was not obtained. Yields, analytical data and results of dye tests are given in Table III.

Preparation of Intermediates.—Most of the methyl esters needed for the condensations with acetonitrile were obtained from the Eastman Kodak Company or were prepared by esterification of the corresponding acids by the conventional procedure. The derivatives of salicylic acid were found to be most readily prepared by etherification of methyl salicylate. The methyl and ethyl ethers were prepared using the corresponding dialkyl sulfates, the propyl derivative using propyl iodide, and the benzyl derivative using benzyl chloride.

The chloroacetyl derivatives of tetralin, acenaphthene, toluene and biphenyl were prepared by the conventional Friedel–Crafts reaction using chloroacetyl chloride.

Thiophene-2-carboxylic acid was prepared by oxidation of methyl 2-thienyl ketone by the procedure recommended for β-naphthoic acid.[14]

The necessary amines and diazo compounds were prepared by conventional procedures.

Methyl 3,4-Dichlorobenzoate.—This appears to be a new compound. It was prepared by esterification of 3,4-dichlorobenzoic acid by refluxing with methyl alcohol and a small amount of sulfuric acid. Recrystallization from methyl alcohol gave white crystals, m. p. 45–47° (cor.); yield, 78.4%. It was not analyzed.

Summary

The preparation of a new type of chromium complex of azo dyes is described. These azo dyes are derived from acylacetonitriles and aromatic aminesulfonic acids containing hydroxyl or carboxyl groups ortho to the amino group. The complexes are stable either when dry or in aqueous solution. They have been shown to contain one atom of chromium for each molecule of azo dye.

The use of the unmetallized dyes as acid colors and chrome colors and of the chromium complexes as wool dyes is discussed with regard to the effect of the chromium and of substituents on the shade. In general, the chromium complexes have much more color value than the unmetallized dyes and the shade varies from yellow to violet depending on the nature of the acylacetonitrile and the diazo component.

The method used by Dorsch and McElvain[6] for the preparation of benzoylacetonitrile has been shown to be applicable to the preparation of numerous acylacetonitriles, not only in the benzene series but also in the naphthalene, furan and thiophene series.

BOUND BROOK, N. J.

RECEIVED SEPTEMBER 6, 1946

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[14] "Organic Syntheses," Coll. Vol. II, p. 428.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF NEW YORK UNIVERSITY]

Aqueous Solubilities of Some Sulfamates, and the System Ammonium Sulfamate–Sulfamic Acid–Water at 25°[1]

BY JOHN E. RICCI AND BERNARD SELIKSON

The technical uses and importance of sulfamic acid and its salts are increasing, but knowledge of the properties and solubilities of its inorganic salts is still rather scanty. Most of the published information on the preparation and properties of the pure acid and its salts, and on their solubilities in various solvents, is summarized in the articles of Cupery and Gordon[2] and in the review article by Audrieth and co-workers.[3] This is a report of preliminary work beginning some systematic studies on the solubility relations of the simple sulfamates in aqueous systems.

I. Preparation and Properties of the Compounds.—A. Sulfamic acid of sufficient purity was obtained by a simple leaching procedure from Eastman Kodak Co. material of technical grade.[4] The leached residue, filtered on a Büchner funnel, was washed successively with cold water, alcohol and ether. The final product, which was found to be sulfate free, was air dried for a day and then ground and stored over Anhydrone. It melted at 205°, in agreement with Cupery's report,[2a] and titration with 0.2 N sodium hydroxide showed it to be 99.9% pure.

The test for sulfate in solutions either of sulfamic acid or of its salts was made by adding about 5 ml. of saturated barium chloride solution to 1 g. of the sulfamate in 2 ml. of distilled water. If a haze of barium sulfate precipitate did not appear within thirty minutes the material was accepted as "sulfate free." It was otherwise rejected or purified further, although it was estimated, by actual tests with added quantities of soluble sulfate, that as little as a few thousandths of a per cent. of sulfate would give a positive test. The retardation of the precipitation of barium sulfate by sulfamic acid, observed by Divers and Haga,[5] was not found to occur under the conditions of the test here employed. Premixing of sulfuric acid with sulfamic acid gave precipitates of barium sulfate of the same intensity almost as quickly as did experiments on pure sulfuric acid.

B. Ammonium sulfamate was prepared both by neutralization of sulfamic acid with aqueous ammonia and by recrystallization of technical grade material. The final, recrystallized salt was sulfate-free, melted without decomposition at 131° in agreement with literature values.[2a,6] and was found to be 99.9% pure on the basis of ammonia content. Ammonia was determined by standard procedure, distilling with excess of potassium hydroxide into boric acid solution and titrating the ammonium borate with 0.2 N hydrochloric acid. The amide group of the sulfamates does not interfere in this ammonia determination, as the hydrolysis, producing ammonia and sulfate, is prevented in alkaline solution. Parallel determinations for ammonia content made on pure samples of sulfamic acid, ammonium sulfamate and mixtures of the two, showed no ammonia in the first set of experiments and no effect of sulfamic acid in the latter two. The effect of acidity on

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[1] From the M.S. thesis of Mr. B. Selikson, New York University, January, 1945.

[2] (a) Cupery, *Ind. Eng. Chem.*, **30**, 627 (1938); (b) Gordon and Cupery, *ibid.*, **31**, 1237 (1939); (c) Cupery and Gordon, *ibid.*, **34**, 792 (1942).

[3] Audrieth, Sveda, Sisler and Butler, *Chem. Rev.*, **26**, 49 (1940).

[4] The nature of this technical material was such that the more elaborate but necessarily more wasteful purification described by Butler, Smith and Audrieth (*Ind. Eng. Chem., Anal. Ed.*, **10**, 690 (1938)) was not necessary.

[5] Divers and Haga, *J. Chem. Soc.*, **69**, 1634 (1896).

[6] Berglund, *ibid.*, **34**, 643 (1878).

this hydrolysis was also shown by the difference in time required for the appearance of a haze of barium sulfate in solutions of pure sulfamic acid as contrasted with solutions of pure ammonium sulfamate: at most two hours for the acid but at least a day for the ammonium sulfamate solution.

C. Potassium sulfamate was made from potassium hydroxide and sulfamic acid; the recrystallized salt was analyzed only by transformation to potassium sulfate, giving a purity, on this basis, of 99.8+%.

In the recrystallization of these three compounds, the following qualitative observations were made concerning the effect of ethanol: very little effect on the solubility of the acid, a marked decrease for the potassium salt, and formation of two liquid layers in the case of ammonium sulfamate solution.

D. The first batch of sodium sulfamate prepared turned out to be the metastable anhydrous salt. It was made by adding sodium carbonate to a mixture of technical sulfamic acid and water with stirring, the heat evolved by the reaction being sufficient to dissolve the materials. Carbon dioxide was expelled by addition of a small excess of sulfamic acid, and the solution was then titrated with dilute sodium hydroxide until neutral to litmus. This solution was filtered and cooled, producing granular crystals similar in appearance to those of the potassium salt. The product was washed as in other preparations, found to be sulfate-free, recrystallized in water by heating, and finally dried in the usual manner with alcohol and ether. After several days over Anhydrone, it was analyzed by transformation to sodium sulfate and found to be 99.8% pure.

When an attempt was made to use this anhydrous salt in ternary mixtures containing water and sulfamic acid, it changed, during the sampling of saturated solutions, to a voluminous, hydrated form, and thereafter it was impossible in this Laboratory to repeat the preparation of the anhydrous salt by precipitation. The hydrated salt forms in large, long, soft, silky, fibrous crystals, tending to enclose the mother liquor. This behavior resulted in the setting, or apparent solidification, of mixtures containing very small amounts of the hydrate in excess of that required for saturation. Such mixtures frequently became mobile when shaken, only to set again on standing. The hydrate would not settle from a saturated solution, it formed supersaturated solutions very easily, and its solubility relations seemed to be very sensitive to slight changes in temperature, at room temperature. Purification of the monohydrate by recrystallization therefore did not seem advisable, and for the same reason the ternary work involving this salt was postponed for the time being.

A sample of the hydrate for analysis was made by adding a solution of C. P. sodium hydroxide to pure aqueous sulfamic acid until neutral and then evaporating until very slightly moist but not dry, thus preventing any dehydration. This material, kept under a bell jar together with a beaker of water, was the source of the sodium sulfamate used in further work. It was sulfate free and apparently consisted simply of water and pure sodium sulfamate. Heated to constant weight at 110°, the anhydrous residue was found to be 100.2% pure (calculated as sodium sulfamate) upon transformation to sodium sulfate.

The monohydrate of sodium sulfamate is not mentioned in the literature, and its formation was a surprise in the present work. Its formula was determined by both direct and indirect analysis; namely, from the loss of weight on heating and by application of the Schreinemakers "wet residue" method[7] using sodium iodide as a third component. Some of the hydrate was partially dehydrated at 90° and used as a desiccant to bring another portion of the moist hydrate to constant weight at room temperature. The product thus obtained was presumably the pure hydrate, and its loss of weight at 110° was then determined. The molar ratio of water to salt was found to be 1.018. The second method involved the determination of a small portion of the ternary system sodium sulfamate–sodium iodide–water at 25° (but strict control of temperature is here of no importance), in the region of low sodium iodide concentration, where hydrated sodium sulfamate is the saturating phase. Algebraic extrapolation of the tie-lines[8] through wet residue and saturated solution gives a precise determination of the hydration of the solid phase. Three mixtures of saturated solution and monohydrate were prepared, containing approximately 5, 10 and 15% of sodium iodide, respectively. After a few days of stirring at 25°, samples of both liquid and wet solid were analyzed. Two samples of the liquid were drawn into pipets fitted with filtering tips; one was titrated for iodide content with 0.15 *N* silver nitrate using eosin as indicator, while the second was analyzed for total solid by heating for two days at 110° and then for ten minutes at 250° to complete the dehydration of the sodium iodide. After removal of the liquid sample, the wet solid was squeezed between filter papers, weighed, dissolved and aliquoted for similar analysis, both for iodide and for total solid. The extrapolations gave 13.6% water, in very good agreement with the theoretical value of 13.1% for the monohydrate. The data are given in Table I.

TABLE I

HYDRATION OF SODIUM SULFAMATE AT ROOM TEMPERATURE

Direct method

Hydrate, g.	Anhydrous salt, g.	Water, mole	Anhydrous salt, mole
0.4925	0.4264	0.366	0.358
.6666	.5778	.493	.486

Indirect method

Satd. soln.		Wet residue		% Water in solid phase, by extrapolation
% Solid	% NaI	% Solid	% NaI	
56.74	17.61	66.19	12.02	13.5
55.81	10.78	61.23	8.87	13.6
55.54	4.38	59.68	3.79	13.6
		Per cent. in monohydrate		13.1

II. Solubilities of the Compounds.—The solubilities of these substances were determined by analysis of saturated solutions obtained by stirring excess solid with water in Pyrex tubes. Equilibrium was proved by constancy in respect to approach from higher and lower temperatures, and in respect to time. The latter seemed especially important in the case of sulfamic acid which is more subject to hydrolysis than the more nearly neutral or alkaline solutions of its salts. The analytical determinations used were titration with standard alkali for sulfamic acid, evaporation to constant weight for the sodium and potassium salts, and both determination of ammonia (Kjeldahl) and evaporation to constant weight at 105–110°, for the ammonium salt. The agreement of determinations by various analytical methods and by approach from super- and under saturation was in every case very close. The average, individual solubilities are listed in Table II, in which they are also compared with some determinations in the literature.

III. System: Ammonium Sulfamate–Sulfamic Acid–Water at 25°.—The isothermal relations of this ternary system at 25° were investigated in the usual manner, equilibrating known

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(7) Schreinemakers, *Z. physik. Chem.*, **11**, 76 (1893).

(8) Hill and Ricci, THIS JOURNAL, **53**, 4306 (1931).

Table II

Solubilities of the Pure Substances

	Temp., °C.	Wt. %	Cupery[2a]
Sulfamic acid	25	18.78 ± 0.03	~19.2
Ammonium sulfamate	20	67.0 ± .2	66.7
	25	68.87 ± .11	~68.4
	35	72.9 ± .25	~71.9
Potassium sulfamate	20	40.05 ± .02	
	25	43.74 ± .02	
	35	50.38 ± .03	
Sodium sulfamate monohydrate	25	55.30 ± .30	51.5[9]

complexes of the three components and analyzing the filtered saturated solution at equilibrium. The temperature of the bath was 25 ± 0.02°. Solubility equilibrium was reached after one day of stirring, as proved by constancy of analytical results after three more days. Separate experiments were also made on solutions of sulfamic acid and ammonium sulfamate alone and together, to estimate the extent of hydrolysis to be expected in such periods of time. Determination of the ammonia in excess of that present in the ammonium sulfamate itself showed that the maximum decomposition was not greater than four parts per thousand in five days.

The saturated ternary solutions were analyzed for sulfamic acid by titration with alkali, and for ammonium sulfamate by the Kjeldahl method as already described. The results are listed in Table III and shown graphically in Fig. 1. Incidentally, various attempts were made to substitute an evaporation to dryness for the Kjeldahl determination, to measure the total percentage of both dissolved components, but with no success. The solution of the free acid, with or without ammonium sulfamate, could not be heated without decomposition even at moderate temperatures and in a vacuum oven. Complete hydrolysis of the acid by prolonged heating of the solution and consequent weighing as ammonium bisulfate was also unsuccessful. Heating to dryness with excess of ammonia which prevents hydrolysis and weighing a residue consisting entirely of ammonium sulfamate was possible, but the process of drying such a residue without decomposition was inconvenient and tedious. The Kjeldahl determination was both faster and more reliable.

Table III

System Ammonium Sulfamate–Sulfamic Acid–Water at 25°

Orig. complex % Salt	Orig. complex % Acid	Satd. soln. % Salt	Satd. soln. % Acid	Solid phases
...	0.00	68.87	0.00	Salt
72.03	4.73	65.99	5.73	Salt
65.37	10.59	63.59	11.00	Salt
72.28	10.06	62.96	13.65	Salt
64.46	14.83	62.24	15.12	Salt + acid
60.43	20.33	62.20	15.16	Salt + acid
55.06	25.14	62.14	15.19	Salt + acid
Average		62.19	15.16	Salt + acid
49.50	30.62	60.72	15.26	Acid
40.52	28.29	47.39	16.19	Acid
25.12	30.07	29.89	17.06	Acid
10.35	29.64	12.18	17.72	Acid
0.00	...	0.00	18.78	Acid

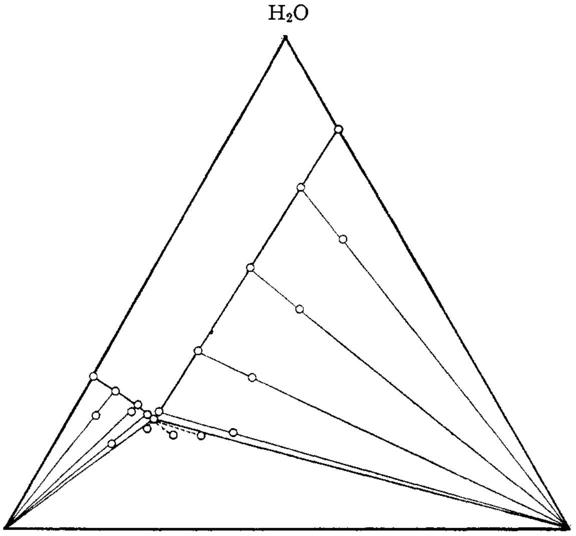

Fig. 1.—System ammonium sulfate–sulfamic acid–water at 25°.

The numerical results tabulated are averages of closely agreeing duplicate analyses. It is clear from the diagram that neither solid solution nor compound formation occurs in the system at this temperature. The tie-lines converge sharply and with negligible errors at the compositions of the separate anhydrous solid components. The isothermally invariant solution saturated with both solids has the composition 62.19% salt and 15.16% acid, as compared with 18.78% for the solubility of the acid alone in pure water. This is a remarkably small effect, for such high concentration of the salt, upon the solubility of the acid. The shape of the curve for saturation with respect to the acid is not as expected; it is practically a straight line and does not show the usual fall in solubility at low concentrations caused by the "common ion effect." The study of the conductivity and other electrolytic properties of these solutions would probably yield information concerning the complexity of species which seems to be indicated by this phase diagram.

Summary

1. Sodium sulfamate has been found to be a monohydrate at room temperature, the anhydrous salt being metastable.

2. Aqueous solubilities are given for pure sulf-

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[9] Given by Cupery as the solubility of "sodium sulfamate" at 25° (106 g./100 g. of H_2O), without specification or identification of the solid phase. It is to be noted that the anhydrous salt, as a metastable phase, must be even more soluble than the monohydrate.

amic acid (at 25°), ammonium sulfamate (at 20, 25, 35°), potassium sulfamate (at 20, 25, 35°) and sodium sulfamate monohydrate (at 25°).

3. The system ammonium sulfamate–sulfamic acid–water was studied at 25°; it forms neither solid solution nor double compounds, and is marked by the very small effect of high concentrations of the salt on the solubility of the acid.

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[CONTRIBUTION FROM INSTITUTT FOR UORGANISK KJEMI, NORGES TEKNISKE HØGSKOLE]

Investigations on the Equilibria in the System V_2O_4, V_2O_5, $VOSO_4$, SO_2, SO_3

BY H. FLOOD AND O. J. KLEPPA

Introduction

In the presence of three solid phases the system V_2O_4, V_2O_5, $VOSO_4$, SO_2, SO_3 is univariant. To each temperature corresponds a pressure of SO_2, determined by the equilibrium

$$2VOSO_4 + V_2O_4 = 2V_2O_5 + 2SO_2 \qquad (1)$$

From the equilibrium

$$2VOSO_4 + V_2O_5 + SO_2 = 2V_2O_4 + 3SO_3 \qquad (2)$$

it is seen that p_{SO_3} is also determined.

When two solid phases are present, the system provides 1 univariant and 2 bivariant equilibria

$$2VOSO_4 = V_2O_4 + 2SO_3 \qquad (3)$$

$$2VOSO_4 = V_2O_5 + SO_2 + SO_3 \qquad (4)$$

$$V_2O_5 + SO_2 = V_2O_4 + SO_3 \qquad (5)$$

Figure 1 illustrates the conditions which at a given temperature allow for the existence of the three solid phases as functions of the partial pressure of SO_2 and SO_3 in the gas phase.

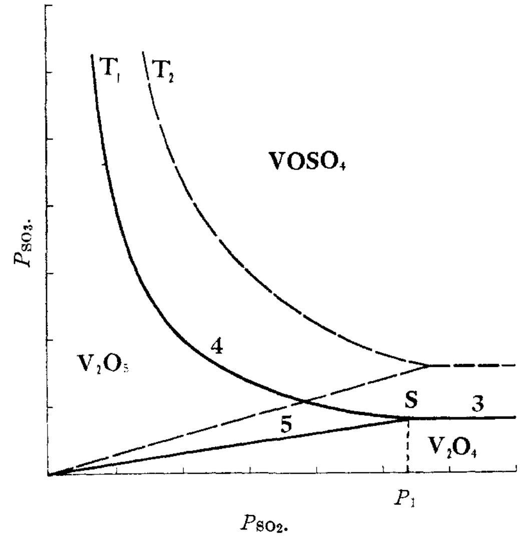

Fig. 1.—Conditions of existence of V_2O_4, V_2O_5 and $VOSO_4$ as functions of the partial pressure of SO_2 and SO_3.

The curves 3, 4 and 5 indicate the coexistence of two solid phases

$$p_{SO_2} = K_3 \text{ (curve 3)}$$

$$p_{SO_2} \cdot p_{SO_3} = K_4 \text{ (curve 4)}$$

$$p_{SO_3} \cdot p_{SO_2} = K_5 \text{ (curve 5)}$$

When $VOSO_4$ is heated in air it normally decomposes into V_2O_5, SO_2 and SO_3 according to equation 4. Only when the partial pressure of SO_2 exceeds a certain limit (p_1, see Fig. 1) will the decomposition proceed according to 3.

It will be seen that the intersection of the three curves (S) corresponds with the coexistence of all three solid phases.

The only information previously available on these equilibria refers to reaction 4. B. Neumann and A. Sonntag[1] measured K_4 using a static method. A. Ditte[2] has shown qualitatively that SO_2 at 500–600° reduces V_2O_5 to V_2O_4.

Under the present investigation all three equilibria have been measured by a flow method. A current of SO_2 was led through a plug consisting of mixtures of V_2O_4–$VOSO_4$, V_2O_5–$VOSO_4$ or V_2O_4–V_2O_5, respectively. After having passed the contact the content of SO_3 was determined and the corresponding equilibrium constants for 3, 4 and 5 were calculated. The results of these investigations are given below.

Experimental

Preliminary investigations and calculations on these equilibria showed that at 500–600° a partial pressure of sulfur trioxide of 1–2% should be expected. The apparatus was constructed in accordance with this assumption.

From the bottle of sulfur dioxide (liquid) a slow current of gas was led at a constant rate through the two-phase-contact. Fig. 2a illustrates the arrangement of the contact. The gas is pressed from above through the contact-plug which is placed in a quartz tube. The temperature was measured by an iron–constantan thermoelement, checked at the melting points of tin, zinc and aluminum (99.99%). The temperature along the contact zone was within the limits of ±1°, even before the contact proper was introduced. A constant temperature was secured by a lamp bank in the usual way.

Having passed the contact the gas mixture was led down through an Ahlintube, where the content of sulfur trioxide was adsorbed on asbestos as described by K. Schiel and H. Sieber[3] (Fig. 2b). The adsorbed sulfur trioxide was removed by repeated washing with hot, boiled, distilled water. Afterwards sulfur dioxide was boiled out in a current of carbon dioxide, and the content of sulfur trioxide determined by titration with sodium hydroxide. The amount of sodium hydroxide was empirically corrected for the oxidation of sulfur dioxide to sulfur trioxide during the analytical procedure. This correction represented a con-

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[1] B. Neumann and A. Sonntag, *Z. Elektrochem.*, **39**, 799 (1933).

[2] A. Ditte, *Compt. rend.*, **101**, 1487 (1885).

[3] R. Schepp and K. Schiel, *Papier-Fabr.*, **29**, 761 (1931); H. Sieber, *ibid.*, **23**, 209 (1925).