

STUDIES ON THE ELECTROCHEMICAL PREPARATION OF SODIUM HYDROSULPHITE.

PART VII. STUDIES ON TRANSITION POINT OF SODIUM HYDROSULPHITE CRYSTALS

by C. C. PATEL, *Department of General Chemistry, Indian Institute of Science, Bangalore.*

(Communicated by Dr. J. C. Ghosh, F.N.I.)

(Received July 7; read October 4; 1952.)

It is well known that anhydrous hydrosulphite keeps well, while the hydrated salt is quite unstable. The usual commercial practice, therefore, is to render the hydrosulphite anhydrous. According to the patent literature on hydrosulphite, the dehydration of the salt is carried out at about 60° C. by heating the crystals alone (Badische Anilin- und Soda-Fabrik, 1906) or with reagents like alcohol (Höchst, 1906) or sodium chloride (Badische Anilin- und Soda-Fabrik, 1905) or by heating in vacuum the solution of hydrosulphite in presence of a salting out agent above its transition point (Nitzschke, 1941). K. Jellinek (1911) heats the crystals over the range 50° C. to 70° C., either with alcohol or with a saturated solution of sodium chloride. Pratt (1924) carries out the dehydration in presence of sodium chloride at about 60° C. In connection with the dehydration of hydrosulphite, accurate information about the transition from the dihydrate to the anhydrous form, is of considerable value. In chemical literature, however, information about this transition is very meagre, the only reference to any determination of the transition point being the work of Bazlen (1905) who found that transition took place at about 52° C., in presence of alcohol. In the present investigation, a systematic study was made of the transition point of sodium hydrosulphite dihydrate since it was available in pure form.

EXPERIMENTAL.

Preliminary experiments were carried out to determine, in the case of hydrosulphite, the suitability of the usual methods of determining transition temperature. It was found, however, that some of these methods were not at all suitable. The dilatometric method, for example, was tried employing toluene, kerosene or alcohol as the liquid medium surrounding the crystals. This, however, did not succeed, as practical difficulties were encountered owing to the evolution of sulphur dioxide in the dilatometer, due to the decomposition of the hydrosulphite. In fact, when the salt ($\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) is heated in an inert atmosphere, the solid is decomposed at about 80° C. with an evolution of heat. The solubility method and the electrical conductivity method of determining the transition temperature were not practicable due to continuous decomposition of hydrosulphite at elevated temperatures. Owing to this decomposition, the dehydration in industrial practice is carried out by heating the crystals of hydrosulphite in presence of sodium chloride (Riegel, 1942). Information about the transition temperature of hydrosulphite in presence of sodium chloride is, therefore, of particular importance. The methods mentioned above could not be employed for the determination of transition temperature in presence of sodium chloride. The thermometric method, however, was found to be fairly satisfactory.

Transition Point of Sodium Hydrosulphite crystals in presence of Sodium Chloride.

For the determination of the transition temperature, the apparatus used was the same (Fig. 1, Part VI) as previously described. The modification introduced was that the vessel *P* was surrounded by an air-jacket. The water bath was well insulated and heated electrically so as to ensure uniform rise in temperature. The water in the bath was stirred well. The crystals of sodium hydrosulphite were prepared by electrochemical method and purified at 0°C., as described in Part VI. The crystals were then washed twice at 0°C., with about 10 ml. of a saturated aqueous solution of sodium chloride. The analysis of the wash liquor showed that the hydrosulphite was free from thiosulphate, bisulphite and other sulphur compounds.

For the determination of the transition temperature, the mercury in the apparatus was brought to the sintered glass plate *S* and 8 ml. of the saturated solution of sodium chloride was added to the crystals. In order to confirm the attainment of equilibrium, the hydrated crystals were mixed with anhydrous hydrosulphite. The crystals were gently stirred by the thermometer and the supply of nitrogen maintained in the vessel *P*. The water bath was heated gradually. The temperatures were noted at one minute intervals. The results obtained are given in Fig. 1.

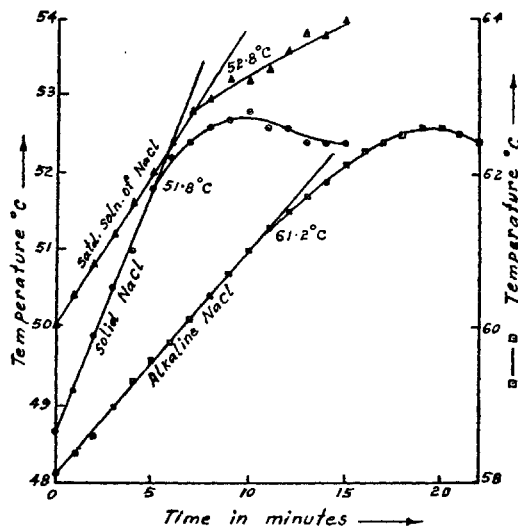


FIG. 1. Transition temperature of sodium hydrosulphite in presence of sodium chloride.

It is seen that the break in the curve, Fig. 1, occurs at 52.8°C. This temperature is, therefore, taken to be the transition point of sodium hydrosulphite in presence of solution of sodium chloride, which is practically saturated.

The temperature of the bath was raised by 0.4°C., per minute. Slower rate of heating was not desirable on account of the decomposition of the hydrosulphite. During the transition, the crystals of the dihydrate changed over to a sand-like granular powder, which settled down on the filter plate in the vessel *P*. In order to determine roughly the extent of decomposition of hydrosulphite during transition, the liquid phase was analysed for hydrosulphite, bisulphite and thiosulphate at the end of the experiment. The solid was washed and dried as described later and the composition determined. The results obtained are given in Table I.

Employing the same technique, the transition temperatures of sodium hydrosulphite were determined in presence of (a) a suspension of solid sodium chloride in its saturated aqueous solution, and (b) an aqueous solution of sodium chloride containing 5% sodium hydroxide. The latter system was tried, in view of general impression that alkali stabilises hydrosulphite. The corresponding curves are given in Fig. 1; the transition points as read from these graphs and the data pertaining to decomposition of hydrosulphite are presented in Table I.

TABLE I.

Transition Temperature of Sodium Hydrosulphite Crystals in presence of Sodium Chloride.

Expt. No.	Reagent used. 8 ml. in each case.	Transition temperature obtained. °C.	Approx. weight of anhydrous hydrosulphite obtained. g.	Salts present in liquid phase at the end of the dehydration process in 100 ml. solution, g.		
				Na ₂ S ₂ O ₄	NaHSO ₃	Na ₂ S ₂ O ₃
1	Saturated NaCl soln.	52.8	12	5.9	1.3	..
2	Saturated NaCl soln. + 1.5 g. of solid NaCl.	51.8	14	2.8	1.1	..
3	Alkaline NaCl soln.	61.2	13	4.8	4.0	0.7

It is clear from the data represented above that the dehydration of crystals of hydrosulphite is best effected in presence of a saturated solution of sodium chloride containing purified common salt. While in presence of a saturated solution of sodium chloride, the transition takes place at 52.8° C., the point is further lowered to 51.8° C., by the presence of solid salt; the alkali, on the other hand, raises the temperature to 61.2° C.

Transition Point of Sodium Hydrosulphite in presence of various Sodium salts.

The dehydration of sodium hydrosulphite crystals was also studied in presence of various foreign substances such as sodium sulphate, sodium nitrate, tri-sodium

TABLE II.

Expt. No.	Reagent surrounding the crystals. 8 ml. in each case.	Transition temperature obtained. °C.	Salts present in liquid phase at the end of the dehydration process in 100 ml. solution, g.		
			Na ₂ S ₂ O ₄	NaHSO ₃	Na ₂ S ₂ O ₃
1	Saturated solution of Na ₂ SO ₄ at 40° C.	67.7	9.2	1.8	..
2	100 g. NaNO ₃ dissolved in 100 ml. water.	57.3	4.4	3.1	..
3	Saturated solution of Na ₃ PO ₄ at 50° C.	62.1	12.6	0.1	..
4	Saturated soln. of Na ₂ HPO ₄ at 50° C.	61.7	7.5 (lower layer) 0.2 (upper layer)	9.8 0.6	4.4 ..

phosphate and di-sodium hydrogen phosphate, employing about 15 g. of the crystals. The transition temperatures obtained with various media are given in Table II. Data relating to decomposition products of hydrosulphite in liquid phase are also given in Table II. It was noted that two layers were formed in the liquid phase during the dehydration of hydrosulphite in presence of disodium hydrogen phosphate.

The results given in Table II indicate that the transition temperature varies with the nature of the foreign substance surrounding the crystals. Hydrosulphite decomposition was minimum in presence of tri-sodium phosphate.

Transition Point of Sodium Hydrosulphite in presence of different concentrations of alcohol.

Employing the procedure already described, a study was made of the transition temperature of sodium hydrosulphite in presence of the following concentrations of alcohol (by volume): (a) 70%, (b) 85%, and (c) 99.8%. The transition temperatures are given in Table III, as read from data plotted in Fig. 2. Data relating

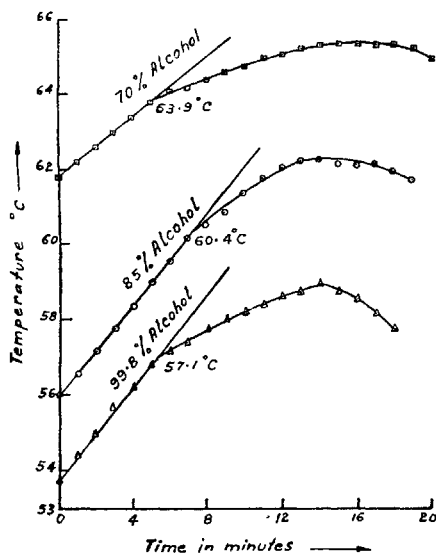


FIG. 2. Transition point of hydrosulphite in presence of various concentrations of alcohol.

TABLE III.

Transition Temperature of Sodium Hydrosulphite in presence of various concentrations of alcohol.

Expt. No.	Concentration of alcohol % (by volume).	Transition temperature obtained. °C.	Salts present in the liquid phase at the end of dehydration process in 100 ml. solution, g.		
			Na ₂ S ₂ O ₄	NaHSO ₃	Na ₂ S ₂ O ₃
1	70.0	63.9	2.78	3.08	0.78
2	85.0	60.4	0.92	2.02	0.34
3	99.8	57.1	0.14	1.50	..

to decomposition products of hydrosulphite in liquid phase are also given in the same table. Unlike the granular type of anhydrous hydrosulphite obtained in the case of dehydration in presence of sodium chloride, the product obtained with alcohol was a fine powder, which was found to have comparatively poor keeping quality.

The results of the above table indicate that hydrosulphite decomposition is least in presence of absolute alcohol.

The transition temperature of the hydrosulphite in presence of 60% alcohol was only 60° C. This abnormally low value was due to the appreciable decomposition of hydrosulphite at the elevated temperature.

The transition temperature of sodium hydrosulphite, in absence of stabilising foreign substances, cannot be determined experimentally, owing to the marked decomposition that takes place, during transition. An approximate idea of the transition temperature can, however, be obtained by extrapolation to zero alcohol concentration of the data presented in Table III. The value was found to be 79.4° C.

Stability of anhydrous Hydrosulphite on storage.

To obtain anhydrous hydrosulphite, the crystals were heated with various reagents till the dehydration was complete. The mother liquor was drained off and the anhydrous salt was washed twice with hot 95% alcohol and dried in vacuum at 92° C. The sample was stored in glass stoppered bottles and kept over calcium chloride in a desiccator and analysed after one month. The percentage decomposition of hydrosulphite on storage is given in Table IV.

TABLE IV.

Comparison of the stability of Hydrosulphite on storage.

Method of dehydration.	Purity of hydrosulphite.		Decomposition %
	When prepared.	After one month's storage.	
Saturated solution of NaCl containing solid NaCl.	96.8	94.04	2.9
		93.90 (after 10 months).	3.0
Saturated solution of Na ₃ PO ₄ at 50° C.	95.0	92.85	2.3
Solution of NaCl + 5% NaOH ..	92.4	90.96	1.6
Absolute alcohol	92.4	86.12 (after 15 days).	6.8

It is seen from the above table that hydrosulphite dehydrated in presence of sodium salts is more stable than that dehydrated in presence of alcohol.

DISCUSSION.

Transition Temperature of Sodium Hydrosulphite.

When sodium hydrosulphite is heated near the transition temperature, there is absorption of heat due to the dehydration of the salt. At the same time, there is the evolution of heat due to the decomposition of the hydrosulphite (10,350 cal./mol., Deines and Elstner, 1930). The temperature recorded experimentally will be the resultant of these two opposing factors. Hence the transition point curves are not typical.

That the transition temperature of sodium hydrosulphite is influenced by the nature of the surrounding media, is well established by the data presented in Tables I, II and III. This important fact was overlooked by Jellinek (1911) who states that the transition temperature of hydrosulphite should change very little with a change in the medium. In fact, the transition point, as a general rule, is dependent on the activity of water in the surrounding media. If the surrounding medium contains other salts, the transition temperature will naturally be lowered. In the present investigation, the transition point of sodium hydrosulphite was found to range from 51.8° C., in presence of sodium chloride (Table I) to 67.7° C., in a saturated solution of sodium sulphate (Table II). These results also indicate that the transition point of sodium hydrosulphite is not 52° C., as claimed by Bazlen (1905) and accepted by subsequent authors (Pratt, 1924; Seidell, 1940). The extrapolated value for the transition temperature of the hydrosulphite, in absence of foreign substances, is 79.4° C.

The transition temperatures of the salt determined by the solubility method (Part VI) are compared with those obtained by the thermometric method in Table V. It is clear from this table that there is close agreement between the values obtained by the two methods.

TABLE V.

Comparative values of Transition Point of Sodium Hydrosulphite as obtained by the thermometric and solubility methods.

Strength of alcohol. %	Transition temperature in °C.	
	By solubility method.	By thermometric method.
60	64.3	..
70	63.8	63.9
85	60.5	60.4
99.8	..	57.1

Influence of the media on the nature of the anhydrous Sodium Hydrosulphite.

It has already been pointed out that when hydrosulphite was dehydrated by heating in presence of alcohol, the anhydrous substance obtained was in the form of very fine powder; while that dehydrated in presence of sodium chloride was in the form of granules. The maximum purity of the alcohol treated hydrosulphite was only 92.4%; while salt of 96.8% purity was obtained by treatment in presence of sodium chloride. Jellinek (1911) could obtain hydrosulphite of only 82% purity by treatment with alcohol. The physical condition of hydrosulphite is of considerable practical importance as this determines the keeping quality of the product (Table IV). Finely divided hydrosulphite is more liable to decomposition than the coarse powder. Christiansen and Norton (1922) also observed rapid decomposition with finely ground hydrosulphite.

The best process of dehydration of hydrosulphite was to heat the crystals at 52° C., in presence of solid sodium chloride enough to form saturated solution with the water of dehydration of the crystals. The anhydrous hydrosulphite obtained in this way was found to have good keeping quality.

SUMMARY.

Dehydration of sodium hydrosulphite has been carried out in presence of aqueous ethanol, sodium chloride, sodium nitrate, sodium sulphate, tri-sodium phosphate and di-sodium hydrogen phosphate. The transition temperature varies considerably (52° C. to 67.7° C.) with the nature of

the medium employed for dehydration. The transition temperature in the absence of foreign substances has been found to be 79.4°C ., by extrapolation. Direct determination of this temperature is not practicable owing to the decomposition that sets in during transition. Dehydration of hydrosulphite is best effected by heating the crystals at 52°C ., in presence of a saturated solution of sodium chloride.

The author wishes to acknowledge his indebtedness to Dr. M. R. A. Rao and Dr. B. Sanjiva Rao for their keen interest and instructive suggestions during the progress of the work.

REFERENCES.

- Badische Anilin- & Soda-Fabrik, (1905). Verfahren zur Darstellung haltbarer, wasserfrier Hydrosulfite. D.R.P. 171,991, Apr. 2 and 188,139, July 30; *Chem. Centr.*, 2, 379 (1906); 2, 1283 (1907).
- (1906). Verfahren zur Darstellung haltbarer wasserfrier Hydrosulfit. D.R.P. 200,291, Nov. 16. *Ibid.*, 2, 356 (1908).
- Bazlen, (1905). Zur Kenntniss der hydroschwefligen Säure. *Ber.*, 38, 1057.
- Christiansen and Norton, (1922). Purifying sodium hydrosulphite: A modification of Jellinek's method. *Ind. Eng. Chem.*, 14, 1126.
- Deines and Elstner, (1930). Ueber die Konstitution der hydroschwefligen Säure. *Z. anorg. allgem. Chem.*, 191, 340.
- Höchst (to Farbwerke vorm. Meister Lucius und Brüning) (1906). Verfahren zur Herstellung von Krystallisiertem Natriumhydrosulfithydrat. D.R.P. 191,594, Sept. 27. *Chem. Centr.*, 1, 313 (1908).
- Jellinek, (1911). Ueber die Herstellung von reinen Hydrosulfit und ueber das System Hydrosulfit-Wasser. *Z. anorg. Chem.*, 70, 93.
- Nitzschke (to I. G. Farbenind. A.-G.), (1941). Anhydrous stable sodium hydrosulphite. D.R.P. 706,869, May 8. *C. A.*, 37, 2525.
- Pratt, (1924). The manufacture of sodium hydrosulphite. *Ind. Eng. Chem.*, 16, 676.
- Riegel, (1942). Sodium hyposulphite. Industrial Chemistry, Reinhold Publishing Corporation, New York, 4th Edition, p. 91.
- Seidell, (1940). Sodium hydrosulphite. Solubilities of Inorganic and Metal Organic Compounds. D. van Nostrand Co., Inc., New York, 3rd Edition, p. 1299.

Issued April 23, 1953