

A STUDY OF THE LYOPHILIC NATURE OF CELLULOSE  
ACETATE IN LIQUID AMMONIA

By

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Introduction:

Many organic substances disperse spontaneously in water and other solvents, and their properties differ from those of true solutions due to the fact that there is apparently strong attraction of the two phases for each other. These substances are called lyophilic substances or lyophilic colloids.

Liquid ammonia possesses many properties similar to the solvent properties of water and many of these same lyophilic substances disperse in liquid ammonia just as they do in water or any other solvent<sup>1</sup>. Also, some substances disperse in liquid ammonia which do not disperse in water. Cellulose acetate is one of these substances and it disperses readily in liquid ammonia as has been pointed out by Fenton and Berry<sup>2</sup>, Clancy<sup>3</sup>, and Taft<sup>4</sup>.

Due to the fact that little attention has been given to the study of lyophilic sols and gels in liquid ammonia, an investigation has been made on cellulose acetate, comparable to the studies made on other lyophilic substances in the water system, to determine whether or not this system is of colloidal character.

Some of the more important properties that were in-

investigated are:

1. Extent of dispersion at various temperatures.
2. Chemical action of the dispersion medium.
3. Gel formation.

### Procedure:

The cellulose acetate was dispersed in calibrated Dewar flasks containing liquid ammonia obtained from an ordinary commercial cylinder of the same. Moisture of the air was excluded from the system as far as possible by fitting the flask with a one-hole rubber stopper which contained a simple valve made by slitting a rubber tube and stopping up one end of it with a short glass rod. This allowed ammonia gas to escape from the flask and very little moisture to enter. This method was employed while transporting the ammonia from the supply tank to the laboratory. During experimentation the valve was replaced by a tube of soda lime attached to a long rubber hose to allow free agitation of the flask. However, for absolutely anhydrous conditions the ammonia was dried with metallic sodium and distilled. The details and diagram of the apparatus will be given later.

The tests on given samples were carried out in sealed tubes of Pyrex glass by adding the dispersed sol to the tubes immersed in a bath of liquid ammonia where they were sealed off by means of an oxygen-gas flame. Dispersion, of higher concentrations especially, could not be carried out in the tubes directly because the circulation of the solvent was insufficient and the surface of the cellulose acetate exposed was comparatively small. Agitation by hand was also insufficient to disperse the cellulose acetate, mainly because

the tube was necessarily removed from the ammonia bath and as the temperature rose, chemical reaction began which caused flocculation to occur. This flocculent precipitate produced was not redispersible at the temperature of boiling ammonia and its appearance led us to investigate the possibility of gel formation at room temperatures, the results of which will be considered later.

### Experimental:

In order to disperse the cellulose acetate, Dewar flasks were employed to insure the necessary circulation of ammonia and also to allow the surface of the dispersing phase to be large. The latter was accomplished by stirring the ammonia with a glass rod while the cellulose acetate was added.

Apparently there is no limit of dispersion of the cellulose acetate as long as the above requirements are fulfilled. Concentrations of the emulsoid (lyophilic substances are emulsoidal) were prepared ranging from 0 - 60 per cent cellulose acetate. Per cent here and throughout this paper is used as the number of grams of cellulose acetate dispersed in 100 c.c. of ammonia at its normal boiling point. In the higher concentrations the emulsoid became light brown in color and translucent to light. The viscosity was exceedingly high as considerable resistance to stirring and flowing was shown. It was impossible to work with concentrations any higher than 60 per cent as the residue became gummy or plastic and its concentration was hard to estimate. This concentration could be obtained only by evaporating a 30 per cent emulsoid to one-half its original volume.

Owing to the high viscosity of these concentrated emulsoids the vapor pressure of the ammonia decreases because the bubbles of gaseous ammonia formed, as it boils away, obviously have much difficulty in reaching the surface. A decrease

in vapor pressure is accompanied by a rise in boiling point, consequently a rise in boiling point should be expected here. This was shown to be the case in a sample containing 30 per cent cellulose acetate which indicated (using a toluene thermometer) a temperature five degrees higher than that of the pure boiling ammonia. The equilibrium resulting here between the emulsoid and vapor is a case of false equilibrium because, although the pressure on the system is atmospheric, the vapor pressure of the ammonia in the emulsoid is suppressed by its viscosity and lags behind the apparent vapor pressure of the system. As the concentration rapidly and continuously increases, equilibrium has no chance to result. Thus one would be led to think that this difference in boiling points would be quite small if true equilibrium resulted.

A point which makes the high viscosity and filmlike texture of the concentrated emulsoids more comprehensive is the fact that the bubbles of ammonia gas, which form in these emulsoids as the liquid ammonia boils away, do not rise rapidly to the surface and break immediately as they do in pure ammonia, but they rise slowly, reach the surface and disappear without breaking. The film of the bubble is apparently quite strong and elastic and, thereby, causes the gas either to diffuse through the film during contraction or to dissolve in it. Another factor which probably plays a part here is vaporization of ammonia on the surface of the film, causing heat to

be absorbed from the interior of the film and thus producing condensation of the ammonia.

When the sealed tubes are allowed to warm up to room temperature the viscosity rapidly decreases at first but after a few hours begins to increase again. This is due to the chemical action of the ammonia on the cellulose acetate at elevated temperatures with the result of a change in the dispersed phase. On the whole it may be said that the viscosity of this system is affected by concentration, temperature and age just as other lyophilic colloidal systems are.

Dispersions containing 1 per cent or less of cellulose acetate were quite fluid, especially at room temperature. Some attempt was made to transfer the dispersed phase of these more dilute emulsoids to other media which may or may not be capable of dispersing cellulose acetate. Clancy<sup>2</sup> points out that the emulsoid after being dispersed in ammonia can be transferred without precipitation to media which are not capable of dispersing the cellulose acetate otherwise. Confirmation of his statement was not successfully obtained in the following cases.

#### Symbols

- (a) The dispersion medium is precooled in liquid ammonia before the cellulose acetate is added.

(b) The dispersion medium is not precooled as in (a).

(c) The dispersion medium is applied directly to the undispersed cellulose acetate.

#### Data

1. 10% ethyl alcohol and 90% chloroform

(a) Dispersion is good at first but total precipitation results inside of three weeks.

(b) Immediate precipitation.

(c) Permanent dispersion.

2. Ethyl alcohol (95%)

(a) No dispersion.

(b) No dispersion. (Permanent dispersion in absolute alcohol).

(c) No dispersion.

3. 10% ethyl alcohol and 90% carbon tetrachloride

(a) No dispersion.

(b) No dispersion.

(c) No dispersion.

4. 25% ethyl alcohol and 75% chloroform

(a) Dispersion with slow precipitation.

(b) Some dispersion but slight residue.

(c) Good dispersion.

5. Amyl acetate

(a) No dispersion.

(b) No dispersion.

(c) No dispersion.

6. 50% butyl alcohol and 50% ethyl alcohol

(a) No dispersion.

(b) No dispersion.

(c) No dispersion.

The dispersibility of cellulose acetate in a few media other than liquid ammonia is shown by the following data.

	Substance	Dispersibility
1.	Acetone . . . . .	+
2.	Chloroform . . . . .	+
3.	Acetic acid . . . . .	+
4.	Ethyl acetate . . . . .	+
5.	Amyl acetate . . . . .	-
6.	10% ethyl alcohol & 90% chloroform. .	+
7.	25% ethyl alcohol & 75% chloroform. .	+
8.	Benzyl alcohol . . . . .	+
9.	Diethylene chloride . . . . .	+
10.	Ethylene trichloride . . . . .	-
11.	Benzene . . . . .	-
12.	Ether . . . . .	-
13.	Kerosene . . . . .	-
14.	Glycerol . . . . .	-
15.	Turpentine . . . . .	-
16.	Carbon tetrachloride . . . . .	-
17.	Ethyl alcohol . . . . .	-

## Heat-irreversible Gels.

As was indicated previously, chemical action of the dispersion medium upon the cellulose acetate caused a marked increase in the viscosity of the emulsoid after a few hours at room temperature. This increase in viscosity was accompanied by gel formation of the heat-irreversible type. Several of the gels were cooled again in liquid ammonia for a week without any noticeable changes. Thus a gel was formed which is similar in appearance and properties to gels of silicic acid. It was found that gels of many concentrations could be prepared and that the time of gelation was a function of the concentration.

Figure 1 shows a graph of the above relationships, the data for which are given below. These values are an average of several trials, which, of course, have some deviation due to the previous history of the sample (e. g. age, temperature, concentration and mechanical treatment). But with conditions the same for any series of observations the data listed below are typical.



<u>Conc. of Cell. Ac.</u>	<u>Gelation Time</u>	<u>Properties of the gel</u>
0.1%	54 hours	Soft, clear gel; marked syneresis.
0.2	46	{ Firm, translucent gel; marked syneresis.
0.5	38	
1.	31	Striated; some syneresis.
2.	24	Vertical crack.
5.	18	{ Opaque, rigid, white; sine curve crack; syneresis.
10.	12	
15.	8	{ Striated; oblique cracks; marked syneresis of brownish color; contraction of the gel.
20.	6	
30.	4.5	
35.	3.5	

Figure 2 shows some of the characteristic markings of the gels of various concentrations. The very dilute gels show marked syneresis, and parabolic striations occur in gels of 1% cellulose acetate, while it will be noticed that peculiar sine curve breaks characterize the gels of 5 - 10 per cent. This break in gel structure occurs usually in one or two days after gelation, depending again upon the previous history of the sample. The wave length of the curve was found to be practically constant and independent of the concentration but as the bore of the tubes used was constant it was thought that the size of the tube might be the controlling factor of this peculiarity. In order to

Gels of various concentrations

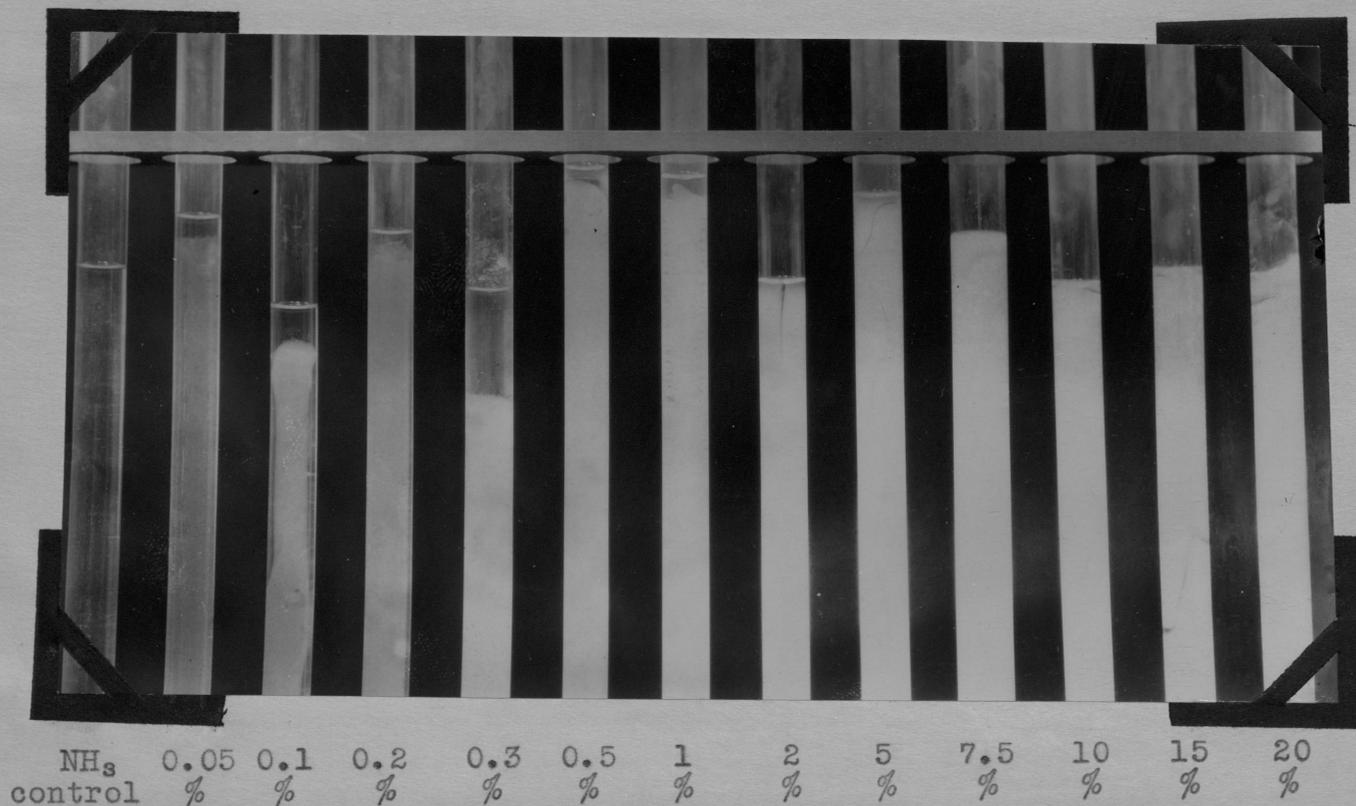


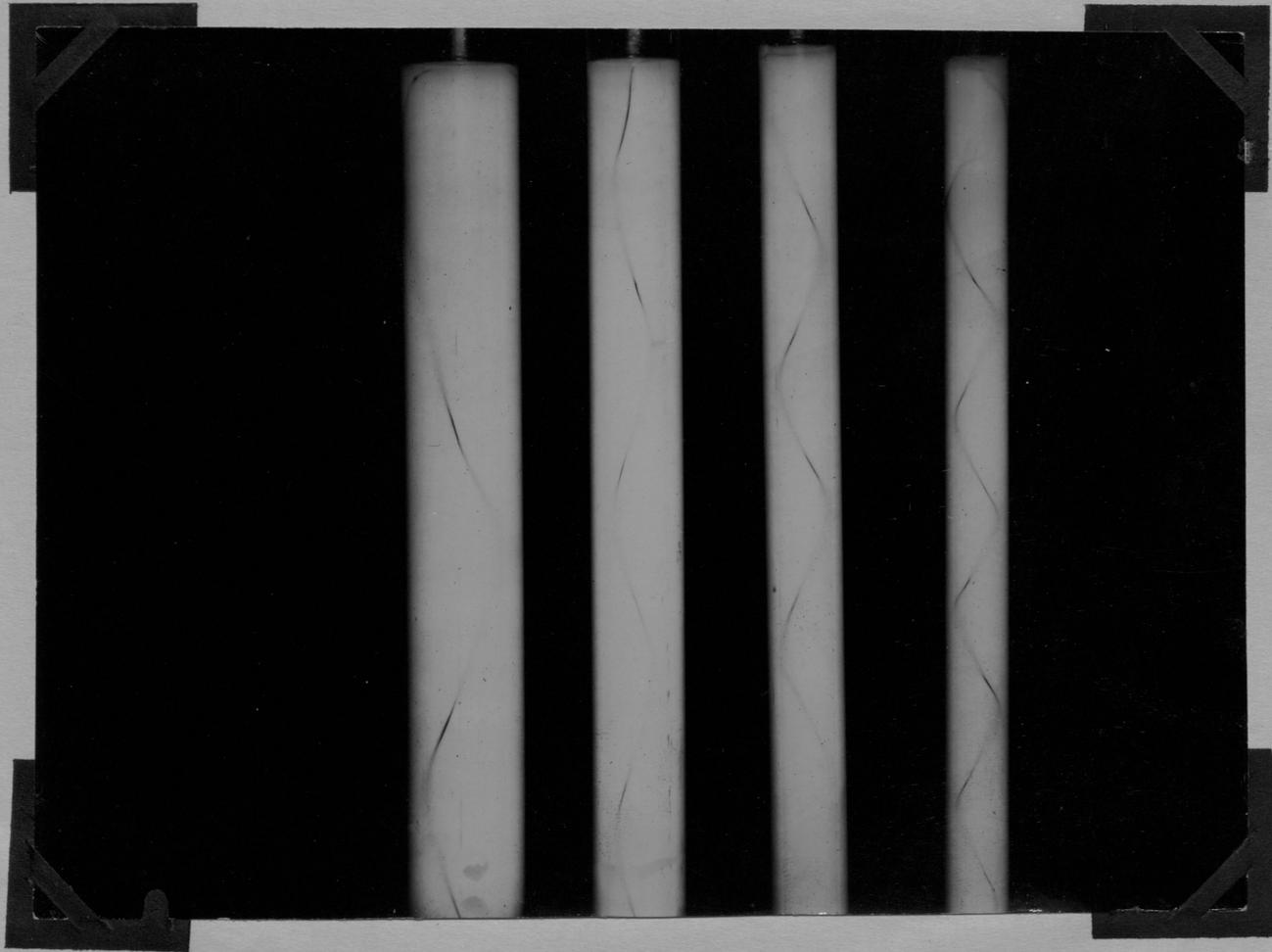
Figure 2

Age ?

confirm this suspicion a number of samples of 5, 7.5, and 10 per cent cellulose acetate were sealed in tubes of four different sizes, with the result that increasing the diameter of the tube also increased the wave length of the curve as is shown in Figure 3.

The break is undoubtedly caused by the gel's contraction which begins shortly after gelation but since the glass surface adheres to the gel it cannot contract and thus a strain is set up. This strain is followed by absorption of all the liquid of syneresis, giving the surface of the gel a dry appearance. As contraction proceeds, the stress produced finally becomes sufficient to rupture the structure. Since the structure is thinner near the walls of the tube it will also tear more easily, for resistance to strain is proportional to cross sectional area, but also, as the membrane becomes thinner, it will stretch more for a given load or stress; consequently the stress is relieved on that side before the break reaches the edge. But the stress on the other side must also be relieved, and since it is now greatest at the opposite side of the tube, a break is set up in that direction. After completion of the break, the pores of the gel once more contract and syneresis is produced a second time.

Gels of 15 per cent cellulose acetate usually show parts of a sine curve break with horizontal cracks at each crest



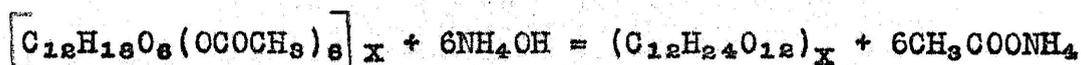
7.5% Cellulose Acetate

Figure 3

of the wave as shown in Figure 2, a fact which indicates brittle structure. More concentrated gels became slightly striated with occasional oblique cracks in the structure but here the gel is either so tough that it breaks away from the glass before its structure is ruptured or else it does not adhere to the glass as tightly as the less concentrated ones. These gels are characterized by a brownish opalescence with very marked syneresis, which is also brown.

Several of the gels were cooled in liquid ammonia and unsealed for examination. The 5 per cent gels were quite rigid and brittle, but shrank rapidly and increased in toughness as ammonia evaporated. A gel four inches by one-half inch shrank to one inch by one-eighth inch, leaving a transparent yellow residue, which would not swell or disperse again when treated with liquid ammonia. This horn-like structure was not only inert toward ammonia but also to all the other dispersing media previously tried for cellulose acetate. Hydrochloric acid had no effect upon it and concentrated sulfuric acid only softened it slightly in a few hours, while the ordinary cellulose acetate was attacked rapidly. The substance was thought to be free cellulose, liberated by the action of the ammonia upon the cellulose acetate with the formation of acetamide as the other product. A point supporting this idea is the

fact that the dried gel disperses in Schweizer's reagent, a common solvent for cellulose. In the above reaction acetamide would be formed only in anhydrous samples for if small traces of water were present, as was the case here, ammonium acetate would form immediately according to the following reaction.



The liquid synerized by the gel was analyzed qualitatively for the acetate ion by adding amyl and ethyl alcohols to separate tubes containing the above liquid in dilute sulfuric acid. The characteristic odors of banana oil and ethyl acetate were obtained.

The inert cellulose structure was also observed to form slowly from the dispersed cellulose acetate in the Dewar flasks. The emulsoid could be spread in films to form a very resistant covering, and under proper conditions might prove useful. This fact points to the probability of ammonia's reacting with the cellulose acetate also at the boiling point of ammonia. Investigation was made on the effect of temperature on the rate of reaction of the dispersion medium. Samples of 5 and 10 per cent of cellulose acetate were placed in baths of ice and ammonia to compare their time of reaction to that at room temperature already observed. Figure 4 shows the relation-

ship graphically.

The 5 per cent sample was kept in the ammonia bath for two weeks without setting although slight cloudiness was noticeable. On taking it out of the bath gelation took place in eight hours or in about one-third of the normal time; consequently it was assumed that two-thirds of the reaction had taken place and that gelation should have resulted in twenty-one days — hence the graph. In the case of the 10 per cent emulsoid, a gel formed in a few hours but on being examined it was of the heat-reversible type which will be discussed later. On warming, it melted and set to the heat-irreversible type in about the regular time. This seems unusual at first for it should set more quickly than the 5 per cent emulsoid, but apparently the reversible gel structure (which is truly a gel of cellulose acetate) prevented the ammonia from reacting with it. This might be expected since a gel is not as intimately associated with its dispersion medium as a lyophilic sol, but contains most of the dispersion medium in its pores.

These curves seem to show that the rate of reaction of the dispersion medium upon the cellulose acetate is a function of the absolute temperature — a fact which is in accordance with an analogous set of data worked out by Holmes<sup>4</sup> with silica gels. He showed that the time of setting of these gels was greatly increased at 0° C. and decreased with

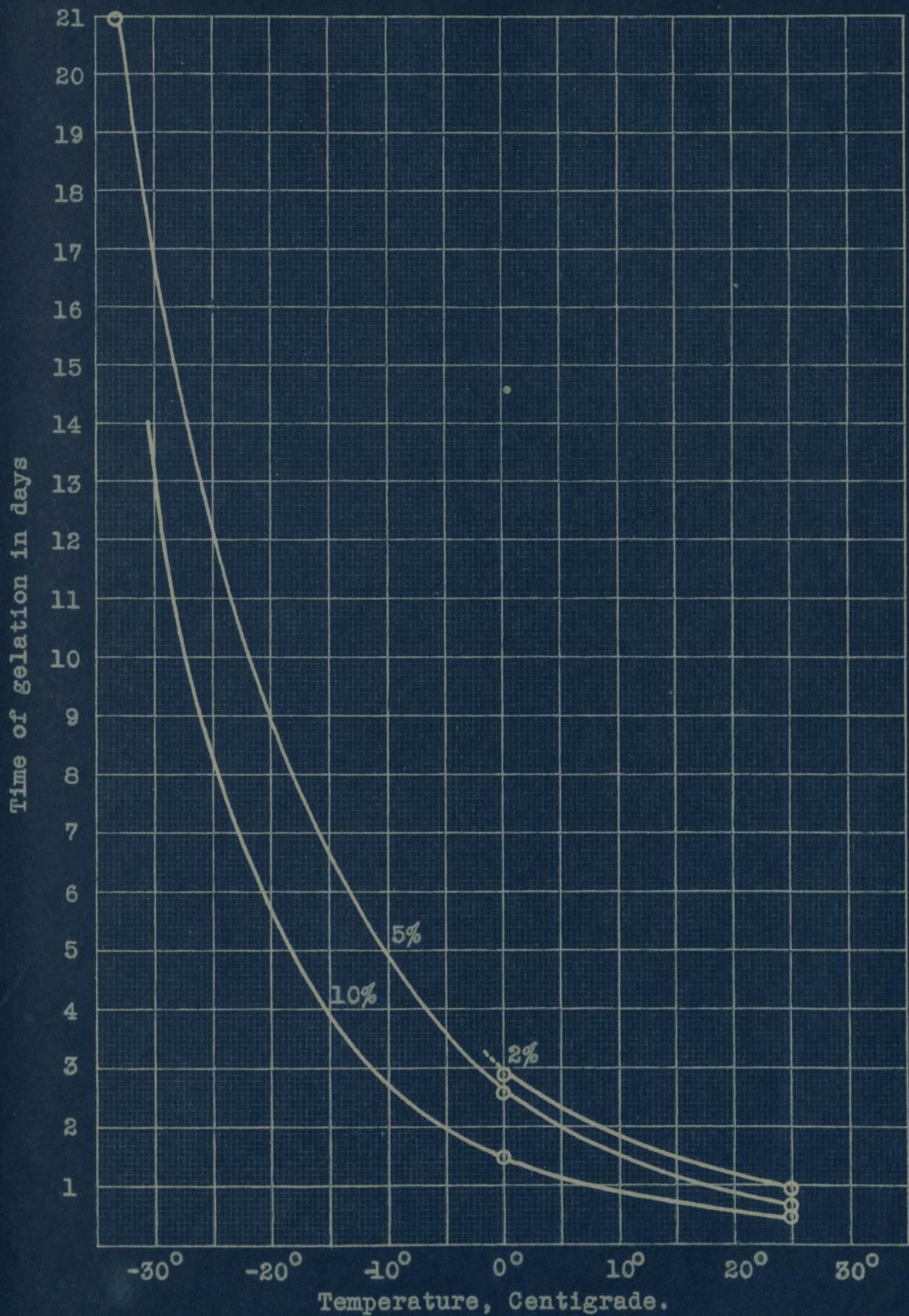
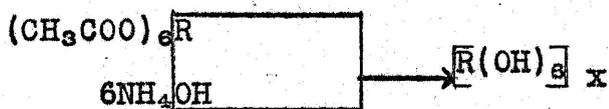
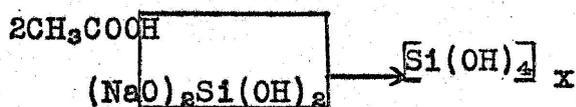


Figure 4

rising temperature on a curve similar to the one just outlined. Flemming<sup>5</sup> also points out that the time of gelation of silica gels decreases with rising temperature.

Silica gels seem to be strikingly analogous in properties to those of cellulose. They will even form sine curve breaks under proper conditions and their color is from a translucent, opalescent white in dilute solutions to an opaque white in concentrated solutions just as in the case of cellulose gels. A graphical representation of the two reactions will illustrate their close analogy:



In the most dilute gels considerable diversion in results was experienced at first, a fact which was found to be caused by small traces of water in the ammonia. It was thus necessary to work under anhydrous conditions and in some cases known amounts of water were added in order to find out just what effect water had on the properties of the gel.

A simple means of obtaining anhydrous ammonia was worked out as illustrated in Figure 5. Enough metallic sodium was added directly to the supply cylinder G to react with all the water present and by means of stopcocks, con-

tact with the air was completely cut off. A is a two-way stopcock which switched the ammonia gas from the apparatus to the atmosphere, thereby decreasing the pressure in tube E so stopcock B could be shut off without blowing off any connections. Valve H was not sensitive enough to regulate easily, hence the use of A and B. The tube I contained soda lime to prevent moisture from entering the apparatus. Tube E is graduated to hold 10 c.c. of liquid ammonia at the mark on the tube. A sample of cellulose acetate is dried, weighed, and placed in the tube E which is stoppered and connected to stopcock B by means of a rubber tube at J.

The rubber stopper was now loosened and ammonia gas allowed to escape for a while to sweep out all air. Then it was stoppered again and the slight pressure produced, raised the boiling point of the ammonia in the tube sufficiently to cause condensation when the tube was in a bath of the liquid at its normal boiling point. Condensation is continued until the liquid reaches the desired mark on tube E, when valve A is turned to switch the ammonia from the apparatus to tube I. H is then shut off and also B, after which the tube E is sealed off by means of the oxygen-gas flame F without being disconnected from the apparatus.

By this means, samples containing anhydrous ammonia were obtained which gave results that were reproducible for very dilute emulsoids but for those more concentrated than

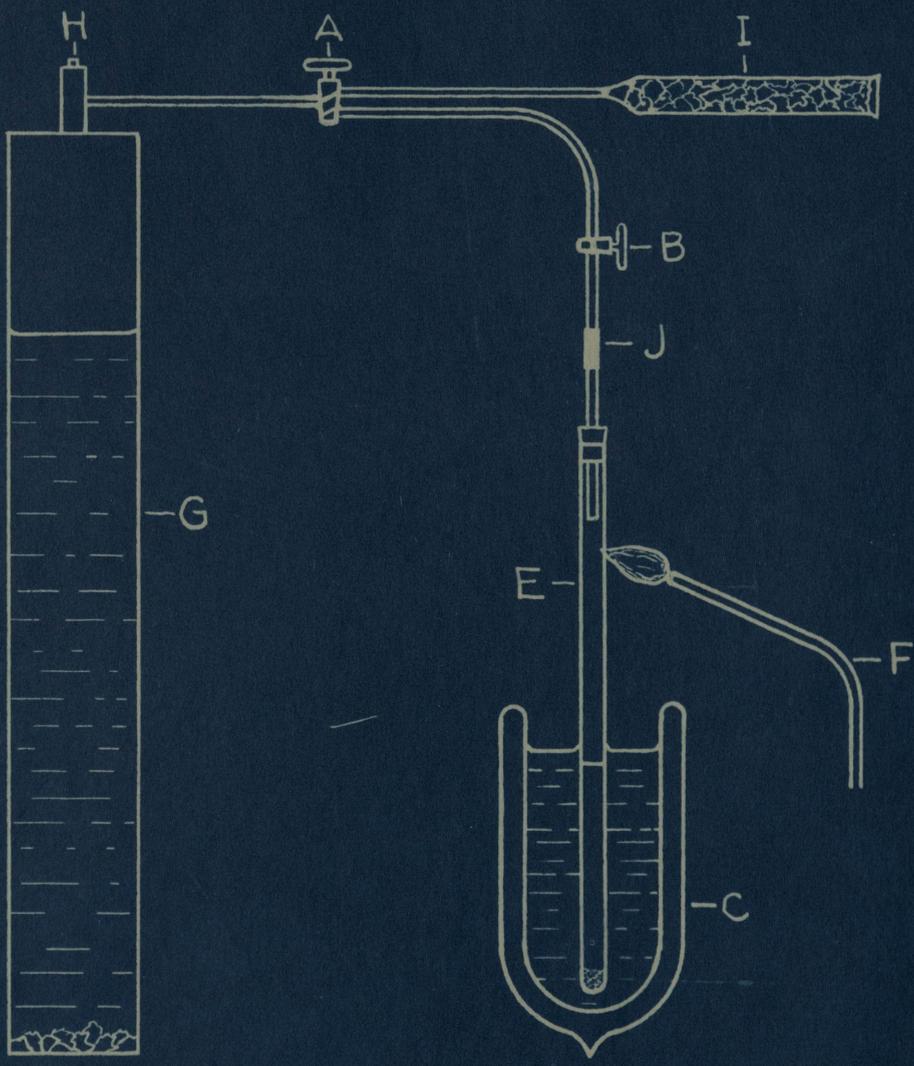


Figure 5

0.5 per cent cellulose acetate, dispersion would not take place quickly enough to obtain a uniform system.

To show how water affected the structure of the gel and time of gelation a series of experiments was tried for emulsoids of 0.5, 0.2, 0.1 and 0.05 per cent cellulose acetate with the following results which are shown graphically in Figure 6.

0.5% Cellulose Acetate

<u>Amount H<sub>2</sub>O</u>	<u>Time of Reaction</u>	<u>Structure</u>
None	38 hours	Coarse gel, gradually settling
1%	32	Slightly grainy gel
2%	27	Fine gel
5%	20	Fine, opalescent gel

0.2% Cellulose Acetate

<u>Amount H<sub>2</sub>O</u>	<u>Time of Reaction</u>	<u>Structure</u>
None	46 hours	Gelatinous precipitate
1%	36	Coarse, granular gel
2%	28	Fine gel
5%	22	Fine, opalescent gel

0.1% Cellulose Acetate

None	54 hours	Flocculent precipitate
1%	42	Opalescent gel
2%	26	Precipitate
5%	21	Gelatinous precipitate
10%	15	Grainy, coarse gel

0.05% Cellulose Acetate

None	41 hours	Precipitate
0.5%	41	Precipitate
1%	35	Opalescent, soft gel
2%	25	Precipitate
5%	17	Precipitate
10%	9	Gelatinous precipitate
20%	3 - 6	Precipitate

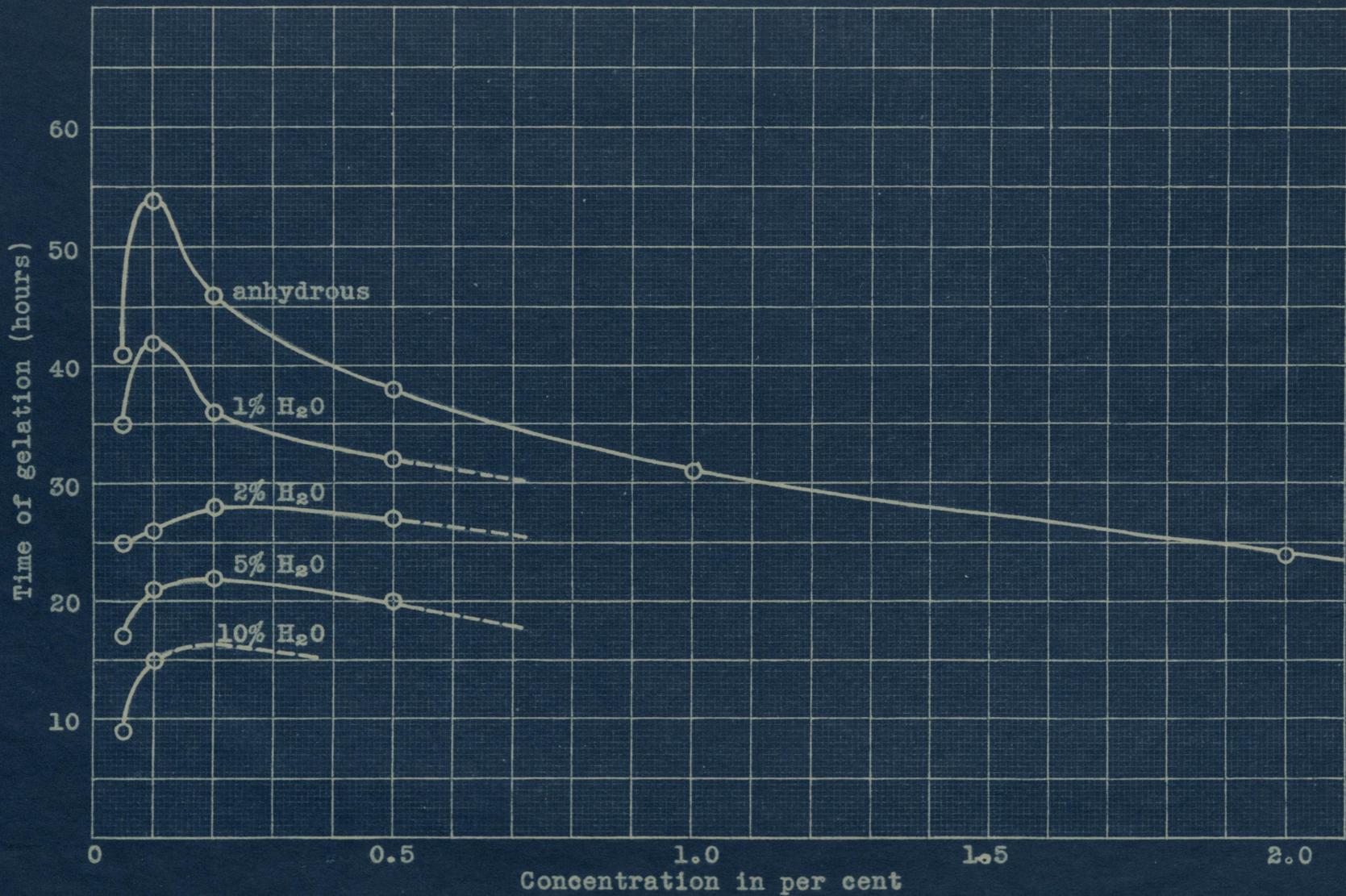
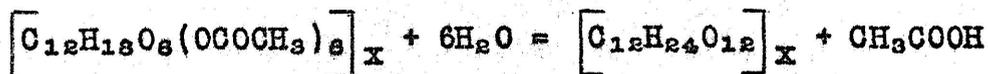


Figure 6

The results of the last two sets of data are shown clearly in the photographs, Figures 7 and 8. It will be noticed that reaction goes on just the same in anhydrous ammonia as it does in commercial, but more slowly. Also, the result of the reaction brings about precipitation rather than gelation; thus it is necessary for a certain amount of water to be present in order to get a good gel structure in these dilute systems. It also will be noticed that in higher concentrations of cellulose acetate less effect of water is produced. However, the best gels contain considerable water.

It was thought that the relationship between water content and concentration of the emulsoid might give a means of determining the molar weight of cellulose since the amount of water necessary for permanent gelation increases with the concentration of the gel in most cases. (See data above.)

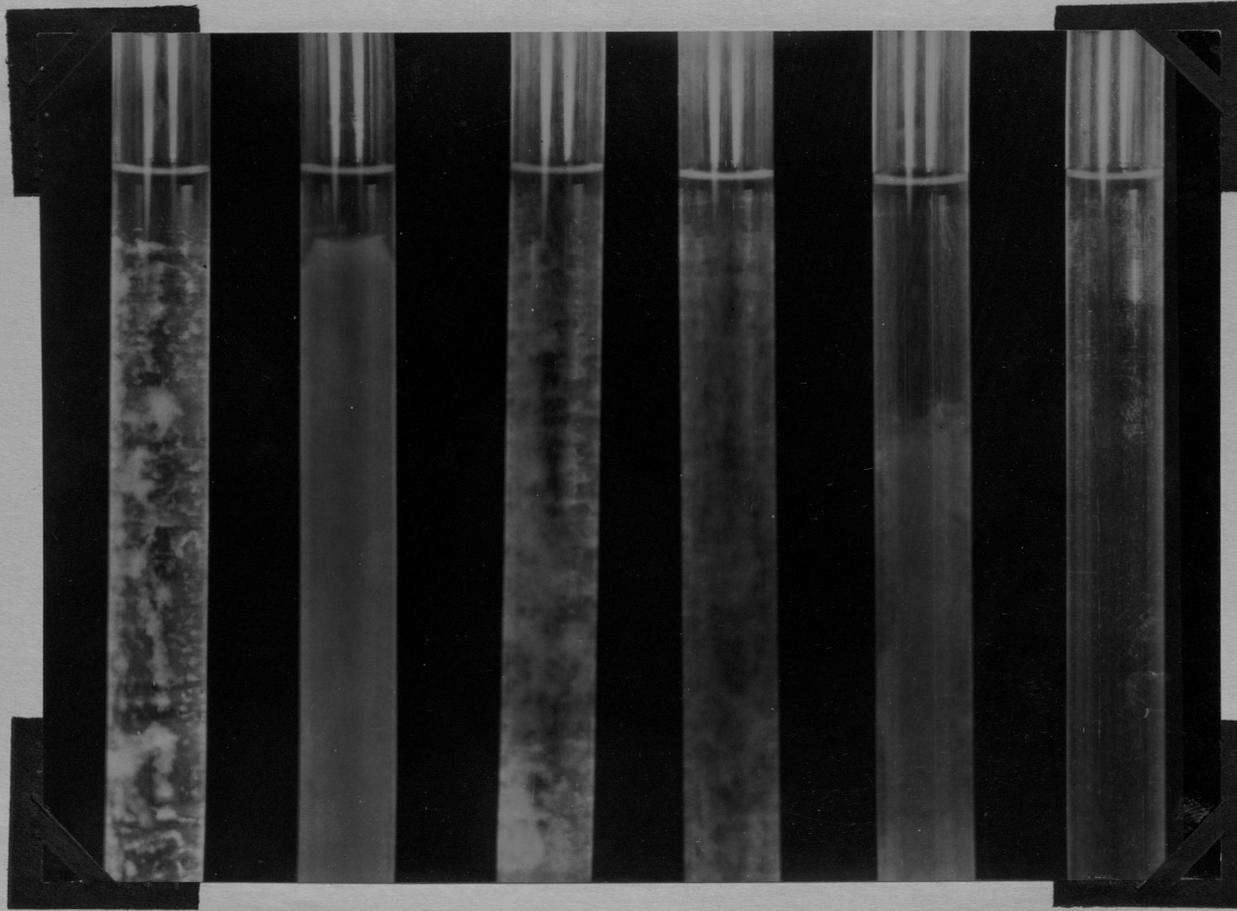
From an examination of the following reaction



when  $x$  is 1, the mass of cellulose acetate that would react with water would be roughly five times as great as the mass of the water, but in the experimental case (see Figure 8)

0.5 gram of cellulose acetate required 1 gram of water for best gelation; consequently, the presence of water must af-

0.1% Gels



Anhyd.  
NH<sub>3</sub>

1%  
H<sub>2</sub>O

2%  
H<sub>2</sub>O

5%  
H<sub>2</sub>O

10%  
H<sub>2</sub>O

NH<sub>3</sub>  
control

Figure 7

0.05% Gels

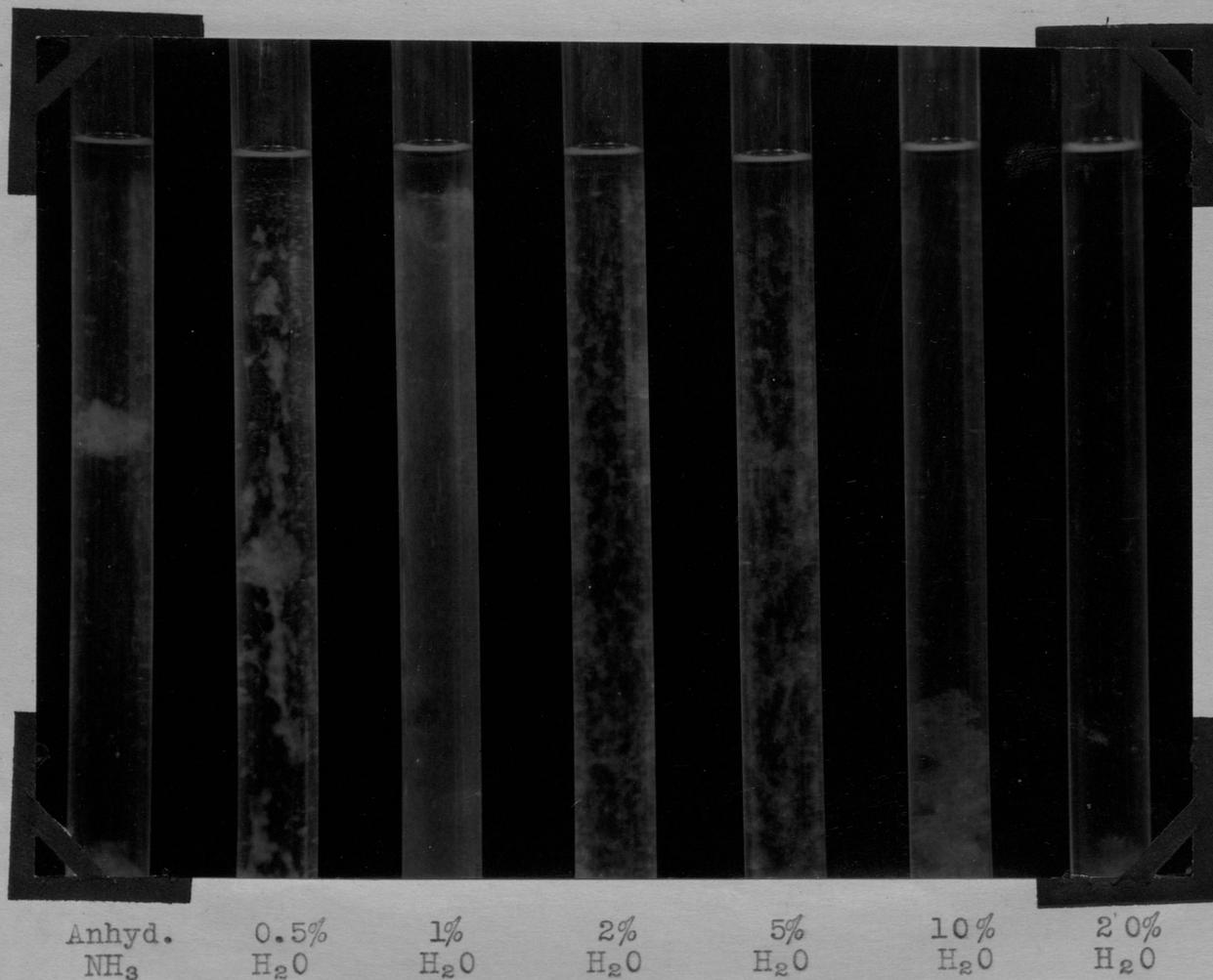


Figure 8

fect the structure and adsorptive power of the gel rather than react with it chemically. Furthermore, cellulose is deposited even in the absence of water, but no gel is formed.

The limits of gel formation are rather wide, ranging from 35 to 0.05 per cent cellulose acetate. Concentrations higher than 35 per cent were not tried as the emulsoid became so viscous that it could not be transferred from the Dewar to the test tube. The higher concentrations studied were obtained by pouring the emulsoid into a test tube through a funnel in order to keep the cellulose acetate from clinging to the walls of the tube and there be decomposed when the tube was heated and sealed.

The lower limit of gel formation is at least as low as 0.05 per cent cellulose acetate. Lower concentrations were not tried. This is the smallest concentration of gel that has been recorded as far as the writer is aware. Many gels have been studied at relatively low concentrations. Weiser<sup>6</sup> reports that firm gels can be obtained containing 0.18 per cent  $\text{Cr}_2\text{O}_3$  and soft gels containing but 0.09 per cent  $\text{Cr}_2\text{O}_3$ ; this is the lowest concentration of a gel recorded, as far as the writer knows. Weiser and Bloxson<sup>7</sup> also have made gels of  $\text{MnHAsO}_4$  as dilute as 0.25 per cent, while higher concentrations were necessary for gelation of the arsenates of iron and aluminum. B rjeson<sup>8</sup> has made gels of metallic

cadmium in concentrations as low as 0.2 per cent, while Gortner<sup>9</sup> has produced gels of the same concentration from dibenzoyl-l-cystene. Hatchek<sup>10</sup> reports gels in concentrations of 0.25 per cent from camphorylphenylthiosemicarbazide. He also states<sup>11</sup> that sols of gelatin of the same concentration will not set to gels even at 0° C., while Kruyt<sup>12</sup> reports that agar as dilute as 0.14 per cent will gel at room temperature. Many other systems have been studied — none of which give gels more dilute than the ones already mentioned.

The liquid ammonia gels herein discussed make a system suitable for diffusion experiments. It will be recalled that suspensoids of the water system can be distinguished from true solutions of the same by testing their relative rates of diffusion through gels. Since sulfur, treated with liquid ammonia, gives a solution which is green by transmitted light and red by reflected ( a property characteristic of suspensoids) it was thought to be of interest to try the rate of diffusion of this solution in one of the cellulose gels. An inverted Y tube, with the ends of the lateral branches sealed, was made so that the cellulose acetate emulsoid could be placed in one branch and the sulfur solution in the other until gelation took place, when by tipping the tube the sulfur solution was added on top of the

gel. Diffusion took place at the rate of about two inches in twenty-four hours. This fact would lead one to think that sulfur in ammonia did not form a colloidal system. It could be either a true solution of molecular sulfur or a true solution of a sulfur compound of ammonia. This last is the most probable. These experiments were carried out in the dark as it was found that the solutions of sulfur were reversibly light sensitive, turning pale yellow in the light and deep blue in the dark.

#### Heat-reversible Gels.

As was stated previously, when the 10 per cent emulsoid of cellulose acetate was placed in an ammonia bath for several days a gel structure appeared. This led to the investigation of the possibility of gel formation of the heat-reversible type upon cooling the ammonia below its boiling point. Reversible gels of cellulose acetate have been prepared in benzyl alcohol by Mardles<sup>13</sup> and Poole<sup>14</sup>, consequently one <sup>might</sup> expect an analogous system in liquid ammonia.

Samples of 5 and 10 per cent cellulose acetate were prepared and cooled in a bath of gasoline treated with solid carbon dioxide with the result that at  $-45^{\circ}\text{C}$ . the 10 per cent emulsoid changed to a beautiful opalescent gel which was quite rigid and brittle with springiness similar to that of gelatin gels. The color was also less intense for a giv-

en concentration than it was in the irreversible type. The 5 per cent emulsoid remained fluid until a temperature of  $-60^{\circ}$  C. was reached, when a similar opalescent gel appeared. Thus it will be seen that the higher the concentration of the gel, the higher its temperature of gelation — a characteristic of heat-reversible gels such as agar or gelatin in water and cellulose acetate in benzyl alcohol.

On warming up the bath gradually, it was found that the gels would not melt at the same temperature at which they jelled, but a temperature of about ten degrees higher was necessary to bring about this change. This is similar to what Poole<sup>14</sup> found in studying cellulose acetate in benzyl alcohol. ~~The effect is termed hysteresis~~ and is characteristic of heat-reversible gels. [Hatchek<sup>11</sup> discusses hysteresis of agar and of gelatin in which the phenomenon is reported to range as widely as 50 degrees for agar and 10 degrees for gelatin, depending upon the relative concentrations of each.]

The above data were taken on samples sealed in Pyrex tubes which were afterward allowed to warm up to room temperature, when the emulsoid became more fluid at first and later set to the heat-irreversible type of gel, previously discussed. The characteristic sine curve break already noted for gels of these concentrations formed in about twenty-four hours after gelation with the usual syneresis following.

**Summary.**

1. Cellulose acetate disperses in liquid ammonia in concentrations ranging from 0 - 60 per cent to form a true lyophilic colloid.
2. Chemical action of ammonia on cellulose acetate is a function of the absolute temperature.
3. Heat-irreversible gels of cellulose form from cellulose acetate in liquid ammonia at room temperature and have a very wide range of concentrations. Exceedingly low concentrations of these gels have been prepared and the effect of water upon their structure studied. Gels of 5 - 10 per cent cellulose acetate are characterized by sine curve breaks, the wave length of which is proportional to the size of the tube in which they are contained. These gels are suitable for diffusion experiments of suspensoids in liquid ammonia.
4. Heat-reversible gels of cellulose acetate form in liquid ammonia at temperatures below its boiling point. They show hysteresis and concentration effects characteristic of ordinary heat-reversible gels such as gelatin and agar in water.

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