

STUDIES ON THE ELECTROCHEMICAL PREPARATION OF SODIUM HYDROSULPHITE.

PART VI. STABILITY AND SOLUBILITY OF SODIUM HYDROSULPHITE IN AQUEOUS SYSTEMS AT VARIOUS TEMPERATURES

by C. C. PATEL and M. R. A. RAO, *Department of General Chemistry, Indian Institute of Science, Bangalore.*

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The solubility of sodium hydrosulphite in water has been studied by K. Jellinek (1911) but the purity of hydrosulphite was not ascertained by him. Artamonov and Shadrina (1937) have studied the solubility of sodium hydrosulphite in aqueous sodium chloride, sodium hydroxide and alcohol at 20°C., using a sample of hydrosulphite whose purity was only 90%. The effect of temperature on the solubility of hydrosulphite was not determined by these authors.

A need for the systematic investigation on the solubility and stability of pure hydrosulphite in aqueous sodium chloride was keenly felt during the standardisation of optimum conditions for the preparation of sodium hydrosulphite by the electrochemical method (Part IV). The temperature effect on the solubility of hydrosulphite was also very important in this connection. The data were of particular interest since the sample of hydrosulphite was very pure. Since alcohol was employed in washing of sodium hydrosulphite, the effect of aqueous alcohols on the stability and solubility of sodium hydrosulphite was also investigated. In this section, water, aqueous sodium chloride and aqueous alcohol have been employed at various temperatures to determine the solubility and stability of pure hydrosulphite at various temperatures.

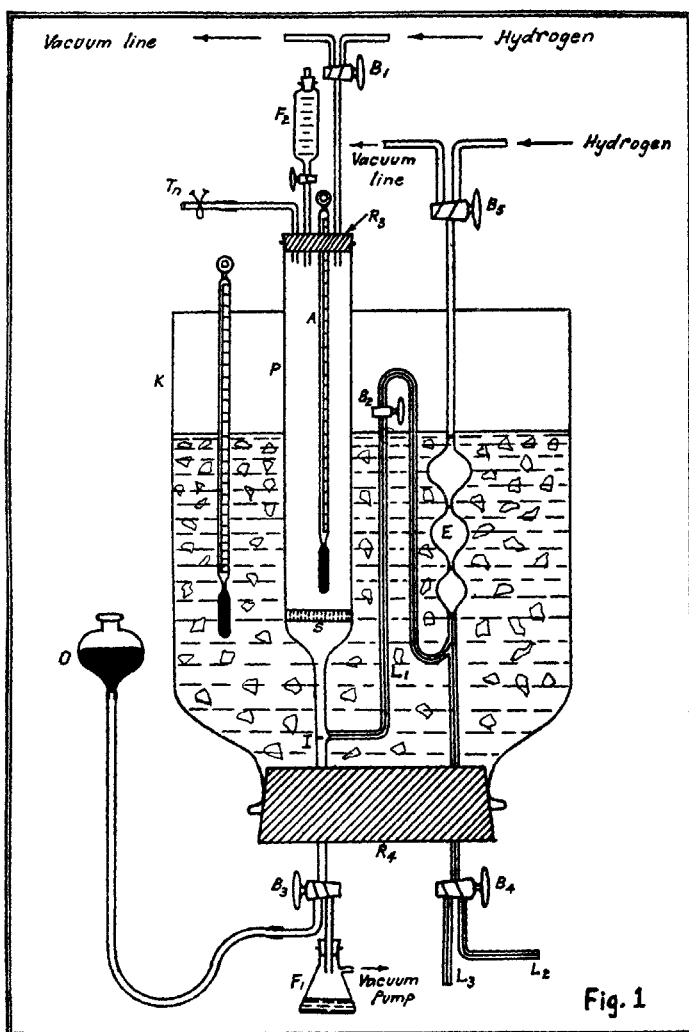
EXPERIMENTAL.

Preparation of pure Sodium Hydrosulphite.

Owing to the susceptibility of hydrosulphite to atmospheric oxidation, the preparation of sodium hydrosulphite in a state of purity, presents many difficulties. Furthermore, sodium hydrosulphite in aqueous solution is liable to decompose, even when air is excluded (Meyer, 1903). Hence the filtration and washing of the hydrosulphite had to be carefully controlled and suitable precautions had to be taken in the preparation of hydrosulphite solution prior to the analysis of the salt. After a great deal of experimental work, the following technique was finally adopted.

The hydrosulphite crystals were prepared by the electrochemical method described in Part IV, employing an aqueous solution of 27% bisulphite and 20% sodium chloride in catholyte. The suspension of the hydrosulphite crystals produced in the catholyte was conveyed through the filter tube T_1 to the pyrex sintered glass filter P of 120 ml. capacity (Fig. 1) while an inert atmosphere was maintained in the electrolytic cell. P was closed with a rubber stopper R_3 , through which the hydrosulphite delivery tube T_2 , thermometer A , a graduated separating funnel F_2 , and a three-way stop-cock B_1 passed. P was surrounded by a glass vessel

K which served as a water-bath for the maintenance of constant temperature. At its lower end, *P* was provided with a three-way stop-cock *B*₃ to connect it either to



the filter flask *F*₁, or to the mercury reservoir *O*. The calibrated pipette *E* could be connected to *P* by means of the stop-cock *B*₂ to take out the filtered solution for analysis. The pipette *E* had three-way glass stop-cocks *B*₅ and *B*₄ as in the figure.

PROCEDURE.

The mercury level was first raised to fill the bore of the stop-cock *B*₃ and all air in the entire apparatus was displaced by hydrogen by suitable manipulation of the stop-cocks *B*₁, *B*₂, *B*₃, *B*₄ and *B*₅. The temperature of the bath *K* was lowered to about 0°C., by addition of ice. *B*₂ was closed and the mercury was brought up to the sintered glass plate *S*. The cathode slurry was then sucked into the filter *P*. The filter *P* was then connected to the hydrogen supply to push back the slurry remaining in the tube *T*_n. The pinch-cock at *T*_n was closed. The

mercury in the filter *P* was then lowered to the level *I*, *B*₂ was opened and some mother liquor was sucked into the pipette *E*. *B*₂ was then closed, *E* was connected to the hydrogen supply and the liquid was allowed to drain off through *L*₃. The pipette *E* was refilled with the mother liquor and aliquots were taken through *L*₃ for analysis. The sample was analysed for hydrosulphite, bisulphite, thiosulphate, chloride and total sulphur as described in Part IV.

After removal for analysis, the entire mother liquor was drained off into the flask *F*₁. All the wash liquids and water that were added to the hydrosulphite crystals were free from dissolved air and pre-cooled to 0° C. The wash liquids in the funnel *F*₂ were added in small quantities at a time into the filter *P*. The contents of *P* were then intimately mixed by pulsations in the liquid caused by moving the mercury reservoir up and down and the wash liquid analysed to know the extent of removal of impurities and the superfluous wash liquid was drained off into flask *F*₁. It can be stated that the hydrosulphite does not get decomposed in presence of mercury (Rabinowitsch and Fokin, 1930). The crystals were washed with a small quantity of air-free distilled water (0° C.), followed by three washes with 60% alcohol to remove the contamination of sodium chloride and sodium bisulphite. The crystals were then washed with 5 ml. of aqueous sodium hydroxide (0.5%) to avoid any acidity. It was then followed by two washes with distilled water and finally dissolved in 20 ml. of distilled water and the solution was well stirred by inducing pulsations in the mercury. In order to determine the purity of hydrosulphite, aliquots were analysed for hydrosulphite, bisulphite, thiosulphate, chloride and 'total sulphur'. The following table gives the purity of a representative sample.

TABLE I.

Purity of Hydrosulphite crystals.

1.	Na ₂ S ₂ O ₄ in 100 ml. solution	= 11.64 g.
2.	NaHSO ₃ " "	= 0.032 g.
3.	Na ₂ S ₂ O ₃ " "	= nil.
4.	NaCl " "	= 0.010 g.
5.	BaSO ₄ gravimetrically corresponding to total sulphur in 1 ml. solution	= 0.3136 g.
6.	BaSO ₄ corresponding to hydrosulphite + bisulphite in 1 ml. solution	= 0.3129 g.

The above results indicate that the sample of hydrosulphite prepared was at least 99.6% pure.

Solubility of hydrated Sodium Hydrosulphite in water.

For the determination of the solubility of sodium hydrosulphite in water at low temperatures, the pure crystals of hydrosulphite prepared in the filter *P* were cooled to -2.8° C. by means of ice and salt, and air-free distilled water at 0° C. was added to the crystals. The mixture was stirred by pulsations of mercury for about fifteen minutes for the attainment of the equilibrium. The mercury in the filter was then moved up and down to rinse the lower parts of the vessel thoroughly. The solution in equilibrium with the solid was then transferred to the graduated pipette *E* under the hydrogen atmosphere as described already. Aliquots of the solution were employed for the analysis of hydrosulphite, thiosulphate, sulphite and 'total sulphur'. It was found that the solution was free from sulphur compounds other than hydrosulphite. Duplicate analytical values were obtained to confirm the attainment of the equilibrium between the solid hydrosulphite and the solution. After determining the solubility at -2.8° C., the temperature of the bath was raised to 0° C., and the solubility determined at this temperature. The

same procedure was adopted to determine the solubility of hydrosulphite at 10° C. and 20° C., employing fresh samples of hydrosulphite. It has to be stated, however, that at 20° C., the stability of hydrosulphite was poor and the measurements had to be made very rapidly. The results are given in Table II.

TABLE II.
Solubility of hydrated Sodium Hydrosulphite in water.
Purity of hydrosulphite crystals = 99.9%.

Temperature 0° C.	Weight in g. of solid in 100 ml. Solution.		
	Na ₂ S ₂ O ₄	NaHSO ₃	Na ₂ S ₂ O ₃
-2.8	11.06
0.0	11.86
10.0	15.55
20.0	18.16

The results (Table II) indicate that the solubility of hydrosulphite in water increases gradually with a rise in temperature.

Solubility of hydrated Sodium Hydrosulphite in aqueous sodium chloride.

For the determination of the solubility of hydrosulphite in sodium chloride solutions, the purified crystals of hydrosulphite were rinsed twice with about 8 ml. of 10% aqueous sodium chloride (A.R.) solution (at 0° C.). The wash liquid was removed into the flask *F*₁. The solid in the filter was then mixed with about 12 ml. of 10% sodium chloride solution and the contents were well stirred for the attainment of the equilibrium. The rest of the procedure was the same as described for the determination of solubility in water. Similarly, solubility determinations were carried out employing fresh samples of hydrosulphite in 20% aqueous sodium chloride solution. The results obtained for solubility of hydrosulphite in 10% and 20% sodium chloride solutions are given in Table III.

TABLE III.
Solubility of hydrated Sodium Hydrosulphite in 10% and 20% sodium chloride solutions at various temperatures.

Concentration of NaCl soln.	Temperature °C.	Weight in g. of solid in 100 ml. soln.			Remarks.
		Na ₂ S ₂ O ₄	NaHSO ₃	Na ₂ S ₂ O ₃	
10%	-2.2	5.90	} Slight decomposition. Decomposition of hydrosulphite.
"	1.0	7.04	
"	10.8	8.74	0.85	0.11	
"	20.4	10.44	1.78	0.65	
"	30.0	10.27	4.13	2.69	
20%	-2.0	2.50	} Slight decomposition. Decomposition of hydrosulphite.
"	0.2	2.72	
"	10.6	3.61	0.51	0.23	
"	20.2	4.64	n.d.	n.d.	
"	30.5	5.73	1.51	0.78	
"	40.8	6.44	2.84	1.82	
"	50.7	4.53	8.57	7.23	

The results of Table III indicate that there is a considerable diminution in solubility of hydrosulphite with the increase in concentration of sodium chloride. The stability of hydrosulphite, however, diminishes considerably with an increase in temperature.

Solubility of hydrated Sodium Hydrosulphite in aqueous ethanol at various temperatures.

The procedure adopted for the determination of the solubility of sodium hydrosulphite employing aqueous alcohol as the solvent was very similar to that used in the case of aqueous sodium chloride. The results are given in Table IV.

TABLE IV.

Solubility of hydrated Sodium Hydrosulphite in different concentrations of aqueous alcohol at various temperatures.

Concentration of alcohol % (by vol.)	Temperature °C.	Weight in g. of solid in 100 ml. soln.			Remarks.
		Na ₂ S ₂ O ₄	NaHSO ₃	Na ₂ S ₂ O ₃	
20	0.5	4.71	} Decomposition of hydrosulphite.
..	11.0	6.07	
..	21.0	7.83	
..	31.2	9.87	0.35	..	
..	40.5	11.66	1.18	0.12	
..	51.0	10.27	5.38	3.27	
40	11.0	1.82	} Decomposition of hydrosulphite.
..	20.0	2.56	
..	30.4	3.41	
..	41.0	3.74	1.56	0.14	
..	50.6	4.60	3.22	2.19	
50	0.2	0.89	} Decomposition of hydrosulphite.
..	10.2	1.00	
..	20.1	1.16	
..	30.2	1.31	
..	40.6	1.96	1.47	0.15	
..	50.4	2.64	2.27	1.15	
..	60.0	2.96	4.18	2.08	
..	64 ± 0.5	2.42	5.92	2.87	
..	68 ± 1	1.63	7.11	5.07	
60	31.0	1.03	} Decomposition of hydrosulphite.
..	40.0	1.22	0.10	..	
..	55.0	1.36	1.52	1.01	
..	60.0	1.49	2.37	1.57	
..	70 ± 1	1.23	2.62	1.80	
..	75 ± 1	0.95	3.58	2.52	
70	1.2	0.10	} Decomposition of hydrosulphite.
..	20.6	0.12	
..	40.6	0.24	
..	51 ± 0.5	0.38	0.95	0.43	
..	55.0	0.45	1.40	0.78	
..	60.0	0.58	1.52	0.88	
..	63.4	0.62	1.98	1.20	
..	70 ± 1	0.46	1.80	0.91	
..	74 ± 1	0.36	1.66	1.18	

It will be observed from the results (Table IV) that the solubility of hydrosulphite diminishes with the increase in concentration of alcohol. The stability of hydrosulphite, however, is increased considerably in presence of alcohol. The effect of temperature on the solubility of hydrosulphite becomes less marked as the concentration of alcohol increases. The solubility data are not very accurate beyond 30° C., because of the presence of large quantities of products of decomposition of hydrosulphite. The solubility values are decreased beyond 60° C., due to the dehydration of the hydrosulphite at its transition temperature. At this temperature, it was noticed that the crystals would become powdery and dense.

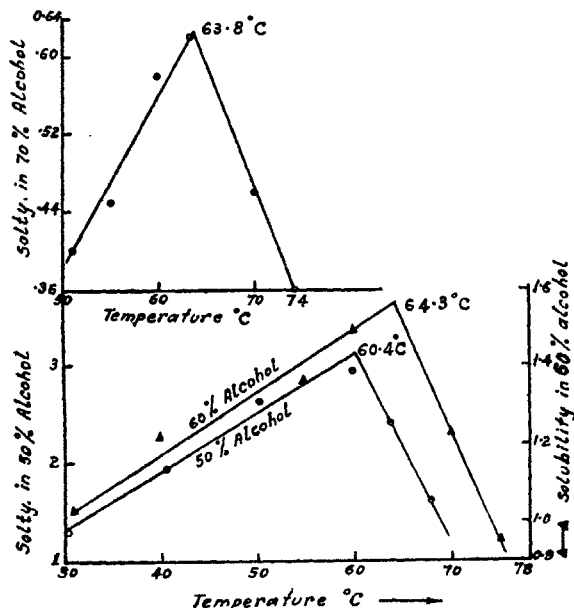


Fig. 2. Transition point of sodium hydrosulphite in presence of different concentrations of alcohol.

The transition point of the hydrosulphite as read from Fig. 2 is 60.4° C., 64.3° C., and 63.8° C., in 50%, 60% and 70% alcohol respectively. The solubility in 85% alcohol was also determined but it was found to be very low (0.062%). The effect of temperature was also noticed to be comparatively small. The transition point was noticed to be about 60.5° C.

DISCUSSION.

Solubility of Hydrosulphite in aqueous media.

The determination of solubility of hydrosulphite in water has been studied only by K. Jellinek who carried out two sets of determinations: one published in 1911 (Jellinek, 1911) and the second a year later (Jellinek, 1912). In the following table, the values obtained by K. Jellinek are compared with those obtained by the present authors.

The present values are in general, intermediate between the values obtained by Jellinek in 1911 and in 1912. In determining the solubilities, Jellinek (1911) obtained the hydrosulphite at 20° C., by salting it out with sodium chloride. At 20° C., it has been shown in the present work that the hydrosulphite suffers appreciable decomposition and it is, therefore, likely that this factor has to a certain extent

TABLE V.

Comparison of solubility of Sodium Hydrosulphite in water at various temperatures.

Temperature °C.	Solubility of hydrosulphite by K. Jellinek in %		Solubility of hydrosulphite determined in %
	1911	1912	
1.0	14.9	12.85	12.25
10.0	16.7	14.40	15.55
20.0	19.1	16.46	18.16

affected the values obtained by Jellinek. The purity of hydrosulphite crystals used in the present work was at least 99.6%. Furthermore, in each solubility determination, the saturated solution was analysed for impurities like bisulphite and thiosulphate, produced by hydrosulphite decomposition. It can, therefore, be claimed that the solubility data presented in this paper are of greater accuracy.

As is to be expected, the solubility of sodium hydrosulphite is much less in salt solutions than in water, owing to the common ion effect (compare Tables II and III).

The solubility of the hydrosulphite (Table II) is also diminished by an increase in the concentration of alcohol (Table IV).

Using sodium hydrosulphite of 90% purity, Artamonov and Shadrina (1937) have found that the solubility of hydrosulphite at 20°C., in aqueous solutions containing 20% sodium chloride and 20% alcohol are 10.2% and 9.9% respectively. The corresponding values obtained in the present work are much lower, 4.6% (Table III) and 7.7% (Table IV). As the details of the procedure employed by the above workers are not known, it is difficult to account for the divergence in values. It can, however, be stated that the hydrosulphite employed in the present investigation is far purer (99.6%) than that employed (90%) by the previous workers.

The results of Tables II and III show that with a rise in temperature, the solubility in water and aqueous sodium chloride increases. In aqueous alcohol of lower than 50% strength (Table IV), the effect of temperature is pronounced, but the temperature effect is diminished as the strength of alcohol increases.

Stability of Hydrosulphite in aqueous media.

As already pointed out the solubility of hydrosulphite in water could not be measured with great accuracy at temperatures above 20°C., owing to the rapid decomposition of the salt. Thus when the temperature of the aqueous hydrosulphite was raised to 30°C., the solution darkened rapidly and on standing for about 15 minutes, was found to have a good deal of bisulphite and thiosulphate, the strength of hydrosulphite dropping to 11.15 g., while the saturated solution at 20°C., had 18.16 g. of hydrosulphite in 100 ml. solution. Even at 20°C., the hydrosulphite solution was markedly unstable and yielded 2.5% bisulphite in 25 minutes, the hydrosulphite concentration dropping to 16.34% from its original value of 18.16%. Thus, concentrated solutions are more susceptible to decomposition, and the rate of decomposition increases with rise in temperature. Seyewetz and Kalmar (1932) also came to the same conclusion. Saturated solutions of hydrosulphite can, however, be preserved only at very low temperatures (at 0°C. or below). Thus a saturated solution of hydrosulphite in contact with solid dihydrate, in an inert atmosphere, when preserved for about 20 hours at 0°C., during the present work, suffered a decomposition by about 1% only. On account of the greater stability of hydrosulphite at low temperatures, MacIntyre (1920) patented

a process for preservation of hydrosulphite liquors at about 0° C., in the absence of oxidising gases.

It is evident from Table IV that the stability of hydrosulphite solution is enhanced by the presence of alcohol in the solution. Hydrosulphite in 20% alcohol is found to be stable only up to 21° C., while in 70% alcohol the hydrosulphite is comparatively stable even at higher temperature (up to 50° C.).

Transition point of Hydrosulphite in Alcohol.

The transition temperatures as determined from Fig. 2 are 60.4° C., 64.3° C., and 63.8° C., while the corresponding alcoholic concentrations are 50%, 60% and 70%. The value for 50% alcohol seems to be vitiated by the high rate of decomposition of hydrosulphite.

CONCLUSION.

It can be stated that the stability of hydrosulphite is relatively high at low temperatures. For the electrochemical preparation of hydrosulphite, therefore, low temperatures have to be employed. The addition of sodium chloride to the catholyte, is also highly beneficial as it considerably reduces the solubility of hydrosulphite and thus increases the stability of the salt.

The presence of alcohol increases the stability of hydrosulphite. Alcohol (60%) is, therefore, a very good reagent for washing out the impurities from hydrosulphite. Absolute alcohol cannot, however, be employed for washing since the impurities present in hydrosulphite are almost insoluble. 60% alcohol as a wash liquid has definite advantages over the reagents (aqueous sodium chloride and water) employed by Jellinek (1911), and Christiansen and Norton (1922).

SUMMARY.

(1) A new design has been given for the construction of an apparatus to determine the solubility of unstable substances in an inert atmosphere.

(2) Using this apparatus, the solubility of sodium hydrosulphite crystals has been determined (a) in water over the range -2.8° C. to 20° C., (b) in 10% and 20% aqueous sodium chloride over the range 0° C. to 20° C., and (c) in aqueous alcohol of different strengths from 0° C. to 70° C.

(3) Solubility studies with 60%, 70% and 85% aqueous alcohols indicate that the transition temperatures of the dihydrate to anhydrous sodium hydrosulphite are 64.3° C., 63.8° C., and 60.5° C., respectively.

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