Evaluation of the Solubilities of the Calcium and Magnesium Salts of 2,4-Dichlorophenoxy Acetic Acid

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Knowledge of the solubilities of calcium and magnesium salts of 2,4-dichlorophenoxy acetic acid would yield valuable information concerning the fate of this aquatic herbicide in lakes and reservoirs and the possible use of limestone products for its chemical removal at potable water treatment plants. The solubilities and activity coefficients for $Ca(2,4\text{-}D)_2$ and $Mg(2,4\text{-}D)_2$ were determined in distilled water and in KCl solutions ranging from 0.001M to 0.100M. The solubility of $Ca(2,4\text{-}D)_2$ was $9.05 \times 10^{-3}M$ and the solubility of Mg $(2,4\text{-}D)_2$ was $2.51 \times 10^{-2}M$ in distilled water. The activity solubility product constants were 1.096×10^{-6} for $Ca(2,4\text{-}D)_2$ and 1.55×10^{-5} for $Mg(2,4\text{-}D)_2$. Consequently, the usual aquatic herbicide dosages of 1 to 3 mg./liter of 2,4-D would be unaffected by normal calcium and magnesium ion concentrations of natural surface water or by that employed in potable water treatment plants.

THE 2,4-DICHLOROPHENOXY derivative of acetic acid (2,4-D) is used extensively as a herbicide for control of aquatic vegetation in lakes and reservoirs. Much concern has been expressed about the chemical effect of 2,4-D on water quality, its fate and persistence in surface waters, and its removal from water. Knowledge of the solubilities of calcium and magnesium salts of 2,4-D, therefore, would give valuable data concerning the fate of this herbicide in hard surface waters and the possible use of limestone products for its chemical removal at potable water treatment plants. A survey of the chemical literature did not reveal any pertinent information on the solubilities of the 2,4-dichlorophenoxy acetates of calcium and magnesium.

EXPERIMENTAL

Reagents. Reagent grade calcium acetate, magnesium sulfate, and potassium chloride were used. The 2,4-dichlorophenoxy acetic acid was Eastman's No. 5532 white label grade.

Preparation of Salts. The calcium and magensium derivatives were prepared from 1% solutions of sodium 2,4-dichlorophenoxy acetate, calcium acetate, and magnesium sulfate. The appropriate solutions were mixed slowly with heating until precipitation occurred, cooled to room temperature, and filtered. These salts were purified by three crystallizations from distilled water.

Determination of Solubility. Two grams of the appropriate salt were added to 100 ml. of deionized distilled water and placed in a shaking water bath thermostated at $25° \pm 0.5°$ C. for 48 hours. The pH values of the saturated solutions were 7.2 for the calcium salt and 5.1 for the magnesium salt. These values were high enough to suppress hydrolysis of the 2,4-dichlorophenoxy acetate ion. An aliquot of these suspensions was filtered through No. 41 Whatman paper, appropriately diluted with 95% ethanol, and 2,4-D determined spectrophotometrically at 284μ (*1, 2*).

Results. Table I lists the precipitation reactions and the formulas used to calculate the solubilities, solubility products, and activity coefficients of $Ca(2,4\text{-}D)_2$, and $Mg(2,4\text{-}D)_2$. Table II shows the solubilities and activity coefficients of the calcium and magnesium salts of 2,4-D that were determined in pure water and in KCl solutions ranging from 0.001*M* to 0.100*M*. The ionic strengths ranged from 0.027 to 0.138 for the $Ca(2,4\text{-}D)_2$, solutions and from 0.075 to 0.192 for the $Mg(2,4\text{-}D)_2$ solutions.

The activity coefficients of $Ca(2,4\text{-}D)_2$ and $Mg(2,4\text{-}D)_2$ were evaluated from increased solubilities in the presence of KCl. The usual extrapolation of the pk *vs.* $(\mu)^{1/2}$ curve to zero ionic strength for determination of M_o values would have been inaccurate because of the initial high solubilities, hence high ionic strengths of the calcium and magnesium salts. Therefore, the Debye-Hückel expression (Equation 5, Table I) was used to calculate the activity coefficients. The average effective diameter of the $Ca(2,4\text{-}D)_2$ and $Mg(2,4\text{-}D)_2$ salts were calculated by simultaneous solution of Equation 5 at the KCl concentrations of 0.000 and 0.100*M*. The values of 2.5 *A* for $Ca(2,4\text{-}D)_2$ and 3.5 *A* for $Mg(2,4\text{-}D)_2$ are acceptable since the activity solubility product constants and M_o values are in good agreement throughout the range of ionic strengths. The average $p\underline{K}$ values of 25° C. for $Ca(2,4\text{-}D)_2$ and $Mg(2,4\text{-}D)_2$ were

Table I. Equations and Formulas (*3*)

$$K = \frac{[Ca^{++}][2,\bar{4}\text{-}D]^2}{[Ca(2,4\text{-}D)_2)]} \quad (1)$$

$$2[Ca^{++}] = [2,\bar{4}\text{-}D] \quad (2)$$

$$k = [2M]^2[M] = 4M^3 \quad (3)$$

$$\underline{K} = (V+^{v-}\ V-^{v-})\ M^v f^v_{\pm} = 4M^3 f^3_{\pm} = k f^3_{\pm} \quad (4)$$

$$\log f_{\pm} = \frac{-0.509\ Z + Z - \mu^{1/2}}{1 + 0.329\ a\ \mu^{1/2}} \text{ at } 25° \text{ C.} \quad (5)$$

$$\log \underline{K} = \log k + 3 \log f_{\pm} \quad (6)$$

$$\log M = \log M_o + \frac{0.509\ Z + Z - \mu^{1/2}}{1 + 0.329\ a\ \mu^{1/2}} \quad (7)$$

$$pk = \log k \quad (8)$$

$$\rho\underline{K} = \log \underline{K} \quad (9)$$

Table II. Solubilities and Activity Coefficients of $Ca(2,4\text{-}D)_2$ and $Mg(2,4\text{-}D)_2$ at 25° C.

KCl, M	2,4-D, G./L.	$M \times 10^3$	μ	$f_{\pm}$	pk	$p\underline{K}$	$M_0 \times 10^3$
Calcium salt (a = 2.5 A)							
0.000	4.00	9.0477	0.1646	0.712	5.53	5.97	6.44
0.001	4.05	9.1608	0.1688	0.707	5.51	5.96	6.48
0.005	4.20	9.5001	0.1830	0.689	5.46	5.95	6.55
0.010	4.30	9.7263	0.1979	0.671	5.43	5.95	6.53
0.050	4.90	11.083	0.2902	0.578	5.26	5.98	6.41
0.100	5.60	12.666	0.3712	0.513	5.09	5.96	6.50
					Av.	5.96	6.48
Magnesium Salt (a = 3.5 A)							
0.000	11.1	25.107	0.2744	0.614	4.20	4.83	15.4
0.001	11.3	25.559	0.2787	0.610	4.18	4.82	15.6
0.005	11.7	26.465	0.2904	0.600	4.13	4.79	15.9
0.010	12.0	27.143	0.3023	0.596	4.10	4.78	16.2
0.050	12.7	28.726	0.3688	0.545	4.02	4.81	15.7
0.100	13.5	30.536	0.4380	0.505	3.94	4.83	15.4
					Av.	4.81	15.7

determined as 5.96 and 4.81, respectively, by Equations 4 and 9. The average M_o values at 25° C. for $Ca(2,4\text{-}D)_2$ and $Mg(2,4\text{-}D)_2$ were determined as 6.48×10^{-3} and 1.57×10^{-3}

The effect of temperature on solubility of these two salts was examined in distilled water. The solubilities increased from 3.26 grams/liter as 2,4-D at 4° C. to 5.21 grams/liter at 35° C. for $Ca(2,4\text{-}D)_2$ and from 8.4 grams/liter at 4° C. to 14.2 grams/liter at 35° C. for $Mg(2,4\text{-}D)_2$.

DISCUSSION

The calcium and magnesium salts of 2,4-D are quite soluble in distilled water at 25° C., 4000 mg./liter and 11,100 mg./liter, respectively. Therefore, the ordinary concentrations of calcium and magnesium ions in a surface water would not remove 2,4-D through precipitation reactions. Likewise, limestone products could not be used to remove 2,4-D at water treatment plants since formulations of this herbicide are applied to concentrations less than 3 mg./liter as the acid equivalent.

The assumption indicated in Equation 1, Table I, appears to be valid since the Debye-Hückel expression is followed up on ionic strengths of 0.138 for $Ca(2,4\text{-}D)_2$ and up to 0.192 for $Mg(2,4\text{-}D)_2$. This is substantiated by the close agreement of the $p\underline{K}$ value and of the M_o values.

NOMENCLATURE

A = activity coeflcient
K = equilibrium constant
M = solubility, moles/liter
k = classical solubility product
$\underline{K}$ = activity solubility product
$f_{\pm}$ = mean activity coefficient of $Ca(2,4\text{-}D)_2$ and $Mg(2,4\text{-}D)_2$
Z = valence
μ = ionic strength
a = average effective diameter of the ions of $Ca(2,4\text{-}D)_2$ and $Mg(2,4\text{-}D)_2$, A.
M_o = solubility at zero ionic strength, moles/liter
v = total number of ions—*i.e.*, $v+$ + $v-$ produced from one molecule upon ionization
p = negative logarithm

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A Calorimetric Study of Nickel-Cadmium Cells

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NICKEL-CADMIUM batteries have been used as energy storage devices in many space power systems. They are usually employed in conjunction with solar cells. They are also utilized in many commercial and industrial applications where a rechargeable and portable power supply is required.

The thermal design of such a battery requires the availability of accurate and reliable thermal data. This article describes a calorimetric study of the heats generated during the discharge of some nickel-cadmium cells. This study has provided an experimental determination of the enthalpy of the cell reaction and thermal data for the