Part II

ORGANIC CHEMISTRY
PHYSICAL PROPERTIES
EVALUATION OF COMPOUNDS AND MATERIALS

Some Physical Properties of Sodium Chromate, Sodium Dichromate, and Potassium Dichromate, and Their Aqueous Solutions

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Solubilities of Na_2CrO_4 (I), $Na_2Cr_2O_7 \cdot 2H_2O$ (II), and $K_2Cr_2O_7$ (III) from 0° to the boiling points at saturation are given. Viscosities and densities of solutions of various concentrations are given for temperatures between −20° and 90°. Boiling points are given for solutions of various concentrations. Saturated solution boiling points and compositions are: I, 115.7°, 55.5%; II, 139.5°, 93.7%; and III, 104.5°, 51.3%. Hydrate transition points above 30° are: I, $4H_2O = 1.5H_2O$, 62.2°; $1.5H_2O$ = anhydrous, 68.9°; II, $2H_2O = H_2O$, 82.6°; H_2O = anhydrous, 87.3°. $Na_2Cr_2O_7 \cdot H_2O$ is a new phase, for which x-ray powder diffraction data are given.

THE LITERATURE on the physical properties of sexivalent chromium compounds was critically reviewed in 1949 (*4*). Work recently undertaken in these Laboratories required confirmation of some of the published values, and determination of others at temperatures and concentrations not previously investigated, for sodium chromate, sodium dichromate, and potassium dichromate. Properties studied were solubilities; boiling points, densities, and viscosities of solutions; and hydrate transition points at the higher temperatures.

EXPERIMENTAL

Reagent grade $Na_2CrO_4 \cdot 4H_2O$, $Na_2Cr_2O_7 \cdot 2H_2O$, and $K_2Cr_2O_7$, and distilled water, were used in these measurements.

Solubilities were determined by two methods. In the first, the salt was mixed with sufficient water in tightly capped bottles to make a thin slurry. The containers were rotated end over end for several hours in a constant temperature bath (±0.1° C.). Samples of the solution were removed, with filtration in some cases, after undissolved solids had settled, and analyzed. Equilibrium was approached from both higher and lower temperatures. In the second method, slurry was stirred in a round-bottom flask immersed in a constant temperature bath (±0.3° C.). Samples of solution were removed by pressure filtration, at temperature, through a sintered glass filter, after 1 and 2 day intervals. Solubilities were checked at several points by noting visually the temperature at which prepared compositions in sealed ampoules completely dissolved.

Boiling points of solutions were determined in a Cottrell molecular weight apparatus, Washburn and Read modification, using a thermometer accurate to 0.1° C. Barometric corrections, which never exceeded 10 mm. of Hg, were applied. Solutions prepared for boiling point, viscosity, and density determinations were analyzed and readjusted, where necessary, to give the concentrations desired.

Viscosities of solutions were measured in Ostwald-type viscosimeters, Fenske-Cannon modification. Temperatures were controlled to ±0.1° C. The viscosimeters were calibrated with water and checked with Bureau of Standards Oil D, and with several solutions of sulfuric acid or sucrose.

Densities of solutions were determined with Babcock bottles of about 42 ml. capacity, calibrated with water at 25° and 80° C. Weighed quantities of solutions of known concentration were immersed in a constant temperature bath (±0.1° C.), and volumes were read after no further changes were noted.

Temperatures of transition of hydrates were measured by heating and cooling curves, and by dilatometric analysis. Quantities of material up to 500 grams, mechanically stirred, were used in the thermal analyses. Temperatures were measured with a thermometer accurate to 0.1° C., although in some cases a four-junction iron-constantan thermopile, actuating a recording potentiometer, was used to trace the curves. The dilatometers consisted of glass bulbs of about 40 ml. capacity to which were attached capillaries of 3 or 4 mm. bore. The bulbs were filled with slurry and slowly heated in a water bath, periodic readings of liquid level in the capillary being taken with a cathetometer. Temperature as registered by a thermometer (0.1° C.) with its bulb located in the center of the slurry was noted at each reading of liquid level.

RESULTS

The data on solubility in the long, continuous portions of the curves were mathematically analyzed by the method of multiple correlation in order to reject points falling outside the 95% confidence limits. Acceptable data were then treated by the method of least squares to determine the second degree curve of best fit. Values in other portions of the curves were plotted and connected, consideration being given to the location of eutectics and transition points. The values given in Table I, read from the smooth curves, represent the acceptable experimental data within 0.3%, relative. Note that concentrations of sodium dichromate solutions are expressed in terms of the dihydrate in Tables I–IV, conforming with industrial practice.

Boiling points are shown in Table II. In determining boiling points of the saturated solutions, saturation was assured by visually noting the presence of undissolved solids during the measurements. Compositions of these solutions were determined by short extrapolation of the boiling point–composition curves to the saturated solution boiling temperatures.

Viscosities are shown in Table III. The values given represent the averages of four determinations; standard deviations are 0.6% or less.

Averaged density values, which have standard deviations of 0.3% or less, are shown in Table IV.

Table I. Solubilities of Sodium Chromate, Sodium Dichromate, and Potassium Dichromate in Water

Temp. °C.	Na_2CrO_4 Wt. %	$Na_2Cr_2O_7 \cdot 2H_2O$, Wt. %	$K_2Cr_2O_7$, Wt. %
0.0	23.9	70.3	4.9
10.0	32.1	71.6	7.4
19.5	43.9[a]	...	...
20.0	44.2[b]	73.4	11.0
25.9	46.2[c]	...	...
30.0	46.7	75.2	15.7
40.0	48.4	77.2	20.6
50.0	50.8	79.2	25.4
60.0	54.0	81.5	30.2
62.2	54.9[d]	...	...
68.9	54.9[e]	...	...
70.0	54.9	84.6	35.4
80.0	55.0	88.5	40.8
82.6	...	90.8[f]	...
87.3	...	91.1[g]	...
90.0	55.0	91.2	45.8
100.0	55.1	91.8	49.8

[a] $Na_2CrO_4 \cdot 10H_2O = Na_2CrO_4 \cdot 6H_2O$ (7).
[b] $Na_2CrO_4 \cdot 10H_2O = Na_2CrO_4 \cdot 4H_2O$ (metastable) (7).
[c] $Na_2CrO_4 \cdot 6H_2O = Na_2CrO_4 \cdot 4H_2O$ (7).
[d] $Na_2CrO_4 \cdot 4H_2O = Na_2CrO_4 \cdot 1.5H_2O$ (Table V).
[e] $Na_2CrO_4 \cdot 1.5H_2O = Na_2CrO_4$ (Table V).
[f] $Na_2Cr_2O_7 \cdot 2H_2O = Na_2Cr_2O_7 \cdot H_2O$ (Table V).
[g] $Na_2Cr_2O_7 \cdot H_2O = Na_2Cr_2O_7$ (Table V).

Transition points as determined by thermal analysis and dilatometer are shown in Table V. The values shown are averages of a number of determinations, with standard deviations indicated beside each.

DISCUSSION

Solubilities, viscosities, and densities generally confirm previously published data (1, 3–6, 8–10), but are, in most instances, more extensive with respect to concentration and temperature. Solubilities of sodium chromate above 80° C., and of potassium dichromate throughout the temperature range, are a little lower than the published data. A lowering of viscosity when small amounts of potassium dichromate are dissolved in water, indicated by the data of one investigator (*4*), was not substantiated.

The boiling point of saturated sodium chromate solution has been reported as 115.6° C. (*2*), after correction to standard pressure is applied. This value agrees within 0.1° C. with the present determination. With respect to sodium dichromate, the saturated solution boiling point has been reported

Table II. Boiling Points of Aqueous Solutions of Sodium Chromate, Sodium Dichromate, and Potassium Dichromate

	Boiling Point, ° C.		
	Na_2CrO_4	$Na_2Cr_2O_7 \cdot 2H_2O$	$K_2Cr_2O_7$
10.0	100.8	...	100.7
20.0	102.0	101.3	101.3
30.0	103.7	...	102.2
40.0	106.8	103.8	103.2
50.0	112.5	...	104.3
51.3	...	...	104.5[a]
55.0	115.5	...	...
55.5	115.7[a]	...	...
60.0	...	109.8	...
70.0	...	115.3	...
79.6	...	122.5	...
85.2	...	128.5	...
90.9	...	135.9	...
93.7	...	139.5[a]	...

[a] Saturated solution.

Table III. Viscosities of Aqueous Solutions of Sodium Chromate, Sodium Dichromate, and Potassium Dichromate

Concn., Wt. %	Temp., ° C.					
	0.2	25.0	39.8	59.4	74.3	89.3
	Viscosity, Centipoises					
	Na_2CrO_4					
10.0	2.26	1.16	0.85	0.62	0.50	0.42
20.0	3.40	1.68	1.23	0.87	0.70	0.59
30.0	...	2.88	1.98	1.35	1.08	0.89
40.0	...	6.14	3.90	2.47	1.90	1.48
45.0	...	10.03	5.94	3.47	2.56	1.97
50.0	...	...	...	5.16	3.63	2.75
	$Na_2Cr_2O_7 \cdot 2H_2O$					
20.0	2.07	1.09	0.82	0.61	0.51	0.44
40.0	3.18	1.65	1.22	0.89	0.73	0.62
60.0	8.58	3.85	2.70	1.87	1.50	1.26
70.0	21.26	7.90	5.16	3.36	2.60	2.07
80.0	...	...	...	...	...	4.29
	$K_2Cr_2O_7$					
2.0	1.78	0.89	0.66	0.47	0.38	0.32
5.0	...	0.90	0.67	0.49	0.40	0.34
10.0	...	0.91	0.68	0.50	0.41	0.34
20.0	...	...	0.73	0.54	0.45	0.38
35.0	...	...	...	...	0.54	0.47
40.0	...	...	...	...	...	0.52

Table IV. Densities of Aqueous Solutions of Sodium Chromate, Sodium Dichromate, and Potassium Dichromate

Concn., Wt. %	Temp., ° C.							
	−19.5	−8.5	0.0	25.0	40.0	60.0	75.0	90.0
	Density, G./Ml.							
				Na_2CrO_4				
10.0	...	...	1.103	1.088	1.082	1.072	1.064	1.054
20.0	...	...	1.209	1.193	1.184	1.172	1.162	1.154
30.0	...	...	...	1.308	1.300	1.290	1.280	1.271
40.0	...	...	...	1.436	1.428	1.417	1.408	1.400
45.0	...	...	...	1.506	1.498	1.486	1.477	1.468
50.0	...	...	...	...	...	1.560	1.544	1.535
				$Na_2Cr_2O_7 \cdot 2H_2O$				
20.0	...	1.157	1.154	1.138	1.130	1.119	1.109	1.099
40.0	...	1.346	1.342	1.320	1.306	1.293	1.279	1.274
60.0	1.587	1.581	1.576	1.550	1.539	1.523	1.512	1.497
70.0	...	...	...	1.695	1.678	1.663	1.647	1.642
80.0	...	...	...	...	...	...	...	1.808
				$K_2Cr_2O_7$				
2.0	...	...	1.021	1.011	1.006	0.996	0.988	0.980
5.0	...	...	1.044	1.032	1.026	1.017	1.008	0.999
10.0	...	...	...	1.070	1.063	1.052	1.044	1.035
20.0	...	...	...	...	1.142	1.134	1.122	1.112
35.0	...	...	...	...	...	...	1.262	1.253
40.0	...	...	...	...	...	...	...	1.306

as 139° C. (*11*), again agreeing with the present value within the implied accuracy of measurement. Another reference (*12*) cites heating sodium dichromate solution to 145° C., but this was not intended as a boiling point measurement, and the high reading probably reflects some superheating caused by thermometer immersion. Boiling points of unsaturated solutions of sodium chromate and of sodium dichromate, and of potassium dichromate solutions generally, appear not to have been reported previously.

Two hydrate transition temperatures above 30° C. in the system Na_2CrO_4–H_2O were found, corresponding to transition of the tetrahydrate to the sesquihydrate (*2*) and of this to the anhydrous salt. (The composition of the sesquihydrate was confirmed by analysis of solids isolated from slurry at 65°C.: Na_2CrO_4 calculated, 85.7%; found, 85.4%.) Although the three methods of determination gave somewhat different values for the lower transition, the values obtained by thermal analysis agree well. Their average, 62.2° C., is taken as the best estimate of this temperature. Two earlier determinations, 63.0° C. (*4*) and 62.8° C. (*7*), may represent the metastable transition of tetrahydrate to anhydrous salt, while a third, 64.0° C. (*2*), corresponds to the present dilatometric determination, and is probably too high. In the higher transition, heating and cooling curves gave fair agreement (70.8° C. and 67.0° C., respectively), whereas the dilatometer gave a considerably higher value, 76.1° C., which is not far removed from the previously published value of 75.4° C. (*2*). Since the dilatometric measurements were conducted without disturbance of the crystals being studied, it is probable that there was a considerable amount of superheating before transition occurred with this method. In support of this conjecture, heating curves traced without agitation of the sample showed this transition at approximately 75° C. The previously reported transition temperature was determined by heating curves, but no mention was made of agitation, and it is assumed that superheating occurred in that work as well. The best value is probably the average of values obtained by thermal analysis, 68.9° C.

Table V. Transition Points Above 30° C. in the Systems Na_2CrO_4–H_2O and $Na_2Cr_2O_7$–H_2O

Method	Transition Temperature, ° C.	
	Na_2CrO_4–H_2O	
	$4H_2O = 1.5H_2O$	$1.5H_2O$ = anhydrous
Cooling Curves	61.9 ± 0.1	67.0 ± 0.6
Heating Curves	62.4 ± 0.3	70.8 ± 0.5
Dilatometer	64.0 ± 0.8	76.1 ± 1.3
Probable Value[b]	62.2	68.9
	$Na_2Cr_2O_7$–H_2O	
	$2H_2O = 1H_2O$	$1H_2O$ = anhydrous
Cooling Curves	82.2 ± 0.4	87.7 ± 0.6
Heating Curves	83.1 ± 0.1	86.9 ± 0.6
Dilatometer	...[a]	87.2 ± 0.9
Probable Value[b]	82.6	87.3

[a] A small, poorly defined effect was noted at about 83° C., indicating that the volume change accompanying this transition is slight.
[b] Average of determinations by heating and cooling curves.

The sesquihydrate has been incorrectly reported to be unstable with respect to the pair Na_2CrO_4–$Na_2CrO_4 \cdot 4H_2O$ at room temperature (*2*) because the sesquihydrate x-ray pattern was absent from a sample of partially dehydrated tetrahydrate. In calculated hydrate decomposition pressures cited as supporting evidence, enthalpy changes per mole of hydrated salt were used in the Clausius-Clapeyron equation. Recalculation using enthalpy changes per mole of vapor formed, which is proper, shows that $Na_2CrO_4 \cdot 1.5H_2O$ is stable at all temperatures up to its transition point, at which it becomes unstable with respect to the pair saturated solution-anhydrous Na_2CrO_4. This behavior is normal. Failure of the sesquihydrate to form during dehydration of

Table VI. X-Ray Powder Diffraction Data[a] for Sodium Dichromate Monohydrate

d, A.	I/I_o	*d*, A.	I/I_o	*d*, A.	I/I_o
8.65	33	4.10	20	2.384	13
7.89	13	4.037	100	2.26	10
7.13	10	3.076	21	2.236	10
6.70	10	2.976	21	2.111	10
6.03	33	2.877	75	2.008	13
5.75	25	2.808	50	1.959	10
5.64	25	2.631	42	1.850	16
4.88	35	2.50	10	1.79	12

[a] X-ray diffraction data were measured from patterns obtained with CuK α radiation (35 kv., 15 ma., nickel filter) and a Norelco Diffractometer. Relative intensities (I/I_o) were obtained from peak heights.

the tetrahydrate at room temperature is not surprising, since metastable transition to the anhydrous salt, even at the higher temperatures at which the sesquihydrate exists in contact with saturated solution, occurs with such ease that the sesquihydrate was not detected by the careful work of at least two previous investigators (*4*, *7*).

In the system $Na_2Cr_2O_7$–H_2O, transition temperatures were found at 82.6° C. and 87.3° C., although only one transition, at 84.6° C. (*3*), has been reported previously. These temperatures represent transition from the dihydrate to the monohydrate, which is a new crystal form, and thence to the anhydrous salt, while the previously reported temperature very likely represents the metastable transition from the dihydrate to the anhydrous salt. The monohydrate was identified by analysis of the solid phase isolated from slurry at 85° C. in a heated centrifuge ($Na_2Cr_2O_7$ calculated, 93.6%; found, 93.4%); that it was not a mixture of the two known forms was indicated by its x-ray pattern, of which the principal lines are shown in Table VI. Crystals of $Na_2Cr_2O_7 \cdot H_2O$ are intermediate in color between the dihydrated and anhydrous forms.

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Measurement of Ultraviolet Indices of Refraction with a Differential Refractometer

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Modifications of a commercial differential refractometer are described which permit using the instrument in the ultraviolet. Dispersion data and Lorentz corrections from 5461 to 2655A. are given for fourteen solvents.

IN ORDER TO RELATE macroscopic optical phenomena such as absorption and optical rotation to molecular properties, one must obtain an estimate of the internal electric field on the molecule or on a particular group in the molecule. Numerous formulas have been proposed to relate the local field to the applied macroscopic electromagnetic field (*1*, *3*) of which the Lorentz correction $[(n^2+2)/3]$ is the most widely used, where n is the refractive index at the wavelength of interest. Though the derivation of this factor asserts its applicability only for gases and cubic lattices, it is customarily used by both experimentalists and theoreticians as a first order estimate of internal field effects in solutions.

In our own work we frequently have to compare absorption and optical rotation measurements obtained in media of differing refractive index either because of a variation in wavelength (dispersion studies) or in solvent composition. The spectral region of interest is normally in the ultraviolet. Since refractive dispersion data on many important solvent systems was nonexistent, a commercial refractometer was adapted for measurements in the ultraviolet and dispersion curves were obtained for a number of widely used solvents.

EXPERIMENTAL

The apparatus was a Pheonix Precision Differential Refractometer supplied by the manufacturer with the modifications described below. Figure 1 is a schematic diagram of the optical parts of the instrument as normally supplied by the manufacturer. Light from a tungsten bulb passes through a narrow band-pass filter and then through a lens which focuses an image of the slit on the nearest edge of the prism, where it is split into two beams of equal intensity when the prism is in balance position. During operation the transverse position of the prism is automatically brought to balance by a servo-controlled micrometer drive. In making a measurement a reference liquid of known refractive index is placed in compartment R and

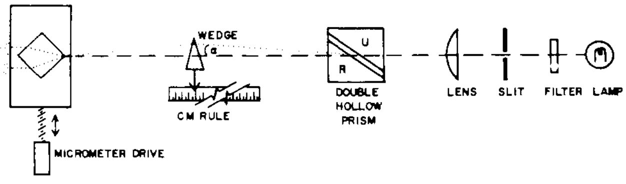

Figure 1. Differential refractometer

Symbols are explained in text. Small deflections are measured by the transverse motion of the micrometer-driven prism. Large deflections are compensated by moving the wedge closer to the double hollow prism.

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