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**SOLUBILITY OF CELLULOSE IN AMMONIA SALT SOLUTIONS**

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The fact that cellulose may be dispersed in solutions of neutral salts has long been known. Dubose<sup>1</sup> noted that hot thiocyanate solutions were cellulose solvents. The action of such reagents was carefully studied by Williams,<sup>2</sup> who proposed a theory to account for such phenomena. According to this the cellulose units combine with the salt-water complex in place of the water molecules and are considerably swollen by such combination. The cellulose unit is so brought into the molecular range of the salt-water complex. A rise in temperature frees the water from the salt complex, upon which the water migrates to the cellulose, causing further swelling until eventually the highly swollen cellulose is dispersed into colloidal solution.

Having noted during a series of experiments that a saturated solution of sodium iodide in ammonia dissolved cellulose, the author was led to investigate the action of a series of the more soluble salts upon cellulose in liquid ammonia solution. In the first series of experiments the ordinary chemically pure salts were made into solution with the ordinary liquid ammonia of commerce with no precautions as to drying. Eight salts were tried in various concentrations and in the case of five of them definite dispersion of cellulose was obtained. Ammonium thiocyanate, sodium nitrate, sodium iodide and sodium thiocyanate dissolved both regenerated and cotton cellulose to give clear colorless solutions from which cellulose could be precipitated in a flocculent condition by dilution with water. Ammonium iodide appeared to dissolve regenerated cellulose but not the cotton. For each salt there was a definite range of concentration in which solution occurred and beyond which no dispersion took place.

Since water has a marked influence upon the solubility of salts in liquid ammonia, it was felt that the solubility of cellulose in the solutions might be greatly influenced by the presence of moisture in the cellulose, the salts and the ammonia. A series of experiments was then run, using the five salts found to give solvent solutions, but using all the precautions against moisture as described in a previous paper by the same author.<sup>3</sup> The cellulose was dried to constant weight in an oven at 105°. In this series it was found that only sodium thiocyanate and ammonium thiocyanate were solvents for both regenerated and cotton cellulose. Sodium nitrate and sodium iodide dissolved regenerated cellulose very slowly but did not dis-

<sup>1</sup> Dubose, *Bull. Rouen.*, **33**, 318 (1905); *Rev. prod. chim.*, **26**, 507 (1923).

<sup>2</sup> Williams, *J. Soc. Chem. Ind.*, **40**, 221T (1921); *Mem. Proc. Manchester Lit. Phil. Soc.*, **65**, 12 (1921).

<sup>3</sup> Scherer, *THIS JOURNAL*, **53**, 3694 (1931).

solve cotton cellulose, so that in the case of such salts it appears probable that moisture plays some part in the solvent action. A peculiar circumstance should be here noted since the addition of water to the anhydrous suspension of cellulose in the liquid ammonia salt solution does not cause the cellulose to disperse. This is true even though 25-30% of water is added to the solution. On the other hand, the addition of only 3-5% of water to the salt before condensing the ammonia caused the cellulose to dissolve. Some such explanation as that of Williams apparently fits these facts. In the case of the solutions studied the ammonia molecule probably plays the part of the water molecule and again the similarity of water and ammonia is emphasized. It is also of interest to note the difference in the case of solution of regenerated cellulose and of cotton cellulose which in these experiments was most marked. Regenerated cellulose usually dissolved very rapidly and easily, whereas the cotton required long stirring to give a solution and, further, regenerated cellulose dissolved in several salt solutions which would not dissolve the cotton. This may confirm the well-known assumption that regenerated cellulose exists in a different physical state from other forms of the substance.

Attempts have been made to use ammonia-salt solutions of cellulose for the production of films but difficulty was encountered owing to the rapid boiling off of ammonia causing blow-holes, and to the very great difficulty of washing the product entirely free of salts. These solutions are being used at this Laboratory for the study of reactions between cellulose and reagents also soluble in the ammonia-salt solutions. It is evident that homogeneous reactions of this type may give interesting results.

### Experimental Part

**Materials.**—The salts used in these experiments were all Baker's Analyzed chemicals from freshly opened bottles. Those salts requiring drying in the second series of experiments were dried as described in a previous paper.<sup>3</sup>

The regenerated cellulose used was prepared by finely dividing a bleached desulfurized viscose rayon yarn spun at this Laboratory from Brown Company alpha spruce pulp. The cotton cellulose was a highly purified cotton linter pulp produced by the Hercules Powder Company. The ammonia was the ordinary liquid ammonia of commerce which in the second series of experiments was dried by distillation over sodium and passage through a drying train of potassium hydroxide and Bentonite.

**Apparatus.**—Two types of apparatus were used. In the first series the reaction vessel consisted of a large Pyrex Dewar tube graduated so that the volume of solution could be read within one or two cubic centimeters. This was provided with a motor-driven stirrer and an outlet tube held in a large rubber stopper.

In the second series of experiments the reaction tube was a large Pyrex test-tube essentially as described in a previous paper.<sup>3</sup> In this apparatus the hand-driven ring stirrer was replaced by a motor-driven screw stirrer of glass acting through a long mercury cup seal.

**Procedure.**—In the first series a weighed quantity of the salt used was placed in the Dewar tube and, by means of another Dewar tube, the required amount of liquid ammonia was added to give a saturated solution. The mixture was then stirred to

solution and a weighed amount of cellulose added. The suspension was stirred for fifteen minutes and if solution had not occurred, more ammonia was added in 10-20 cc. portions with fifteen-minutes' stirring between each addition until solution occurred. The volume was read and the point noted as the solution point. The addition of ammonia was continued in the same manner until the last addition caused the precipitation of flocculent cellulose from the solution. The volume was read and noted as the precipitation point. A series of such experiments was run on each salt used and the average result recorded. In cases where solution did not occur several experiments were tried with various proportions of water present in an attempt to cause solution.

In the second series of experiments the carefully dried salt was weighed into the reaction tube with the dried cellulose and immersed in a bath of boiling liquid ammonia. Anhydrous ammonia was condensed onto the mixture to a concentration within the range found in the first series of experiments. The pressure was removed and the mechanical stirrer started and continued for at least one hour. At the end of the period the solution was examined through a magnifying glass for completeness of solution. If solution did not occur, several per cent. of water was added and the stirring continued for another half hour in an attempt to cause dispersion. Other experiments were then run with the salts in which several per cent. of water was added to the anhydrous salt before condensation of the ammonia.

## Results

**Experiments in Series I.**—In this series the ordinary c. p. chemicals and ammonia were used. The compositions and temperatures given are the average of several experiments in each case.

### SERIES I EXPERIMENTAL DATA

Cellulose used	Salt	Composition of solution		Temp. of solution point, °C.
		Solution point (g. per 100 cc.)	Precipitation point (g. per 100 cc.)	
Cotton	NaI	47	31	-30
Viscose	NaI	49	31	-29
Cotton	NaNO <sub>3</sub>	46	35	-26
Viscose	NaNO <sub>3</sub>	50	36	-25
Cotton	NaCNS	40	25	- 9
Viscose	NaCNS	48	38	- 2
Cotton	NH <sub>4</sub> I	Partly soluble		
Viscose	NH <sub>4</sub> I	70	39	
Cotton	NH <sub>4</sub> CNS	65	30	- 4
Viscose	NH <sub>4</sub> CNS	65	33	- 5
Viscose	KI	Does not dissolve		
Cotton	KI	Does not dissolve		
Viscose	NH <sub>4</sub> NO <sub>3</sub>	Does not dissolve		
Cotton	NH <sub>4</sub> NO <sub>3</sub>	Does not dissolve		
Viscose	NH <sub>4</sub> Br	Does not dissolve		

**Experiments in Series II.**—These experiments were run in the absence of moisture as described under the procedure.

#### 1. Sodium Iodide

(a) 13.5 g. of anhydrous sodium iodide was placed in the reaction tube with 0.25 g. of regenerated cellulose. Ammonia was condensed to a total volume of 35 cc. No

solution occurred after fifteen minutes; 20% of total volume of water was added and the mixture stirred for fifteen minutes. No solution occurred.

(b) 10.0 g. of sodium iodide was placed in a reaction tube with 0.1 g. of cotton cellulose. Ammonia was added to a total volume of 25 cc.: no solution after one hour's stirring; 5 cc. of distilled water was added and stirring continued for one-half hour without solution occurring.

(c) 10.0 g. of sodium iodide with 1 g. of distilled water and 0.25 g. of regenerated cellulose were placed in the tube and ammonia condensed to 25 cc. Solution was complete and rapid.

(d) Repeated (c) using 0.1 g. of cotton cellulose in place of regenerated cellulose. Solution was complete in thirty minutes.

## 2. Sodium Thiocyanate

(a) 10 g. of sodium thiocyanate and 0.25 g. of regenerated cellulose were placed in the tube and ammonia condensed to 22 cc. Solution occurred rapidly and completely.

(b) 10 g. of sodium thiocyanate and 0.10 g. of cotton cellulose made up to 26 cc.: solution was complete after one hour's stirring.

## 3. Ammonium Thiocyanate

(a) 10 g. of ammonium thiocyanate and 0.25 g. of regenerated cellulose made up to 16 cc.: solution occurred very rapidly and completely.

(b) As in (a) except used 0.10 g. of cotton cellulose: complete solution in fifteen minutes.

## 4. Sodium Nitrate

(a) 10 g. of sodium nitrate and 0.25 g. of regenerated cellulose made up to 23 cc.: fiber swells but does not dissolve.

(b) As in (a), using 0.10 g. of cotton cellulose and diluting to 26 cc.: does not dissolve.

(c) 10 g. of sodium nitrate + 1 cc. of water + 0.25 g. of regenerated cellulose made up to 24 cc.: soluble in fifteen minutes.

(d) As (c), using 0.10 g. of cotton cellulose. Soluble only after one hour's stirring.

(e) 10 g. of sodium nitrate + 0.25 g. of regenerated cellulose made up to 22 cc.: not soluble in fifteen minutes; 3 cc. of water added: does not dissolve.

## Summary

1. The solubility of cellulose in certain salt-liquid ammonia solutions was studied. Ammonium thiocyanate, sodium thiocyanate, sodium nitrate and sodium iodide were found to dissolve both regenerated cellulose and cotton linter cellulose. Ammonium iodide dissolved regenerated but not cotton cellulose.

2. The solubility was also studied in anhydrous solutions. Only ammonium thiocyanate and sodium thiocyanate readily dissolved cellulose in the absence of moisture.

3. Sodium nitrate and sodium iodide solutions could dissolve cellulose provided the water was present before the addition of ammonia. Addition of water to the salt-ammonia solution did not appear to increase its solvent action.

4. The new solvent solutions are being used to study certain single phase reactions of cellulose.

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### NOTE

**Copper Selenate Tetrammonate Dihydrate.**—In a recent communication the isolation of copper selenate tetrammonate dihydrate,  $\text{CuSeO}_4 \cdot 4\text{NH}_3 \cdot 2\text{H}_2\text{O}$ , was reported,<sup>1</sup> and as Hurd and Lenher<sup>2</sup> did not succeed in preparing this compound, the detailed description of the preparation of this salt will be given.

Alcohol is added to a strong ammoniacal solution of copper selenate, the resulting blue precipitate filtered on a sintered glass plate, washed several times with alcohol and acetone and rapidly dried on a porous plate in the open air. Ten grams of this product, finely powdered, is dissolved by warming in 7.5 cc. of 25% ammonia solution and after filtering through a sintered glass plate is cooled to 15–20° in a closed Erlenmeyer flask. If needle-like crystals appear, two drops of concentrated ammonia should be added and the solution warmed until the crystals have dissolved. The solution is again cooled and if needles appear the process of adding ammonia and warming should be repeated. Eventually, after six to twenty-four hours, large six-sided tables will crystallize out. In most cases only one crystal forms, the edges having a length of about 1 cm.

These crystals are the copper selenate tetrammonate dihydrate. They are of a pure blue color and are easily soluble. After being dried with filter paper, the crystals tarnish in a short time as a result of incipient decomposition. The yield best obtained was 2 g.

Even if the crystals appear perfectly pure and faultless, they always include solvent. For analysis they should be broken up, pressed between filter paper and the pieces pulverized on a porous plate until the powder is perfectly dry. This drying requires practice and must be carried out rapidly, for even the unbroken crystals begin to decompose as soon as the surfaces are dry. The powder is pure blue in color, differing from the monohydrate, which is blue-violet.

The compound analyzes correctly for copper selenate tetrammonate dihydrate, as indicated by the analytical data for the last products which each of us has made and analyzed.

*Anal.* Calcd. for  $\text{CuSeO}_4 \cdot 4\text{NH}_3 \cdot 2\text{H}_2\text{O}$ : Cu, 20.45;  $\text{NH}_3$ , 21.91;  $\text{H}_2\text{O}$ , 11.59. Found (W. L.): Cu, 20.68;  $\text{NH}_3$ , 21.97;  $\text{H}_2\text{O}$ , 11.52; (G. v. K.) Cu, 20.34;  $\text{NH}_3$ , 21.81;  $\text{H}_2\text{O}$ , 11.70.

In view of these results we consider the existence of copper selenate tetrammonate dihydrate as proved. It is improbable that in every experi-

<sup>1</sup> Willy Lange, *Ber.*, **59**, 2113 (1926).

<sup>2</sup> L. C. Hurd and V. Lenher, *THIS JOURNAL*, **52**, 3861 (1930).