[CONTRIBUTION FROM THE RESEARCH LABORATORIES, MUTUAL CHEMICAL COMPANY OF AMERICA]

Some Properties of Lithium Dichromate

BY WINSLOW H. HARTFORD AND KEITH A. LANE

Lithium dichromate has been described[1,2] and the system Li_2O–CrO_3–H_2O has been investigated at 30°,[3] while Heydweiller[4] has investigated the density and equivalent conductance of dilute solutions at 18°. The black or brownish-black crystals of lithium dichromate dihydrate previously described were suspected of being impure in view of the characteristic red to orange color of the other alkali dichromates. The growing importance of lithium salts and of the dichromates has rendered the reevaluation of the properties of this salt desirable.

Experimental

Preparation of Lithium Dichromate Dihydrate.—Lithium carbonate of N. F. grade was employed as a source of lithium. This material assayed 99.60%, the principal impurities being other alkalies and sulfate.[5] Technical chromium trioxide, 99.7% pure, was used as the source of chromium, the principal impurities in this material being Cr(III), sulfate and moisture. The procedure for the preparation of a typical batch of lithium dichromate dihydrate was as follows:

Three and one-half kilograms of chromium trioxide was dissolved in water to give 7.5 liters of solution. Solid lithium carbonate was added, with agitation, until a *p*H of 3.5 was reached, about 1.3 kg. of lithium carbonate being employed. Cr (III) was converted to Cr (VI) by electrolysis of the solution at 4.5 volts, using lead electrodes. The oxidation of Cr (III) was judged complete when the solution became bright orange-red in color. The batch was filtered free of lead chromate, concentrated to a volume of 4.0 liters and allowed to cool with agitation, when a crop of crystals separated which were centrifuged and dried in a stream of warm air in a small rotating dryer. Additional yields may be obtained from reconcentration of the mother liquor. The crystals are bright red-orange in color, deliquescent, and consist of thin plates with crystal angles resembling those of sodium dichromate dihydrate. The black color reported by the original investigators[1,2] was evidently due to trivalent chromium present in the chromium trioxide used. Their identification of the salt as the dihydrate was confirmed by the following analyses: For $Li_2Cr_2O_7 \cdot 2H_2O$: calcd.: Li_2O, 11.24, CrO_3, 75.21; H_2O, 13.55. Found: Li_2O (as sulfate) 11.23, 11.31; CrO_3 (by electrometric titration with $FeSO_4$) 74.91, 74.91; H_2O (by weight loss), 13.54.

Existence of the Anhydrous Salt and Behavior on Heating.—The dihydrate is converted to the anhydrous salt on heating. All water is removed on heating four days at 110°; Schulerud[1] reports dehydration at 130°. On heating the crystalline dichromate slowly with saturated solution to the boiling point and then cooling with agitation, no evidence was obtained of any transition point on plotting a time–temperature curve. The anhydrous salt does not exist as a crystalline phase in contact with solution at temperatures below the boiling point of a saturated solution, 149°.

When the solid dihydrate is slowly heated with agitation in air, it melts with partial decomposition at 187°. Water and oxygen are evolved and the salt is partially decomposed to lithium chromate and chromic chromates.

Density of the Solid Dihydrate.—The density of the solid dihydrate was measured in a pycnometer at 30°, using light mineral oil as the immersion liquid, giving $d^{30}{}_4$ 2.34.

Density of the Solution.—The salt dissolves congruently in water, and no difficulty was experienced in measuring the density of the solution in a pycnometer. The following values were obtained at 30°.

% $Li_2Cr_2O_7 \cdot 2H_2O$ by weight	$d^{30}{}_4$	% $Li_2Cr_2O_7 \cdot 2H_2O$ by weight	$d^{30}{}_4$
0.00	0.9957	36.64	1.2575
4.05	1.0195	38.79	1.2777
6.15	1.0320	41.48	1.3026
8.16	1.0455	44.64	1.3325
12.13	1.0705	46.10	1.3470
15.37	1.0930	50.72	1.3954
18.98	1.1178	52.67	1.4177
22.38	1.1427	56.44	1.4602
26.82	1.1767	61.96	1.5246
30.82	1.2082	65.11	1.567[a]

[a] Extrapolated to saturation concentration.

The data are plotted in Fig. 1, and may be shown to fit the empirical equation

$$d^{30}{}_4 = 0.9957 + 0.00586\,C + 0.000233\,C^2 + 0.000000303\,C^3$$

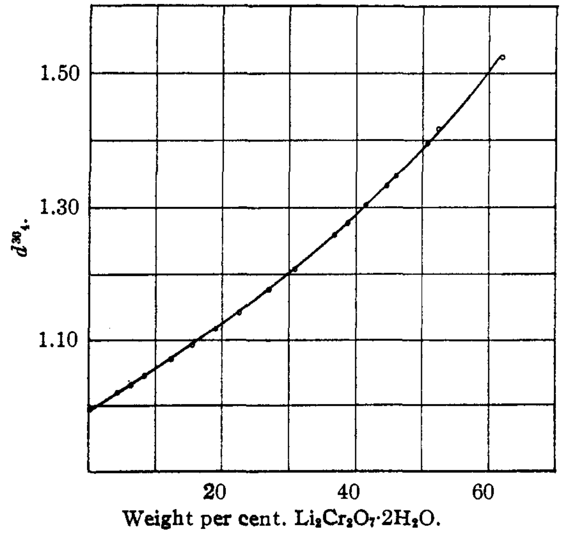

Fig. 1.—Density of lithium dichromate solutions at 30°.

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(5) Foote Mineral Co., Philadelphia, Pa., private communication.

where C is concentration in weight per cent. of $Li_2Cr_2O_7\cdot 2H_2O$, with an average error of 0.0006 in the density. These data are in substantial agreement with those of Heydweiller,[4] which cover the range up to 23%, when the temperature difference is taken into consideration.

Solubility in Water.—This was determined by agitating about 2 liters of solution with an excess of the solid phase in a covered container at a constant temperature provided by an immersion heater and a vapor-mercury sensitive element. After reaching equilibrium (about six hours) a sample of the clear solution was removed by means of a sintered glass funnel and analyzed. The results given are the average of duplicate analyses for chromate on each of two samples, which checked with an average error of 0.04%. The value for 0.8° was obtained by surrounding the solution container with crushed ice, and represents an average of temperatures varying from 0.6 to 1.0°. The following data were obtained:

Temp., °C.	Soly., % by weight $Li_2Cr_2O_7\cdot 2H_2O$	Temp., °C.	Soly., % by weight $Li_2Cr_2O_7\cdot 2H_2O$
0.8	62.36	70.0	69.49
30.0	65.11[a]	80.0	70.76
40.0	66.08	90.0	72.26
50.0	67.28	100.0	73.55
60.0	68.39		

[a] Schreinemakers' data[3] at 30° give 65.4% $Li_2Cr_2O_7\cdot 2H_2O$ for the solubility.

These data, when plotted, deviate an average of 0.06% from the empirical equation: $S = 62.18 + 0.0890t + 0.000243t^2$, where S is solubility in weight per cent. and t is temperature in degrees C. The maximum deviation is 0.12%.

Freezing Point of Solutions.—Five hundred milliliter portions of analyzed solutions were cooled in an insulated container by means of solid carbon dioxide and alcohol. Time-temperature heating and cooling curves were employed to determine the ice-point for each solution, and these data further checked by observation of the appearance and disappearance of ice-crystals. The following data were obtained:

% $Li_2Cr_2O_7\cdot 2H_2O$ by weight	Ice point, °C.	% $Li_2Cr_2O_7\cdot 2H_2O$ by weight	Ice point, °C.
0.0	0.0	41.10	−24.0
20.14	− 6.2	47.39	−35.4
29.97	−12.0	52.32	−49.8
34.82	−17.2	57.53	No crystallization at −60

A smooth curve may be drawn through these points with an average deviation of 0.4°.

Eutectic Point.—Facilities did not permit investigation of the system below −60°. Graphical analysis indicates the eutectic composition to be close to 56.5% $Li_2Cr_2O_7\cdot 2H_2O$ and the eutectic temperature below −70°.

Solubility in Organic Liquids.—Lithium dichromate dihydrate is insoluble in ether, carbon tetrachloride and hydrocarbon solvents. It dissolves in ethyl alcohol to the extent of about 20 g. per 100 ml. of solvent at room temperature. No exact measurement is possible because of the rapid oxidation of the alcohol and reduction of the dichromate. In acetone solution occurs at first, then the dichromate decomposes with precipitation of yellow lithium chromate.

Summary

1. Lithium dichromate dihydrate has been prepared and shown to consist of red-orange crystalline plates when pure.
2. Its density, solubility and behavior on heating have been described.
3. Data have also been presented giving the density and freezing point of aqueous solutions, and the eutectic composition and temperature estimated.
4. The solubility in common organic liquids has been qualitatively examined.

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[Contribution from the Cobb Chemical Laboratory of the University of Virginia]

Colorimetric Determination of Iron with 4-Hydroxybiphenyl-3-carboxylic Acid[1]

By John H. Yoe and Aubrey E. Harvey, Jr.[2]

As early as 1834,[3,4,5] the color reactions between ferric ions and phenolic derivatives were observed and used as a qualitative test for the aromatic hydroxyl group. Salicylic acid was the first phenol to be used for the detection of ferric ions,[6,7,8,9] and for its quantitative determination.[10-16] Derivatives of salicylic acid which have been used as quantitative colorimetric reagents for iron are: sulfosalicylic acid,[17,18,19] salicylaldoxime,[20] and β-resorcylic acid.[21]

This paper introduces 4-hydroxybiphenyl-3-carboxylic acid as a new colorimetric reagent for ferric iron. The reagent is very sensitive and is

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(1) Abstracted from the Ph.D. thesis of Aubrey E. Harvey, Jr., University of Virginia, 1946.

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