[CONTRIBUTION NO. 176 FROM THE RESEARCH LABORATORIES, MUTUAL CHEMICAL DIVISION, ALLIED CHEMICAL AND DYE CORPORATION]

Magnesium Dichromate Hydrates[1]

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$MgCr_2O_7 \cdot 6H_2O$ has been isolated as a new compound and the stable phase in the system $MgCr_2O_7$–H_2O at ordinary temperatures. Solubilities in this system have been measured over the range 30–82°. The transition to $MgCr_2O_7 \cdot 5H_2O$ is unusual in that it occurs with no measurable break in the solubility curve and with a very small heat of transition of 0.20 ± 0.06 kcal./mole at 26°. For this reason the transition temperature can only be determined approximately as $48.5 \pm 0.5°$, the saturation concentration being 61.16% $MgCr_2O_7$. The two phases have been shown microscopically and by X-ray analysis to be crystallographically different: $MgCr_2O_7 \cdot 6H_2O$: orthorhombic, a = 11.9 Å., b = 12.42 Å., c = 7.71 Å., $d^{25}{}_4$ 2.002; $MgCr_2O_7 \cdot 5H_2O$: triclinic, a = 9.32 Å., b = 11.9 Å., c = 7.72 Å., α = 140° 40′, β = 99° 13′, γ = 82° 5′, $d^{25}{}_4$ 2.001. Other optical data are also given.

In earlier work by one of us,[3] a pentahydrate and monohydrate of magnesium dichromate were described. No evidence of any higher hydrate was obtained at temperatures down to 0°. Since that time, several batches of the pentahydrate have been prepared by the described procedure without difficulty. On one occasion, however, a product resulted which when carefully dried in a laboratory rotary drier and analyzed for hexavalent chromium, gave an assay corresponding to 69.26% $MgCr_2O_7$. Since the pentahydrate theoretically contains 72.74% $MgCr_2O_7$ and the hexahydrate 68.98%, there was a strong presumption that the crystals obtained were a new hydrate $MgCr_2O_7 \cdot 6H_2O$. Further examination of the properties of the two hydrates showed unusual characteristics attending the transition, so that measurements of solubility heat of transition, transition temperature, solid phase composition and crystal structure were necessary to establish beyond doubt the existence of both hydrates.

Experimental

Preparation.—The preparation of magnesium dichromate hexahydrate was carried out using the same procedure as that previously described for the pentahydrate.[3] Analyses of several samples for hexavalent chromium confirmed a chemical composition corresponding to the hexahydrate. Calcd. for $MgCr_2O_7 \cdot 6H_2O$: CrO_3, 57.40. Found: CrO_3, 57.51, 57.45, 57.39, 57.39, 57.41, 57.43, 57.43, 57.38. Batches were also analyzed for magnesium. Calcd.: MgO, 11.57. Found: MgO, 11.60. Once the hexahydrate had been prepared, it was found necessary to carry out crystallizations at temperatures around 50° to ensure formation of the previously reported pentahydrate.

Measurement of Transition Temperature.—An attempt was made to measure transition temperature by the slow heating and cooling of a large sample of heavy crystal slurry. Much the same behavior was observed as in the case of calcium dichromate,[4] except that breaks at the same temperature on heating and cooling could not be obtained at rates of temperature change as low as 0.015°/minute. However, evidence of a heat effect was obtained, the low point of the "break" on heating being 50.3° and the high point of the "break" on cooling being 47.8°. With 100 g. of crystals and 400 g. of saturated solution in a Dewar flask, the heat effect lasted about 1 hr.

Solubility.—The same technique for solubility measurement was used as in previous work from this Laboratory.[5] Excellent checks were obtained on duplicate samples, the precision being better than 0.1% of the measured value. The results obtained were

Temp., °C.	Solubility, % $MgCr_2O_7$ by wt.	Temp., °C.	Solubility, % $MgCr_2O_7$ by wt.
30.3	58.52	52.0	61.72
39.4	59.75	53.5	61.82
42.2	60.23	53.6	61.92
44.2	60.53	54.0	61.96
45.9	60.68	55.2	62.32
47.5	61.03	55.7	62.40
47.8	61.08	56.4	62.34
48.0	61.01	57.8	62.60
48.2	61.05	60.2	62.85
49.4	61.35	70.0	64.39
49.8	61.40	78.6	66.53
50.4	61.44	80.0	66.51
51.0	61.57	81.7	67.21
51.6	61.72		

Plottings of these data show no break in the curve, either when examined as a whole, or when the data in the region of the suspected transition are examined in detail.

Chemical Analysis of Solid Phase.—Solid phase from slurries agitated at constant temperature for 24 hours in the region of the suspected transition temperature was separated by centrifuging at 1200 × g in a preheated centrifuge, dried carefully, examined under the microscope and analyzed. The results were

Temp., °C.	% $MgCr_2O_7$ in solid[a]	Hydrate present
43.7	68.7	6
45.8	69.4	6
46.3	68.6	6
47.0	69.9*	6
48.2	68.9	6
48.2	71.2**	5, 6
48.4	70.2**	5, 6
49.0	72.6	5
49.3	72.1	5
49.8	72.6	5
51.2	73.1	5
54.0	72.9	5

[a] The sample indicated * was evidently overdried; those indicated ** showed two crystal phases under the microscope.

Heat of Solution.—Samples of the supposed penta- and hexahydrate were crystallized at 60° and room temperature, respectively, then carefully dried in a laboratory rotary drier. The "pentahydrate" sample analyzed 72.75% $MgCr_2O_7$ (theory 72.74%), the "hexahydrate" 69.01% (theory 68.98%). The heat of solution was measured by weighing about 20 g. of salt in a thin-walled Pyrex bulb, im-

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(1) Much of the experimental work was performed in partial fulfilment of the requirements for the degree of Master of Science from The Johns Hopkins University. A preliminary report of this work was also made at the meeting-in-miniature of the Maryland Section of the American Chemical Society on November 18, 1955.

(2) Inquiries regarding this paper should be addressed to the junior author, Solvay Process Division, Allied Chemical and Dye Corporation, Syracuse, New York.

(3) W. H. Hartford, THIS JOURNAL, **68**, 2192 (1946).

(4) W. H. Hartford, K. A. Lane and W. A. Meyer, Jr., *ibid.*, **72**, 3353 (1950).

(5) W. H. Hartford and K. A. Lane, *ibid.*, **70**, 647 (1948).

mersing the bulb in a weighed amount of water (about 350 g.) in a covered Dewar, the entire system being maintained at room temperature, which was 26 ± 1°. The temperature was recorded at one-minute intervals using a differential thermometer until equilibrium was established, and the bulb was then broken. The instantaneous change in temperature, extrapolated to the time of breaking of the bulb, gives a measure of the heat of solution. The following data were obtained for the heat of solution in calories per mole

	"Penta-hydrate"		"Hexa-hydrate"
Av. (7 detns.)	−782	(11 detns.)	−979
Std. dev.	49		40

The heat of transition of the hexahydrate to the pentahydrate is the difference between these figures. Statistical breakdown of the figures shows the difference to be small but highly significant. For 99% confidence limits the heat of transition at 26 ± 1° is 198 ± 62 cal./mole.

Optical Properties of the Hydrates.—Considerable difficulty was encountered with microscopic examination of the crystals because of their extreme deliquescence. Oil immersion was used even at the low magnifications needed. The optical properties determined were

	$MgCr_2O_7 \cdot 6H_2O$	$MgCr_2O_7 \cdot 5H_2O$
Optical character	Biaxial positive	Biaxial positive
Probable system	Orthorhombic	Triclinic, pseudo-hexagonal
n_D	1.62, 1.63, 1.70	1.61, 1.65, 1.70
2V (axial angle)	21°	49°
Dispersion	Moderately strong	Weak

Density.—Density of the two types of crystal was measured in a pycnometer, using pure toluene as the immersion liquid, which was previously compared against freshly distilled, deaerated water as a primary standard. Results were (calculated as $d^{25}{}_4$)

$MgCr_2O_7 \cdot 6H_2O$ 2.000, 2.005, 2.000, 2.004, 2.001; av. 2.002
$MgCr_2O_7 \cdot 5H_2O$ 2.000, 2.002, 2.002; av. 2.001

X-Ray Diffraction Measurements.—Of the foregoing data, heating and cooling curves, chemical analysis and heats of solution indicate the existence of distinct solid phases; microscopic studies show two different physical entities and some difference in optical character, while solubility and density measurements fail to give evidence of more than one solid phase. X-Ray diffraction photographs with powder samples were unsatisfactory; in preparation of the samples, there was sufficient moisture absorption that no difference in pattern was noted. Satisfactory single crystal pictures were obtained by embedding selected single crystals in plastic cement before photographing. Some specimens of the pentahydrate showed marked twinning. Results of the X-ray diffraction studies were

Crystal system	$MgCr_2O_7 \cdot 6H_2O$ orthorhombic	$MgCr_2O_7 \cdot 5H_2O$ triclinic
a, Å.	11.9	9.32
b, Å.	12.42	11.9
c, Å.	7.71	7.72
α	...	140° 40′
β	...	99° 13′
γ	...	82° 5′
Density, calcd.	2.03	2.06

Discussion

The data presented above establish without doubt the existence of $MgCr_2O_7 \cdot 6H_2O$ as the stable hydrate of the salt at room temperature. Chemical analysis of the existence of a heat of transition and crystal structure study distinguish it from the previously reported $MgCr_2O_7 \cdot 5H_2O$, which has been further confirmed in this work as a definite hydrate. The solubility curve in the vicinity of the transition point and the heat of transition indicate that the transition between the two hydrates is unusual.

Blasdale[6] states: "Since the form of the solubility curve depends in part upon the change in heat content and in part upon the change in volume accompanying the process of solution, and since it is *not probable* that any two solids should give identical values for the relations existing between these constants, the entire solubility curve *must* be made up of as many separable parts as there are solid phases concerned." (Italics ours). More logically, this statement should be modified to read "the entire solubility curve is *usually* made up of as many separable parts. . ." Magnesium dichromate appears to be an unusual salt, in that the slope of the solubility curve is continuous, within experimental error, at the transition point. If, as is frequently done, solubility is expressed as a power function of temperature, it may be shown that curves meeting the requirements of the phase rule can be constructed using four virial constants. If, in the present case, S_1 is the solubility of the pentahydrate, S_2 the solubility of the hexahydrate, t the temperature. and t_0 the transition temperature

$$S_1 = at_3 + bt^2 + ct + d$$

$$S_2 = et^3 + ft^2 + gt + h$$

$$at^3{}_0 + bt^2{}_0 + ct_0 + d = et^3{}_0 + ft^2{}_0 + gt_0 + h$$

at t_0, $dS_1/dt = dS_2/dt$, or $3at^2{}_0 + 2bt_0 + c = 3ct^2{}_0 + 2ft_0 + g$

at $t < t_0$, $S_2 < S_1$ at $t > t_0$, $S_1 < S_2$

from which it may be shown that $a < e$ is a further condition on the solubility curves. The development of numerical values for the constants from the data lies outside the scope of this paper. From Blasdale's statement above, it may also be inferred that the change in slope of the solubility curve at transition is independent of the heat of transition. However, a large heat of transition denotes profound structural changes during the hydrate transition, and the heats of solution and volume changes on solution of the two phases would be expected to differ markedly. A large heat of transition thus usually occurs with a sharp break in the solubility curve and, accordingly, the very small heat of transition observed in the present instance is entirely consistent with the absence of a measurable break in the solubility curve.

The heat of transition observed, 0.20 kcal./mole, is the smallest ever recorded for a hydrate transition, to our knowledge. The loss of one mole of water from $MgSO_4 \cdot 7H_2O$, for instance, is attended by a heat effect of 3.78 kcal./mole.[7]

Also in support of the small heat effect and lack of break in the solubility curve are the X-ray data. It will be noted that the c dimensions of both hydrates are identical, while the b cell dimension of the pentahydrate is identical with the a dimension of the hexahydrate. The very nearly identical densities are also of interest, since this shows the

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(6) W. C. Blasdale. "Equilibria in Saturated Salt Solutions," A.C.S. Monograph no. 31, Reinhold Publ. Corp., New York, N. Y., 1927, p. 55.

(7) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," U. S. Govt. Printing Office, Circular of the National Bureau of Standards 500, 1952, p. 379.

volume changes attending solution for the two hydrates to be nearly equal.

The small heat effect and the relatively high viscosity of saturated solutions of magnesium dichromate also give a reason why measurement of the transition temperature with precision is difficult. The average temperature of the heating and cooling "breaks" is 49.0 ± 1.3°, but two solid phases were identified unequivocally only at 48.2° and 48.4°. The best estimate available appears to be 48.5 ± 0.5° for the transition temperature, at a solubility of 61.16% $MgCr_2O_7$. The transition occurs exceptionally slowly, twenty-four hours agitation being required for equilibration in the tests described above. These same characteristics explain why $MgCr_2O_7 \cdot 6H_2O$, actually the stable phase at room temperature, went so long undiscovered.

While visual examination of the solubility curve shows no apparent break, statistical methods were also used to verify this point. Over the temperature range 39.4 to 60.2°, the equation $S = 53.73 + 0.15325T$ fits the data with an average deviation of 0.05% solubility and a maximum error of 0.13%. An appreciably better fit cannot be obtained by the use of curves of higher order, and the precision of fit of the above straight line is substantially the same as the precision of the solubility data itself.

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[CONTRIBUTION FROM THE SPECTROSCOPY LABORATORIES AT CANISIUS COLLEGE]

Niobium and Tantalum 8-Quinolinolates[1]

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A preparative technique was developed for an interaction of niobium and tantalum compounds with 8-quinolinol (8-hydroxyquinoline) which minimized contamination of the product with basic salts. A modification of the originally proposed method for the preparation of niobium 8-quinolinolate was used and a new formula for the compound of niobium 8-quinolinolate proposed. Infrared spectroscopy was utilized to verify some of the results. Products with the empirical formula $MO(C_9H_6ON)_3$ and $M(C_9H_6ON)_5$ have been prepared in the pure form.

Discussion

The compounds of 8-quinolinol with niobium or tantalum have been described as of indefinite or of inadequately described structures.[3] Niobium 8-quinolinolate was first prepared by Sue[4] and a formula was proposed.

$$Nb_2O_5 \cdot 5.5(C_9H_6ON) \cdot 4(H_2O)$$

Schwarz[5] reported having prepared niobium and tantalum 8-quinolinolates in connection with an analytical study of niobium and tantalum but no formulas were proposed. Doan and Duval[6] reported from a thermogravimetric study that the compound of niobium 8-quinolinolate as prepared by Sue has no definite composition.

Experimental

Niobium 8-Quinolate.—One-tenth g. of very high purity niobium oxide was fused with 5 g. of potassium bisulfate. The melt dissolved in 100 ml. of 10% sulfuric acid solution containing 1 g. of oxalic acid. 8-Quinolinol (1.5 g.) in 12% acetic acid solution was then added. Upon neutralizing with ammonium hydroxide a finely crystalline yellow precipitate of niobium 8-quinolinolate formed. After digesting for one hour, the precipitate was filtered on a weighed glass-frit crucible and washed with hot water. To produce a substance free of water and excess 8-quinolinol, the precipitate was dried overnight at 155°.

Anal. Calcd. for $NbO(C_9H_6ON)_3$: Nb, 17.16; C_9H_6ON, 79.88. Found: Nb, 17.1; C_9H_6ON, 80.3.

Anal. Calcd. for $NbO(C_9H_6ON)_3$: Nb, 17.16; C_9H_6ON, 79.88. Found: Nb, 17.1; C_9H_6ON, 80.3.

Tantalum 8-Quinolinolate from Tantalum Pentachloride.—A small excess of a benzene solution of 8-quinolinol was added to a benzene solution of tantalum pentachloride. A bright, orange-yellow precipitate was formed which was filtered and washed with benzene.

Anal. Calcd. for $Ta(C_9H_6ON)_5 \cdot 5HCl$: Ta, 16.7; C_9H_6ON, 66.5; HCl, 16.8. Found: Ta, 18.4; C_9H_6ON, 66.1; HCl, 15.2.

Niobium and Tantalum 8-Quinolinolates from Mixed Oxides.—Equal weights of niobium and tantalum oxides were mixed and fused with potassium bisulfate. The same procedure by which niobium 8-quinolinolate was prepared, was followed. The yellow precipitate which formed was digested, then filtered and dried overnight at 155°.

Anal. Calcd. for $TaO(C_9H_6ON)_3$ and $NbO(C_9H_6ON)_3$: Ta + Nb, 21.9; C_9H_6ON, 75.4. Found: Ta + Nb, 22.2; C_9H_6ON, 74.0.

Analysis of Compounds.—The determination of niobium in niobium 8-quinolinolate was determined from the weight of the starting material. The niobium oxide starting material was determined by X-ray fluorescence analysis to be 99.5+% pure. In the mixed compounds of niobium and tantalum and in the tantalum compound prepared from tantalum pentachloride, weighed portions of the final products were ignited to the oxides. The 8-quinolinol content was determined by a volumetric titration with sodium bromate solution as recommended by Berg.[7] The hydrogen chloride content of the tantalum compound was determined by a Volhard titration of the chloride.[8]

The infrared spectrum of the dry compounds (made in Nujol-mull) showed no bands for water and free 8-quinolinol and no shift in bands of the complex as water was removed.

A change in the technique of precipitation of niobium 8-quinolinolate was used to avoid contamination of the final product with basic salts. When a pure compound, free of

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[1] Supported in part by a grant from Research Corporation, New York, N. Y.

[2] Abstracted from the Master's Thesis of John H. Archibald.

[3] J. P. Phillips, *Chem. Revs.*, **56**, 271 (1956).

[4] P. Sue, *Compt. rend.*, **196**, 1022 (1933).

[5] V. Schwarz, *Angew. Chem.*, **47**, 228 (1934).

[6] V. M. Doan and C. Duval, *Anal. Chim. Acta*, **6**, 83 (1952).

[7] R. Berg, *Pharm. Ztg.*, **71**, 1542 (1926).

[8] J. Volhard, *J. prakt. Chem.*, **117**, 217 (1874).