substitution reaction is induced by the addition reaction, the heat of formation of ethylene dichloride being utilized to promote the formation of trichloro-ethane.

In the absence of water and light the reactions are autocatalytic.

Oxygen inhibits the utilization of the reaction energy to promote substitution. Nitrogen and water have little effect in this respect. Oxygen and excess chlorine reduce the specific reaction rate to the same minimum value. It is suggested that besides the induced substitution reaction there is also an induced addition reaction.

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THE FRACTIONAL PRECIPITATION OF CELLULOSE ACETATE AND SOME PROPERTIES OF THE FRACTIONS

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Introduction

It is well known that cellulose acetates may be prepared that have widely different physical properties but identical chemical compositions. These differences are commonly ascribed to some difference in state of aggregation or molecular weight of the cellulosic micelles. Several synthetic organophilic colloids—polyvinyl acetate,[1] polyindene,[2] polycinnamalfluorene[3] and polystyrene[2]—have been shown to be mixtures of polymers representing a rather wide range of polymerization of the monomer; it also has been shown that the physical properties of these colloids are intimately connected with the range of sizes of the molecular aggregates present.

The easiest method yet found for fractionating such mixtures is a precipitation process which makes use of the fact that the more highly polymerized components are the first to precipitate from a solution when a precipitating liquid is added. It has been found possible to adapt this method to the case of cellulose acetate and show that a representative material is a mixture of acetates having widely different characteristics.

Materials.—All the experiments reported here were made on a single sample of cellulose acetate prepared by subjecting a dope acetylated triacetate to acid hydrolysis until the product was soluble in acetone. The acetyl number determined by the Eberstadt[4] method was 44.50.

Methods of Fractionation.—Two procedures were used to separate

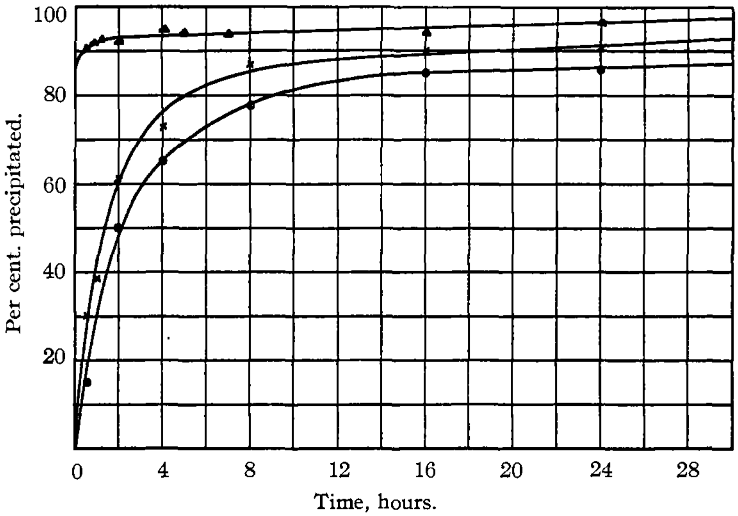
[1] G. S. Whitby, J. G. McNally and W. Gallay, *Trans. Roy. Soc. Canada*, **22**, 27 (1928).

[2] H. Staudinger, *Ber.*, **59**, 3019 (1926).

[3] G. S. Whitby and J. R. Katz, THIS JOURNAL, **50**, 1160 (1928).

[4] Eberstadt, "Dissertation," University of Heidelberg, **1911**; Knoevenagel, *Z. angew. Chem.*, **27**, 507 (1914).

the cellulose acetate into fractions. In Method A a 10% solution of the acetate in acetone was made and either water or a mixture of three parts of water and one of acetone added in insufficient amount to completely precipitate the acetate. It is essential that the formation of large clots of precipitate be avoided if a true fractional precipitation is to be effected. In our experiments the precipitation was carried out in a 250-cc. centrifuge bottle fitted with a rubber stopper provided with holes for the shaft of a Cenco stirrer and the tip of a buret. The solution to be fractionated was placed in the bottle and water added slowly through the buret, rapid stirring being maintained during the operation. Near the latter end of the precipitation, it is advantageous to substitute a 3:1 mixture of water and acetone as the coagulating liquid. The precipitated acetate was separated by centrifuging and more precipitant added to the liquid. In this manner a series of fractions was obtained that differed in their solubility in acetone–water mixture.



⊙, 34% water; ×, 36% water; △, 45% water.

Fig. 1.

On attempting to repeat quantitatively the fractionation outlined above, it was found that the amount of acetate that could be separated on centrifuging under standard conditions depended very much on how long the solution was allowed to stand after the precipitant had been added.

Fig. 1 shows the percentage of acetate separated by centrifuging partially precipitated solutions that had been allowed to stand for different periods of time after the addition of 34, 36 and 45% of water to a 10% solution of the acetate in acetone. A convenient method of fractionation consists, then, in adding a suitable amount of water to the acetone solution of cellulose acetate and collecting the precipitates that form after various lengths of time. This will be called Method B. By controlling the length of time the solution stands before centrifuging, Method A could be quantitatively repeated. Fig. 2 shows the percentage of cellulose acetate precipitated by various water concentrations after standing for thirty minutes. The water concentration is given as percentage by volume of the total amount of liquid.

Changes in the Properties of Cellulose Acetate Caused by Precipitation, Drying and Re-solution.—De Mosenthal[5] found that the viscosity of cellulose nitrate was *decreased* by repeated precipitation and re-solution while McBain[6] states that cellulose nitrate recovered from solution either by evaporation or precipitation is more insoluble and gives solutions of *higher* viscosity than the original material. No similar experiments appear to be on record for cellulose acetate, but if any difference in the properties of fractions collected by either Method A or B is to be attributed to the heterogeneity of the original material, it should first be shown that the treatment involved in the precipitation process does not appreciably alter the characteristics of the acetate. To obtain data on this point, 500 g. of a 10% acetate solution in acetone were precipitated by thoroughly mixing with 2 liters of distilled water. The precipitate was dried to a constant weight at 105° and a 5-g. sample set aside. The remainder was redissolved and the procedure repeated until all of the acetate was used up. In Table I the acetyl numbers and viscosities of 4% acetone solutions are given. Sample A was precipitated once, B twice, etc. Viscosity measurements were made at 25° with an Ostwald viscometer. The samples did not give sharp melting points but they all showed the same behavior on heating, softening at 255–260° and decomposing at 260–265°.

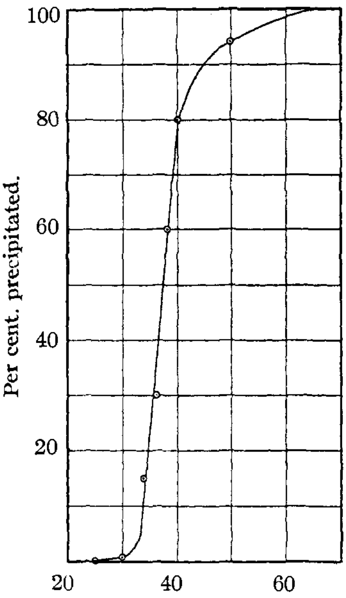


Fig. 2.

These experiments indicate that not much change is produced by repeatedly precipitating cellulose acetate. An increase in viscosity of 13% showed after nine precipitations. It will be noted from the table that a small part of the acetate was lost during each precipitation. This portion

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[5] H. de Mosenthal, *J. Soc. Chem. Ind.*, **30**, 782 (1911).

[6] J. W. McBain, C. E. Harvey and L. E. Smith, *J. Phys. Chem.*, **30**, 347 (1926).

TABLE I

ACETYL NUMBERS AND VISCOSITIES

Sample	Acetate in soln., g.	Acetate recovered, g.	Recovered, %	Viscosity, centipoises	Acetyl number
Original	..	..	..	6.85	40.4
A	50	49.1	98.2	6.75	40.6
B	45	43.4	96.5	7.05	40.5
C	39	38.1	97.8	7.25	40.45
D	33	32.7	99.2	7.35	40.6
E	27	26.0	96.4	7.51	40.4
F	21	21.0	100	7.56	40.5
G	16	15.4	96.3	7.60	40.45
H	10	9.3	93.0	7.78	40.6
I	5	4.6	92.0	7.72	40.45

remained suspended in the water as a finely divided suspensoid and the increase in viscosity may be reasonably attributed to the loss of this probably less highly polymerized fraction rather than to any change in the remaining fraction. It will be noted that in Fraction F, where this suspended material was collected by filtration, only a very slight increase in viscosity was noted over the preceding sample.

Melting Points, Acetyl Numbers and Viscosities of the Fractions.—Typical results obtained by both methods of fractionation will now be given.

Method A.—Seventy grams of cellulose acetate was dissolved in 630 g. of acetone and 250 cc. of water and 250 cc. of 3:1 water–acetone mixture was added. The precipitate collected was labeled Fraction A. One hundred and twenty-five cc. of the 3:1 mixture was added to the filtrate and Fraction B separated. Fraction C was obtained on the addition of 120 cc. of water to the filtrate from B. On distilling off the acetone from the filtrate from C, Fraction D was obtained.

Fraction A contained the bulk of the precipitate. About 80% of this material was dissolved in 500 cc. of acetone, and 153 cc. of water and 180 cc. of 3:1 mixture were added to give Fraction A-1. This filtrate was mixed with 25 cc. of 3:1 mixture and Fraction A-2 precipitated. The addition of 170 cc. of 3:1 mixture to this filtrate gave A-3, and A-4 appeared on distilling off the acetone from the filtrate from A-3.

Fraction A-1 was then refractionated as follows. The precipitate was dissolved in 300 cc. of acetone and 110 cc. of water added. The resulting precipitate was marked A-1-a. The addition of 25 cc. of water and 100 cc. of 3:1 mixture precipitated A-1-b; 150 cc. of water added to this filtrate gave A-1-c. A-1-d was obtained by distilling the acetone from the filtrate of A-1-c.

The melting points, acetyl numbers and viscosities of these fractions are given in Table II, with their weights and the composition of the liquid from which they precipitated.

Method B.—Thirty-six per cent. of water was added to a 10% solution of cellulose acetate in acetone and the precipitate separated after the mixture had been standing for thirty minutes at room temperature. The filtrate was then set aside and allowed to stand for four hours, when it was again centrifuged and a fraction obtained. Two other fractions were obtained in like manner and the data for all of them are given in Table III.

TABLE II

PROPERTIES OF CELLULOSE ACETATE FRACTIONS OBTAINED BY METHOD A

Fraction	Weight, g.	% Original wt.	Water by vol. when pptd., %	Acetyl number	M. p., °C.	Viscosity, centipoises
Original	..	..	...	40.4	266	6.68
A	15.7	24.1	32	39.6	287	5.28
B	6.2	9.5	35	39.7	250	4.08
C	6.65	10.2	39	39.9	236	1.68
D	2.6	4.0	100	39.9	217	0.65
A-1-a	0.6	0.9	27	39.65	301	..
A-1-b	10.1	15.5	32	39.2	292	23.6
A-1-c	4.0	6.2	44	39.6	264	7.16
A-1-d	0.05	0.08	100	39.6	255	..
A-2	10.3	15.9	33	40.4	264	9.41
A-3	6.2	9.5	39	..	255	3.79
A-4	0.7	1.1	100	39	240	..

TABLE III

PROPERTIES OF CELLULOSE ACETATE FRACTIONS PREPARED BY METHOD B

Fraction	Elapsed time, hours	Per cent. pptd.	Viscosity, centipoises	Acetyl number	M. p., °C.
A	0.5	49.5	12.85	40.6	270
B	4.5	7.75	4.96	40.8	257
C	22.5	14.50	4.32	40.8	252
D—Residue, filt. from C.		21.25	2.22	40.8	239

Specific Rotation.[7]—The optical rotary powers of Fractions A, B, C and D were determined by using the green mercury line (546 mμ) in a 20-cm. tube. The solvent was a mixture of 85 parts of chloroform and 15 of alcohol by volume. At a concentration of 1% the observed α for each of the fractions was $-0.34°$ and $[\alpha]^{20}_{546} = -17°$.

The data in the two preceding tables make it clear that the original sample of cellulose acetate was a mixture of a large number of components with widely different physical constants. The acetyl numbers of all of the fractions remained sensibly constant, indicating that an explanation of the difference in properties is not to be found in a difference in the degree of acetylation of the components. This conclusion receives further support in the constancy of the specific rotation. The changes in melting point, viscosity and solubility of fractions of the same chemical constitution all point to the conclusion that the original cellulose acetate contains a series of micelles differing either in the number of elementary glucose anhydride units they contain or in the manner in which they are joined together to form the micelle. In this respect cellulose acetate resembles the synthetic organophilic colloids already mentioned.

Solubility of Cellulose Acetate Fractions in Organic Liquids.—Cellulose acetate fractions that were separated by a procedure that made use of

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[7] We are indebted to Mr. Murray of the Organic Research Laboratory for these measurements of optical rotation.

their different solubilities in acetone–water mixtures might well be expected to show different solubility relationships in other solvents. Such was found to be the case. The fractions used in these solubility tests were prepared by Method B. The concentration of water was 36%. Fraction A was collected after standing for twenty minutes and contained 29.7% of the original acetate; B, three hours, 17.85%; C, twenty hours, 28.5%. D was obtained by adding a large volume of water to the filtrate of C and amounted to 19.3% of the original.

Solubility was estimated by placing about 0.1 g. of the sample in a test-tube and adding 20 cc. of the liquid in question. The test-tube was stoppered and placed on a tumbling machine for twenty-four hours. The appearance of the samples was noted at frequent intervals during this time and final notations were made three days later.

The data obtained in these tests are compiled in Table IV, these observations representing the final condition of the acetate.

TABLE IV

THE SOLUBILITY OF CELLULOSE ACETATE FRACTIONS IN ORGANIC LIQUIDS

Solvent	Fraction[a]				Solvent	Fraction[a]			
	Esters					Alcohols			
	A	B	C	D		A	B	C	D
Methyl formate	4	5	5	5	Methyl alcohol	0	0	0	0
Ethyl formate	4	5	5	5	Ethyl alcohol	0	0	0	0
n-Propyl formate	2	3	4	5	Benzyl alcohol	2	2	2	2
Methyl acetate	4	5	5	5	Cyclohexanol	0	0	1	4
Ethyl acetate	1	1	3	5		Ketones			
n-Propyl acetate	0	0	0	1	Di-methyl ketone	5	5	5	5
n-Butyl acetate	0	0	0	1	Methyl ethyl ketone	4	5	5	5
n-Heptyl acetate	0	0	0	0	Di-ethyl ketone	0	0	1	2
*Iso*propyl acetate	0	0	0	1	Cyclohexanone	5	5	5	5
Phenyl acetate	5	5	5	5	Methylcyclohexanone	4	5	5	5
Benzyl acetate	4	4	4	5		Halogenated hydrocarbons			
Resorcinol acetate	4	5	5	5	Chloroform	5	5	5	5
Methyl phthalate	4	5	5	5	Bromoform	0	0	0	0
Ethyl phthalate	0	0	1	2	Trichloro-ethane	5	5	5	5
Butyl phthalate	0	0	0	1	Tetrachloro-ethane	5	5	5	5
Mono-acetin	5	5	5	5	Pentachloro-ethane	3	4	4	5
Tri-acetin	0	1	1	1	Dichloro-ethylene	2	2	2	3
					Trichloro-ethylene	1	2	2	3
					Tetrachloro-ethylene	1	2	2	2

[a] The meanings of the symbols are as follows: 0, insoluble, that is, no apparent change; 1, slightly swollen; 2, highly swollen—almost solated; 3, turbid solution; 4, blue opalescent solution; 5, clear solution.

It appears on examination of the above data that the fractions of cellulose acetate that precipitate first from an acetone–water mixture are more insoluble in solvents in general than are those which precipitate later. It will be remembered that the observations recorded in the table were made after the cellulose acetate had been in contact with the solvent for three days and, therefore, indicate an equilibrium state of affairs with no description of the rate at which this equilibrium was reached. In every case where all the fractions ultimately dissolved, the rate of solution was invariably in the order D:C:B:A. Thus, with methyl acetate, the D fraction dissolved in eight minutes, C in twenty minutes, B in one hour and A in three hours.

All the fractions show a greater tendency to swell and dissolve in the lower member of an homologous series. If the most prominent atomic grouping in the cellulose acetate molecule is taken, as $H{-}\overset{|}{\underset{|}{C}}{-}O{-}CO{-}CH_3$, it may be said in a broad sense that cellulose acetate tends to swell and dissolve in those liquids that resemble it most closely in chemical structure. This is in general agreement with the views of Sheppard[8] and Whitby.[9]

Summary

1. A sample of a commercial acetone-soluble cellulose acetate has been fractionally precipitated. The fractions have the same chemical composition but different physical properties; this has been attributed to a difference in the state of aggregation of the glucose anhydride units in the micelles.

2. The solubility of cellulose acetate in organic liquids has been shown to be a function of its state of aggregation as well as its acetyl content.

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[Contribution from the Chemical Laboratory of Bryn Mawr College]

THE REDUCTION POTENTIALS OF VARIOUS PHENANTHRENEQUINONES

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The problem of correlating the structures of the quinones with their reduction potentials divides itself naturally into two distinct parts: a comparison of the potentials of the parent quinones which are derived from the various aromatic hydrocarbons and heterocycles, and a study of the manner in which substituent groups influence the oxidizing power of a given substance. The results of the present electrochemical study of a number of quinones of the phenanthrene series thus fall into two groups and each of these may be considered in the light of one or the other of the two aspects of the general problem.

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[8] S. E. Sheppard, *Nature*, **73**, March 17 (1921).

[9] G. S. Whitby, "Colloid Symposium Monograph," The Chemical Catalog Company, Inc., New York City, Vol. IV, **1926**, p. 203.