

The average areas occupied by each molecule of sodium oleate, potassium stearate and potassium palmitate, were found to be 48, 27 and  $30 \times 10^{-16}$  sq. cm., respectively. These areas agree rather closely with those found for the corresponding fatty acids in unimolecular films on the surface of water.

4. In case there is insufficient soap to form a unimolecular film the emulsion is not stable.

5. The excess soap remains in water solution.

WASHINGTON, D. C.

---

[CONTRIBUTION FROM THE COLOR LABORATORY, BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE, No. 74]

## ADSORBED MOISTURE AND WATER OF CRYSTALLIZATION IN CERTAIN COMMON DYES

BY H. WALES AND O. A. NELSON

Received April 24, 1923

A discrepancy between the observed and calculated results for different samples of pure methylene blue when the molecular weight as given in the United States Pharmacopeia ( $C_{16}H_{18}N_3SCl \cdot 3H_2O$ ) was used, always occurred during the work done on this dye in the Color Laboratory. As the authority for assuming the presence of 3 mols. of water of crystallization in this compound failed to give reliable experimental data, it was considered desirable to determine, if possible, whether or not the moisture in this dye, as well as in a few others, was present as adsorbed moisture or as water of crystallization.

From the literature, reference to which will be made as each dye is considered, it appears that no investigator has attempted to show by experiment how the moisture in his sample was held. The customary method was to heat the dye at a definite temperature for a definite period of time and calculate the amount of water present from the analytical determinations of elements. The water thus found was then considered in terms of mols. of water of crystallization when, from the data given, it might as readily be adsorbed water. Since adsorbed water is often held more tightly than the so-called water of hydration or crystallization, it seems obvious that the results obtained by such a method cannot be conclusive.

The primary object of this work was not so much to determine the quantity of water present in the dyes studied as to ascertain whether the water was present as adsorbed moisture or as water of crystallization.

Theoretically, if the vapor pressure of a hydrate be plotted against the weight of water present at constant temperature, the pressure remains constant until the last of the hydrate corresponding to this pressure has been removed. At this point the pressure drops to that of a lower hydrate,

if one is present, or to that of the anhydrous substance. Practically, however, these breaks are not always sharp. Beutell and Blaschke<sup>1</sup> found that in all cases where there was more than one hydrate, the dehydration on the surface of the particles proceeded further than in the interior, "where cohesion hindered the evolution of water vapor." The inside of the particles, therefore, consists of hydrates higher than those at the surface. This prevents a sharp transition from one hydrate to the next, and causes a rounding of the breaks in the curve which becomes more pronounced with increase in the pressure difference between two hydrates. (Compare the curves for oxalic acid, crystal violet and tartrazin.)

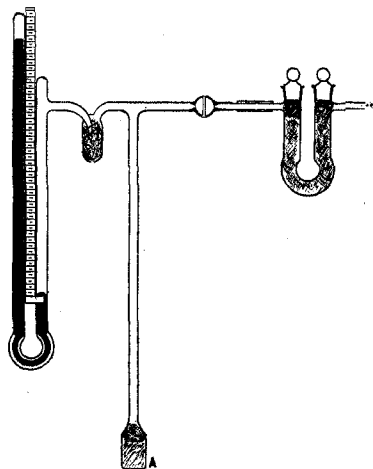


Fig. 1

If, however, the water in a compound is present as adsorbed water, the curve showing the relation of vapor pressure to water content will not have the breaks characteristic of the hydrate curves, but will be perfectly smooth and have a slope depending on the tenacity with which the water is being held. These two types are illustrated by the curves for hydrates, such as cupric sulfate pentahydrate or sodium carbonate decahydrate,<sup>2</sup> and by that of vapor pressure against water content curve of a substance containing adsorbed water.<sup>3</sup> A vapor pressure-water content curve for oxalic acid  $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$  at  $50^\circ$  was determined to test the apparatus and also to obtain a curve for a known hydrate. The results are tabulated in Table I and shown diagrammatically in Fig. 2, Curve A.

**Method.**—Since the vapor pressure-water content curves of hydrates and substances containing adsorbed water are so distinctly different, the method used in determining which dyes are hydrates and which contained adsorbed water was that of determining the vapor pressure after removing a small increment of water, at constant temperature. The apparatus used was essentially the same as that described by Nelson and Hulett,<sup>4</sup> a portion of which is shown diagrammatically in Fig. 1. About 1.5 g. of dye was weighed into Bulb A and a wad of fine glass wool was packed in, to prevent the dye from being carried over mechanically when the pressure in the system was lowered. The bulb was then sealed to the manometer

<sup>1</sup> Beutell and Blaschke, *Centr. Mineral. Geol.*, 1915, 199.

<sup>2</sup> *Z. physik. Chem.*, 7, 241 (1891).

<sup>3</sup> Hulett and Nelson, *Trans. Am. Electrochem. Soc.*, 38, 103-119 (1920).

<sup>4</sup> Nelson and Hulett, *J. Ind. Eng. Chem.*, 12, 40 (1920).

as indicated in the illustration. The moisture was absorbed in phosphoric anhydride and the system was evacuated by means of a Toepler mercury

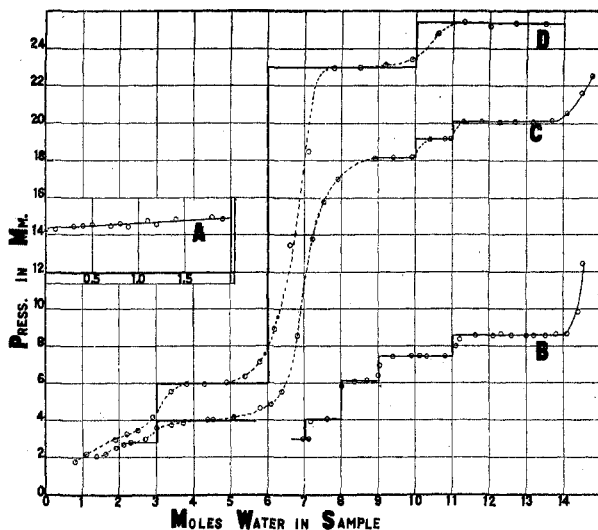


Fig. 2.—A, oxalic acid  $2\text{H}_2\text{O}$  at  $50^\circ$ ; B, crystal violet at  $26^\circ$  (subtract 5 mols.); C, tartrazin at  $26^\circ$ ; D, tartrazin at  $30^\circ$

pump. The pressure was read with the naked eye, directly from the manometer with an accuracy of about  $\pm 0.2$  mm.

TABLE I  
OXALIC ACID AT  $50^\circ$

$\text{H}_2\text{O}$ removed %	$\text{H}_2\text{O}$ to pure acid %	$\text{H}_2\text{O}$ in sample Mols.	Pressure Mm.	$\text{H}_2\text{O}$ removed %	$\text{H}_2\text{O}$ to pure acid %	$\text{H}_2\text{O}$ in sample Mols.	Pressure Mm.
1.2	38.2	1.9	14.9	19.2	13.0	0.7	14.5
4.4	33.6	1.7	15.0	21.1	10.3	0.5	14.6
9.2	27.0	1.4	14.9	23.3	8.0	0.4	14.5
11.0	24.5	1.2	14.6	24.9	5.0	0.3	14.5
13.2	21.3	1.1	14.8	26.8	2.3	0.1	14.3
15.4	18.3	0.9	14.5	28.5	0.0	0.0	..
17.2	15.7	0.8	14.6				

**Methylene Blue** ( $\text{C}_{16}\text{H}_{18}\text{N}_3\text{SCl}$ ).—Previous work on the water content of methylene blue is very contradictory. Koch<sup>5</sup> prepared 2 samples of methylene blue under identical conditions and found that one contained the equivalent of 4 molecules of water and the other the equivalent of 1.5 molecules. Both samples gave up the water completely at  $110^\circ$ . Bernthsen<sup>6</sup> found that the salt dried in a desiccator lost an equivalent of 2 mols. of water at  $100^\circ$ , 2.5 at  $130^\circ$  and 3 at  $150^\circ$ . He claims to have heated to constant weight in each case. The American and French Pharmacopeias

<sup>5</sup> Koch, *Ber.*, 12, 592 (1879).

<sup>6</sup> Bernthsen, *Ann.*, 230, 139 (1885).

accept Berntsen's figures and give the formula as  $C_{16}H_{18}N_3SCl \cdot 3H_2O$ . The German Pharmacopeia makes no mention of moisture in this compound.

Four samples of methylene blue made by different manufacturers were analyzed in the Color Laboratory and contained 11.44%, 11.58%, 12.42%

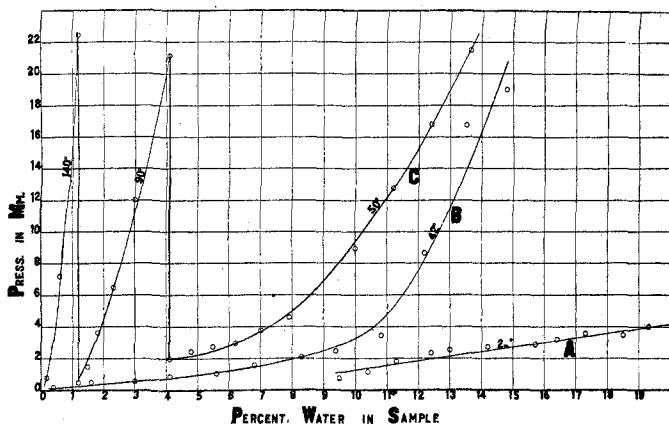


Fig. 3.—A, methylene blue at 28°; B, methylene blue at 42°; C, erythrosin at 50°, 90° and 140°

and 17.06% of water (calc. for 3 mols. of water: 14.46%). In every case the salts could be completely dehydrated by drying them at 110° for 1 day, thereby confirming Koch's results.

TABLE II  
METHYLENE BLUE HYDROCHLORIDE

28°			42°		
Water removed %	Water to pure color %	Pressure Mm.	Water removed %	Water to pure color %	Pressure Mm.
0.0	20.6	7.5	4.9	14.8	19.0
0.5	20.1	4.2	5.6	13.5	16.8
1.0	19.3	4.0	6.8	12.2	8.7
1.7	18.5	3.5	8.2	10.8	3.5
2.8	17.3	3.6	9.4	9.4	2.5
3.5	16.4	3.2	10.3	8.3	2.1
4.1	15.7	2.9	11.5	6.8	1.6
5.3	14.2	2.8	12.5	5.6	1.1
6.3	13.0	2.6	13.7	4.1	0.9
6.9	12.4	2.4	14.6	3.0	0.6
7.8	11.3	1.8	15.8	1.6	0.3
8.5	10.4	1.2	16.8	0.4	0.2
9.2	9.5	0.8	17.1	0.0	0.0

The vapor pressure-water content curves of the sample containing 17.06% were determined at 28° and 42°, with the results shown in Table II and Fig. 3, Curves A and B. The curves show no indication of breaks,

thus indicating that the moisture in this dye is not present as water of crystallization. In the following tables the percentage of water has been recomputed to a pure color basis,<sup>7</sup> for convenience in determining the degree of hydration.

**The Zinc Chloride Salt of Methylene Blue.**—The formula for the zinc chloride double salt of methylene blue is usually given as  $(C_{16}H_{18}N_3SCl)_2 \cdot ZnCl_2 \cdot H_2O$ . Apparently the only authority for this is Bernthsen<sup>8</sup> who found 2.13% of moisture (calculated for  $1H_2O$ : 2.27%). No mention was made of the temperature at which the moisture was evolved. Three samples of the zinc chloride salt of methylene blue analyzed in the Color Laboratory yielded 4.0%, 3.4% and 3.1% of moisture. Heating in an oven for 1 day at  $110^\circ$  was sufficient to remove all but very minute traces of water.

The vapor pressure-water content curve was determined on the sample containing 4.0% of water. The results again indicated the absence of water of hydration. It should be noted that the total percentage of water obtained by the authors' method agreed well with that obtained by heating in an oven.

TABLE III  
METHYLENE BLUE ZINC CHLORIDE AT  $40^\circ$

H <sub>2</sub> O removed %	H <sub>2</sub> O to pure color %	Pressure Mm.	H <sub>2</sub> O removed %	H <sub>2</sub> O to pure color %	Pressure Mm.
0.0	4.2	24.0	2.0	2.1	2.9
0.3	3.9	18.4	2.4	1.65	1.0
0.6	3.5	13.5	2.8	1.2	0.8
1.2	2.9	8.0	3.2	0.8	0.3
1.5	2.6	6.0	3.4	0.6	0.2
1.7	2.3	3.4	4.0	0.0	...

**Crystal Violet,  $C_{23}H_{30}N_3Cl$ .**—Crystal violet or hexamethyl-*p*-rosaniline hydrochloride is stated to contain 8 molecules of water of crystallization.<sup>9</sup> Green<sup>10</sup> gives the same figure, and Schultz<sup>11</sup> gives 9 molecules.

A sample of commercial crystal violet was found on analysis to contain 4% or about 1 molecule of water. After recrystallization from water and drying for 24 hours at room temperature in a desiccator, this sample yielded 29.5% of water. The vapor pressure-water content curve for this sample (Fig. 2, Curve B), determined at  $26^\circ$ , showed breaks corresponding to hydrates containing 9, 6, 4, 3 and 2 molecules of water. The presence

<sup>7</sup> By pure color basis is meant the parts of water per 100 parts of anhydrous dye. A dye containing 20% of water, therefore, would contain 25% on a pure color basis.

<sup>8</sup> Bernthsen, *Ann.*, 251, 81 (1889).

<sup>9</sup> Kraft, *Ber.*, 32, 1611 (1899).

<sup>10</sup> Green, "Organic Coloring Matters," The Macmillan Co. N. Y., 1908.

<sup>11</sup> Schultz, "Farbstofftabellen," Weidmannsche Buchhandlung Berlin, 1914.

of lower hydrates was not determined, owing to appreciable sublimation of the dye at pressures below 3 mm.<sup>12</sup>

TABLE IV  
CRYSTAL VIOLET AT 26°

H <sub>2</sub> O removed %	H <sub>2</sub> O to pure color %	H <sub>2</sub> O in sample Mols.	Pressure Mm.	H <sub>2</sub> O removed %	H <sub>2</sub> O to pure color %	H <sub>2</sub> O in sample Mols.	Pressure Mm.
0.0	41.9	9.5	12.5	13.0	23.5	5.3	7.5
0.3	41.4	9.4	9.9	13.5	22.8	5.1	7.5
1.2	40.2	9.1	8.7	14.2	21.5	4.9	7.5
2.1	38.8	8.8	8.7	15.8	19.4	4.4	7.5
3.0	37.6	8.5	8.6	17.0	17.7	4.05	7.0
4.1	36.1	8.2	8.6	17.1	17.6	4.0	6.5
4.8	35.2	8.0	8.6	18.0	16.3	3.7	6.2
5.6	33.9	7.6	8.6	19.1	14.8	3.35	6.1
7.3	31.5	7.2	8.7	20.1	13.3	3.0	5.9
7.4	31.4	7.1	8.6	21.3	11.6	2.6	4.1
9.1	29.0	6.6	8.6	22.4	10.1	2.3	4.0
10.4	27.1	6.2	8.4	23.0	9.3	2.1	3.0
10.5	26.9	6.1	8.0	23.4	8.6	1.95	3.0
11.4	25.5	5.8	7.5				

**Magenta.**—Both rosaniline and *p*-rosaniline-hydrochlorides are stated to contain 4 molecules of water of crystallization.<sup>9,10,11</sup> As neither of

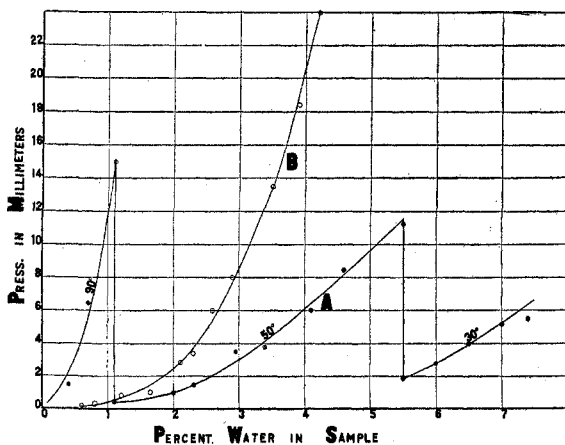


Fig. 4.—A, magenta at 30°, 50° and 90°; B, methylene blue ZnCl<sub>2</sub> at 40°

these compounds was available, carefully purified magenta, which is an approximately equimolecular mixture of the two, was examined. Table V and Fig. 4, Curve A, show the results obtained on this sample. The vapor

<sup>12</sup> Green and Schultz (Ref. 10; Ref. 11) also record the anhydrous dye as existing in cantharides-green, glistening crystals and the hydrated form as bronzy crystals. This is perhaps due to the state of subdivision, as there was no noticeable change in color on dehydration in the sample used.

pressure-water content curve of this mixture is perfectly smooth, with no indication of a break.

TABLE V  
MAGENTA

H <sub>2</sub> O removed %	H <sub>2</sub> O to pure color %	Pressure Mm.	Temperature ° C.	H <sub>2</sub> O removed %	H <sub>2</sub> O to pure color %	Pressure Mm.	Temperature ° C.
0.0	7.4	5.5	30	4.5	2.95	3.6	50
0.7	7.0	5.2	30	5.1	2.3	1.5	50
1.2	6.5	4.0	30	5.3	2.0	1.0	50
1.6	6.0	2.8	30	6.2	1.1	0.2	50
2.1	5.5	1.9	30			15.0	90
		11.2	50	6.5	0.7	6.5	90
2.9	4.6	8.5	50	6.8	0.4	1.5	90
3.4	4.1	6.8	50	7.2	0.0	...	90
4.0	3.4	3.8	50				

While the vapor pressure-water content curve of a mixture may indicate the absence of hydrates, this evidence alone cannot be considered conclusive. That either rosaniline or *p*-rosaniline contains 4 molecules of water of crystallization does not seem likely, however, from other observations made in this Laboratory. For example, the highest percentage of water obtained in any sample prepared or purified was 7.2, against 17.9 required for 4 molecules (the calculations are based on an equimolecular mixture of rosaniline and *p*-rosaniline). If one of the components of the mixture contained 4 molecules of water of crystallization and the other was anhydrous, the amount of water present in an equimolecular mixture of the two should be approximately 8.5%. If this were the case, however, the vapor pressure-water content curve should show the breaks characteristic for hydrates. This it failed to do.

**Erythrosin.**—Erythrosin, or disodium tetra-iodo-fluoresceinate, has received much attention in the analytical work on food colors, because of the constant discrepancy in its analysis. Determinations of iodine in dried samples of this dye give results about 1% low, while those made on the pure acid agree very well with the theoretical value. Gomberg and Tabern<sup>13</sup> found an average of 56.99% of iodine in the sodium salt (calc. for C<sub>20</sub>H<sub>6</sub>I<sub>4</sub>O<sub>5</sub>Na<sub>2</sub>: 57.70), and of 60.67% (calc. for C<sub>20</sub>H<sub>5</sub>O<sub>5</sub>I<sub>4</sub>: 60.75) in the free acid. Their results for iodine content in samples of technical erythrosin were approximately 0.6% low. These investigators account for this discrepancy by assuming the presence of a small amount of water, equivalent to approximately 1 molecule, held very tenaciously. Similar conclusions have been reached by W. C. Holmes<sup>14</sup> of the Color Laboratory in connection with a gravimetric method for determining erythrosin.

A vapor pressure-water content curve was obtained on a sample of re-

<sup>13</sup> Gomberg and Tabern, *J. Ind. Eng. Chem.*, **14**, 1117 (1922).

<sup>14</sup> Holmes, Estimation of Erythrosin, *Color Trade J.*

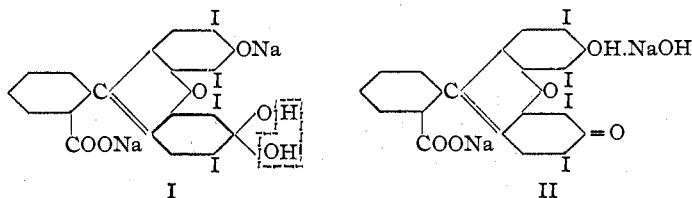
crystallized erythrosin containing 13% of water. No trace of hydrate formation was observed. (Table VI, Fig. 3, Curve C.) However, the sample which had been subjected to prolonged evacuation under pressure of less than 0.2 mm., and at a temperature of 160°, gave on analysis 56.58% of iodine, which agrees well with the value 56.55% required for a sample containing the equivalent of 1 molecule of water. Therefore, all work indicates that there must be an equivalent of 1 molecule of water in the sodium salt of erythrosin and that this water is bound much more firmly than ordinary water of crystallization.

TABLE VI  
ERYTHROSIN

H <sub>2</sub> O removed %	H <sub>2</sub> O to pure color <sup>a</sup> %	Pressure Mm.	Temp. °C.	H <sub>2</sub> O removed %	H <sub>2</sub> O to pure color <sup>a</sup> %	Pressure Mm.	Temp. °C.
1.2	13.65	21.5	50	9.4	4.1	2.0	50
2.2	12.4	16.8	50			21.1	90
3.3	11.2	12.8	50	10.4	3.0	12.0	90
4.3	10.0	9.0	50	11.0	2.3	6.5	90
5.2	9.0	6.5	50	11.5	1.8	3.6	90
6.2	7.9	4.6	50	11.7	1.5	1.5	90
6.9	7.0	3.8	50	12.0	1.2	0.5	90
7.6	6.2	3.0	50			22.5	140
8.2	5.5	2.8	50	12.5	0.6	7.2	140
8.8	4.8	2.5	50	12.9	0.2	0.8	140
				13.0	0.0	...	140

<sup>a</sup> Computed from water actually removed.

No definite evidence as to how this water is held is available at this time. Gomberg and Tabern<sup>13</sup> suggest that the quinoid tautomer of the dye combines with water to give Formula I. This formula does not seem to explain the characteristics of this compound. There is no reason to expect a difference in structure between the sodium salt and the free acid which can easily be obtained in the anhydrous form. Pending further work on this subject, it is suggested that this seeming irregularity might be explained on the basis of an addition compound formed by the union of 1 molecule of the monosodium salt with 1 molecule of sodium hydroxide, such as shown in Formula II.



**Tartrazin**, C<sub>16</sub>H<sub>9</sub>N<sub>4</sub>S<sub>2</sub>O<sub>9</sub>Na<sub>3</sub>: This is of especial interest as it is one of the 11 permitted food dyes. Anschütz<sup>15</sup> records that tribarium tartrazin

<sup>15</sup> Anschütz, *Ann.*, 294, 288 (1897).



$((C_{16}H_9N_4S_2O_9)_2Ba_3)$  contains 6 molecules of water. All investigators report that the di- and trisodium forms are anhydrous, although users of this dye know that the sodium salt very rapidly takes up approximately 17% of moisture on exposure to the air.

A pure sample of trisodium tartrazin was recrystallized from water and partially dried in the air. A moisture determination on this product showed approximately 33% of water. Vapor pressure-water content

TABLE VII  
TARTRAZIN

26°				30°			
H <sub>2</sub> O removed %	H <sub>2</sub> O to pure color %	H <sub>2</sub> O Mols.	Pressure Mm.	H <sub>2</sub> O removed %	H <sub>2</sub> O to pure color %	H <sub>2</sub> O Mols.	Pressure Mm.
0.2	49.9	14.8	22.6	3.7	45.5	13.5	25.4
0.9	48.9	14.5	21.7	4.8	42.9	12.7	25.4
1.8	47.5	14.1	20.6	6.4	40.5	12.0	25.3
2.8	46.1	13.7	20.2	8.0	38.1	11.3	25.5
3.8	44.5	13.2	20.1	9.5	35.8	10.6	24.8
4.8	42.9	12.7	20.1	11.2	33.3	9.9	23.5
5.8	41.4	12.3	20.1	12.7	31.1	9.2	23.2
6.9	39.7	11.8	20.1	14.3	28.7	8.5	23.0
8.0	38.1	11.3	20.1	15.9	26.2	7.8	23.0
8.3	37.6	10.9	19.2	17.4	23.9	7.1	18.5
9.2	36.4	10.8	19.2	18.6	22.2	6.6	13.5
10.2	34.9	10.4	19.2	19.5	20.8	6.2	9.0
11.3	33.3	9.9	18.2	20.4	19.5	5.8	7.2
12.4	31.7	9.4	18.2	21.2	18.3	5.4	6.4
13.5	30.1	8.9	18.2	22.3	16.6	4.9	6.1
15.6	26.7	7.9	17.0	23.6	14.6	4.3	6.0
16.6	25.3	7.5	15.9	24.8	12.9	3.8	6.0
17.3	24.1	7.2	13.8	25.9	11.3	3.4	5.6
18.3	22.8	6.8	8.6	27.0	9.6	2.9	4.2
19.2	21.4	6.4	5.6	27.7	8.5	2.5	3.5
19.8	20.4	6.1	4.9	28.4	7.5	2.2	3.3
20.5	19.5	5.8	4.7	29.0	6.6	1.9	3.0
21.9	17.3	5.1	4.2	30.8	3.8	1.1	2.2
23.2	15.3	4.5	4.0	31.4	3.0	0.7	1.8
23.5	15.0	4.4	4.0	32.9	0.7	0.2	1.0
25.0	12.6	3.7	3.9	33.3	0.0	0.0	...
25.8	11.3	3.4	3.8	..	...	...	...
26.6	10.3	3.0	3.6	..	...	...	...
27.3	9.2	2.7	3.0	..	...	...	...
28.2	7.9	2.3	2.9	..	...	...	...
28.5	7.3	2.1	2.7	..	...	...	...
29.2	6.3	1.9	2.5	..	...	...	...
29.9	5.3	1.6	2.2	..	...	...	...
30.2	4.7	1.4	2.1	..	...	...	...
33.3	0.0	...	...	..	...	...	...

curves on this sample were obtained at 26°, and repeated at 30° because of certain irregularities observed at the lower temperature. Curves C

and D, Fig. 2, show that breaks in the curve obtained at 26° occur at points corresponding to hydrates of 14, 11, 10, 6 and 3 molecules of water. As the presence of the hydrates containing 10 and 11 molecules of water seemed a little doubtful, owing to the slight change in pressure (1 mm.) between them and the next higher hydrate, and in order to obtain more information regarding the location of the curve between the hexa- and octahydrate, this experiment was repeated at 30°. The curve obtained at the higher temperature indicates the presence of hydrates containing 14, 10, 6 and 3 molecules of water. The rounding-off effect due to the presence of higher hydrates in the interior of the particles, as suggested by Beutell and Blaschke,<sup>1</sup> is clearly demonstrated between the deca- and hexahydrates which differ in pressure by 13 mm.

As already mentioned, tartrazin after exposure to air contains about 17% of water. This corresponds to the hexahydrate, which has a vapor pressure approximately that of the aqueous tension of the air.

### Summary

Vapor pressure-water content curves have been obtained for methylene blue, crystal violet, erythrosin, magenta and tartrazin, for the purpose of determining whether the water present in these dyes is adsorbed or held as water of crystallization. Crystal violet and tartrazin alone show hydrate formation. Further proof was also obtained that the equivalent of 1 molecule of water in erythrosin is present as part of the molecule and a new theory of the structure of this dye is offered.

WASHINGTON, D. C.

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]  
**THE USE OF BROMATE IN VOLUMETRIC ANALYSIS. III. THE DETERMINATION OF BROMATE IN THE PRESENCE OF FERRIC IRON**

BY G. FREDERICK SMITH

Received April 27, 1923

In the former papers of this series,<sup>1</sup> the stability of boiling solutions of potassium bromate in the presence of mineral acids was demonstrated and the relation of this stability to further applications in the use of bromate for volumetric analysis suggested. The use of bromate in acid solution in the presence of mercuric ion was shown to alter the course of several reactions of analytical importance, increasing the oxidation value of the bromate from 5 to 6 equivalents of oxygen, thus preventing the troublesome formation of free bromine and in other ways increasing the flexibility and value of bromate oxidimetric processes.

Determinations involving the use of bromic acid in excess generally

<sup>1</sup> THIS JOURNAL, 45, 1115, 1417 (1923).