyndall effect end-point observations. These correspond with literature values, determined potentiometrically, of 5×10^{-30} (Lacroix, 1947) and 5×10^{-31} (Borrel and Paris, 1952). The value obtained through Tyndall effect end-point observation is not only more accurate than the normally observed one, but also more precise; the pK_{sp} data for the Tyndall effect experiments show a standard deviation of 0.40, as compared with 0.75 for the normal observations. The confidence limit, at the 90% probability level, for the pK_{sp} results shown in Table 2 is 30.45 ± 0.20 .

An experiment based on the precipitation of aluminum tris-(8-hydroxyquinolate), or any of the other readily precipitated metallic oxinates, may be adapted quite readily to student performance. Other organic precipitating agents, such as dimethylglyoxime for nickel, which operate in a manner similar to 8-hydroxyquinoline may also be studied. In most instances, literature values for corresponding K_{sp} 's are available for comparison of results. In cases involving divalent metals, an equation analogous to equation 4 must be derived by the experimenter for evaluation of the solubility product constant from experimental data.

ACKNOWLEDGMENTS

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TABLE 1.—Solubility Product for Aluminum Oxinate Calculated from Normal Visual Observation of Incipient Precipitation. $[Al^{+++}] = 0.033$ M, $[OxH_2^+] = 0.095$ M.

Solution Composition			Final Volume ml.	pH at Incipient Pptn.	pK _{sp}
Al ⁺⁺⁺ ml.	OxH ₂ ⁺ ml.	H ₂ O ml.			
10.0	10.0	0	31.5	3.82	28.35
			31.0	3.45	30.53
		10.0	43.0	3.65	29.92
			44.0	3.82	28.94
		20.0	49.0	3.55	30.73
			48.0	3.80	29.19
30.0	61.5	3.89	29.09		
	61.5	3.88	29.15		
20.0	20.0	10.0	70.5	3.70	29.27
			72.0	3.85	28.41
10.0	20.0	20.0	69.5	3.75	29.23
			71.5	3.65	29.91

Mean: 29.39

TABLE 2.—Solubility Product for Aluminum Oxinate Calculated from Tyndall Effect Observation of Incipient Precipitation. $[Al^{+++}] = 0.033$ M, $[OxH_2^+] = 0.095$ M.

Solution Composition			Final Volume ml.	pH at Incipient Pptn.	pK _{sp}
Al ⁺⁺⁺ ml.	OxH ₂ ⁺ ml.	H ₂ O ml.			
10.0	10.0	0	31.0	3.41	30.77
			30.0	3.48	30.31
		10.0	41.5	3.52	30.63
			40.5	3.62	29.99
		20.0	48.5	3.58	30.55
			52.0	3.52	31.03
30.0	61.0	3.71	30.17		
	60.5	3.70	30.19		
20.0	20.0	10.0	71.5	3.62	29.79
			70.5	3.56	30.11
			71.5	3.50	30.50
10.0	20.0	20.0	70.0	3.45	31.07
			66.0	3.48	30.77

Mean: 30.45

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