The Solvation of Nitrocellulose in Acetone-Water Mixtures

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V. *The Solvation of Nitrocellulose in Acetone-Water Mixtures.*

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Introduction.

The process of solution is, considering its enormous importance, remarkably little understood. With nitrocellulose as with many other technical products the " solution " formed is of a colloidal nature ; that is to say, the ultimate units of dispersion are very large compared with the solvent molecules, and osmotic phenomena play an unimportant part. It is clear that solvation, or attachment of some or all of the solvent to the dispersed particles must be essential to the process of solution, but so far, comparatively little work has been done on solvation probably because of the lack of an unequivocal method for its determination. Yet the uncertainty concerning the solvation of colloidal particles is a source of difficulties in many investigations, to mention only a few, in the determinations of particle-size by settling or centrifuging, in viscosity work, and in light scattering experiments.

Acetone is an excellent solvent for nitrocellulose. It forms solutions with materials within a wide range of viscosity and degree of nitration ; its vapour is rapidly absorbed. Water, on the other hand, has no evident solvent action on nitrocellulose ; its vapour is little absorbed. It is of interest therefore to investigate the action of these two liquids when they are used together as a solvent. As might be expected the contrast between the two liquids results in critical solution phenomena which, for a system containing a colloidal solute, are unusually definite.

To determine completely the solvation in such a system, *i.e.*, to find directly the quantities of acetone *and* water which are removed from the active mass of the solvent does not seem possible by any means of which we know, but the amount of solvate acetone *relative to that of water* can always be found. Such figures, for various nitrocelluloses and various acetone-water mixtures, form the main part of the experimental work.

There are properties of nitrocellulose which it may be profitable to touch on at this point, especially as an account of some of them has not yet been published. The product of the action of nitric acid on cellulose is never a homogeneous cellulose nitrate, but always consists of a mixture of an apparently infinite number of elements. Any property of nitrocellulose, while differing only infinitesimally from one element to another, may yet, over the whole number of elements, exhibit quite a considerable variation.

Thus the elements will each dissolve in a characteristic concentration of acetone in water. With less acetone they will not dissolve. If the nitrocotton is "fractionated" by treating it with more and more concentrated acetone solution, it is found that the viscosity of successive fractions shows a difference which, however, becomes smaller the smaller the fractions.

The nitrogen content of an unfractionated nitrocellulose may be anything less than 14·14%; the inferior limit for complete solubility in acetone is about 10%, but it is found that although the fractions into which any nitrocellulose may be divided certainly differ from each other in nitrogen content, the difference in comparison with the whole possible range of nitrogen percentages (from, say, 10 to 14%) is small.

In a previous discussion of these matters CRAIK and MILES* showed that the critical solution concentrations of (unfractionated) nitrocelluloses rise with increase of nitrogen content and with increase of viscosity, but without there being any obvious quantitative relationship between these properties. The use of unfractionated material is unsatisfactory for several reasons; it is easy to see, for instance, that the critical solution concentration, determined by either a precipitation or a solution method, will be that of the elementary fraction which has the highest nitrogen content and viscosity. Homogeneous fractions cannot, however, be obtained in sufficient quantity. For the work to be described each nitrocellulose was extracted with an aqueous acetone sufficient to remove 15% or more of the solid, including the most degraded fractions of the nitrocellulose which are always the most soluble and may have an appreciable osmotic pressure.

The critical concentrations of acetone-water range from about 72 to 87% of acetone for commercial nitrocelluloses. It will be convenient to refer to an acetone-water mixture as "above" or "below the compatibility point" in regard to a particular nitrocellulose, in accordance with such a mixture being more or less concentrated than the critical solution mixture. Below the compatibility point the mixed solvent cannot effect solution, but it causes swelling, accompanied by a sorption of acetone which can be measured. It has been found (unpublished work) that this sorption rises from about 0·4 gm. per gram of nitrocellulose in 30% acetone to 1·0 in 70% acetone. All nitrocottons give the same general result, with the exception of those containing 13% or more of nitrogen (guncottons), which have lower sorption values. (See fig. 4, Curves C and D.)

A considerable amount of work has been done on the sorption of vapours by nitrocotton. Work by McBAIN and others† has shown that the best solvents by repute

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* 'Trans. Faraday Soc.,' vol. 27, p. 756 (1931).

† 'Trans. Faraday Soc.,' vol. 29, p. 1086 (1933)

are sorbed to the greatest extent, and that the weight of a solvent sorbed is of the order of 1 gm. per gram of nitrocotton for 90% saturation. JENKINS and BENNETT* and RUBENSTEIN† have extended this work to different nitrocottons with the same vapour pressure, and have found that there is a maximum sorption of a given vapour with a nitrocotton of 12% nitrogen. Before proceeding to the experimental work we shall define the sense in which some terms are used.

"Solvation" is the phenomenon by which a part or the whole of the solvent is bound to the dissolved substance. The "apparent solvation" refers here to the amount of acetone attached, calculated on the assumption that no water is attached. In passages where it is desired to refer to the whole of the bound solvent, the term "total solvation" is used. "Absorption" we have employed to designate the same process in the region of acetone-water concentrations where the nitrocotton is not in solution. To cover both processes we have used a more general term "Sorption."

We shall give the composition of acetone-water mixtures as the percentage of acetone by weight, and the concentration of nitrocotton in acetone-water solutions will be given in grams per 100 c.c. of solvent. Sorption values will be given as grams of acetone sorbed per 1 gram of nitrocotton.

By the "free" solvent is meant the solvent not sorbed, and by the "final" concentration of acetone is meant the concentration of the acetone in the free solvent after the nitrocotton has abstracted its solvation layer.

EXPERIMENTAL.

In the following treatment the nitrocellulose in solution is considered as if it were a phase separate from the solvent. This is justified because it can be separated from the solvent by ultrafiltration, or ultracentrifuging, and because it exerts only a negligible osmotic or swelling pressure of about 2 cm. of mercury for a 3% solution in 95% aqueous acetone. Following out this conception, we may say that the nitrocellulose phase removes acetone from the solvent phase, and leaves it with an acetone percentage lower than before. In the method which we have developed a measurement is made of the total vapour pressure above the solution and since this will be characteristic of the solvent phase one can deduce from it the acetone concentration of the "free" solvent. The following is a general description of the method.

The total vapour pressures of solutions of known acetone concentration containing no nitrocellulose are first determined, and graphs constructed so that the composition of the solvent can be read off when its total vapour pressure is known. If now nitrocotton is added to the aqueous acetone some of the acetone is taken up by the nitrocotton to form a solvate. The "free" solvent then corresponds to a mixture with less acetone and has a lower total vapour pressure. This decrease in pressure can be

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* 'J. Phys. Chem.,' p. 2318 (1930).

† 'J. Phys. Chem.,' p. 2330 (1930).

measured, and reference to the above figures will give the change of composition of the solvent and hence, *assuming no water is absorbed*, the amount of acetone in the solvate.

The greater part of the work may therefore be described in three sections. (1) The determination of the total vapour pressure of acetone-water mixtures. With this is included measurements of the partial pressures of acetone and water at 20°. (2) The modification of this method used to find the change of concentration of the "free" solvent when nitrocotton is introduced, and (3) the experimental results.

Measurement of the Total Vapour Pressure of Mixtures of Acetone-Water Mixtures.

To obtain the curves connecting acetone concentration with the total vapour pressure, it was necessary to obtain air-free aqueous acetone, measure the vapour-pressure above it, and then determine its composition by density measurement.

Apparatus.—Figs. 1A and 1B show the apparatus used. B was sealed to A at *f*. The dotted lines in A indicate a connecting tube which was removed after the experiments described here. The tube *a* at this time was rounded off at the bottom like *b*, *j i h g* being added at a later date.

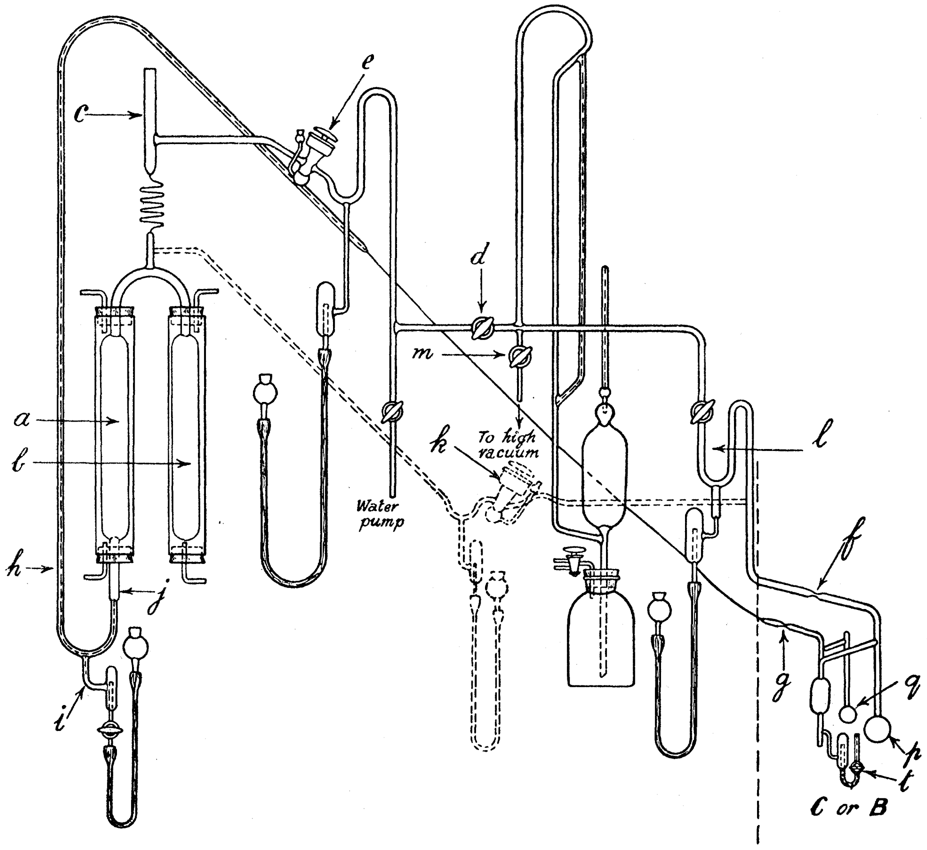

FIG. 1A.

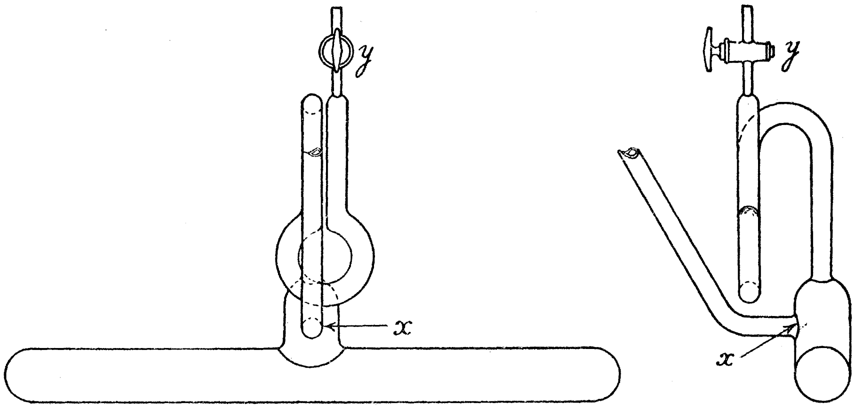

FIG. 1B.

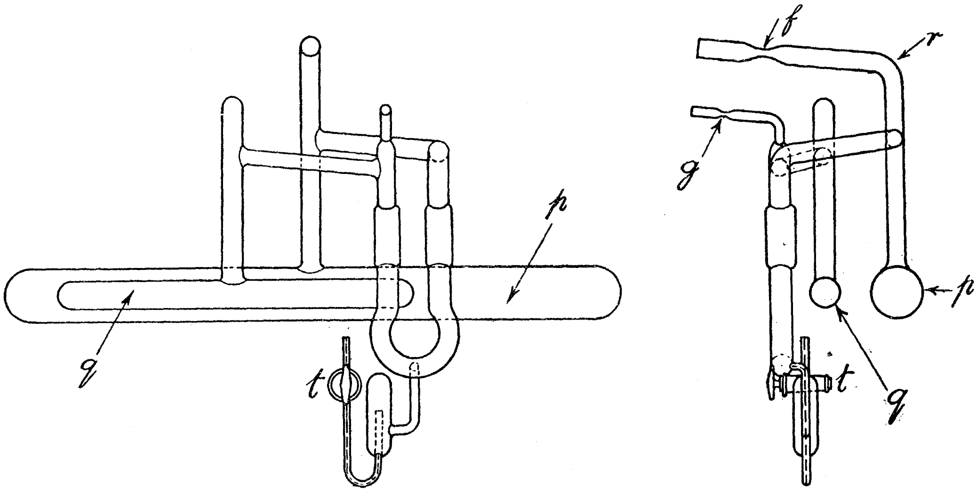

FIG. 1C.

Acetone.—The acetone, as shown by analysis, contained no impurity except water, nevertheless, it was fractionated before use, the first and last portions being discarded ; it was not dried. The density was used as a measure of the acetone concentration since only water and acetone were present. A table of densities of acetone-water mixtures by YOUNG was used.*

Introduction of Acetone and Water.—Air was withdrawn from bulbs *a* and *b*, acetone was admitted through *c*, then water and finally air ; by maintaining this order it was safe to seal off with a flame, since the spiral prevented the inflammable acetone vapour from diffusing up again. The spiral has two other uses : it prevents flooding of the connecting tubes when the liquid bumps during distillation, and it gives some flexibility to the apparatus. About 200 c.c. of aqueous acetone was thus introduced, the mixture initially containing a larger percentage of acetone than was finally required, to allow for the loss of acetone in the process of removing air.

Freeing Acetone from Air.—After sealing off, the system was evacuated through

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* 'J. Soc. Chem. Ind.,' vol. 52, p. 449T (1933)

tap *e*. An ordinary tap could not be used here because of the action of the acetone on the grease, and a mercury seal is inconvenient except at low pressures. Tap *e* combining the advantages of both, is sealed with mercury and is backed by an ordinary tap leading to the water pump. Tap *k* was also of this design. The aqueous acetone was then distilled from *a* to *b* by passing hot water through a jacket surrounding *a*, and cold water through a jacket surrounding *b*. Towards the end of the distillation the system was again evacuated. This was best done at the point when the distillate, rich in acetone, had a vapour pressure equal to the residue rich in water but at a higher temperature. This distillation process was continued till the pressure of air was 10^{-4} mm. or less (about 6 or 8 distillations were necessary). This was tested by withdrawing vapour through tap *d* into a McLeod gauge and compressing it; only a rough estimate, however, could be obtained in the presence of acetone, which condensed and might have dissolved some of the air. The McLeod gauge was constructed as in the sketch, with a view to separating as much as possible of the liquid acetone before the pressure inside the gauge had risen to a value where the permanent gas would be appreciably soluble in the liquid. In reading the pressure of the permanent gas, allowance was of course made for the vapour pressure of the acetone present.

Adjustment of Acetone Concentration.—The acetone was then free from air and the composition was adjusted to the value required by drawing off vapour with a waterpump. The percentage of acetone was thus lowered as the more volatile constituent of the mixture was withdrawn. Several small floats similar to those described by ROBINSON and SMITH* were present in bulb *a*, and were sufficiently small to withstand the bumping during distillation without breaking. By means of these a rough estimate of the composition of the acetone could easily be obtained, and in several experiments the density was determined to 0·0001. This method is as accurate as any for determination of the density, but because of the difficulty in bringing the composition of the aqueous acetone exactly to that corresponding to a float, it was later used only to adjust the composition approximately to that desired.

Transferring Aqueous Acetone to B.—In the meantime B had been shut off from A by the tap *k*, which was mercury-sealed and free from grease. B was evacuated to 10^{-4} mm. and sealed off from the pump by the mercury seal *l*, and a tap which prevented the mercury in the seal from being blown out when the pressure rose on one side. *k* was then opened, and the whole of the aqueous acetone distilled over into B, which was then sealed off at *f*.

The Thermostat.—A very constant temperature was required in order that the mixed vapours of acetone and water, which give rise to the total vapour pressure, should attain equilibrium. This was achieved by using a double thermostat. The temperature fluctuations of the outer thermostat were not transferred to the inner thermostat and with efficient stirring the temperature was constant to ± 0·001° at 20° C. and ± 0·003°

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[*] 'J. Chem. Soc.,' p. 1262 (1926).

at 50° C. A rocking arrangement was provided by means of which the tube C could be mixed while in the thermostat.

Manometer.—The manometer must be at the same temperature as the vapour, the pressure of which is being measured and tube C was accordingly designed with a short U-tube which could be connected by a rubber tube to a longer manometer outside. This U-tube was surrounded by a coil of wire embedded in nitrocellulose cement and a small current was passed, except when readings were being taken, to heat the tube slightly and prevent condensation on the mercury. The U-tube was immersed in the water of the thermostat so that the vapour space was all at constant temperature, a necessary precaution with mixed vapours. The distance from the surface of the mercury to the surface of the aqueous acetone was as short as possible, and constructed of relatively wide glass tubing to enable the vapour to become homogeneous. A bulb was connected to the external manometer and immersed in the thermostat, thus preventing any appreciable change from occurring with change in room temperature during a reading. The barometer tube used as a reference was prepared by boiling out under a vacuum and sealing off while a McLeod gauge registered 10^{-5} mm. The manometer and barometer tubes were enclosed in an air jacket to avoid sudden changes in temperature, which might cause the temperature of the mercury to lag behind that registered by the thermometer.

Readings.—The pressure in the tube connecting the U-tube to the external manometer was fixed at approximately the pressure expected by evacuating and admitting dry air, and tap y was opened. The manometer was read, then tap y, fig. 1B, was closed again. The barometer was read, and finally the two sides of the U-tube. The capillary correction was taken as cancelling out, since the tubes were all the same bore ($\frac{3}{8}$ inch). The readings were corrected to the density of mercury at 0° C. Three sets of readings or more were taken at each temperature. The readings were steady after a short time, and did not change on further shaking or standing. The effect of temperature variation is considerable. 0·01° causes a variation of 0·1 mm. at 20°, and 0·2 mm. at 50°. As examples of the accuracy of measurement one series of readings at 20° and one at 50° are given.

20°	170·13	170·05	169·94	170·06 mm.
50°	539·07	538·77	538·88	539·13 mm.

The results are collected in Table I. Working graphs were constructed from these figures to the following scale :—

Acetone concentration axis 1% . . . . . . = 2 cm.
Pressure axis . . . . 1 mm. = 2 cm. (10°).
= 1 cm. (20°, 30°).
= 0·5 cm. (40°, 50°).

Partial Vapour Pressures of Acetone-water Mixtures.—In view of the fact that there is an acetone-water complex formed, it seemed desirable to have measurements of the partial pressure of acetone-water mixtures, as this figure is proportional to the activity of the acetone in the solution: for where there is a complex the concentration alone may give quite an erroneous measure of the "active mass" of the acetone. The apparatus just described was suitable for the measurements.

TABLE I.—Total Vapour Pressure of Acetone-water Mixtures.

Experiment No.	% Acetone	Total vapour pressure (mm.)				
		10°	20°	30°	40°	50°
2	99·48	114·97	183·25	282·17	421·38	611·13
1	96·09	109·71	175·74	272·73	407·71	594·56
5	92·48	106·27	170·08	263·48	395·76	578·23
7	88·02 *88·02	103·18	165·00	255·15	382·86	560·64
3	83·78 83·80	100·80	161·09	249·17	374·47	547·62
6	80·26 *80·32	99·18	158·34	245·28	368·38	538·95

* Density by float.

Some of the vapour in equilibrium with the acetone-water was collected, condensed, and from its density the composition was determined. Then, since the total vapour pressure (acetone-water) was already known, the two partial pressures could be found. Apparatus B was modified in two ways. First, the capacity was increased to 500 c.c., and secondly a small 10 c.c. tube was connected by a flexible thin-walled capillary tube, four feet long, with the vessel. This capillary was bent in a half-circle so that the small tube could be clamped outside the thermostat, while the main apparatus was rocking in the thermostat.

Aqueous acetone was rendered free from air as usual, and about 250 c.c. passed into this apparatus, which was sealed off. The apparatus was placed in the thermostat at 20° and rocked till thoroughly mixed. It was necessary to have the room temperature over 20°, otherwise acetone might begin to condense in the 10 c.c. tube before the solution had taken up the exact temperature. When thoroughly mixed, cooling was applied to the 10 c.c. tube and acetone-water condensed. This distillation was conducted while the main apparatus was rocking; moreover, it took place slowly, about 5 c.c. in one or two hours, and since there was only one-way passage of vapour through the capillary it followed that the distillate must have had the same composition as the vapour. The capillary was then sealed off and removed along with the small 10 c.c. tube which contained about 5 c.c. of distillate for the measurement of density. All that remained then was to measure the total pressure just as before. The composition of the liquid undergoing distillation only changed appreciably in experiment 3, where the change was from 28·78% to 27·40%; the mean value of the composition was taken, and the reading of the total pressure was corrected to refer to this composition also. At higher compositions of acetone the change in concentration was neglected. The results are given in Table II and in fig. 4.

Table II.—Partial Pressure of Acetone-water Mixtures.

Experiment No.	Composition (final) %	Composition distillate %	Partial pressure acetone mm.	Partial pressure water mm.	Total pressure mm.
3	28·09	94·89	96·8	5·21	102·0
5	54·92	96·96	135·9	4·26	140·1
2	58·36	97·17	139·4	4·06	143·5
1	80·75	97·37	154·8	4·18	159·0
6	87·43	97·87	161·0	3·50	164·5
4	93·18	—	—	—	170·8

Determination of Total Vapour Pressure of Nitrocellulose Solutions.

It was originally intended to measure the total vapour pressure in solutions of nitrocotton directly in the same apparatus that has already been described, but a few experiments showed that the experimental error was too large. This was a consequence of the results depending on a small difference between two large numbers—the total vapour pressures of pure solvent and of the solution. The method was accordingly modified to a differential one; the acetone was syphoned over instead of being distilled, and this made possible its separation into three samples of the same composition, one of which was used for density determination, one for making up the nitrocotton solution, and one, so to speak, to balance against the solution. Now, since the vapour pressure difference between solvent and solution is being read directly, only the slope of the reference graphs enter into the calculation. The slope is much more accurately defined by the points than the actual position of the curves. The fact that there are now only two readings to take instead of four will also reduce errors. This method will now be described in detail.

Apparatus.—Figs. 1A and 1C show the apparatus used. In A, the tube shown in dotted outline was removed, and the syphon $j\ i\ h\ g$ added.

Nitrocotton.—The samples of nitrocotton were extracted according to the methods of Craik and Miles (*loc. cit*), with a strength of aqueous acetone which would remove the most soluble 15%. It was anticipated that this would separate any degraded material; the precipitation and drying also left the nitrocotton in a form more easily introduced into the tubes. The analyses of the nitrocottons are given in Tables VII and IX.

Acetone.—The acetone was purified as before.

The introduction of the acetone and water, and the processes of freeing the mixture from air and adjusting the composition, have already been described.

Filling Tube C with Nitrocotton.—The tube had a total capacity of 170 c.c. and a convenient volume of solution was 100 c.c. The requisite weight of nitrocellulose was introduced into the tube *p*, fig. 1C, through *r*. The entrance tube *r* was cleaned thoroughly with cotton-wool, and clamped behind a lead screen (in case of ignition); it was then drawn out in a flame at *f*, ready for sealing off later. *g* and *f* were sealed on to the appropriate connections of A, the mercury seal *h i j* filled with mercury, and the air in C withdrawn through *m*. The tap *t* was sealed with mercury, which did not, however, reach the level of the U-tube, and so did not interfere with the evacuation of the apparatus. Surrounded with water at 60° for several hours, the nitrocotton was exposed to the vacuum of a mercury pump backed by a Hyvac oil pump, and then left overnight sealed with mercury at *l* under a pressure of about 10^{-4} mm. The vacuum usually fell to about 10^{-3}. It was then re-evacuated to 10^{-4} mm., and sealed off carefully with a flame at *f*. As soon as air was withdrawn from C the evacuation of *a* and *b* was begun and the process of freeing the acetone from air could proceed so that at this stage the acetone was ready to be transferred.

Transferring Aqueous Acetone to Tube C.—The difficulties lay in avoiding any separation of the acetone by distillation. The aqueous acetone was collected in *a*. It was mixed thoroughly by heating locally at *j*, which caused bubbles to rise through the liquid, and, finally, by raising and lowering the mercury in *j*. Apparatus C was tilted slightly to avoid any acetone passing into the solvent tube *q*, and *q* was heated with hot water to prevent any acetone condensing there. The mercury was then lowered to *i* and the mercury seal broken by entrapping some acetone in the capillary and heating it. Then, on cooling *p* acetone rose over the syphon *j i h g* and through the U-tube into the nitrocotton. When a suitable volume had passed over as read by rough graduations on *a*, mercury was admitted into the U-tube of C, and the remainder of the acetone passing over was retained on the other side of the U-tube in *q*, which was now cooled. When an additional 20 c.c. had passed over, the flow of acetone was stopped by allowing mercury to rise to *i*. By heating the capillary about *h*, the mercury column was broken, and a bead of mercury could be caused to pass through the syphon carrying all the acetone in the capillary tube into *q*; the apparatus was then sealed up with a flame at *g*. A sample of acetone for exact analysis was left in *a*.

Removal of Liquid from Surface of Mercury.—At this stage the apparatus C contained some aqueous acetone and some nitrocotton solution made up from it, on opposite sides of a U-tube. The mercury surfaces were, however, covered with acetone. This could be removed as follows :—

(1) The tube was tilted and as much acetone as possible poured into p and q.

(2) Ice was applied to the U-tube, and some acetone thus distilled on to the mercury ; this distillate was rich in acetone.

(3) As much distillate as possible was poured back again. The tube could then be placed in the thermostat, when the remaining acetone on the mercury would be reduced to about one-fifth to one-tenth of its volume by distillation, and this trace did not interfere with the readings.

The Pressure Readings.—The tube was rocked until solution was complete, and readings could be taken. The U-tube had limbs $\frac{5}{8}$ inch bore, and since the surface was wet with approximately the same aqueous acetone on both limbs the capillary corrections could be taken as equal. The difference between the extreme readings once a steady state was reached was seldom as much as 0·05 mm. A typical series is shown below :—

2·00 2·03 2·05 2·05 2·06 2·06 2·06 2·06 mm.

The first two were probably taken before equilibrium had quite been attained. The manometer and barometer are of course not now used.

Calculation.—After the pressure difference had been noted at one or two temperatures the experiment was concluded with the measurement of the total weight of the solution in the tube.

If g = gm. nitrocotton.
w = weight of solution.
c_1 = percentage of acetone by weight in solvent.
c_2 = percentage of acetone by weight in solution (" free " solvent).
s = solvation in grams acetone per gram nitrocotton.
Δp = pressure difference between solution and solvent.

Since g, w, c, and Δp are known, and $C_2 = C_1 - \Delta p \dfrac{dc}{dp}$ (dc/dp is the slope of the reference graph) it is evident that, from the equation :—

$$\frac{\dfrac{(w-g)\,c_1}{100} - gs}{w - g - gs} = \frac{c_2}{100}$$

s can readily be found.

Accuracy.—The reading error is small and is not important except in very weak solutions. The volume of the solution and the weight of nitrocotton can be accurately determined ; the slope of the graph may introduce an error of 1–2%, but the greatest possible sources of error are (1) the osmotic lowering of the vapour pressure and (2) the possibility of the three parts into which the acetone is divided being of unequal concentration. The measure of these errors was found by some blank experiments.

(1) 100 c.c. of pure acetone was syphoned over into the tube containing 10 gm. ML nitrocotton. There was no difference in the vapour pressure of this solution compared with that of the solvent.

Since a difference of pressure as low as 0·05 mm. should have been quite definitely detected the effective molecular weight of the nitrocotton must be greater than 30,000. Indeed, since a 15% fraction of the lowest molecular weight has probably been extracted this is no higher than one would expect. The only results which may possibly be affected by lowering of the osmotic pressure are those for the MX nitrocotton which will have a lower molecular weight than the ML and possibly a lowering of osmotic pressure greater than the limit imposed above for the ML.

(2*a*) 100 c.c. of 89·05% acetone was syphoned over into the tube *p*, from which, however, nitrocotton had been left out. 20 c.c. was collected in the solvent tube *q*. The reading of the U-tube showed that *q* was more volatile than *p*, the difference in the readings being 0·10 mm. Here there was evidence of unequal concentration in the three parts.

(2*b*) This was a repetition of (2) with 89·95% acetone, with particular attention to drawing over all the acetone in the capillary tube, and it gave a similar result, 0·20 mm. difference. Evidently the acetone was not mixed properly before syphoning over.

(2*c*) A new system of mixing was introduced where, by heating locally at the bottom of the tube *a*, large bubbles were caused to rise and the acetone was thoroughly mixed. This time the difference in readings in the U-tube was nil.

In conclusion, the total error from this cause may be taken as less than 0·05 mm.; that is, 25% of the smallest reading taken (with 1% solution) and 2% of the largest reading taken.

The Effect of Various Factors on the Apparent Solvation of Acetone by Nitrocellulose.

The value of the solvation may be expected to be influenced by a number of factors.

(*a*) The acetone concentration of the solvent.

(*b*) The concentration of nitrocellulose in the solution.

(*c*) The degree of nitration of the nitrocellulose. (Measured by the percentage of nitrogen.)

(*d*) The characteristic viscosity of the nitrocellulose (in a standard solution).

(*e*) The temperature.

(*f*) The age and history of the solution.

Each of these factors has been investigated by conducting a few experiments in which, as far as possible, the other conditions were held constant, but the given factor was varied.

(*a*) *The Acetone Concentration of the Solvent.*—The nitrocotton concentration was fixed at as high a value as practicable, about 14%. The actual nitrocotton was the one designated ML, the first letter indicating a medium nitrogen (H = high, L = low) and the second letter indicating a low characteristic viscosity (H = high, M = medium, X = very low). This was considered to be an average and representative nitrocotton. The results are given in Table III and fig. 2.* Fig. 2 brings out an unexpected and surprising result—the acetone solvation apparently falls while the activity of the acetone increases.

TABLE III.—Apparent Solvation of Acetone by Nitrocotton in Various Acetone-water Mixtures.

Experiment No.	Gm. N/C per 100 c.c. solvent.	Final acetone concentration 20°	Solvation gm./gm.	
			20°	30°
20	12	85·25	1·00	0·95
23	14	92·77	0·56	0·45
24	9	86·44	0·84	—
25	13	94·00	0·42	0·41
27	13	86·90	0·81	0·74
28	13	89·24	0·75	0·67
29	13	92·07	0·52	0·43
32	14	96·96	0·22	0·24
34	13	81·37	1·09	1·05
35	13	88·90	0·81	0·68
42	12	89·09	0·75	0·68

The most probable explanation is that the water is also absorbed and that while the total solvation may increase or remain constant, the apparent solvation of acetone becomes less.

There is no direct evidence on the value of the solvation between 97% and 100% acetone. The relation between the pressure reading in mm. and the solvation value calculated from it is 2·1 mm. to 1 gm. per gm. at 80% acetone, and 1 mm. to 1 gm. per gm. at 97% acetone, and the experimental error is practically constant, so that the percentage error is doubled in the range 80% to 97% for this reason alone. In addition, the solvation values are always decreasing and thus increasing the percentage error. Hence, the value recorded for 97% acetone had a probable error of about 20%, and it was useless to proceed beyond 97%, but the curve has been extrapolated to a value of zero solvation at a concentration of 100% acetone.

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* In this and some of the other figures we have preferred to use instead of the concentrations the activities (p/po) of acetone; that is, the ratios of the partial pressures of acetone at the concentrations to the vapour pressure of pure acetone. In making this substitution the data of Table II were used.

An interesting experiment may be mentioned here. One might think it possible to obtain points on an extension of the absorption curve above the compatibility point by allowing nitrocotton to swell in aqueous acetone *without stirring.* The system then is very like those below the compatibility point. The nitrocotton swells, but the swelling is slow, and on the top is aqueous acetone containing very little nitrocotton. Such a system, however, is found to have the same vapour pressure before and after stirring. This means, then, that the process of solvation above the compatibility point does not depend directly on the break-up of the nitrocotton into small units by mixing.

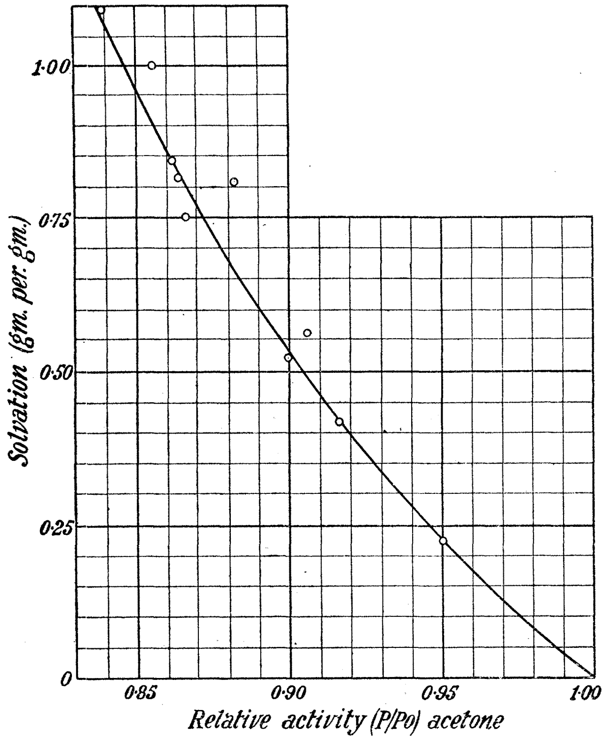

FIG. 2.—Change of solvation of nitrocotton with acetone activity in acetone-water mixtures.

(*b*) *The Concentration of Nitrocellulose in the Solution.*—The first experiments were directed to obtaining results for the solvation value with different concentrations of ML nitrocotton in a constant acetone concentration. The acetone concentration was chosen as 87%, which is within a range giving relatively high readings for a given solvation, and yet not too near the compatibility point where disturbing irregularities might occur. The nitrocotton was extracted as previously. The results are tabulated in Table IV and shown graphically in fig. 3. The solvation values are evidently almost the same from solutions of about 12% nitrocotton (see fig. 2) until the concentration is reduced to 5%. After that, the value increases rapidly with falling concentration as far as the measurements have been made.

The question then arose whether similar curves would be found with acetone concentrations other than 87% and for other nitrocottons. The additional experiments are given in Table V, and the analyses of the guncotton and nitrocotton in Table VII.

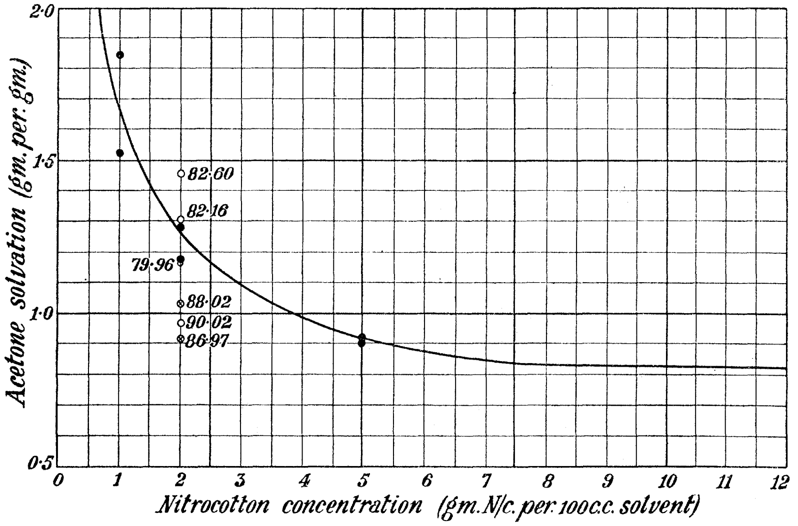

FIG. 3.—Change of solvation with nitrocotton concentration. ● ML nitrocotton, 87% acetone; ○ ML nitrocotton; ⊗ guncotton.

TABLE IV.—Solvation Values for Different Nitrocotton Concentrations.

ML Nitrocotton.

Experiment No.	Gm. N/C per 100 c.c. solvent.	Final acetone concentration.	Solvation gm./gm.	
			20°	30°
36	5	86·89	0·92	0·84
37	5	86·66	0·91	0·82
40	2	87·37	1·27	1·15
44	2	85·13	1·18	1·21
47	1	85·89	1·85	1·65
49	1	86·81	1·52	1·52

TABLE V.—Solvation Values for a Low Nitrocotton Concentration.

Experiment No.	Description of nitrocellulose.	Gm. N/C per 100 c.c. solvent.	Final acetone concentration.	Solvation gm./gm.	
				20°.	30°.
66	Guncotton 2 . .	2	86·97	0·92	0·73
67	,, . .	2	88·02	1·04	1·04
70	ML	2	82·60	1·46	1·38
71	,, ...	2	82·16	1·29	1·27
72	,, ...	2	79·96	1·17	1·25
76	,, ...	2	90·02	0·97	—

If one compares the solvation at a concentration of 12% (from fig. 2) with the figures for 2%, the following pairs are obtained for the ML nitrocotton—80% 1·15, 1·17; 82% (average) 1·00, 1·37; 86% 0·87, 1·23; 90% 0·73, 0·97. Evidently in one pair only is there no difference between the solvation with 2% and with 12% nitrocotton; in the other pairs the solvation rises with diminishing concentration. The exception is 80% acetone which corresponds to the compatibility point of the nitrocotton. The two experiments with guncotton also show that this concentration effect does not occur at the compatibility point. Since the effect occurs in the one pair in 80% and in the other at 87% acetone, it is obviously dependent not on the solvent but on the nitrocellulose.

Some 0·5% values were obtained with the object of deciding whether the solvation was approaching some fixed value at zero concentration of nitrocotton or not, but the results were so variable that they have not been included in the tables. They were not in disagreement with the other results, but failed to give any information on the progress of the curves.

The solvation in extremely dilute solutions may reach quite high values.

(*c*) *Degree of Nitration of the Nitrocellulose.*—A series of three nitrocottons of approximately the same viscosity was used. In addition, a guncotton which had been boiled under pressure until its viscosity was comparable with that of the others was examined. Unfortunately, its nitrogen content was so lowered by this treatment that it was not much higher than the HL. There was also included a guncotton of high nitrogen content, but of high viscosity. The analyses of the nitrocottons, which were carried out on the residue after extraction, are given in Table VII.

Each estimation of solvation took about 2 days. For this reason it was decided to determine only a few points on the curve connecting solvation and acetone concentration for each nitrocotton. In the absence of any contrary evidence the form of the curve was then assumed to be the same as for the ML material, for which the whole curve had been explored. The nitrocotton concentration was fixed at 12%, and the aqueous acetone at 87%, or near there.

These experiments are collected in Table VI and in fig. 5.

The series shows that while the essential shape of the curves appears to be the same, there are between the nitrocottons differences which are outside the experimental error.

When the compatibility points are determined and marked in the graph as has been done by short vertical lines, there is indicated that value of the solvation at the compatibility point which is apparently the maximum sorption over the whole range of acetone-water mixtures. In spite of the rather small number of points it seems safe to say that this greatest value of the sorption attains a maximum with a nitrocotton of nitrogen about 12·3%.

The significance of this still escapes us, but the phenomena should be compared with the sorption of acetone vapour by dry nitrocotton. JENKINS and BENNET* and

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* 'J. Phys. Chem.,' p. 2318 (1930).

Rubenstein* found that a series of nitrocottons of different nitrogen content showed a maximum sorption of acetone vapour with 12% nitrogen.

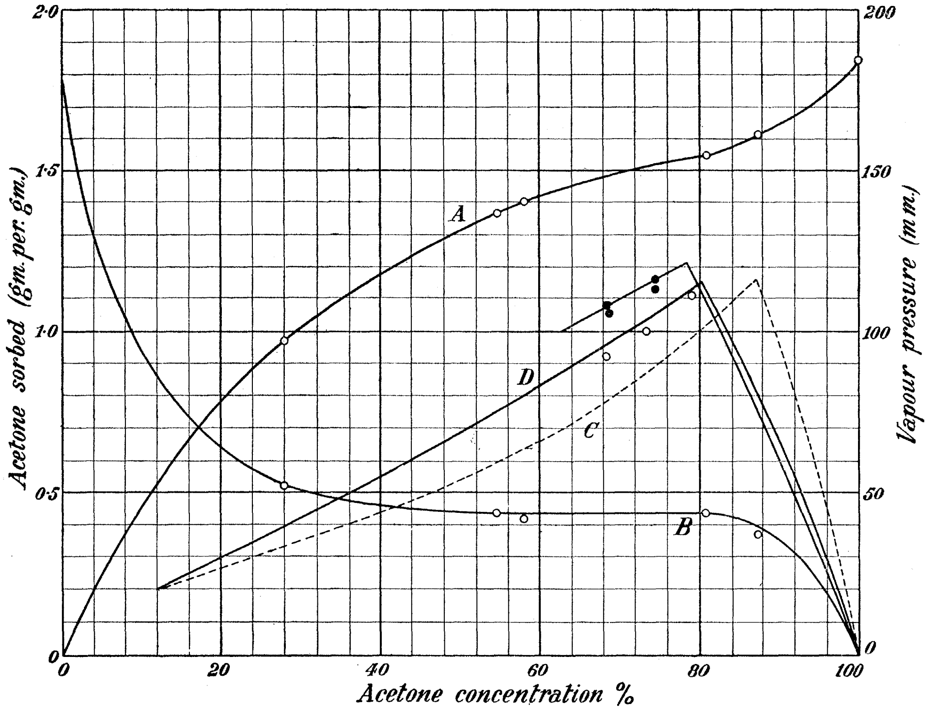

Fig. 4.—A. Acetone partial pressure; B. Water partial pressure × 10; C. - - - guncotton; D. ML nitrocotton, ○ at 20°, ● at 30°.

Table VI.—Solvation Values for Nitrocottons of Different Nitrogen Content.

Experiment No.	Description of nitrocellulose.	Gm. N/C per 100 c.c. solvent.	Final acetone concentration 20°.	Solvation gm./gm.	
				20°.	30°.
51	HL	14	83·65	1·02	0·93
52	,, ...	13	83·04	1·14	1·08
73	,, ...	11	81·75	1·25	1·23
53	LL	14	82·73	0·93	—
55	,, ...	13	88·35	0·61	0·53
57	,, ...	14	86·36	0·84	0·70
74	,, ...	13	78·70	1·04	1·03
56	Guncotton 1 . .	14	87·6	0·85	0·80
58	,, . .	13	87·45	0·90	0·82
77	,, . .	12	84·41	1·15	1·10
79	,, . .	12	90·53	0·72	—
45	Guncotton 2 . .	12	87·48	1·07	0·97
48	,, . .	13	89·29	1·02	0·99

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* 'J. Phys. Chem.,' p. 2330 (1930).

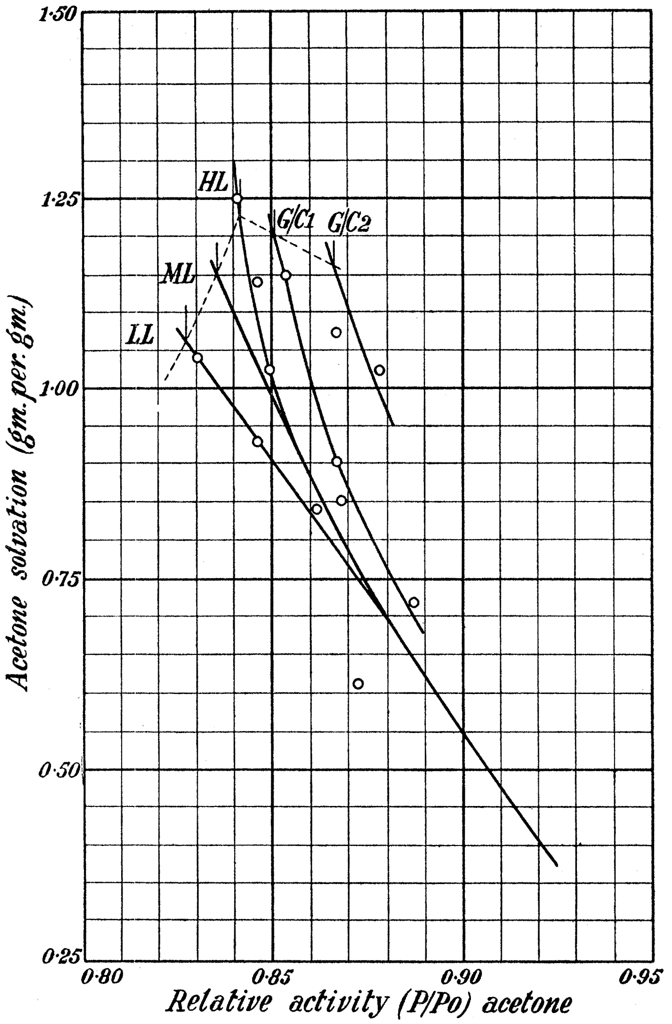

FIG. 5.—Change of solvation with nitrogen content.

TABLE VII.—Analyses of Nitrocottons in Tables V and VI.

	LL.	ML.	HL.	Guncotton 1.	Guncotton 2.
Extracted with acetone of strength = %	70·39	76	78·31	80·18	83·5
Residue gm. %	86	85	88·5	88	83
Critical solution concentration	77·7	80·2	82·1	83·9	87·1
N_2 ash free	10·83	11·68	12·33	12·65	13·41
Ash	0·12	—	0·08	0·23	—
Viscosity 20% solution . .	101	161	194	1300	1590

(*d*) *The Characteristic Viscosity of the Nitrocellulose in a Standard Solution.*—Solvation values of a series of nitrocottons of different viscosities, MX, ML, MM, and MH were determined; the nitrogen was approximately the same in each specimen. In addition, two experiments were carried out with "ML extract." It has already been noted that all the nitrocottons used were extracted before use with aqueous acetone. The "ML extract" was the soluble fraction from the ML nitrocotton. The nitrogen content was lower than the original, and also the viscosity, but it is included in this series to illustrate the effect, on the curves obtained, of the mixed nature of the nitrocotton. The critical solution concentration of this extract is of course that of the acetone used to extract it. The results are given in Table VIII and fig. 6, and the analyses of the nitrocottons in Table IX. The figures for the viscosities of the nitrocottons determined in different concentrations of solution in 95% acetone have been calculated for a common hypothetical concentration of 20% by using empirical factors.

These factors are simply the ratio of the viscosities of a representative nitrocotton in the two concentrations.

TABLE VIII.—Solvation Values for Nitrocottons of Different Viscosities.

Experiment No.	Description of nitrocellulose.	Gm. N/C per 100 c.c. solvent.	Final acetone concentration 20°.	Solvation gm./gm.	
				20°.	30°.
59	MX	14	91·03	0·44	0·42
60	,, ...	12	88·69	0·63	0·52
61	,, ...	12	81·40	0·98	0·98
82	,, ...	14	81·08	1·09	1·04
62	MM	13	86·50	0·91	0·78
63*	,, ...	12	87·52	0·67	0·60*
65	,, ...	13	85·82	0·85	0·77
68	LH	13	86·96	0·82	0·69
69	,, ...	14	89·43	0·70	—
75	,, ...	17	79·96	1·10	1·08
38	ML extract . .	12	83·56	0·94	0·88
39	,, . .	13	85·18	0·82	0·75

* Omitted from graph.

This series shows less definite agreement than the last series of different nitrogen percentage. Nevertheless, some conclusions may be drawn. If the points are considered with reference to the continuous line, which is copied from fig. 2 and represents the ML nitrocotton, it is clear that there is a tendency for the points belonging to nitrocottons of lower viscosity to lie below the curve. The points representing nitrocottons of higher viscosity as nearly as possible coincide with the line. The compatibility points of these nitrocottons all lie near one another, so evidently there can be no great difference between the values of the sorption at the compatibility points such as was

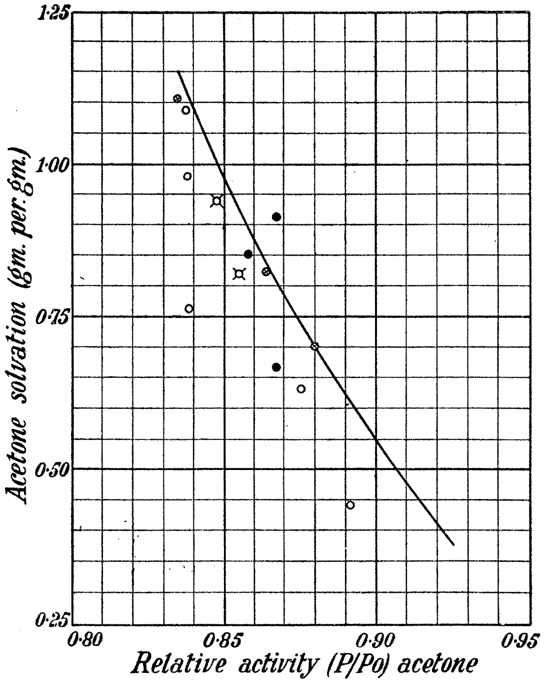

Fig. 6.—Change of solvation with viscosity. ○ MX; ● MM; ⊗ MH; ¤ ML extract; —— ML.

Table IX.—Analysis of Nitrocottons in Table VIII.

	MX.	ML.	MM.	MH.	ML extract.
Extracted with acetone of strength = (%)	71·9	76	76·97	77	—
Residue gm. %	87	85	90	89	—
Critical solution concn. .	79·9	80·2	79·9	81·3	76
N_2 ash free	11·41	11·68	11·73	11·61	9·52
Ash	0·14	—	0·12	0·11	—
Viscosity 20% solution . .	25	161	450	2770	120

apparent with the last series of nitrocottons, fig. 5; there is no viscosity of maximum sorption, analogous to the nitrogen content of maximum sorption which was found in that series. The solvation at the compatibility point, however, may fall off with nitrocottons of low viscosity.

One is struck by the fact that a viscosity change from 25 to 120 and to 161 has a perceptible change on the solvation while one from 161 to 2770 makes no difference.

With low viscosity and short chain lengths, the ends of the chains will play an increasingly important part, while with increasing chain length and viscosity the influence of the chain-ends will tend to become smaller and smaller. This may explain why the nitrocottons MX and ML extract differ from the others. A similar effect is apparent with the critical acetone concentration, which rises at first with increasing viscosity, but with higher viscosities becomes almost constant. A further point is of interest in considering the absolute value of the solvation at the compatibility point. Since a nitrocotton consists of an infinite number of fractions of constantly varying viscosity, critical solution concentration, and nitrogen content, solvation values of an ordinary nitrocotton are the integrated values for all these fractions. Consideration shows that the integral solvation curve will be more rounded near the compatibility point, and will have a maximum value slightly lower than would be shown by a uniform fraction having a viscosity and nitrogen equal to that of the nitrocotton. This effect is comparatively small.

(*e*) *The Temperature.*—In all the experiments, the solvation has been found at 20° and 30°. The temperature coefficient is calculated on the difference between the 20° and 30° solvation values divided by the 20° value, and is shown as a negative value in Table X when there was an increase in the solvation with rise of temperature. In this particular calculation, many of the sources of error are eliminated. The same solution is used for both readings, so that errors in making up the solution are absent. The only errors are the reading error, which may be taken to be quite random, and the error of the graphs, which is small, and probably random, since different parts of the graph are being used.

TABLE X.—The Temperature Coefficient is Calculated as

$$\frac{\text{Solvation at } 20^\circ - \text{Solvation at } 30^\circ}{\text{Solvation at } 20^\circ}.$$

Expt. No.	Temp. coeft.	Expt. No.	Temp. coeft.	Expt. No.	Temp. coeft.	Expt. No.	Temp. coeft.
20	0·05	36	0·09	72	− 0·07	48	0·03
23	0·20	37	0·10	51	0·09	59	0·05
25	0·02	40	0·09	52	0·05	60	0·17
27	0·09	44	− 0·03	73	0·02	61	0·00
28	0·11	47	0·18	55	0·13	62	0·14
29	0·18	49	0·00	57	0·16	63	0·10
32	− 0·09	66	0·21	74	0·01	65	0·09
34	0·04	67	0·00	56	0·06	68	0·16
35	0·16	70	0·06	58	0·09	38	0·06
42	0·09	71	0·02	45	0·09	39	0·09
Average	0·085	Average	0·072	Average	0·063	Average	0·089
General average 0·077.							

There are not sufficient results to separate into classes. The experiments which it might be possible to separate from the rest are those near the critical solution concentration, since in these the percentage error is smallest, and the small number of these results is partly balanced by their greater reliability. Thus, separating out six values with a concentration lower than 84% acetone, the average is 0·043, which is lower than the general average. It is probable that this is a real effect.

(*f*) *The Age and History of the Solution.*—It is known that the viscosity of a nitrocellulose solution depends on the age and manner of mixing. The possible effects of these factors on the solvation were therefore looked for. It was, however, found that mixing, under the limitations of the rocking arrangement, had no effect, and ageing up to a few days showed no perceptible change.

Sorption of Acetone below the Critical Solution Concentration.

At the compatibility point the nitrocotton just fails to dissolve in the aqueous acetone, and below this concentration the nitrocotton swells but does not dissolve. The absorption of acetone in the swelling region can be found by measuring the concentration of the aqueous acetone before and after immersing nitrocotton in it. Fig. 4 (D) shows the results of some unpublished work. Since these results extended only up to 65% acetone several additional determinations were made. 6 grams of dry nitrocotton were immersed in 150 c.c. aqueous acetone and left tightly stoppered for 6 days in a thermostat. From the fall in concentration which is indicated by the rise of density the absorption of acetone can be calculated assuming that no water is absorbed. Some figures at 30° were also obtained; Table XI contains these figures.

TABLE XI.—Sorption of Acetone by Nitrocotton in Acetone-water.
ML Nitrocotton. 6 gm. in 150 c.c Acetone-water.

Final concentration of acetone.	20°.	30°.
68·55	0·92	—
73·63	1·00	—
78·82	1·11	—
79·16	(1·19)	—
68·15	—	1·07
68·35	—	1·06
75·10	—	1·16
74·78	—	1·13

The nitrocotton was, of necessity, extracted before use with an acetone of higher concentration than that used in the experiments. This extraction gives a nitrocotton of uniformly higher compatibility point than the average, and the sorption curve has been continued not through the determined points but about 2%–3% above them. The correction was calculated on the assumption that the sorption curves for each fraction would have the same forms and the same maximum sorption, but at different acetone concentrations, *i.e.*, at their separate compatibility points.

Recently this absorption has been most carefully repeated, and the results, which it is hoped to publish shortly, show that the values below the compatibility point in fig. 4 (D) are about 5% too low. This, however, does not affect any conclusions which we shall draw from them.

Critical Solution Concentration and Temperature.

In fitting together the two portions of the sorption curve which meet at the compatibility point there is occasion to know the change of compatibility point with temperature.

A series of determinations of the compatibility points were carried out at different temperatures. ML, MX, and LL nitrocottons were used, and the concentration was 0·5 gm. per 100 c.c. These figures, which were not corrected for the reduction in acetone concentration caused by the solvation by the 0·5 gm., since the error is practically the same for them all, are given in Table XII.

Table XII.—Change of Critical Concentration of Acetone with Temperature (given as % Acetone).

Nitrocotton.		0°.	20°.	40°.	60°.
ML	Critical solution concn. . . .	82·0	80·2	78·4	76·6
	Differences		1·8	1·8	1·8
MX	Critical solution concn. . . .	80·8	78·9	76·9	74·8
	Differences		1·9	2·0	2·1
LL	Critical solution concn. . . .	79·6	77·5	75·1	72·7
	Differences		2·1	2·4	2·4

Volume of Swollen Nitrocotton.

It was noted in the course of the absorption experiments that much more swelling took place than was accounted for by the comparatively small absorption of acetone. The following experiment shows that in addition to the apparent sorption of acetone a quantity of the surrounding aqueous acetone is imbibed by the gelatinized nitrocotton.

A gel of 5 gm. of nitrocotton and 5·9 gm. of acetone was made up. This was centrifuged and formed a clear layer at the bottom of a 6″ × 1″ test tube. An aqueous solution of acetone, 77·62%, was then poured over the gel. From the sorption curve we know that 5 gm. nitrocotton placed in a large bulk of aqueous acetone of this concentration would take up 5·9 gm. of acetone, so that if no water is absorbed there will be no change in the gel under the conditions of this experiment. Experiment showed that there was a slow increase in the volume of the gel. The aqueous acetone was poured off periodically, its density determined, and the gel re-weighed. Fresh acetone of the same strength was poured on and the system left for a further period. Owing to the room temperature being rather low, there was too much acetone in the gel, and this diffused out during the first week. It is noteworthy that the gel remained clear. The figures are given in Table XIII. The value corresponding to time "infinity" was obtained by shaking up 5 gm. of nitrocotton repeatedly with 77·62% acetone, and then allowing the gelatinized nitrocotton to settle. This gives a system similar to the experimental one, except that the gel is not so clear and may contain some entrapped solvent. On standing, the volume of this gel decreases only very slightly, and therefore this volume may be considered to be the maximum value towards which the gel in the previous experiment tends to swell. The volume occupied by 1 gm. of nitrocotton and its sorbed solvent according to this experiment is 5·2 c.c. A similar experiment at the compatibility point, 80·15%, gave 1 gm. nitrocotton occupying 12 c.c.

TABLE XIII.—Swelling of Acetone-Nitrocotton Gel in Acetone-water. 5 gm. ML Nitrocotton + 5·9 gm. Acetone.

Time (weeks).	0.	1.	2.	3.	4.	6.	9.	19.	∞
Composition of aqueous acetone (%)	77·62	78·36	78·02	77·69	77·65	77·95	77·43	—	—
Increase in weight of N/C gel. in gm.	0	3·60	4·68	5·38	6·06	7·13	8·32	10·61	13·29

Viscosity—Concentration Curves and Solvation.

To determine the bearing of the solvation results on the viscosity relationships of nitrocotton-acetone-water, some measurements were made of the viscosities of solutions of nitrocotton in aqueous acetone.

Solutions of 0·5%, 10%, and 20% nitrocotton, in a range of five acetone-water concentrations were examined. These figures are given in fig. 7.

The acetone and the 0·5% nitrocotton solution were carried out by the Ostwald-Poiseuille method, and the other two concentrations by the falling sphere method. It may be observed that no particular care was taken to attain great accuracy in the determination of these viscosities, but relative to one another they are quite reliable.

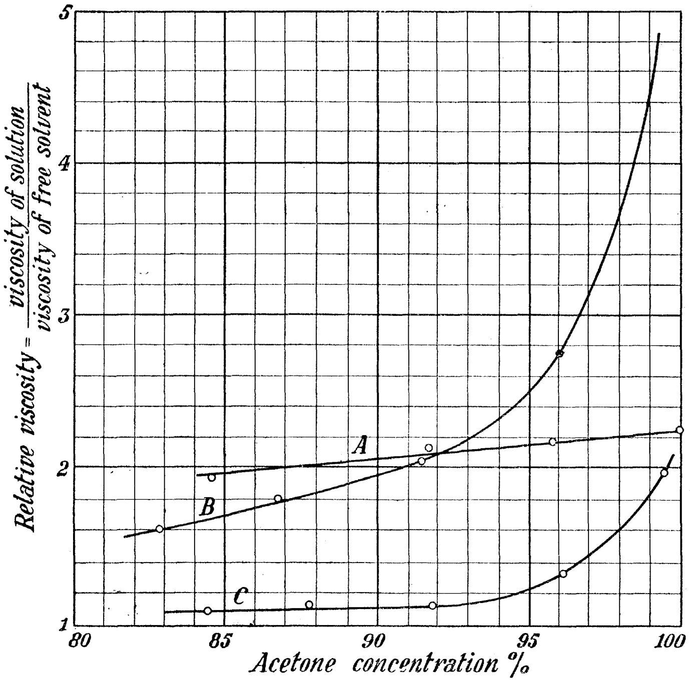

FIG. 7.—Relative viscosities of nitrocotton solutions in acetone-water at 20%. A. relative viscosity, 0·5% nitrocotton; B. relative viscosity × 10^{-4}, 20% nitrocotton; C. relative viscosity × 10^{-3}, 10% nitrocotton.

DISCUSSION.

Since acetone-water is a mixture of a solvent and a precipitant, at the outset of this work it was anticipated that only acetone would take part in the solvation phenomena. Unfortunately it is an extremely difficult thing to prove that no water enters into the solvation layer, or to estimate both acetone and water if both are there. It is necessary to use a reference substance which will not be attached to either of the constituents of the solvent or to the nitrocotton, and will not interfere in any way with the solvation process. This is, as far as we can see impossible, and were a substance to exist which seemed to fulfil these conditions, it would be necessary to prove that it did so, and since information on the solvation would be necessary to prove this, we should only have returned to the original problem. In spite of this, attempts have been made to use reference substances. Recently KOSAKEVICK* has employed CO_2 as a reference substance to determine the solvation of salts in non-aqueous solutions.

SVEDBERG and RINDE† have pointed out a method for determining the solvation layer on particles. This depends on determining the radius of the particle including the solvation shell, by centrifuging, and also the radius of the particle itself by some other means. It appears to be a very useful method, but unfortunately could not be

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* 'Z. phys. Chem.,' vol. 143, p. 216 (1929).

† 'J. Amer. Chem. Soc.,' vol. 46, p. 2692 (1924).

applied without further assumptions to a colloid such as nitrocellulose where the particles are very long and may be of varying shapes and sizes.

For such reasons the question of total acetone solvation in aqueous acetone must be approached rather by making the most reasonable inferences from as many facts as possible, than by rigid experimental proof. The experiments which have been recorded here give only a relative measure of the acetone solvated, but the solvation theory presented is made fairly probable by the fact that it does explain all the data in a reasonable way, and is not in conflict with any known facts.

Below the Compatibility Point.—From acetone-water of less than the critical concentration acetone is absorbed by nitrocotton in amount increasing with the acetone concentration. The nitrocotton swells and if the volume of the swollen mass is measured as has been described it is found that much more solvent has been taken up than is accounted for by determinations of apparent absorption carried out by any analytical means. This can be understood if we consider the nitrocotton as a mass of long molecules packed together nearly at random but with a tendency to associate in parallel bundles. The nitrocotton used had been dissolved and reprecipitated before use and the original micellar arrangement of the fibres is known to be greatly disorganized although not altogether lost by this treatment.

Now, owing to the lateral attraction between the chains there will be regions where they have partly aligned themselves and are firmly joined side by side, and other places where the packing is more open because the chains are tangled. We may then expect that the acetone absorbed penetrates the chains, even the closely packed ones, and by lessening the lateral attraction, allows relaxing of the chains and consequent swelling of the mass. The acetone-water outside enters and fills up the interspaces as these enlarge in the swelling process. This acetone-water is probably not really attached to the nitrocotton or the swelling would take place more quickly; it is more akin to the filling of the pores of a sponge. It is interesting to note that this gel, below the compatibility point, may with very low viscosity nitrocottons become quite liquid. This mobility would be a consequence of the chains being shorter and not interlocking to the same extent as normal nitrocottons. Those parts of the mass where the molecules were more loosely packed must be assumed to have been broken down by absorption of the solvent with the result that other parts in which the micellar arrangement was more complete could move about as a whole. Only by the action of aqueous acetone of greater than the critical concentration can the micelles be completely broken down.

The Compatibility Point.—As the activity of the acetone in the acetone-water increases the sorption of acetone proceeds, until a point is reached when the lateral adhesion of the chains is lost and shaking is sufficient to break up the swollen mass into a solution. The point at which solution takes place is the compatibility point, and the amount of acetone solvated is about 1·1–1·2 gm. per gram of nitrocotton. This corresponds to two acetone molecules per nitrate group or to a unimolecular layer. The calculation which arrives at a unimolecular layer of acetone is, of course, only an approximate one; the coincidence, however, is interesting. It would be impossible to distinguish between these two explanations in the present state of our knowledge.

The Solution Range.—By far the greater part of the work described has been concerned with the solution range above the compatibility point. Most of the experiments were made with solutions containing 12% of nitrocotton. Two outstanding results appear. The first is that as the activity of the acetone increases above that corresponding to critical solution, absorpton appears to fall. The second is that in solutions weaker than 12% the recorded values of solvation are higher.

The first result is very unexpected because all the other available evidence such as that obtained from experiments on the sorption of acetone vapour by nitrocotton makes it almost inevitable that the *total* solvation must increase with the activity of the acetone. It is possible to account for the observed facts only by supposing that in addition to the acetone some water must be absorbed. This absorption of water can hardly be continuous throughout the whole range of acetone concentration but must begin or at least become much more marked at the solution point.

The idea that the apparent sorption of acetone, as determined in this way, was the effect of the attachment of water and acetone separately, say, the acetone on the nitro-groups and the water on the hydroxyl groups, was considered at one time. Two smooth curves of similar shape could be postulated, which when combined would give an apparent acetone solvation rising to a maximum at the compatibility point, and then falling to zero at 100% acetone. That this is not a true explanation is shown by the fact that the apparent sorption calculated from two continuous separate sorption curves would always be continuous. Any theory of the sorption curve must therefore explain the discontinuity. The solution of nitrocotton is apparently a continuous process, but there is some change in the mechanism of solvation which begins when the nitrocotton goes into solution. Bearing this in mind we may proceed to a hypothesis which will explain the observed facts, particularly the second principal result. One supposes that below the solution point water is not appreciably attached to nitrocotton. In the act of solution the nitrocotton molecules surrounded by absorbed acetone separate from each other. If the solution is dilute, ½% or less, each solvated molecule will not interfere much with its neighbours and the solvation will rise as the activity rises without any break being seen at the solution point. This is in accord with the facts because, as has already been noted, the solvation has been found to rise with increasing acetone activity if the solutions are dilute, but in concentrated solutions the conditions are not the same; the chain molecules are in constant contact with one another and it may be supposed that where contact takes place water is also in some form of combination. The results of this are that the apparent sorption of acetone in concentrated solutions is lowered. Thus, although the *total* solvation of acetone continues to rise as the concentration of acetone increases in the concentrated solution, the apparent solvation which alone can be determined is found to fall, owing to the concurrent effect of the absorbed water. To the question of what value the *total* solvation finally reaches in pure acetone we can give no answer.

Temperature and Solvation.—There are several quantities in the region of the compatibility point that exhibit a variation with temperature. These are :—

(1) The value of the maximum apparent sorption.
(2) The critical solution concentration.
(3) The absorption value.
(4) The solvation value.

These four coefficients can all be measured and checked against one another, for if two are known the other two can be calculated. The maximum sorption coefficient thus calculated from the other three is 0·05 for 10 degrees rise. Fig. 4 shows how these coefficients can be obtained from the difference between the sorption curves at 20° and 30°.

An additional proof that the mechanism of sorption of acetone by nitrocotton undergoes a change at the compatibility point, is given by the reversal of sign of the temperature coefficient of sorption which takes place there. We may in a tentative way consider the differential heat of sorption Q to be made up of Q_1, the heat of formation of the acetone-water complex, Q_2 the heat of linkage of the solvated nitrocotton chains to one another, and Q_3 the heat of attachment of acetone to nitrocotton. Then $Q = -Q_1 - Q_2 + Q_3$. We know that heat is given out when nitrocotton is added to aqueous acetone, but this is the integral heat of sorption. Near the compatibility point the temperature coefficient of sorption is positive and accordingly by the Chatelier-Braun principle the differential heat of sorption Q must be negative, therefore we have $Q_1 + Q_2 > Q_3$. The reversal at the compatibility point must be due to changes in $(-Q_1 - Q_2 + Q_3)$. Now Q_1 will become numerically smaller, Q_2 may be expected to become negligibly small, and Q_3 is becoming gradually smaller. Above the compatibility point, since the temperature coefficient is negative, the heat of sorption must be positive and $Q_3 > Q_1 + Q_2$.

With more knowledge of the process of sorption and of the acetone-water-complex system it might be possible to develop these ideas further, but enough is not known yet about the process to allow of a detailed analysis.

Viscosity of Solutions and Solvation.—Turning now to the viscosities shown in fig. 7 we may consider whether the theory outlined above is in agreement with the effects of solvent and concentration on viscosity.

The only formula for the viscosity with a theoretical basis is that of EINSTEIN who deduced that $\eta = \eta_0 (1 + K\phi)$ where η and η_0 are the viscosities of solution and solvent respectively, ϕ is the fraction of the solution occupied by the dispersed phase and K is a constant usually taken as 2·5. The solution of nitrocellulose does not fulfil the conditions to which this formula applies, principally because of the shape of the molecules. It is not surprising, therefore, that substitutions of values for the viscosity at 0·5% in the formula gave a solvation of 100 in 100% acetone and 80 in 85% acetone in disagreement with the results of this work. KRAEMER and SEARS* carried out a similar calculation with the viscosities of a more dilute solution and obtained a similar result.

The factor K has undoubtedly a higher value for long-shaped molecules. JEFFREY† and more recently EISENSCHITZ‡ have developed the hydrodynamic theory of long particles. The latter has concluded that solvation does not cause the high viscosity of such solutions. Nevertheless it is probable that except in the most dilute solutions the solvation shell is a contributing factor towards high viscosity, since otherwise the relative viscosity should be the same in various solvents.

The high viscosity of nitrocotton solutions is, however, primarily due to the long molecules of the dispersed substance. The viscosity is presumably high because the chain-molecules touch each other. The contacts, however, need not be of more than momentary duration. In a qualitative way we can see that the number of contacts in weak solutions will be some function of the lengths of the chains. In stronger solutions the chains are much closer together and it is reasonable to suppose that the thickness of the molecule as well as the length will now determine the number of contacts. The solvation shell will not change the length of the molecule of nitrocotton, though it may alter its mode of vibration, but it will greatly change the thickness. In strong solutions but not in weak ones the viscosity should depend on the solvation.

In 0·5% solution the viscosity does not change much with the increased solvation (which we assume takes place on proceeding from 80% to 100% acetone) because at this concentration the length of the molecule is determining the number of contacts and hence the viscosity. In 10% and in 20% solution when practically all the solvent is to some extent attached the effect of the variation in the thickness of the molecules on the viscosity is apparent; there is a rise in the viscosity on proceeding from 85% to 100% acetone.

The viscosity, then, we consider to be dependent on all three factors: (1) solvation, (2) concentration, (3) length of the molecules. Fig. 6 gives the variation in viscosity when (2) and (3) are kept constant. Numerous graphs are available in the literature for the variation in viscosity when (1) and (3) are kept constant, but until the nature of the relationship between viscosity and chain length is known, no empirical formula can be derived for the viscosity in terms of solution concentration and chain length.

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* ‘J. Rheology,’ vol. 1, p. 231 (1930).

† ‘Proc. Roy. Soc.,’ A, vol. 102, p. 161 (1922).

‡ ‘Z. phys. Chem.,’ A, vol. 158, p. 78 (1932).

Summary.

The addition of an acetone-water mixture to nitrocellulose may cause solution or merely swelling according to the concentration of acetone.

Where swelling results, it is known that the ratio of acetone to water imbibed is more than that existing in the bulk solvent. This may be expressed as an apparent absorption of acetone if in the calculation it is assumed that only acetone is attached.

The work described here consists of measurements of the acetone similarly attached to the nitrocotton where a solution results. The figures have been calculated from the lowering produced in the total vapour pressure of acetone-water mixtures when nitrocotton is added. This lowering is not due to osmosis, but to the abstraction of the volatile acetone by the nitrocotton.

Measurements have been made with several samples of nitrocellulose with various acetone-water mixtures, with different proportions of nitrocellulose to acetone-water and at different temperatures.

It is found that there is always a positive absorption or solvation of acetone which is not greatly different for the various nitrocelluloses. With a concentration of 12% nitrocellulose and different acetone-water mixtures, the solvation is greatest with that mixture which just effects solution, and falls off to zero with 100% acetone.

With lower concentrations of nitrocellulose, however, the solvation is found to be higher, in some mixtures richer in acetone. The effect of temperature is to lower the solvation.

These results are discussed and a tentative theory is advanced to account for them. It is suggested that in mixtures where there is sufficient acetone to cause solution, water is solvated as well as acetone and that this causes the solvation of acetone to seem to fall as the acetone-water ratio becomes greater. In dilute nitrocellulose solutions, however, it is considered that water is not so absorbed and that although actually no more acetone is solvated, the apparent value is much higher. The difficulty of working with more dilute solutions of nitrocellulose unfortunately makes it hard to prove this. The bearing of the results on the viscosity of solutions of nitrocellulose in acetone-water is discussed.