

SOME STUDIES
IN
ELASTIC ORGANIC COLLOIDS

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SOME STUDIES
IN
ELASTIC ORGANIC COLLOIDS

THESIS

BY WILFRED GALLAY, B.A.

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CONTENTS

	<u>Page.</u>
1.- INTRODUCTION	1
2.- SOLVATION	3
3.- VISCOSITY IN ORGANOPHYLIC SOLS	12
4.- VISCOSITIES OF SOME RUBBER SOLS	21
5.- PRECIPITATION OF ORGANOPHYLIC COLLOIDS	31
6.- FRACTIONATION OF POLY VINYL ACETATE	40
7.- FRACTIONATION OF RUBBER	49
8.- WATER ABSORPTION BY RUBBER	61
9.- SUMMARY	67

INTRODUCTION (1)

Some years ago, the study of systems containing particles of colloidal size became sufficiently important to warrant the recognition of a new branch of chemistry. It soon became evident that these disperse systems could be placed definitely under one of two classes, lyophobic and lyophylic. The properties of these two classes of dispersoids are widely different; the most important distinction, and one to which most of the others differences may be ascribed, lies in the mutual attraction between the disperse phase and the dispersion medium.

In a system such as a gold hydrosol, where we have reason to believe that little or no affinity evinces itself between disperse phase and dispersion medium, we have an example of a lyophobic sol, or in this case, hydrophobic, since water forms the continuous phase. In contradistinction to this, in the case of a dispersion of gelatin in water, where the two phases exhibit definite attraction for each other, we have an instance of a hydrophylic sol, differing markedly in many of its properties from those of the former.

Of late years, these hydrophylic systems, previously rather neglected, have sprung more into prominence, the chief reason probably being their physiological and industrial importance. More recently still, that branch of lyophylic colloids which disperse in organic solvents have attracted the attention of chemists. To this group has been ascribed the term "organophylic colloids".(2)

Since water is a powerful ionizing medium, investigators in hydrophylic systems have been severely hampered by the effects of electrical and ionic influences. Just how great a part these influences play in the stability and even structure of a hydrophylic system is not known. It is obvious therefore, that the organophylic systems present a field of research where these complicating factors are present to little or no extent, since the solvent is usually non-ionizing. Furthermore the number of solvents available being virtually unlimited, the number of systems under observation is multiplying rapidly, and many of these will doubtless be directly applicable industrially.

In the present work, no attempt has been made to dwell on any one topic, but, as the title indicates, various studies have been undertaken in different organophylic systems with a view to shedding more light upon several important phases of the subject.

SOLVATION

Since the attraction of the dispersed colloid for the continuous phase constitutes the salient characteristic of an organophylic system, and since the effects of this attraction must necessarily affect to a great extent every discussion of phenomena in such systems, it would be well to devote some time to a consideration of this matter.

Because of this attraction, colloidal particles dispersed in a continuous phase, by means of forces not clearly understood, bind a part of the solvent in some sort of combination; the net result being that less solvent is present in the "free" condition than before. This is known as "Solvation".

The stability of a dispersoid depends upon two factors, the charge of the particles and solvation. Since organophylic systems entail usually only non-ionizing solvents, the charge can play only a very small rôle. Solvation, then, including both imbibition of solvent and presence of a protective layer of bound solvent around the particle, must be the chief factor upon which the very existence of the sol as such, depends.

Experiment has shown that in the swelling of a colloid, imbibition takes place very rapidly at first, reaching an equilibrium more slowly. Since the intensity of solvation is evidently inversely proportional to the amount of solvent already taken up, it may be concluded that varying parts of the solvent are bound with different degrees of firmness. Probably the outermost layers of bound solvent are held by

very loose forces indeed, and the amount of solvation will naturally vary with many different conditions.

Solvation and degree of dispersion.

The attraction between particle and solvent is exercised first at the surface where the two come into contact. It might be concluded that the greater the specific surface of the disperse phase the greater will be the solvation, but it must be admitted that very little direct experimental evidence can be adduced for this reasoning. Kuhn(3) quotes experiments on heats of solution as evidence for this. The heat of solution has been shown to run parallel with the amount of surface. Ariz has shown that a 10% gel swelled much faster than a 20% one, and Freundlich offers the explanation that in the formation of a 10% gel from one of a higher concentration by dilution, more micelles have been formed which can take up more solvent.

Solvation and Temperature.

McBain and Salmon(4) have carried out experiments on the change of solvation with temperature, using a sodium palmitate hydrosol. They found a definite lowering in the amount of solvation with rise of temperature, but they further conclude from their work that this change is very small. The desorption method of measurement was used. For example:

at 90°	-----	2.16 moles H ₂ O / 1 mole Na Palmitate,
" 80°	-----	2.32 " " " "
" 40°	-----	2.40 " " " "
" 16°	-----	2.60 " " " "

There is no doubt that the amount of solvation changes with

change in temperature. From theoretical considerations, it may be explained that the outer layers of bound solvent are more greatly affected by thermal agitation at higher temperatures and will free themselves from the particle to a greater extent with successive rises in temperature. Although conditions differ widely in each system, we may even observe a definite upper limit to solvation. Thus particles of an albumen sol are solvated at lower temperatures but flocculate at a higher temperature.

The total solvation for the purpose of relative measurements, may be divided into two parts. If we consider a dispersion of rubber in benzene, for example, a large amount of the solvent is associated with the disperse phase, but we have no method whereby the amount may be measured. If now there be added to the system sufficient acetone to just produce a visible flocculation, the rubber has been partly desolvated. By allowing the precipitate to settle and then by drying, the second^{stage}/of desolvation may be carried out. In the latter case the difference in weight before and after drying gives direct measurement of the solvation of the highly swollen visible precipitate.

In the present instance an attempt was made to measure directly the change in amount of solvation with change in temperature, assuming that at the end of the first^{stage}/of desolvation, the disperse phase in all cases is brought to the same degree of solvation. If we consider a sol of cellulose acetate in acetone, we may assume that the system is composed of

particles of the disperse phase which have bound a part of the solvent, and that these particles are suspended in the remaining free solvent. If we add water to this system, two forces oppose each other. Both the colloid and the water~~me~~ attract the acetone, but if the water-acetone attraction is great enough, then the particles will be sufficiently de-solvated to flocculate. As will be shown in a later chapter, this de-solvating effect is exactly opposite to swelling. It is very often the case that liquids which do not swell such colloids as rubber or cellulose acetate will de-solvate or precipitate them from a dispersoid, providing, of course, that the liquids added are miscible with the continuous phase of these systems.

Madgen, Peel and Briscoe(5) have investigated these forces among liquids to some extent, and have concluded from their data that an added liquid will distribute itself definitely between two miscible liquids according to the ratio of its attractive forces for these liquids.

Various sols were prepared for this purpose and 50 cc. of sol used in each experiment. A Pyrex tube, about 5cm. in diameter and 30cm. in length, closed at one end, was set up in a thermostat. A mechanical stirrer giving vertical motion was placed inside in order to further ensure constant temperature of the contents of the tube. In each experiment 50cc. of sol were introduced into the tube and allowed to come to the required temperature. The precipitant was then added slowly from a burette, with constant stirring. The addition

of the precipitant was sufficiently slow so that the temperature of the contents of the tube was not appreciably changed. The end-point was taken when the first permanent visible precipitate appeared. Check experiments showed an experimental error of about 1%.

Experiment #1

Sol, ----- Cellulose acetate in acetone,

Concentration, ----- 1%,

Precipitant. ----- Distilled water,

<u>Temp.</u>	<u>No. cc's H₂O req'd,</u>	<u>Vcl.% Precipitant in Sol.</u>
48°C.	25.6	33.9
38°C	23.1	31.6
28°C	21.0	29.5
13°C	16.6	24.9
1.5°C	13.8	21.6

Experiment #2

Sol, -----Cellulose acetate in Benzyl alcchl,

Concentration, ---1%

Precipitant, ---Tertiary Butyl alcchl,

<u>Temp.</u>	<u>No. cc's Alc. req'd,</u>	<u>Vcl.% Precipitant in Sol.</u>
60°C	132	72.5
50°C	74	59.7
40°C	45	47.4
30°C	28	35.9

Experiment #3

Sol, -----Cellulose acetate in Benzyl alcohol,

Concentration,--2%

Precipitant, --Tertiary Butyl alcohol,

<u>Temp.</u>	<u>No. cc's Alc. req'd,</u>	<u>Vcl. % Precipitant in Sol.</u>
60°	108.4	68.4
50°	68.2	57.7
40°	42.2	45.7
30°	25.4	33.7

Experiment #4

Sol, -----Cellulose acetate in Benzyl alcohol,

Concentration, -3%

Precipitant, -Tertiary Butyl alcohol,

<u>Temp.</u>	<u>No. cc's Alc. req'd,</u>	<u>Vcl. % Precipitant in Sol.</u>
60°	85.2	63.0
50°	56.2	52.9
40°	34.8	41.0
30°	23.6	32.0

These results are shown graphically in Figs I and II, where are plotted in the one case the number of cc's of precipitant required against temperature and in the other case the percentage volume of precipitant present in the system.

No comparison can be made, of course, between the acetone sol and the benzyl alcohol sols. Different precipitants were used in each case and different attractive forces naturally obtain in each instance. But it is a striking fact

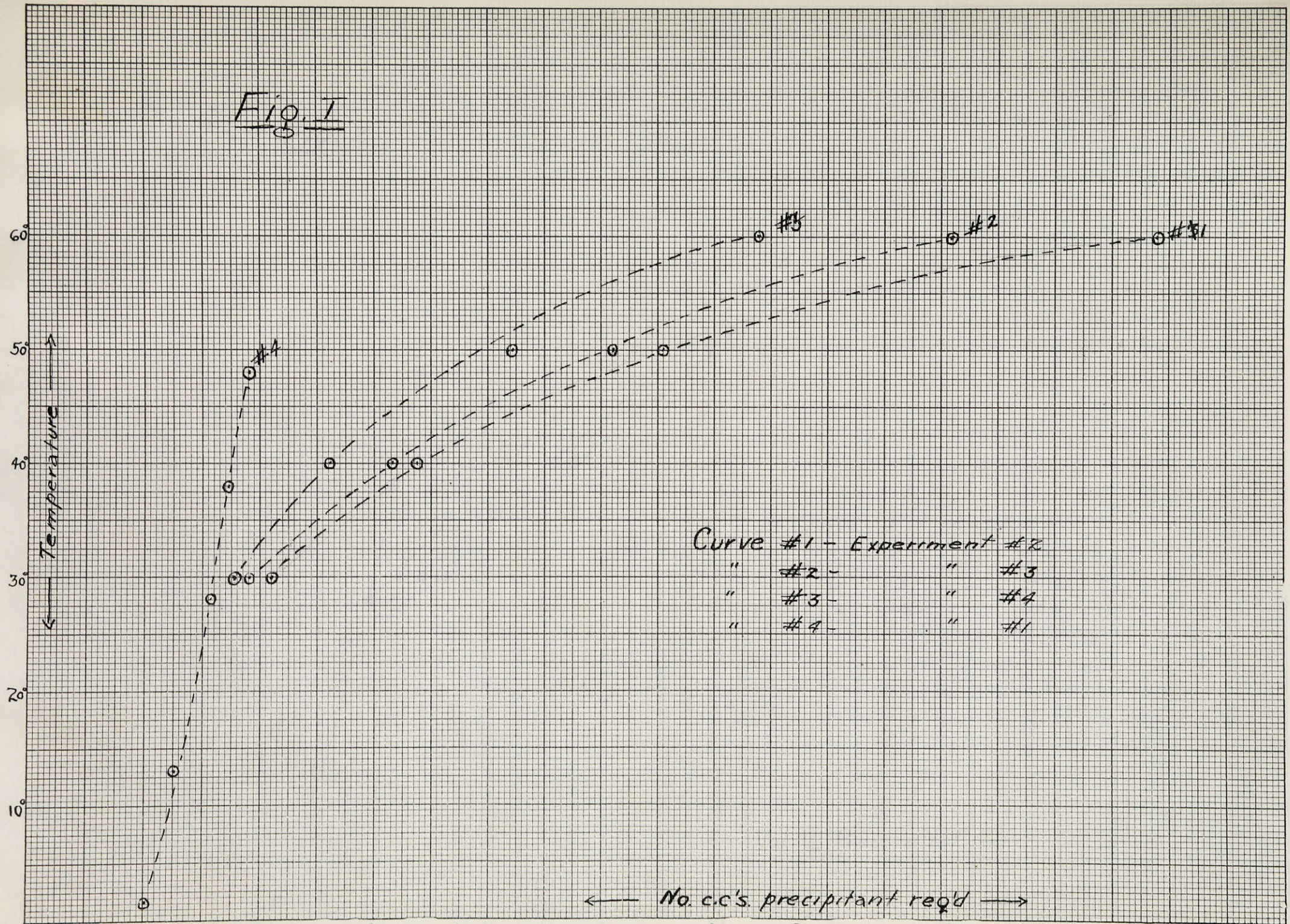
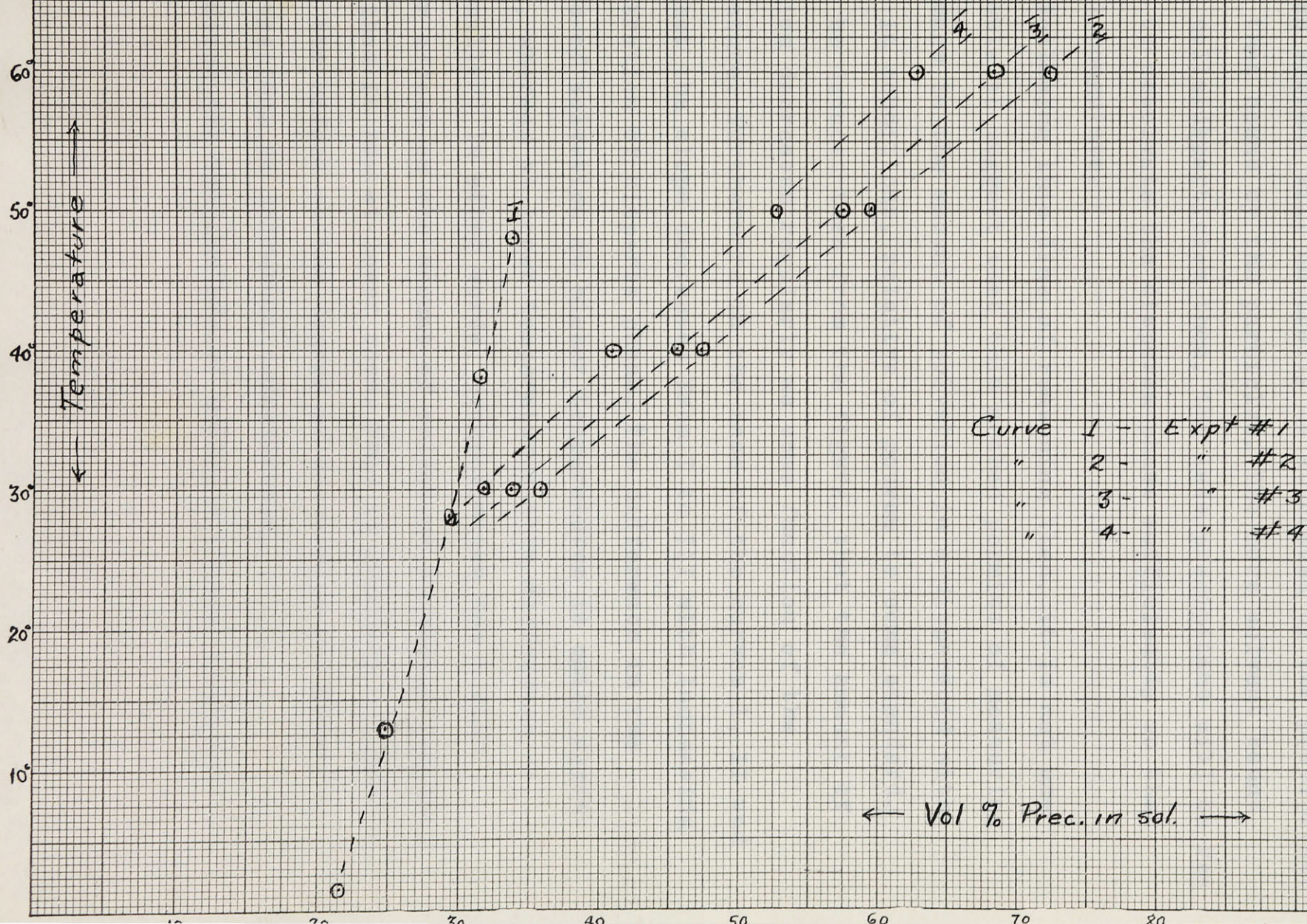
Fig. I

Fig. 2

that in each of the four trials a definite relationship is shown between the amount of precipitant required and the temperature. Furthermore, the amount of precipitant required is a measure of the amount of free solvent in the sol, because the free solvent will naturally be attracted by the precipitant before that bound by the particles. The more solvent bound by the colloidal particles then, the less precipitant will be required to desolvate the disperse phase sufficiently so that it will coagulate.

Following this line of reasoning then, it is not unreasonable to suggest that this method permits of measuring the change in the amount of solvation in a dispersoid with change in conditions, relative of course to some standard. It may be deduced then from the figure, that the amount of solvation decreases regularly as some function of the temperature. Furthermore in the case of the curves I, II and III, that the slope decreases from I to III with increasing concentration of disperse phase. The difference in the amounts of solvation at higher temperatures is quite appreciable, whereas at lower temperatures this difference is much smaller. In other words, concentration has a much greater effect on the amount of solvation at higher temperatures than it has at lower ones. This is probably accounted for by the effect on the degree of dispersion of different concentrations at different temperatures.

Since the temperature of gelation of the 2% sol. is

slightly lower than that of the 3%, and similarly that of the 1% is lower than that of the 2% sol, we have the interesting fact, there is very little difference between the amounts of solvation of these sols at the temperature of gelation.

Solvation and Time.

Time has a very decided effect on solvation. It exerts at first, however, diametrically opposed effects in different cases. For example, it has often been noticed that the viscosity of a rubber sol in benzene falls off with time to an equilibrium value. Opposed to this, we have the case of the gelation of a gelatin sol on standing. It seems probable however that over long periods of time the amount of solvation does decrease in every case, as evidenced by syneresis in the case of a gelatin gel.

Measurement of Solvation.

A tentative relative method has already been advanced for change in solvation with temperature (vide supra). The maximum swelling of a colloid has also been used. The substance is allowed to swell, and either the weight or volume increase measured. It is obvious however, that this cannot be a measure of the amount of solvation for the latter goes further, every molecule of liquid influenced by the micelle must be locked upon as being combined. The viscosity of a solution has also been used as a measure of the amount of solvation. But it must be borne in mind, that if any sort of structure in a sol is admissible, then the viscosity becomes not simply a

measure of the inner friction of the system, but is changed greatly by the deformability of this structure. It would seem then, that both the viscosity and maximum swelling methods used are open to grave objections. The precipitation method mentioned may prove useful for various relative measurements upon more extended trial.

Theory of Solvation.

Beyond the fact that a part of the continuous phase is held bound by the colloid particles, very little is known concerning the forces coming into play. Van Bemmeln(6) classifies the forces as follows:

1.- Adsorption forces. In this case the solvent is held by the surface valencies of the colloid micelle. These forces are very great, instances being observed(7) where as much as 8% H_2O remained combined at $200^{\circ}C$. In a sense, this is not true solvation, since a non-solvated particle would also exercise forces of adsorption.

2.- Absorption. By this means the major part of the solvent is held. Within the micelle, there are probably present spaces of colloid dimensions and here the solvent is held enmeshed.

Von Weimarn(8) speaks also of chemically bound solvent but nothing definite is known regarding this.

3.-Capillary forces. Wherever spaces of capillary dimensions are present, these come into play in holding the solvent.

VISCOSITY IN ORGANOPHYLIC SOLS.

Whether we regard a gel as a liquid-liquid system(9) or a solid-liquid system(10), whether it possesses one or two phases, that a firm structure obtains, is undeniable. Yet we find a very fluid sol of low concentration setting to a gel at a relatively high temperature (loc.cit.). Some change has occurred in this transformation from sol to gel and this change can take place in one of two ways or a combination of both. Either the change is gradual towards a firm structure or an abrupt transformation occurs at the maximum temperature required for gelation.

The effect obviously must be wholly ascribed to the lowering of temperature since this has been the only change made. This effect seems to be two-fold to the writer. It will certainly cause an increased solvation, and hence an increased viscosity, and if any loose structure obtains in the sol, this structure will be rendered firmer by lowering of temperature, since thermal agitation will not be so effective in destroying it. When a temperature has been reached, such that, owing to increased solvation and more definite structure, the latter is sufficiently firm to retain a definite form, then the change from sol to gel will have occurred.

Mardles(11) has determined the viscosity-temperature relationship in sols of cellulose acetate in benzyl alcohol using different concentrations. In the present investigation this has been extended to several other sols.

Sols of cellulose acetate were made up in the following solvents: Benzyl alcohol, phenyl ethyl alcohol, ethyl benzoate, acetone and cyclohexanone, of different concentrations. They were allowed to stand at a temperature of 35°C-40°C for about one month, when dispersion was complete.

The viscosities were measured in an ordinary capillary viscometer of the Ostwald type immersed in a thermostat. The sols were kept above their gelation point throughout. The term relative viscosity here is the ratio of the viscosity of the dispersoid to that of the solvent.

Experiment #1

Sol, -----Cellulose acetate in Phenylethyl alcohol,
Concentration, -2%

<u>Temp.</u>	<u>T.O.F. Sol'n</u>	<u>T.O.F. Solvent</u>	<u>R.V.</u>
33°C	2880	810	3.55
39	2287	650	3.53
45	1835	528	3.48
50	1513	455	3.33
54	1336	410	3.26
64	986	317.4	3.11

Experiment #2

Sol, -----Cellulose acetate in Phenylethyl alcohol,
Concentration, --1%

<u>Temp.</u>	<u>T.O.F. Sol'n</u>	<u>T.O.F. Solvent</u>	<u>R.V.</u>
45°C	1112	528	2.11
50	931	455	2.05
54	824	410	2.01
64	630	317.4	1.97

Experiment #3

Sol, ----- Cellulose acetate in Benzyl alcohol.

Concentration, 2%

<u>Temp.</u>	<u>T.O.F. Sol'n</u>	<u>T.O.F. Solvent</u>	<u>R.V.</u>
27°	3730	520	7.18
30.5	3283	483	6.82
33	2887	446	6.47
38	2368	395	6.00
50	1495	291	5.13
54	1326	265	5.00
64	996	216	4.61

Experiment #4

Sol, ----- Cellulose acetate in Benzyl alcohol.

Concentration, 1%

<u>Temp.</u>	<u>T.O.F. Sol'n</u>	<u>T.O.F. Solvent</u>	<u>R.V.</u>
23.5°	1690	590	2.84
30.5	1338	483	2.77
38	1044	395	2.64
50	719	291	2.47
54	643	265	2.43
64	498	216	2.31

Experiment #5

Sol, ----- Cellulose acetate in Acetone.

Concentration, 1%

<u>Temp.</u>	<u>T.O.F. Sol'n</u>	<u>T.O.F. Solvent</u>	<u>R.V.</u>
9°	200.4	52.0	3.85
25	148.0	47.3	3.13
33.7	128.6	43.0	3.00

Experiment #6

Sol, ----- Cellulose acetate in Acetone,

Concentration, 2%,

<u>Temp.</u>	<u>T.O.F. Sol'n</u>	<u>T.O.F. Solvent</u>	<u>R.V.</u>
9°	775.6	52.0	14.90
25	513.5	47.3	10.86
33.7	419.3	43.0	9.75

Experiment #7

Sol, ----- Cellulose acetate in Cyclohexanone

Concentration, 1%

<u>Temp.</u>	<u>T.O.F. Sol'n</u>	<u>T.O.F. Solvent</u>	<u>R.V.</u>
9°	1406.7	331.4	4.42
25	813.4	238.6	3.83
33.7	642.8	206.4	3.11

Experiment #8

Sol, ----- Cellulose acetate in Cyclohexanone,

Concentration, 2%

<u>Temp.</u>	<u>T.O.F. Sol'n</u>	<u>T.O.F. Solvent</u>	<u>R.V.</u>
9°	4492	331.4	13.55
25	2288	238.6	9.59
33.7	1676	206.4	8.12

Fig. 3.

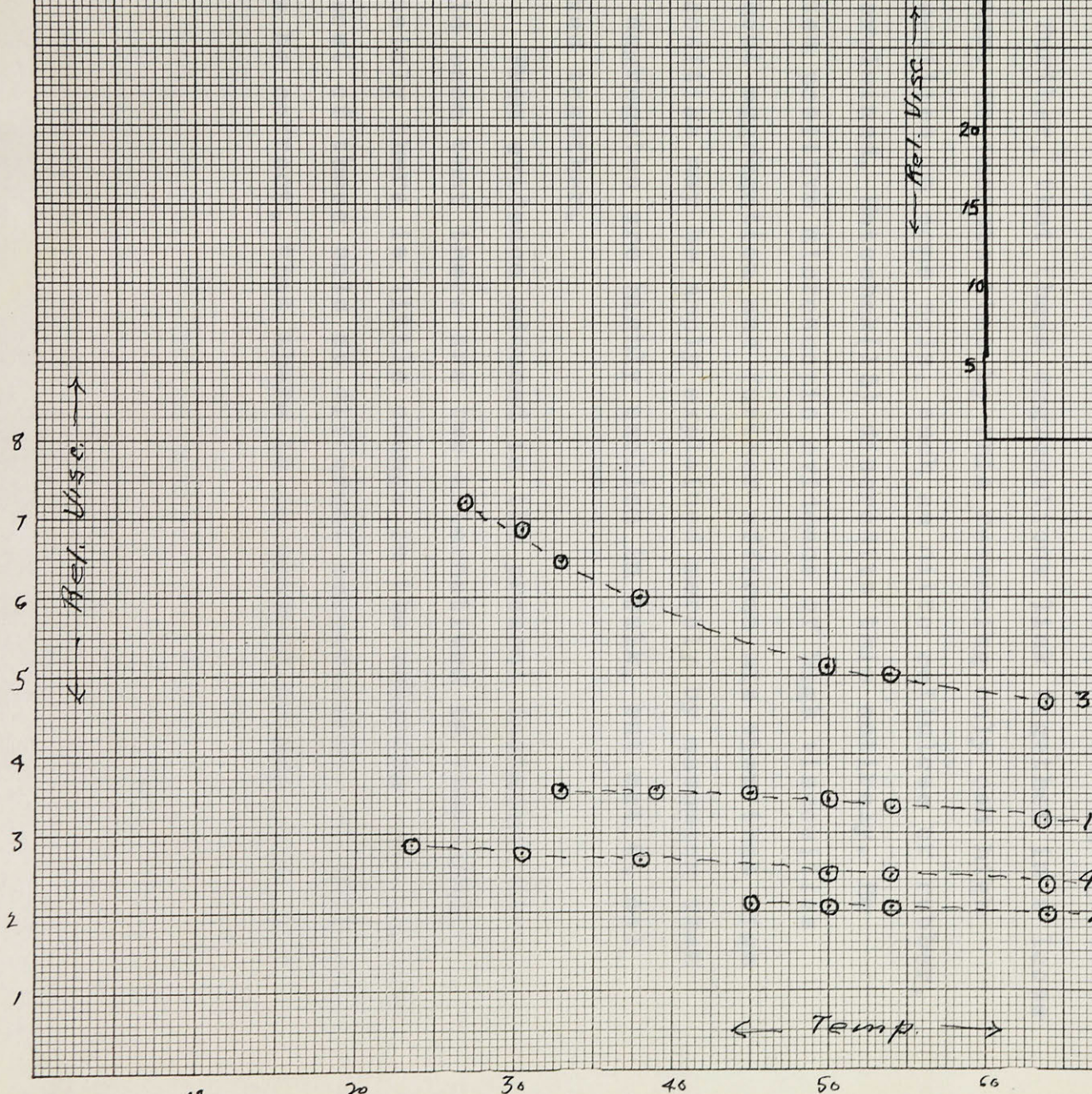
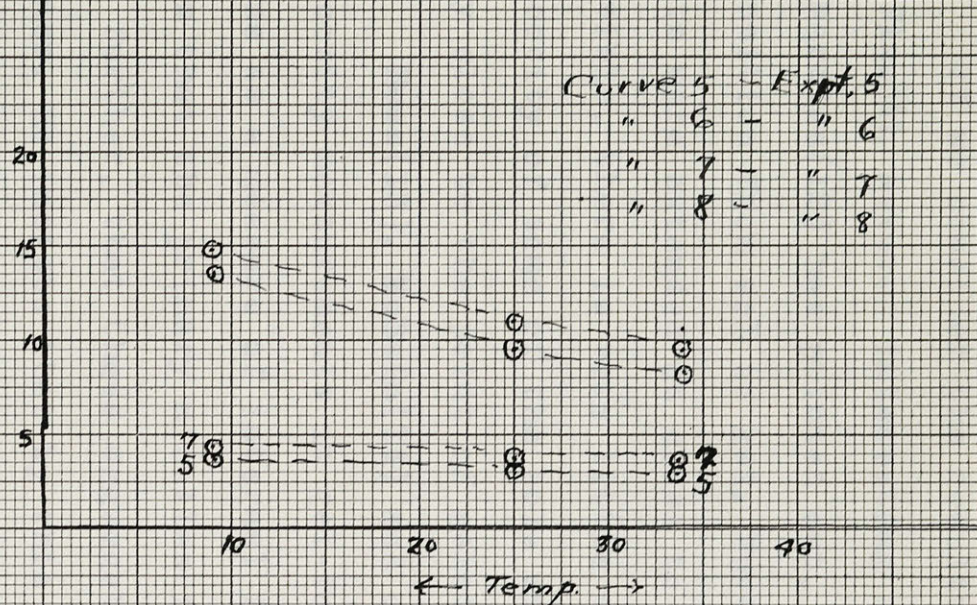


Fig. 4.



Curve 1 - Expt. 1.
" 2 " 2.
" 3 " 3.
" 4 " 4.

If we consider the results as illustrated graphically in Fig. 3&4, several interesting conclusions seem tempting. As Mardles(12) has pointed out, there is certainly no abrupt transition from sol to gel. Furthermore, since the measurements were extended as close to the gelation temperature as possible, there is very little difference in the relative viscosity of some of the sols with change in temperature, even very close to the point of gelation.

Hess(13), McBain(14) and others have pointed out that viscosity measurements in gel-forming sols may be of dubious value as a measure of internal friction. McBain takes the view that the primary micelles form clusters or aggregations and further, that these aggregations link together in a loose manner. He insists that by this reasoning only can high viscosities in some sols, such as nitro cellulose or rubber, be explained. Hatschek(15) discredits this entirely. He quotes positive microscopic evidence of high viscosities without aggregation and further affirms his view that high viscosities may be amply explained merely by assuming that the aggregates are highly swollen in bulk, but not at all linked together.

From evidence adduced in the present instance, it would seem that there are two alternatives in reasoning. Certainly there is little change in the relative viscosities of most of these sols at different temperatures. If Hatschek's view be correct, that there is no network of any sort, it

would seem necessary to assume very highly solvated aggregates at higher temperatures, requiring but little change to assume a definite structure as in a gel. If McBain's view be taken, a loose structure must be presumed at higher temperatures, which, with increased solvation and decreased thermal agitation, becomes firmer with fall in temperature.

McBain views as absolutely untenable Hatschek's contention that, in a highly viscous system, the disperse phase must have taken in practically the whole of the dispersion medium. He quotes sorption experiments on nitrocellulose, where he finds that nitrocellulose takes only its own weight of solvent. Hatschek deprecates the value of this evidence and quite rightly enough, for sorption experiments can give little idea of the magnitude of solvation, since in the sol, all the solvent influenced by the micelles must be regarded as bound.

In the present instance a method at least more direct than sorption was tried. A 2% sol of cellulose acetate in acetone was prepared and distilled water was added slowly with vigorous stirring until a permanent, faintly visible precipitate appeared. This was allowed to settle out and its weight was taken. The swollen mass was then dried in an air oven at 70° and then in vacuo. The difference in weight was the amount of solvation of the precipitate which had been formed.

Experiment #1,

Sol, ----- Cellulose acetate in acetone,

Concentration, 2%

Precipitant, -- Water,

Solvation of precipitate, -- approx. 700%

A check on this gave an identical result within experimental error.

Experiment #2 (16)

Sol, ----- Rubber in Benzene,

Concentration, 1%

Precipitant, -- Acetone,

Solvation of precipitate, -- approx. 1000%

A check on this gave practically the same results.

It is difficult, of course, to conjecture just how much bearing this has on the true solvation of the sol. At the time of appearance of a precipitate, the particles must have been already desolvated to a large extent, so that the amount of actual solvation is probably very much higher than the figures quoted above. At any rate, the latter may certainly be considered as being values far too low for the actual amount of solvation.

The writer finds it difficult to understand ^{why} the two views of McBain and Hatschek are considered to oppose each other absolutely definitely. McBain assumes a structure of ramifying aggregates. But Hatschek(17) himself admits that his well known formula:

$$\eta' = \eta \frac{1}{1 - \sqrt[3]{Q}}$$

$$Q = \frac{\text{Vol. disp. phase}}{\text{Total volume}}$$

expresses a structure, necessarily. Both admit a structure, then; the only difference being that McBain ascribes this structure to ramifying aggregates, and Hatschek's formula

entails the idea of bound solvent - possibly not true solvation but great swollen micelles with practically all of the solvent held bound, in the case of very viscous sols.

It appears to the present writer, first of all, that probably no two sols are alike in structure. With change in temperature, the change in relative viscosity in some instances is very slight, in others very marked. In experiment #1 (vide supra), the change in relative viscosity is very small over a range of 31° . On the basis of Hatschek's idea, this would have to be accounted for by a very small change in solvation. But this is not at all compatible with data on the change of solvation with temperature. It would seem that some structure obtains here, constituting the chief factor causing viscosity in the sol. On the other hand, in experiment #8, change in temperature causes a very marked difference in relative viscosity. Here, change in the amount of solvation with temperature can account for the change in viscosity.

There is of course no doubt that solvation is a factor to be reckoned with in all cases in dealing with viscosity. But from the evidence adduced, it seems very doubtful as to whether it is the only factor. A loose structure of some sort together with solvation would certainly account for some observations much better than solvation alone. The solution might very probably lie in a compromise between the two. In that case, both factors would play a part in the viscosity of every sol. Owing to inherent properties of each sol, however, and the special forces obtaining between dispersion medium and disperse phase in each case, the relative strengths

of these two factors would be different in each instance. A predominance of one or other of these forces would result in such properties of a particular sol as ease of gelation, variability of viscosity with temperature, etc..

It is interesting to note that a sol of cellulose acetate in phenylethyl alcohol of 2% concentration gelled when allowed to stand at a temperature of 35°. Successive gelation and solation was found to have only a very small effect on the viscosity of these sols, the figures varying to a small extent about a mean value.

VISCOSITIES OF SOME RUBBER SOLS.

Kirchhof(18) has determined the viscosities of sols of rubber in several solvents and has calculated the volume of the disperse phase relative to the dispersion medium, on the basis of Hatschek's equation,

$$\phi = \left(\frac{n' - n}{n} \right)^3 \qquad \phi = \frac{\text{Vol. of disperse phase}}{\text{Total volume}}$$

Pcsnjak(19) determined the amounts of these solvents taken up by rubber at equilibrium, using the sorption method.

Hatschek(20), on the basis of the above work, has generalized to the effect that rubber swells more in the solutions in which it exhibits high viscosities. From the discussion in the previous section, it may be readily seen that Hatschek considers this important evidence for his theory that viscosity in a lyophobic sol depends upon solvation or swelling.

It was found also by Kneevenagel and Bregenzner(21) in the case of acetcellulose, that liquids which produced greater swelling prior to dispersion gave more viscous solutions than liquids which produced smaller swelling. Duclaux(22) on the other hand considers it impossible to explain viscosity on the basis of solvation from his data.

Conclusions were drawn in each of the above instances from comparatively few examples. In the present work, the number of sols used has been much extended, covering a variety of types of solvent.

Preparation of Sols.

Pale crêpe of good quality was extracted for a week at room temperature with a 75-25 acetone-petroleum ether mixture. The extraction medium was renewed every 48 hours. Then the crêpe was cut up finely and dried in vacuo for three days.

Whenever impurity was suspected, the solvent was purified by fractional distillation. Solutions were made up to a concentration of 0.328 gms per 100 cc's of solvent. To obviate evaporation in the case of the low boiling solvents, tin foil was wrapped around the stoppers and the latter were sealed with paraffin. The solutions were kept in a dark cupboard at room temperature and shaken frequently.

At the end of two weeks, the solvents could be divided into three classes with respect to their ability to dissolve rubber quickly.

Group I -- All the rubber in solution.

Group II -- Nearly all the rubber dissolved

Group III - Rubber highly swollen, but only partly in solution.

<u>Group I</u>	<u>Group II</u>	<u>Group III</u>
Ethyl iodide	N-Butyl ether	Caprylic acid
Anisole	Is-Amyl salicylate	Pentane
Piperidine	O-Tolyl mustard oil	Hexane
Benzyl chloride	Is-Safrol	Heptane
Ethyl salicylate	N-Butyl benzoate	Octane
Benzotrichloride	Chloroform	Methyl n-butyrate
Methyl iodide	Carbon tetrachloride	Heptaldehyde
Diethyl aniline		N-Butyl thiocyanate
Is-Butyl chloride		N-Heptylic acid
Safrol		Pelargonic acid
Acetal		N-Butyl aniline
Ethylpropyl ketone		
Dipropyl amine		
Methyl cyclohexane		
Benzal chloride		
Tetralin		
Phenetole		
Dimethyl aniline		
Is-Butyl salicylate		
Is-Amyl benzoate		
Is-Butyl benzoate		
Dichloroacetic acid		
Is-Amyl acetate		
Benzene		
Ethyl benzoate		
Phenyl mustard oil		

The viscosities of these sols were measured in an ordinary Ostwald viscometer, immersed in a thermostat constant to 0.002°. By relative viscosity is meant the ratio of the viscosity of the solution to that of the pure solvent. The figures given for the swelling in gms of solvent taken up per gm of rubber, were taken as given by Whitby, Pasternack and Evans(23). The figures for swelling in cc's of solvent taken up per gm of rubber, were calculated on these. The dielectric constants of the solvents, when obtainable, were taken from Landolt-Börnstein.

No.	Solvent	T.O.F.		Rel.Vis.	D.K.	Swelling	
		Solv't	Solv'n			gms/gm	cc's/cc
1	Acetal	68.1	72.8	1.068	3.45	10.13	12.3
2	Ethyl iodide	34.9	37.7	1.080	7.42	v.great	v.great
3	Anisole	112.2	302.7	2.698	4.35	12.72	--
4	Safrol	236.8	557.6	2.355	3.06	9.51	--
5	Methyl iodide	26.7	46.6	1.745	7.1	v.great	v.great
6	Tetralin	237.8	483.9	2.035	--	--	--
7	Phenetole	130.6	387.8	2.969	--	12.90	13.4
8	Diethyl anil.	230.6	391.0	1.695	--	9.62	10.4
9	Benzal chlor.	160.6	242.8	1.512	--	10.11	7.7
10	Dichloroacetic acid	466.4	493.4	1.058	8.22	7.9	5.1
11	Dimethyl anil.	152.1	335.8	2.207	5.07	12.55	13.1
12	Ethyl benzoate	205.6	301.9	1.468	--	6.78	6.5
13	i-Amyl "	372.6	401.8	1.079	--	8.2	8.3
14	Tert. Butyl chloride	63.8	71.2	1.116	--	--	--
15	Methylcyclohexane	96.5	142.6	1.478	--	24.00	31.2
16	i-Amyl acetate	45.0	165.5	3.678	--	8.65	10.0
17	Phenyl mustard oil	135.2	410.0	3.030	--	14.80	13.0
18	Octyl "	176.4	497.6	2.921	--	15.7	14.3
19	Dipropylamine	76.6	216.7	2.828	--	5.51	7.5
20	Benzene	75.6	302.8	4.005	--	24.22	27.7
21	Ethylsalicylate	269.4	512.6	1.903	8.39	6.56	5.7
22	i-Butyl benzoate	315.1	395.6	1.255	5.39	8.04	8.04
23	Benzotrichloride	245.6	451.8	1.839	--	--	--
24	Benzyl chloride	127.0	150.3	1.183	--	13.21	12.0
25	N-Butyl Benzoate	307.2	533.6	1.737	--	7.76	7.76
26	Toluene	72.4	383.0	5.290	--	25.6	29.8
27	Xylene	79.4	430.4	5.421	--	26.4	30.7
28	Piperidine	258.5	618.4	2.392	--	12.3	14.3

Hatschek, as mentioned earlier, has correlated high swelling with high viscosity on the basis of solutions of rubber in benzene and in several halogenated hydrocarbons. If the relative viscosities of the various solvents be compared with their swelling power in the last column, no sweeping generalization such as that made by Hatschek is observable. There appears no general relation between viscosity and swelling in the 28 solvents tested.

However a more detailed analysis of the figures does disclose some interesting relationships which appear to be too regular to be a matter of chance. If we separate the solvents into groups according to structure, we observe that the hypothesis-higher viscosity with higher swelling-does seem to hold for each particular group. The swelling power is the number of cc's of the solvent taken up by the rubber in swelling.

TABLE I - HYDROCARBONS.

<u>Solvent</u>	<u>Relative Viscosity</u>	<u>Swelling Power</u>
Benzene	4.005	27.7
Toluene	5.290	29.8
Xylene	5.421	30.7

TABLE II - ETHERS

<u>Solvent</u>	<u>Relative Viscosity</u>	<u>Swelling Power</u>
Safrol	2.355	8.7
Anisole	2.698	12.7
Phenetole	2.969	13.4

TABLE III - HALOGENATED HYDROCARBONS

<u>Solvent</u>	<u>Relative viscosity</u>	<u>Swelling Power</u>
Benzyl chloride	1.183	2.6
Benzal chloride	1.512	3.1
Benzotrichloride	1.839	4.0

Swelling data available for vulcanized rubber only.

TABLE IV - AMINES

<u>Solvent</u>	<u>Relative viscosity</u>	<u>Swelling Power</u>
Diethyl aniline	1.695	10.4
Dimethyl aniline	2.207	13.1
Piperidine	2.392	14.3
Dipropyl amine	2.828	7.5

TABLE V

<u>Solvent</u>	<u>Relative Viscosity</u>	<u>Swelling Power</u>
Ethyl iodide	1.080	4.2
Methyl iodide	1.745	4.8

TABLE VI

<u>Solvent</u>	<u>Relative Viscosity</u>	<u>Swelling Power</u>
Methyl cyclohexane	1.478	2.6
Tetralin	2.035	5.0

Swelling data for vulcanized sheet.

TABLE VII - ESTERS

<u>Solvent</u>	<u>Relative Viscosity</u>	<u>Swelling Power</u>
Isc-Amyl benzate	1.079	8.3
Isc-Butyl benzate	1.255	8.04
Ethyl benzate	1.468	6.5
N-Butyl benzate	1.737	7.76
Ethyl salicylate	1.903	6.56
Isc-Amyl acetate	3.678	10.0

In the case of the hydrocarbons, the relative viscosities of the solutions rise regularly with rise in swelling power of the solvent, from benzene through toluene to Xylene. In the ethers we have the same regularity from safron through anisole to phenetole. In the halogenated aromatic hydrocarbons the rule holds from benzyl chloride through benzylidene chloride to benzotrichloride. It is interesting to note that toluene, the parent compound of these three derivatives, gives a relative viscosity much higher than the others.

In the amines, we observe the regularity from diethyl aniline, dimethyl aniline, to piperidine, but dipropyl amine forms an exception. Ethyl and methyl iodide obey the rule as do methyl cyclohexane and tetralin.

In the case of the esters, however, although isc-amyl acetate shows the highest swelling power and a solution of highest viscosity, the swelling powers of the others are very nearly the same while the viscosities differ. It may be contended here that in spite of being grouped under the same general heading of esters, they differ rather more widely than the members of the other groups. The swelling powers

and viscosities in the case of the two mustard oils are almost the same so that they really form no exception.

Although much additional information is required in this matter, it does seem as though these relationships cannot be ascribed to chance, and that they do appear to lend support to Hatschek's contention of higher viscosity with higher swelling power - but only if the latter be amended to the effect that we must consider each class of substances separately. This would certainly lead to the belief that solvation is a very important factor in viscosity, but not necessarily that ramifying aggregates play no part in the matter.

Just why a comparison evidently can be made only among the members of the same group is not clear. Why should diethyl aniline and iso-amyl acetate, which swell rubber to practically the same extent, give solutions of such widely varying viscosities - 1.695 and 3.678 respectively? A plausible reason lies in the fact that we are not taking into account here solvation in its widest sense. It is possible for example that the forces acting upon the solvent in the iso-amyl acetate sol are such that mesosolvent is bound in some manner than in the case of the diethyl aniline sol. This may not be true solvation, but it must be borne in mind that all of the solvent which is influenced by the disperse phase will affect the viscosity of the system.

Comparison of the viscosities of rubber sols with meta-styrene
sols in the same dispersion media.

The viscosities of various meta-styrene sols have been determined(24). It is interesting to compare the relative viscosities of the sols of this substance with those of rubber; involving two unsaturated hydrocarbons in a polymerized state, of the same general nature as evidenced by the character of the liquids which they imbibe, the very small change of the viscosities of their sols with change in temperature(25),etc.

The sols were all of the same concentration - 0.328 gms per 100 cc's. The table is listed in the order of the relative viscosities of the meta-styrene sols.

<u>Solvent</u>	<u>Relative Viscosity</u>	
	<u>Meta-styrene</u>	<u>Rubber</u>
Acetal	1.784	1.068
Ethyl iodide	2.320	1.080
Diethyl aniline	2.710	1.695
Ethyl benzoate	2.817	1.468
Methyl iodide	2.912	1.745
Toluene	3.023	5.290
Anisole	3.231	2.698
Xylene	3.369	5.421
Benzene	3.518	4.005

The relative viscosities in the case of the rubber sols are much lower than those of the meta-styrene sols in every case except those where the aromatic hydrocarbons are used as solvents, in which instances those of the rubber sols are much higher. With the exception of the aromatic hydrocarbons, although they also take positions in the last part of each list, there appears broadly the same order in each list.

PRECIPITATION OF ORGANOPHYLIC COLLOIDS

Whitby(26) has discussed the relation between the chemical character of the organophylic colloids and the liquids which they imbibe. In the course of measurements of the swelling of rubber, both raw and vulcanized, in more than 350 organic liquids, very many regularities have been observed. It has been found that there exists a very definite relationship between the swelling power of an organic liquid for rubber, and its polarity.

Rubber is a hydrocarbon of a non-polar character, and with very few exceptions, only non-polar liquids will be imbibed by it. Cellulose acetate, on the other hand, an ester of a fatty acid of low molecular weight, is a polar substance and will in general swell only in liquids of a polar nature.

Very many examples of this relationship might readily be adduced. As typical examples may be cited the following. Hydrocarbons in general are solvents for rubber and non-solvents for the cellulose esters. Aniline, a very polar liquid, is a solvent for cellulose esters but is not imbibed by rubber. Acetyl chloride is a solvent for rubber but not for cellulose acetate.

Solvents for a non-polar substance such as rubber, then, in general are not imbibed by the more polar cellulose esters and conversely, organic liquids which will disperse the latter will not swell rubber. As has been previously stated, solvation is the great stabilizing factor in an organophylic

sol, hence if the micelles be de-solvated, the system will become unstable and the dispersed phase will coagulate.

It has been found to be very often the case that a swelling agent for rubber has the power to de-solvate and precipitate the cellulose esters from solution, and the reverse also. For example, such materials as acetone, methyl acetate, acetonitrile, ethyl oxalate, etc., are all solvents for cellulose acetate and are precipitants for rubber. On the other hand, a liquid such as hexane will precipitate the cellulose esters from their solutions, but is imbibed by rubber,

In any series of compounds containing the same active group, usually the polarity of the lower members is greater than that of the higher ones. In such a series, we find that the solvent power of the liquid decreases as we go up the series. At the same time, what might be termed the negative solvent power or the precipitability for rubber decreases as we go up the series, until we reach compounds which are actually imbibed by rubber.

As will be shown, very often in a series of compounds of the same type, the lower members decrease regularly in their precipitating power for rubber, the next few members will not precipitate rubber nor swell it to any extent, then higher still we encounter increased swellability for rubber with increasing chain length.

The method of precipitation has been discussed in a previous section. The rubber sol used was the same in all cases - a dispersion of smoked sheet in benzene of concentration 1 gm per 100 cc's.

The precipitant was added slowly with vigorous stirring from a burette with divisions of 0.05 cc. The end point was obtained sharply as a first permanent turbidity, observed by the aid of a high-power lamp. Check experiments showed an experimental error of 2 - 3 parts in a hundred, 5 cc's of rubber sol was used each time.

TABLE I - ALCOHOLS

<u>Precipitant</u>	<u>No. cc's req'd</u>	<u>Vol. % Prec.</u>	<u>D.K.</u>
Methyl alcohol	0.95	15.9	31.5
Ethyl "	1.75	25.9	20.8
N-Propyl "	2.20	30.5	13.8
Allyl "	2.40	32.4	--
I-Propyl "	2.85	36.3	13.8
Benzyl "	3.35	40.1	10.6
N-Butyl "	4.85	49.2	8.8
Amyl "	5.30	51.4	6.6
I-Butyl "	5.40	51.9	8.0
I-Amyl "	6.25	55.5	5.7
Hexyl "	8.95	64.1	--
Cyclohexyl "	12.65	71.6	--
Heptyl "	Not a precipitant,		
Octyl "	Swelling agent.		

The figures in the second column represent the number of cc's of precipitant added to produce turbidity and in the next column are given the percentages by volume of the precipitant in the whole system at the end-point. The dielectric constants are those given in the Tabellen of Landolt-Bernstein.

The precipitating power varies inversely as the amount of the precipitant necessary to desolvate the disperse phase to the same extent. Rubber, a non-polar substance, is precipitated most efficiently in this series by the most polar member, methyl alcohol. All these alcohols contain one active hydroxyl group. As the neutralizing hydrocarbon chain is lengthened, or to put it in another form, as the centre of electro-magnetic mass is shifted farther and farther away from the active group, the polarity of the molecule lessens, and consequently the precipitating power is lessened. This holds true for the alcohols with no exceptions.

The straight unbranched-chain alcohols are regular. Allyl alcohol fits in between the normal and iso propyl compounds. Benzyl alcohol, the molecule of which comprises a ring structure, is intermediate in precipitating power between iso-propyl and butyl alcohols. Iso-butyl alcohol is not as efficient as ^{the} n-amyl compound, but iso-amyl alcohol is a better precipitant than n-hexyl alcohol. Cyclohexanol ranks the last of the alcohol precipitants due to the ring structure and heptyl alcohol will neither precipitate rubber from its solution nor will it swell rubber to any extent. The next member, octyl alcohol, is a weak swelling agent for rubber.

A discussion on the forces involved in a series of precipitations of this sort, has been included in the section on "Solvation."

TABLE II - KETONES

<u>Precipitant</u>	<u>No. cc's req'd</u>	<u>Vol. % Prec.</u>	<u>D.K.</u>
Dimethyl ketone	3.95	44.1	21.5
Methylethyl "	11.55	70.0	17.8
Diethyl "	Swelling agent,	--	17.0
Ethylpropyl "	"		
Dipropyl "	"		

Dimethyl ketone or acetone, the lowest member of the series, is a good precipitant for rubber. Methylethyl ketone is also a precipitant but is far less powerful as such than the lower homologue. The next member, diethyl ketone, has actually the power to swell rubber, and this swelling power increases through ethylpropyl ketone to dipropyl ketone.

TABLE III - BASES

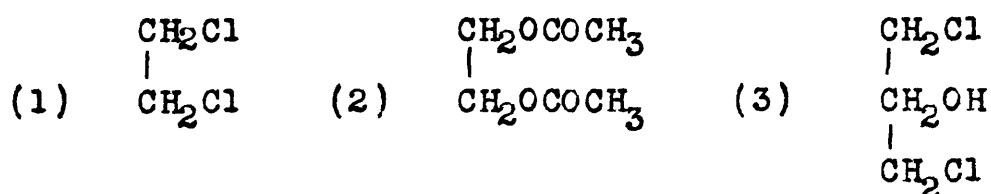
<u>Precipitant</u>	<u>No. cc's req'd</u>	<u>Vol. % Prec.</u>	<u>D.K.</u>
Aniline	3.2	39.0	7.3
Methyl aniline	14.75	74.7	6.0
Ethyl aniline	30		5.9
Propyl aniline	Swelling agent		
Butyl aniline	"		

The same rule holds in the case of the substituted anilines. The first two are precipitating agents, ethyl aniline is really on the border line between a swelling agent and precipitant and the last two are swelling agents for rubber.

TABLE IV - SUBSTITUTED HYDROXY COMPOUNDS

<u>Precipitant</u>	<u>No. cc's req'd</u>	<u>Vcl. % Prec.</u>
Ethylene glycol	Insoluble in benzene,	
Chlorhydrin	1.76	26.0
Ethylene glycol di-acetate	2.12	29.7
Dichlorhydrin, aa,	2.80	36.0

Ethylene glycol itself is insoluble in benzene and could not be used. As we would expect, the mono-chlor compound is more effective as a precipitant than the di-substituted glycol and the latter is in turn more effective than the glycerol derivative where the polarity of the molecule is lessened by symmetry. The order of polarity on this basis would run as follows:

TABLE V - ACETATES

<u>Precipitant</u>	<u>No. cc's req'd</u>	<u>Vcl. % Prec.</u>	<u>D.K.</u>
Hydrogen acetate	2.90	36.7	6.29
Methyl acetate	4.40	46.8	7.03
Phenyl "	6.05	54.7	5.29
Ethyl "	9.15	64.7	5.85
Phenylmethyl "	14.70	74.6	--
N-Propyl "	20 cc's brought faint cloudiness,		5.65
Amyl "	Swelling agent		4.81

In this series the acid radicle is the same in all the members and various groups have been substituted for the

hydrogen of the acetic acid. Phenyl acetate assumes a position intermediate between the methyl and ethyl compounds and phenyl methyl or benzyl acetate between the ethyl and propyl compounds. Normal propyl acetate is on the border line as regards swelling and precipitating power and amyl acetate is a decided swelling agent.

TABLE VI - ETHYL ESTERS

<u>Precipitant</u>	<u>No. cc's req'd</u>	<u>Vol. % Prec.</u>	<u>D.K.</u>
Ethyl Formate	2.00	28.6	8.27
" oxalate	2.78	35.7	--
" acetate	9.15	64.6	5.85
" propionate	20 cc's brought faint cloudiness,		
" butyrate	Swelling agent,		
" valerate	" "		

In contrast to the precipitants of Table V, the members of this series have the same positive group and differ in their acid radicles. Ethyl oxalate is intermediate between ethyl formate and ethyl acetate. Ethyl propionate is the border line compound in this series, which ranges from an excellent precipitant in ethyl formate to a good swelling agent in ethyl valerate. The same holds true, of course, for series of compounds using methyl groups, propyl groups, etc.. For example methyl acetate is a good precipitant for rubber whereas methyl n-butyrate is a swelling agent.

Acetic acid (D.K.-6) was found to be a much better precipitant than propionic acid (D.K.-about 3). Acetophenone was found to be on the border line - a poor precipitating agent and also a poor swelling agent. Benzyl benzoate - an ester of comparatively low polarity was found to be a poor

precipitant for rubber.

Precipitating power and Dielectric Constant.

Since the precipitating power of an organic liquid evidently varies with the polarity and the latter runs parallel with its dielectric constant, it might be expected that there would be a relationship shown between the precipitating power of a compound and its dielectric constant. The literature however is very incomplete in the matter of dielectric constants, and those that are given are not altogether reliable for several reasons. Many different workers have contributed information in this field using different procedures based on unrelated theoretical considerations, working at different temperatures and using different frequencies. The latter two factors are extremely important in dielectric constant determinations and the figures quoted in the tables above were determined in the majority, at the same temperature and at the same frequency, (namely 18° and 91 cm resp.).

There is, however, a broad relationship between the precipitating power and dielectric constant. If we examine Table I, for instance, we see that with drop in dielectric constant, the precipitating power also decreases, and the swelling power naturally increases. In Table III, the anilines, the parallelism holds and in Table V also, with the exception of phenyl acetate. The first member being an acid, it cannot be consistently compared with the remainder of the series.

It might be pointed out that here also, as in the section on "Viscosities of Rubber Sols", comparisons can be made only among members of the same group of compounds. Ethyl aniline and ethyl acetate have approximately equal dielectric constants, but their respective powers of precipitating rubber from its solution in benzene are widely different.

FRACTIONATION OF POLY VINYL ACETATE

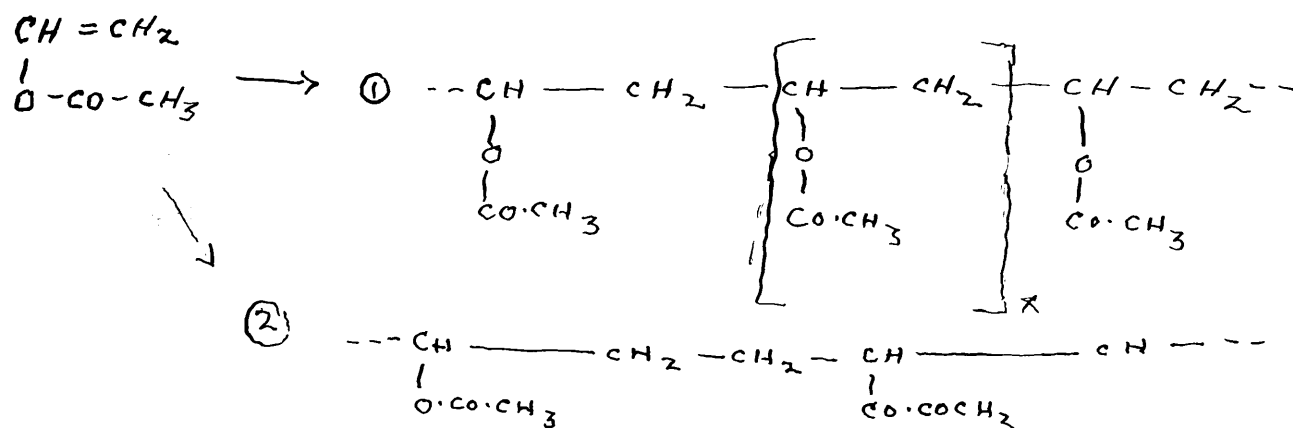
With the exception of a paper by Staudinger, Frey and Stark(27) which has appeared since the present work was complete, references to poly vinyl acetate have been confined to the patent literature. The results of the investigation in this section have already been embodied in a paper communicated elsewhere(28).

Vinyl acetate, an unsaturated ester boiling at 74°C, may be readily polymerized either by the action of heat or with the aid of catalysts. The resultant product is a tough, fibrous mass, greyish white in color. On being swollen or heated, the substance acquires pronounced elastic properties, the extent of which has been measured(29).

Since it yields colloidal solutions in certain types of organic solvents, it may be classed with such materials as rubber, the cellulose esters, etc., as an organophylic colloid. As might be anticipated, it belongs to the group of more polar compounds such as the cellulose esters, in contradistinction to such materials as rubber and meta-styrene. One important exception however was found: poly vinyl acetate, although not soluble in the paraffin hydrocarbons, is soluble in the aromatic hydrocarbons.

A Very considerable number of polymerized substances have been shown to be mixtures of material in various stages of polymerization. As examples/might be cited poly-indene(30, 31), poly cinnamal fluorene(32), meta-styrene(33), etc.

It is probable that the polymerization may be represented as following one of the following two schemes(34):



It may be seen from consideration of either possibility that there is no reason for believing^{ing} that any specified number of molecules will unite to form a larger unit. The size of the latter will be determined only by the strength of the bonds joining the carbon atoms into one structural unit, and will be limited probably only by the instability caused by very large size. Hence it is not difficult to perceive the interpretation of the experimental results.

When the original vinyl acetate is subjected to polymerizing conditions, any number of single molecules(up to a certain maximum) can join together to form a larger unit and there will result a heterogeneous mixture of these various materials of different grades of polymerization. Since then polymers of varying molecular weight are probably intimately mixed in the structure of the whole material, it seems justified to suppose for the present at least, that their relation to one another is such that the whole constitutes a solid solution.

The rough fractionation of these various polymers depends upon their varying solubility in the organic liquids which they imbibe. It was found that the polymers of lower molecular magnitude are far more readily soluble than the more highly polymerized ones and conversely, the latter could be more readily precipitated from solution than the former. Although fractions obtained in this way are, of course, still heterogeneous, in the present work the range of molecular magnitudes found after one fractionation, was surprisingly wide.

Preparation of Polymer.

The writer is indebted to Mr Katz, of this Department, for carrying out the polymerization. A sample of vinyl acetate was distilled and that portion was collected which came over at $73.5^{\circ} - 74^{\circ}$. 100 gms, to which 0.1 gm of benzoyl peroxide had been added, was heated under reflux by means of a hot plate placed a short distance underneath. After refluxing had proceeded for 45 minutes, a vigorous reaction occurred, the temperature rose suddenly to $85^{\circ} - 90^{\circ}$ and polymerization commenced, the liquid beginning to thicken. Heating was continued for three hours in all, at the end of which time, refluxing had ceased.

The transparent, glass-like solid present on cooling, could be readily separated into two layers - an upper, soft, "rubbery" part (52.95 gms), and a lower, harder, resinous part (46.0 gms). The latter clearly represented a part of the vinyl acetate which had set to a solid during the initial vigorous reaction and had then been heated while the

remainder of the liquid was refluxing and gradually undergoing polymerization.

Fractionation of the polymer.

Each of the above mentioned polymers was dissolved in acetone, solution being quite slow. They were then precipitated from the solutions by the addition of distilled water and dried in vacuo. This process of solution and precipitation was repeated three times and the resultant pure products were carefully dried.

A piece of each polymer was then placed in acetone, and as solution proceeded, the supernatant liquid over the swollen mass was poured off and the solvent renewed. From each polymer, solutions representing four fractions were obtained in this way. The fractions were precipitated by water and dried in vacuo. They varied from pure to greyish white, although no definite distinction could be noticed among the fractions of the original low and high polymers in extensibility. All the fractions were fibrous and tough at room temperature and very extensible and elastic at higher temperatures.

Molecular Weights of the Fractions.

Molecular weight determinations were made cryoscopically both in benzene and in bromoform. The procedure followed was the usual one: 0.4 gm of the polymer together with 20cc's of benzene were placed in the inner tube of a freezing-point apparatus. After solution had taken place, the freezing point

of the solution was measured several times on a Beckmann thermometer reading to 0.001°. The freezing point of the same sample of benzene was then taken and the molecular weight of the polymer was calculated from the equation:

$$M = \frac{100 \cdot k \cdot W}{W' \cdot T}$$

Where M Molecular weight,
 k Freezing point constant of benzene,
 W' Weight of the dissolved substance,
 T Lowering of the freezing point.

A similar procedure was used in the case of the determinations using bromoform. Both the benzene and bromoform were carefully purified before use. The following were the results obtained.

TABLE I - Mol. Wts. in Benzene.

A - Softer polymer,		B - Harder polymer.	
	<u>Fraction</u>	<u>Mol. Wt</u>	<u>Aggregation</u>
A)	1st	487	6
	2nd	898	10
	3rd	1198	14
	4th	1376	16
B)	1st	566	7
	2nd	1281	15
	3rd	3483	41
	4th	6192	72

Aggregation - refers to the average number of molecules united to form a larger unit.

TABLE II - Mol. Wts in Bromoform

A - Softer polymer,		B - Harder polymer.	
	<u>Fraction</u>	<u>Mol. Wt</u>	<u>Aggregation</u>
A)	1st	400	5
	2nd	747	9
	3rd	1068	12
	4th	1450	17
B)	1st	462	5
	2nd	1150	14
	3rd	3200	37
	4th	5000	60

The molecular weights of the fractions in the two solvents are not strictly concordant but this is not surprising under the circumstances. The organophylic colloids, solvated in the one case by benzene and in the other by bromoform, might well change sufficiently in aggregation to account for the difference.

Viscosities of the fractions.

Solutions of the various fractions were made up in benzene to the same concentration - 0.328 gm per 100 cc's of solvent. The viscosity measurements were made in an Ostwald viscometer immersed in a thermostat with the temperature constant to 0.002°. The relative viscosity is the ratio of the time of flow of the solution to that of the pure solvent, (in seconds).

TABLE III

A - Softer polymer,

B - Harder polymer.

	<u>Fraction</u>	<u>Time of flow</u>	<u>Rel. viscosity</u>
A)	1st	100.0	1.333
	2nd	118.0	1.561
	3rd	174.2	2.304
	4th	279.6	3.700
B)	1st	98.5	1.303
	2nd	206.0	2.725
	3rd	444.4	5.878
	4th	634.2	8.389

Time of flow of pure solvent - 75.6 seconds.

Poly vinyl acetate, then, is undoubtedly heterogeneous, the product prepared by the aid of benzoyl peroxide being separable into fractions ranging from one having a molecular weight of 566 to one having a molecular weight of 6192 in benzene. The harder polymer, as expected, yielded fractions of much higher molecular weight than those of the softer polymer. The viscosity of sols of the same concentration made of the various fractions is greater, the higher the state of polymerization which the fraction represent. Although, since only one fractionation was carried out and the fractions themselves are undoubtedly still heterogeneous, a linear relation seems to obtain between the grade of polymerization and the viscosity of the sol in benzene, though this relation is only an approximate one.

It is worth noting that the viscosities of sols of this specimen of a given molecular magnitude, are much higher than those of sols of the specimens examined by Staudinger, Frey and Stark(35). The latter were commercial specimens and the exact method of polymerization followed is not described.

Catalysts in the polymerization of Vinyl acetate.

In order to determine which of the commoner inorganic compounds - particularly halides and oxides - could be used as catalysts in the polymerization of vinyl acetate, the following qualitative experiments were carried out.

A 20% solution of vinyl acetate in chloroform was made up and saturated solutions of the following compounds in chloroform were also prepared. The solubility of some of these compounds in chloroform is relatively small, but a very small amount only is sufficient to show catalysis in a qualitative way.

Antimony pentachloride	Thorium bromide
Acetic acid	Ferrous chloride
Zinc chloride	Ferrous bromide
Zinc bromide	Bismuth trichloride
Vanadium chloride	Silicon tetrachloride
Aluminium chloride	Chromium chloride
Aluminium bromide	Cuprous chloride
Phosphorus pentachloride	Cupric chloride
Benzoyl peroxide	Lead iodide
Antimony trichloride	Titanium chloride
Mercuric chloride	Benzoyl chloride
Sodium peroxide	Copper oxy-chloride
Lead peroxide	Stannous chloride
Arsenic trichloride	Stannic chloride

Two cc's of the solution of the catalyst in chloroform were added to about 20 cc's of the vinyl acetate

solution and allowed to stand for three days. Petroleum ether (fraction of boiling point 35° to 40°) was used as a precipitant in throwing out of solution any polymer which might have been formed. None showed polymerization.

Then the solutions of vinyl acetate and the catalyst were heated together in a water-bath to about 80° for two hours and tested again with petroleum ether. Benzoyl peroxide gave the best results as a catalyst. Antimony pentachloride and stannic chloride also gave good results. None of the others, with the possible exception of the tetrachloride of silicon, seemed effective as catalysts.

FRACTIONATION OF RUBBER

Rubber occurs naturally as the disperse phase of a lyophobic dispersoid - latex - secreted by certain plants. The hydrocarbon, probably associated with certain impurities, is suspended in the form of globules in the aqueous medium or serum, which further contains dissolved substances such as carbohydrates, resins and proteins. It is probable also that each globule possesses a protective coating of protein which serves to maintain the disperse phase in the colloidal state. These globules are coagulated by various means and the coagulum, containing besides the caoutchouc much of the protein and resin impurities, is further treated in various ways to give different kinds of rubber.

The extreme importance of rubber is due chiefly to the properties - which it possesses to an unusual degree - of being highly elastic, very resilient to shock and sufficiently durable to withstand long wear. It lends itself very readily to combination with sulphur, to yield the familiar vulcanized product in which form it is most widely used.

It is in order to explain its unusual properties, to explain also many striking phenomena in connection with it - e.g. the Joule effect - and to aid in the search for a good synthetic substitute, that varied attempts have been made to explain the physical and chemical structure of rubber,

Rubber is a polymer of unknown molecular weight, consisting probably of aggregations of a structural unit

which may be formulated as $(C_5H_8)_x$. It is an organophylic colloid yielding colloidal solutions only, in various organic solvents. These possess high relative viscosities, rising steeply with small increases in concentration, but varying only to a small extent with change in temperature.

Weber(36) some years ago, from microscopic investigations declared that the globules in latex are composed of a liquid, oily hydrocarbon which, by more complete polymerization, gives rise to cautchouc upon coagulation. Recently, Hauser(37) by micromanipulation, claims to have succeeded in puncturing the envelope enclosing this liquid and actually to have noticed the escape of the latter from the globule. He considers that this lower polymer is surrounded by a harder shell - a higher polymer chemically identical with the inner fluid. De Vries(38) and Whitby(39) have however, expressed their belief that in all probability, the contents of the globules consist of the true cautchouc itself.

Hauser(40) has also presented microscopic evidence to further prove that the rubber hydrocarbon in latex exists in two stages of polymerization, identical chemically. Many other investigators have taken this view also. Furthermore this two-phase hypothesis has been extended to the structure of rubber itself and various suggestions have been put forth regarding the inter-relation between the alleged two polymers in rubber. It is worth noting that most of these suggestions seem to have been put forward with a view to explaining the unusual properties of cautchouc.

Fessender(41), supported by Lunn, Park and Feuchter, applied the idea of the two-phase structure in latex globules and advanced the view that rubber is composed of grains of solid material floating in a very elastic medium. We have also the isocollidal hypothesis due to Ostwald who considered cautchouc as a colloidal dispersion of solid granules in a medium of the same chemical nature but of different physical properties. A cellular hypothesis, attractive by virtue of its analogy to organic matter of vegetable or animal origin, has been adopted by Hauser. Lastly, a hypothesis of solid solution was first suggested by Chauveau as a results of his experiments on the compressibility of rubber. This suggestion entails two cautchouc of different stages of polymerization dissolved in each other to form a single phase.

The Heterogeneity of Rubber.

As Bary(42) ably points out, most of the investigators in this problem have attempted to carry through ideas of the structure of latex globules to the structure of rubber. If these latex globules be coagulated and the cautchouc coagulum be dispersed in benzene, we obtain particles of disperse phase millions of times smaller than those of latex. If we now obtain back our cautchouc from the benzene sol by evaporation, it seems absolutely impossible that these particles will retake the form of the original globules. It would seem improbable also that globules of the size found in latex could undergo vigorous mechanical treatment and retain their original form.

As has already been mentioned in the discussion of poly vinyl acetate (vide supra), very many polymerized materials have been definitely shown to be of variedly heterogeneous composition - the case of meta-styrene(43) being a particularly analogous one. Among polymers - naturally occurring or synthetic - there is no analogy extant for the idea of a two-phase structure in rubber.

The well known effect of such external forces as heat in changing the state of aggregation, is considered(44) merely to change an equilibrium existing between these two phases. One is naturally led to inquire as to what unusual law must be obeyed in order that two and only two grades of polymerization can be attained by the original molecule in the formation of rubber. What obviates the possibility of the formation of intermediate polymers?

It would appear extremely difficult to present the two-phase hypothesis of rubber on a theoretical basis. There seems to be no logical reason at present, for differentiating the case of rubber from those of other organophylic colloids, whose structures have been proven to be heterogeneous, entailing a mixture of materials of widely varying grades of polymerization.

Fractionation.

Duclaux(45) has separated two distinct fractions from rubber left standing for several years, one solid and insoluble in ordinary solvents and the other semi-liquid and very soluble;

the latter being present in much larger proportion than the former. More recently Pummerer(46) has divided rubber into two components, His method entails - first purification of latex by allowing the latter to stand with 20% NaOH at 50°C, removing the hydrocarbon, dialysing off the NaOH and then fractionating the product by exhaustive extraction with ethyl ether. He speaks of his two fractions as gel-rubber - giving rubber its toughness, and sol-rubber - giving it elasticity.

The sol-rubber is soluble in ether and the gel-rubber is not. Yet when an ether solution of the sol-rubber is evaporated, he finds traces of gel rubber formed which are insoluble in ether. He concludes from these experiments that the parent or unit molecule of rubber polymerizes to two grades of polymers and the latter are reversible by aggregation and disaggregation, association and dissociation.

It is well worth noting that this work appears to yield very imperfect evidence for a two-phase structure in rubber. Each of the two fractions obtained as mentioned might conceivably still be heterogeneous; the only difference between them may be simply in the separation of a preponderance of higher and lower polymers in the gel and sol rubber respectively.

In the present instance, the diffusion method of fractionation was used. As mentioned in the foregoing section, polymers of lower molecular magnitudes possess greater solubilities than those of higher magnitudes and this difference is utilized in their rough separation. Since small traces

of impurities however affect the viscosities of rubber sols to a great extent and the viscosities of the sols of these fractions were to be used later as a criterion of difference in size of polymer, it was necessary to free the rubber from impurities as far as possible.

PART I

Three samples of smoked sheet of known history were extracted with 75-25 acetone-petroleum ether mixture in order to remove the resins. The extraction medium was renewed three times at intervals of 24 hours and then twice at intervals of 48 hours. The liquid poured off from the last extraction was quite colorless and it may be assumed that extraction was complete. Each sample was then dried in vacuo for one week. The loss in weight due to extraction was found to be about 3%.

Each sample was then cut up to expose a large surface and placed in a two litre Erlenmeyer flask. Sufficient benzene was added to each flask so that some 100cc's of liquid was supernatant to the rubber. Care was taken not to shake the flasks throughout the diffusion. At intervals of about four days, the supernatant liquid was siphoned off from the gel below and the solvent renewed - carefully so as to obviate disturbance of the gel.

In this way, six solutions representing six fractions of the original samples, were obtained from each of the three flasks. The solutions were kept till all were prepared, then the rubber was precipitated from each by means of acetone and dried. Then solutions were made up of each fractions

in benzene, to a concentration of 0.328 gm per 100 cc's.

Weights of fractions.

B1 - 0.30	C1 - 1.48	D1 - 1.27
B2 - 0.78	C2 - 1.44	D2 - 1.14
B3 - 0.40	C3 - 3.84	D3 - 0.26
B4 - 0.53	C4 - 1.27	D4 - 0.97
B5 - 0.63	C5 - 0.67	D5 - 0.54
B6 - <u>0.63</u>	C6 - <u>0.60</u>	D6 - <u>2.68</u>
Am't diff'd 3.27gms	9.30 gms	6.86 gms
Orig, wt 13 "	15 "	22 "
% removed 25%	61%	31%

Be the procedure described above, first the resins are removed from the rubber by extraction and then the pure hydrocarbon is diffused out of the skeleton of nitrogenous matter in which it is enmeshed, leaving the proteins behind. That there really is a mesh skeleton of protein in the rubber is supported by the following observations. Although after the fractions had been removed, the remaining swollen mass seemed to resemble the original, yet upon slight shaking of the flask, the gel material seemed to crumble and dispersed in the remaining benzene very quickly.

All the fractions obtained were tested for nitrogen according to the method described in Mulliken's "Identification of Organic Compounds", and the tests all showed negative results. The procedure was briefly as follows: A small sample

was fused with potassium metal, the resultant product mixed with H_2O and the mixture filtered. Any nitrogen present in the original sample would now be dissolved in the form of KCN. Then the usual test for a cyanide was carried out, involving the use of ferrous sulphate, hydrochloric acid and ferric chloride for the production of Prussian Blue. Since the test is a very delicate one, and control tests on ordinary smoked sheet gave decidedly positive results, it may be assumed that the protein impurities present were negligible.

The solutions of the fractions were left to disperse for three months in the dark at room temperature. Then the viscosities of the solutions were measured in a viscometer of the Ostwald type immersed in a thermostat regulated to a variation of 0.002° .

TABLE I - SAMPLE A

<u>Fraction</u>	<u>Time of flow</u>	<u>Relative viscosity</u>
1st	492.0	6.291
2nd	533.8	6.826
3rd	477.6	6.107
4th	536.0	6.854
5th	560.2	7.163
6th	843.6	10.788

TABLE II - SAMPLE B

<u>Fraction</u>	<u>Time of flow</u>	<u>Relative viscosity</u>
1st	603.2	7.713
2nd	593.0	7.583
3rd	647.0	8.273
4th	547.8	7.350
5th	785.0	10.038
6th	750.0	9.591

TABLE III - SAMPLE C

<u>Fraction</u>	<u>Time of flow</u>	<u>Relative viscosity</u>
1st	389.3	4.978
2nd	395.3	5.055
3rd	402.7	5.149
4th	670.3	8.571
5th	703.4	8.995
6th	Not yet properly dispersed.	

In Table I, with the exception of fraction #3, the relative viscosities of the fractions rise regularly from the first to the last. In Table II, more irregularity is encountered, although the same tendency for rise in relative viscosity is shown. In Table III, the rise is regular without exception. It might be noted here that a small proportion of acetone was introduced with the solvent in the case of sample C, and this might possibly have a beneficial effect in the proper fractional diffusion of the rubber.

It must be considered further that since one fractionation only was carried out, the division cannot be a perfectly regular one. It is significant also that in the case of Sample C where the sequence of figures is regular, 60% of the rubber diffused out, while in the other two cases, only 30% of the hydrocarbon was extracted.

PART II

Further experiments on the fractionation of rubber were carried out, varying to some extent the procedure outlined above. Two more samples, D and E were acetone extracted by the procedure of Part I, and allowed to diffuse in the same way, four solutions representing different fractions being collected from each. Then the concentrations of rubber in the various solutions were determined by evaporating a definite volume of each solution and weighing the residue. The fractions all gave negative tests for nitrogen.

By the addition of the proper amount of benzene, each solution was brought to the same concentration of 0.3 gm per 100 cc's. This procedure obviates the necessity of precipitating and redispersing the rubber. The viscosities of these sols of standard concentration were then taken.

TABLE IV - SAMPLE D

<u>Fraction</u>	<u>Time of flow</u>	<u>Relative viscosity</u>
1st	378.0	4.846
2nd	403.2	5.156
3rd	408.6	5.226
4th	415.2	5.309

TABLE V - SAMPLE E

<u>Fraction</u>	<u>Time of flow</u>	<u>Relative viscosity</u>
1st	400.1	5.116
2nd	413.2	5.284
3rd	420.8	5.381
4th	423.6	5.417

These fractions showed a small but regular increase in the viscosities of their sols. The mode of procedure used would seem superior to that used in Part I, since no precipitation and redispersion of the rubber is involved. What effect the rate of coagulation or the coagulant itself may have on the degree of polymerization is not definitely known and furthermore any of the precipitant not removed by drying will have an important bearing on the viscosity of the solution.

The writer clearly recognizes, that the figures adduced above do not constitute a rigid proof of the nonexistence of a two-phase structure in rubber, since it is conceivable that, if the latter hypothesis is correct, mixtures of varying proportions of the two polymers might lead to these results. However, taking into account the great difference in solubilities of the "sol-rubber" and "gel-rubber" described by Pummerer, this criticism does not seem very applicable.

Effect of various precipitants on the degree of polymerization,

From the discussion in the penultimate paragraph, it was deemed interesting to try the effect of precipitating rubber in various ways, redispersing each coagulum in benzene and then determining any change in the relative viscosity of

the sol.

A sample of crêpe rubber was dried and dissolved in benzene to give a concentration of 1 gm per 100 cc's. When dispersion was complete, $\frac{1}{4}$ of the sol was precipitated by the use of acetone, $\frac{1}{4}$ by 90% ethyl alcohol, $\frac{1}{4}$ allowed to evaporate in vacuo, and $\frac{1}{4}$ of the sol was left unchanged. The three coagula were dried and then dissolved in benzene to a concentration of 0.328 gm per 100 cc's; the original solution which had been left unchanged also being made up to the same concentration. The viscosities of the sols were then measured in the usual manner.

<u>Sol</u>	<u>Time of flow</u>	<u>Relative viscosity</u>
Original	377.6	4.936
Alcohol - prec.	410.6	5.396
Acetone - prec.	375.8	4.912
Evaporated	362.0	4.731

The sol where acetone coagulation had been used remained practically unchanged in viscosity. The sol whose disperse phase had been obtained by evaporation showed a definite lowering in viscosity; consequently the average degree of polymerization must have been lowered. The alcohol-precipitated rubber showed a rise in viscosity, although this may have been due in some measure to traces of water remaining in the rubber after drying, 90% ethyl alcohol had been used and, as is well known, water has a comparatively great effect in increasing the viscosity of a rubber sol in benzene.

WATER ABSORPTION BY RUBBER

The efficiency of rubber compounds used for purposes of insulation depends to a large extent on the amount of water which the rubber will absorb from the surrounding medium. Of especially great importance is this in connection with under-water cables, where ^{the} rubber is immersed in water continuously under comparative ^{ly} high pressures.

De Vries(47) and Whitby(48) observed that the water content of raw rubber varied with the humidity of the atmosphere in which it was stored. Van Rossem(49) showed that the amount of water which is absorbed by rubber depends upon the humidity, temperature, and upon a further important factor - the amount of water soluble impurities in the rubber. Obach (50) observed the difference in absorption from sea-water and fresh water, and noted that not only did rubber absorb less from sea-water, but that in the latter case, the rubber soon reached a constant weight, whereas in the case of fresh water, the absorption was continuous over a long period of immersion.

Whitby(51) has further shown that the capacity of rubber to retain moisture is closely related to the presence of hygroscopic serum solids in the rubber. Kirchhof (52) has investigated the relationship between the water absorption and the acidity of the rubber and shown that the former is dependent on the amount of fatty acids present. Recently Beggs and Blake(53) and Lowry and Kohman(54) have discussed the effect of various factors upon the amount of water absorbed and the rate of absorption.

Lowry and Kohman, mentioned above, consider that the most important factor determining the amount of water absorbed is the vapor pressure of water with which it is in equilibrium. They consider that the mechanism of water absorption consists in two processes.

1.-The formation of a true solution of water in rubber.

2.-The formation of solutions internal to the rubber of water soluble constituents of the rubber which can be removed by washing.

They conclude further that increasing the rigidity of a rubber compound decreases greatly the amount of water absorbed.

It would appear to the present writer that, not the vapor pressure of water in the surrounding medium, but the amount of water soluble constituents in the rubber, is the most important factor in water absorption. For of the two processes mentioned in the penultimate paragraph, the second one is by far the more important, as will be shown in this work. Evidently, then, if all of the water-soluble constituents could be removed from the rubber, and granted that the latter were comparatively rigid, the vapor pressure of water in the surrounding medium would make very little difference in water absorption.

The pure caoutchouc hydrocarbon must be considered as possessing practically no affinity for water, hence the latter cannot solvate the rubber. The mechanism of water absorption then with the pure hydrocarbon would lie in the

capillary and adsorption forces which would be exerted. If a sufficiently firm surface could be presented to the water, only the force of adsorption and that over a small surface area, could be exerted to cause an increase in the weight of the immersed hydrocarbon,

Impurities in the cautchouc may be of two kinds, either water-soluble or water-insoluble. In the case of the former, a solution will be formed of these constituents, internal to the rubber. In the case of the latter, as for example with powdered quartz or carbon black as a filler, the absorption of water will be decreased, because a more rigid product will result lessening the effect of capillary forces. The addition of sulphur in the process of vulcanization lessens the water absorption greatly.

In the present work, samples of rubber containing varying amounts of water-soluble constituents were prepared by the following procedure.

Samples #1 and #2 were prepared by extraction of smoked sheet with a 75-25 acetone-petroleum ether mixture, and then diffusing out the pure hydrocarbon from the nitrogenous matter as described in a previous section (Fractionation of Rubber). Both of the samples gave negative tests for nitrogen. Sample #1 possessed much greater rigidity than sample #2.

Sample #3 was prepared by mixing solutions of nitrogen-free, extracted rubber and smoked sheet in the proportion 2 to 1 respectively - thus yielding a rubber containing approximately one third as much water-soluble material as ordinary smoked sheet.

Sample #4 was prepared by mixing solutions of nitrogen-free extracted rubber and smoked sheet in the proportion of 1 to 2 respectively - thus yielding a rubber containing approximately two thirds as much water-soluble material as ordinary smoked sheet.

Sample #5 was ordinary smoked sheet which contained about 2.75% of nitrogenous matter.

Sample #6 was prepared by utilizing the rubber remaining after about 60% of the pure hydrocarbon had been diffused out - thus yielding a rubber containing about two and one half times as much water-soluble material as smoked sheet.

The samples were dried in vacuo, weighed and immersed in the medium. A 3.5% solution of sodium chloride was substituted for sea water and in the case of the water vapor, the samples were suspended over water in closed tubes. At stated intervals, the samples were removed, superficially dried by pressing between pieces of filter-paper and the increase in weight noted. The superficial drying was carried out in as standard a way as possible each time and control tests showed a very small experimental error.

The results are tabulated below.

		<u>Percent increase in weight</u>			
		<u>over original weight after:</u>			
<u>Medium</u>	<u>Sample</u>	<u>5 days</u>	<u>12days</u>	<u>21days</u>	<u>31days</u>
Sea water)	1) <i>N free</i>	0.06	0.32	0.29	0.28
	2)	0.59	0.75	0.78	0.77
	3	0.62	1.93	1.96	2.04
	4	1.10	2.08	2.13	2.19
	5 <i>SS</i>	1.50	1.74	2.15	2.47
	6 <i>Bottom</i>	35.20	36.60	29.87	26.41
Water)	1	0.51	0.86	0.79	0.83
	2	0.74	1.18	1.57	2.00
	3	1.13	3.32	3.68	4.09
	4	3.37	4.32	4.83	5.17
	5	3.87	5.09	5.63	6.82
	6	28.40	32.30	27.12	21.61
Water-vapor)	1	0.20	0.23	0.57	0.33
	2	0.37	0.58	0.71	0.77
	3	0.00	0.88	1.96	2.22
	4	2.04	3.12	3.52	3.91
	5	2.18	3.24	3.93	4.60
	6	7.12	10.56	10.38	10.43

The amount of water absorption is seen to run parallel to the amount of water soluble material present, without exception. Sample #1, presenting a firm surface and containing no water soluble constituents absorbed a negligible amount only, in all cases. The absorption in the case of sample #2

is almost as low, the difference being due to absorption by capillary action and adsorption. The water absorption gradually increases downward until we reach the surprising figure of over 36% in the case of the protein-rich and resin-rich rubber. It will be noticed that in the case of the latter sample, the weight decreased after having come to a maximum, showing diffusion of some of the water-soluble constituents out into the water.

The absorption is less in all cases in sea-water than in pure water (with the exception of #6), which is to be anticipated since the number of water molecules adjacent to unit surface of the sample has been lowered.

Further samples of protein-free, resin-free rubber were prepared and pressed in a mechanical press at an elevated temperature in an effort to obtain a still more rigid material, but it was found that these samples showed marked tackiness and could not be used after a few days immersion.

SUMMARY

1.- The meaning of solvation, the factors affecting it and theories concerning it have been discussed.

2.- Measurements have been made in the temperature-viscosity relation of various cellulose acetate sols and the results discussed in the light of the Hatschek-McBain controversy regarding the cause of viscosity.

3.- The viscosities of various rubber sols have been measured. The results oppose any general correlation of high viscosity with swelling, unless possibly each group of solvents (according to structure) is considered separately. Viscosities of rubber sols and meta-styrene sols have been compared.

4.- The precipitating power of series of organic liquids for rubber has been measured. It has been shown that in any one series, a definite parallelism exists between precipitating power and polarity. Relation has been shown broadly between dielectric constant and precipitating power.

5.- Poly vinyl acetate has been shown definitely to be heterogeneous, the molecular weights of fractions of it and the viscosities of the solutions of these fractions determined. Various catalysts in the polymerization of vinyl acetate have been tried.

6.- An effort has been made to fractionate rubber by the "diffusion" method, using two varying modes of procedure. The results, although not definitely disproving the two-phase hypothesis, seem to indicate that rubber, in common with many other organophylic colloids, is heterogeneous.

7.- Rubber samples with varying nitrogen content have been prepared and treated for water absorption. The latter has been shown to depend very definitely on the water-soluble constituents of the cautchouc. The nitrogen-free, acetone-extracted samples were found to absorb a negligible amount of water.

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