THE INFLUENCE OF THE FIBER STRUCTURE ON THE NITRATION OF CELLULOSE

by

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GENERAL INTRODUCTION

Reactions of fibrous cellulose are always more or less influenced by the fiber structure of the material. Native, mercerized or regenerated celluloses will all be different in this respect, partly because of their distinctive lattice structures, but mostly because of their unequal accessibilities. Reactions such as acetylation or etherification have to be carried out with activated cellulose, made more accessible by preswelling. On the other hand, the nitration of untreated cellulose usually is almost complete after a relatively short time, resulting in derivatives which have hitherto been assumed to be chemically very uniform. In technical nitrations, which involve a true equilibrium reaction, this uniformity is even more likely. In the present study, the influence of the fiber structure of cellulose on its nitration was studied. As shortening of the chain molecules would lead to changes in the fine structure through recrystallization, the nitrating mixture chosen was one containing nitric acid, phosphoric acid and phosphorus pentoxide, which is known to cause no degradation of cellulose. The fiber structure thus remained essentially the same throughout the reaction.

Nitrations were carried out to various degrees of completion in both rate-controlled and equilibrium-controlled reactions. The products obtained were subjected to a fractional solution procedure which would effect fractionation at least partly according to the location of the chains within the microfibrils. The other determining factors in fractionation would be the degree of polymerization and the degree of substitution of the macromolecules, the latter quantity being thought to be of more importance in this procedure than the former one. A considerable

number of fractions was collected until swelling of the material had distorted the fiber structure, and the degree of substitution and degree of polymerization were determined in each case. From the data thus obtained, information was gained as to the course of the nitration and the degree of chemical uniformity of the nitrates.

HISTORICAL INTRODUCTION

The Fiber Structure of Native Cellulose

Approximately forty years ago X-ray diffraction patterns of cellulose were first produced, which indicated the presence of ordered, three-dimensional regions on a polymolecular scale (1). However, these so-called "crystalline" regions did not account for all the properties of the fiber. When the X-ray results were compared with optical orientation data - which showed a lower average orientation for the total fiber than the X-rays did - it was claimed that these highly ordered "crystalline" regions were intermingled with relatively less ordered portions (2). Much attention has subsequently been devoted to gaining more information concerning the quantitative relationship between these two phases. As will be shown later, most studies have only led to the conclusion that there is no sharply defined boundary between the two, but rather that they merge gradually into each other (3).

From chemical and physical data, the basic unit cell of ordered cellulose was derived, and the number and positions of the anhydroglucose units established (4). The geometry of this cell furnished a clue to the type and magnitude of the forces holding the crystalline lattice together. Along the longitudinal axis of the cellulose molecules the units are held together by strong 1-4 glucosidic bonds. In one transverse direction, the distance between glucose rings is only 2.5 Å, suggesting hydrogen bonding between adjacent hydroxyl groups. In the other transverse direction, the interval is 3.1 Å, which is typical for van der Waals' forces (5). Since cellulose reactions depend, in nearly all cases, on the overcoming of one or more of these, the fact that they are of three different strengths would

seem to be quite significant.

At first, the disordered regions were designated as "amorphous", and were considered to be portions of randomly oriented cellulose chains. This rigid concept was gradually altered as experiments showed that this part of cellulose had many properties consistent with a wide range of partial crystallinity. Originally, studies of these disordered regions were based on analogies with completely "amorphous" polymers, such as unstretched natural rubber. The latter had liquid-like physical properties, but it was soon realized that this could not be the case with cellulose, which was relatively inflexible. Baker (6) proposed an intermediate state, or states, between the amorphous and crystalline conditions and even considered using a terminology based on "degree of lateral order". Nickerson and Habrle (7) also conceived the possibility of an intermediate region which they designated as "mesomorphous". Recently, Frey-Wissling (8) has suggested that the less ordered regions be called "paracrystalline".

The above modifications were stimulated mainly by the inconsistent experimental results obtained from measurements of cellulose crystallinity. Hermans (3) has compared various methods for estimating the percentage of crystallinity and has stressed the incompatibility of several of them. In addition, the traditional X-ray diffraction pattern of cellulose may have to be altered, due to some recent studies by Sen and Roy (9) on the effect of water present in the fibers. However, studies with the electron microscope, which is claimed to have a resolving power down to 50 Å, have shown that the only definite structural unit may be a crystalline fibril, about 100 Å in diameter (8)(10). Accordingly, the fiber is composed of these fibrils which, in turn, are made up of chain

molecules. From this information, and other data, a new simplified theory of cellulose fiber reactions has been formulated.

The Reactions of Cellulose Fibers

Cellulose fiber reactions were for a long time considered to be either "micellar-heterogeneous" or "permutoid" (used synonymously with "quasihomogeneous"). The backgrounds of both these theories have been adequately discussed by Sisson (11) and by Spurlin (12), and a critical evaluation of each major investigator's contribution has been made by Timell (13). A "micellar-heterogeneous" reaction was supposed to start at the surfaces of the crystallites and to proceed at a limited rate from layer to layer towards the center of each micelle. In a "permutoid" reaction, on the other hand, the cellulose chains were said to all have equal probability of being converted, with the more accessible, disordered regions reacting more quickly than the crystalline ones (14). The two theories are mutually contradictory, and it has been stated that certain experimental data cited in support of them were, especially in the case of the "micellar-heterogeneous" concept, the result of special, non-typical experimental conditions (13).

At the present time, a trend toward amalgamating the more rational aspects of each theory is evident, and Spurlin has suggested a simplified, general concept of cellulose fiber reactions (15). Partly on the basis of electron microscope studies, he has considered fibrils to be the only essential units of cellulose. This idea appeared as a suggestion in a paper by Astbury and Woods (16), and has recently been advanced by Frey-Wissling (8) and Ranby (10). The fibrils were supposed to be of indefinite length and from 100 Å to 300 Å in diameter. The main departure

from previous concepts was the idea that no distinct material was present between the fibrils. Instead, Spurlin offered a picture of interfibrillar crystallization - enough to maintain a loose bond between the fibrils. Each fibril became less crystalline as its surface was approached and at the interface between fibrils the disorder would be at a maximum.

This concept can be applied in interpreting results obtained in investigations on various cellulose reactions. Studies on the gradual acid hydrolysis of cellulose showed that there was an initial rapid phase followed by a much slower hydrolysis (17). Davidson put forward the explanation that the non-crystalline portion was first being hydrolyzed after which the crystallites were broken down much more slowly (18). When the hydrolysis was stopped after the initial fast reaction, the degree of polymerization (D.P.) of the material was found to reach a limiting value of approximately 250 (19). This was assumed to correspond to the average D.P. of the remaining crystalline regions - the completely hydrolyzed portions having been extracted by the acid. This D.P. was much lower than the original value and it was assumed that considerable chain rupture had occurred. The hydrolysis will also split the fiber lengthwise into basic fibrillar components, resulting in a rod-like micelle which has the same diameter as the original fibril (20). Ultrasonic vibrations have been found to split the fiber structure lengthwise, and when this is combined with a mild hydrolysis, rodlets of the same general size and shape have been produced (21). Ranby has reported that the width of these micelles produced by hydrolysis have a very narrow distribution, while the lengths have a much wider one (20). He compared the measured average lengths of rodlets observed through the electron microscope with viscosity measurements, and showed that the agreement was quite good. In almost all cases of

breakdown, fibrillation precedes transverse splitting, thus illustrating the difference between interfibrillar transverse weak bonding and random points of diminished crystallinity along the chain bundles (22).

Spurlin claimed that the bonding between adjacent fibrils was mainly responsible for the variations in reactivity of different cellulose samples. While the crystal structure at the interfaces of these fibrils was probably at least as disordered as the recurring weak spots along the fibril length, the effect of a small amount of interfibrillar crystallization would be to inhibit strongly the entrance of the reagent into the fibrils. This cross-linking is destroyed by swelling and promoted by favorable crystallizing conditions, e.g., drying from water (23) (24).

With a structure like this there will be three stages of reagent penetration: (1) The surface of the fiber reacts. (2) The reagent penetrates the interfibrillar spaces and reacts on the surfaces of the fibrils (Ranby has estimated that 20 per cent of the chains in native cellulose are on the surfaces of the fibrils (20)). (3) The reagent penetrates the crystalline regions and attacks the individual cellulose molecules there. From comparison of the diameters of the fiber and fibril, the importance of a reagent being able to penetrate to the fibril surface is accentuated; a thousandfold increase in the rate of reaction being involved (25). In line with this picture, swelling agents are classified as either interfibrillar or intrafibrillar. A reagent acting on cellulose must include a component able to act at least as an interfibrillar swelling agent or else the reaction will only take place on the surface of the fiber. This type of phenomenon has been recorded many times in the literature (3). Once the reagent gets to the surface of the fibrils it reacts most quickly at points of greatest disorder, penetrating into the crystallites from all sides. The

situation at any time before the reaction is completed can be depicted as in Figure 1.

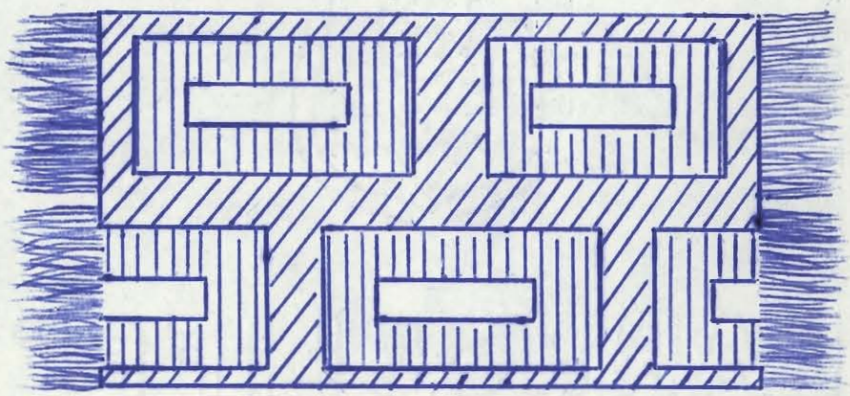

FIGURE 1

The Progress of Reaction Through Cellulose Fibers

Fully Reacted Partially Reacted Unreacted

Both along and across the fibers there will be such zones consisting of fully reacted, partially reacted and unreacted material. In nitration, the completion of the esterification is accompanied by recrystallization, so that the partially reacted portions will be much more swollen by the reaction medium than either of the other two. However, solubility in organic solvents would be expected to remain very low until the unreacted regions were nearly gone (15).

To sum up, it seems that reactions of fibrous cellulose are impeded by either the inability of the reactant to reach the surface of the

microfibrils, or by the amount, size and perfection of the crystalline interior of the fibrils. Factors prohibiting rapid penetration of the surface regions will usually include either lack of a sufficient swelling agent or excessive interfibrillar crystallization, caused, e.g., by drastic drying conditions ("hornification").

The Nitration of Cellulose

Cellulose nitrate was the earliest known derivative of cellulose and the first to reach industrial importance. The early studies on its stabilization were necessitated by explosions at manufacturing plants in various parts of Europe. When reasonable stability was finally achieved, its first use was as a military explosive (26).

The nitration reaction has been studied intensively by workers interested in the fine structure of cellulose and its derivatives. Their interest stemmed from the singular nature of this solid-liquid reaction, in which the initial material and the product remain in the solid state. While originally it was thought that anhydrous nitric acid was the nitrating agent in converting the hydroxyl groups to nitric ester groups (27), Farmer soon postulated that only part of the nitric acid radical was involved and offered a pseudo form, $O_2N \cdot OH$, as the active agent (28). More recently, kinetic studies and the use of isotopic oxygen have strongly indicated that only the hydrogen atoms are removed from the cellulose, and that the actual nitrating agent is the nitronium ion (NO_2^+) (29)(30)(31). However, it must be mentioned that Chedin, one of the most active workers in this field in recent years, claims to have found evidence that non-ionized nitric acid is the main nitrating agent (32).

While differences in reactivity of the three hydroxyl groups in

cellulose have recently been established, it is generally conceded that, for this type of reaction, the fine structure has the predominating influence on the progress of nitration (15). Early investigators were concerned with this problem in studies on technical nitrating mixtures containing sulfuric acid, the prime function of which was assumed to be to swell the fiber and allow the nitrating agent to reach the hydroxyl groups. Later, however, Lunge (33) showed that the sulfuric acid also acted as a dehydrating agent, and it was furthermore found that a small amount of water was needed for efficient nitration, as a necessary aid to swelling (34). The need to eliminate the water formed during the esterification indicated that cellulose nitration was an equilibrium reaction and this belief was strengthened when it was established that specific ternary mixtures of water, nitric acid, and sulfuric acid would nitrate cellulose to an extent solely dependent on the composition of the mixture (14). This equilibrium condition was considered proven when Berl and Hefter (35) showed that nitrates of different D.S. would attain the same nitrogen level if left in the same acid mixture, irrespective of whether their D.S. was higher or lower than the final value.

Nearly all theoretical studies on the mechanism of nitration have been based on X-ray investigations. Naray-Szabo and co-workers (36) first found that highly nitrated cellulose had a definite X-ray structural pattern. Since they could not get definite diffraction patterns of lower nitrates, they claimed that the latter were mixtures of the trinitrate and unchanged cellulose. Miles and Milbourne (37) studied swelling phenomena in the middle range of substitution and concluded that the indefinite X-ray patterns were the result of swelling brought about by the disordered crystalline structure of partially nitrated cellulose. Miles and Craik (38)

denitrated a series of nitrates and showed that the samples with a lower degree of substitution gave a mercerized cellulose while the higher ones did not. In another paper, the same authors visualized the reaction as proceeding in three stages. Up to 7.5% nitrogen, the diffraction pattern of the product remained the same as that of mercerized cellulose, the reaction evidently being limited to the hydroxyl groups at the internal and external surfaces of the fiber. During the second stage the internal forces holding the micelles together were partly destroyed, and the nitration occurred at random throughout the material. The amount of unreacted cellulose soon became too insignificant to produce a definite diffraction pattern; although the overall chain structure probably remained intact, since denitrated products gave relatively sharp patterns. This stage ended at 10.3% nitrogen and the third one was accompanied by an increasing order until 12.8% nitrogen, when the known pattern of "cellulose trinitrate" appeared (39). The nitration of cellulose would thus begin as an intermicellar and gradually develop into an intramicellar reaction.

Concurrent with the above work, Hess and Trogus (40) proposed another mechanism for the nitration of cellulose. They accepted the idea that only cellulose and the trinitrate were present in the product and suggested that this was due to a strictly micellar-heterogeneous reaction, proceeding from the surfaces of the micelles towards the crystalline centers. All chains were supposed to be completely nitrated on contact with the reagent, and the diffused diffraction patterns noted for the intermediate nitration range due to the mixture of the two crystalline forms.

Miles (41), in a critical review of the nitration mechanism, presented several facts in support of a permutoid type of reaction. The

formation of almost 100 per cent mercerized cellulose by denitrating nitrates of a low degree of substitution strongly suggested that the entire fiber structure had been penetrated. The previously-mentioned swelling phenomenon accompanying the middle range of nitration was also presented as incompatible with a trinitrate-cellulose mixture. Nitrates with a high degree of substitution were shown to be hardly swollen by nitrating mixtures, and Miles claimed that the swelling occurring during the nitration could only be explained by the presence of nitric acid inside the micelles. Miles also pointed out that the equilibrium nature of the nitration reaction could only be satisfactorily explained by a relatively random reaction throughout the chain structure. But he cautioned that the presence of a considerable amount of sulfuric acid would lead to increased disorganization, and thus to difficulties in interpreting the mechanism.

Both Miles and Trillat (42) studied the variation in crystallinity during the third stage of the nitration. The former author reported that the crystalline spacings increased slowly as the nitrogen content rose from 10.3% to 12.8%, and then rose abruptly to a maximum final value at 12.9%. Trillat, working with films, found an amorphous structure below 12.95% nitrogen and a crystalline form above this value. The results of these studies were confirmed by Mathieu (43) who showed that, in addition, the crystallinity of films depended on the drying temperature.

In 1944, Chedin and co-workers (32) initiated a series of investigations by means of Raman spectrography on the technical nitration of cellulose. Among other things they showed that the degree of hydration of the nitric acid might be the factor determining the nitration equilibrium - high nitration was achieved when there was little or no hydration.

Chedin and Tribot (44) studied the rate of nitration and claimed to be able to distinguish between two different reactions, an initial rapid one followed by a slow reaction. Only the planar nitric acid was said to be able to penetrate the crystalline portions, the sulfuric acid being restricted for steric reasons to the disordered regions (45)(46). This might be compared to an earlier study by Sakurada (47), who derived a theoretical equation based on diffusion as the controlling factor. This equation was applicable during the early stages of nitration, but was inadequate as the reaction proceeded.

Although the technical nitration is known to proceed very rapidly under favorable conditions, it was soon established that removing the water, the chief swelling agent, noticeably decreased the rate of nitration (40). As soon as other nitrating agents were tried, it became quite evident that the rate of nitration was often governed by the velocity of diffusion. Rogowin and Tichonow (48) compared the reaction rate of gaseous nitric acid to a liquid medium of the same strength, and found that the former reacted more slowly as it did not have the swelling capacity of the liquid. Lunge (33) used an increase in temperature to speed up the reaction with a mixture of nitric and sulfuric acid, but found that the effect decreased at higher temperatures. Rogowin and Tichonow (48) also reported a considerable increase in reaction rate with gaseous nitric acid when the temperature was raised. In another paper (49) these authors showed that adding N_2O_5 to 95% nitric acid raised the nitrating ability of this reagent, and explained this as a result of a more rapid diffusion. Chedin and Tribot (50) considered the case of aqueous nitric acid and developed an equation describing the nitration as depending on the presence of non-ionized, non-hydrated nitric acid. Taking

into account the water formed during the esterification, they showed that this equation fitted the experimental data only if the reagent was a strong swelling agent, i.e., if free movement throughout the structure was possible. To demonstrate the importance of a reagent's ability to diffuse, they attempted to nitrate dry fibers with acetyl nitrate, either alone or dissolved in carbon tetrachloride. Only 2% nitrogen could be introduced in this way, obviously because of insufficient swelling.

Early workers such as Sakurada (47) found an alternate method of increasing the rate of nitration, pretreating to facilitate diffusion. Chedin and Tribot (46) found that both water and pyridine could alter the fiber structure enough to increase noticeably the reaction rate. In addition, they were able to nitrate to 12.2% with acetyl nitrate in carbon tetrachloride provided the fibers were first swollen in water, then in glacial acetic acid and finally in carbon tetrachloride (50). They also showed that dissolving and precipitating a nitrate could make it susceptible to additional nitration with anhydrous nitric acid. Originally, this reagent could nitrate only to 13.3%, and the interior of the fiber seemed to be gelatinized by the heat and water formed during the reaction (51).

Excessive bulk alone has been shown to cause slow nitration, both with cotton cellulose (52) and pulpboard (26). Schiemann and Kuhne (34) compared cotton linters to wood pulp and found that the rate of nitration of the former was noticeably higher. The importance of the physical structure was accentuated by Brown and Purves (23), who reversed the pretreatment effect. Instead of swelling the fibers, they collapsed them by first wetting and then drying. This treatment not only slowed down the nitration, but also decreased the maximum nitrogen content which

could be reached with a specific nitrating agent. This work was later duplicated by Keays (53).

Spurlin has evaluated the studies on cellulose fiber reactions, and has come to the conclusion that interfibrillar crystallization is the main factor in limiting the reaction rate (15). He stresses the fact that water and pyridine are both known to have little effect on the crystalline regions, yet they activate cellulose reactions. Another point mentioned, which is consistent with Chedin's work, is that reduced accessibility brought about by "hornification" is not as marked when the reagent is mainly nitric acid. The latter is said to penetrate crystalline cellulose easily, and Spurlin describes "hornification" as induced interfibrillar crystallization.

As a catalyst in the nitration of cellulose, a mixture of phosphoric acid and phosphorus pentoxide has attracted wide interest. These reagents were first used by Berl and Rueff (54), who reported that the resulting cellulose nitrate had much higher viscosities and nitrogen contents than comparable ones prepared in the presence of sulfuric acid. The same authors also found that the minimum time required to produce a highly nitrated (13.8% - 13.9%) product was less than five minutes (55)(56). They claimed that cellulose suffered little or no degradation in this reaction, and this most important point has been confirmed by Davidson (57) and Nicolas (58). In an attempt to explain why the theoretical cellulose trinitrate (14.14% N) could not be made in this way, Davidson claimed that some ester groups of phosphoric acid were also formed, but the amount found was not sufficient to account completely for the failure to attain the theoretical nitrogen level.

Alexander and Mitchell (59) have described the preparation of an

optimum nitrating mixture: nitric acid, 64%; phosphoric acid, 26%; and phosphorus pentoxide, 10%, which was effected by mixing 90% fuming nitric acid with excess phosphorus pentoxide, the latter reacting with the water to produce the required amount of phosphoric acid. These workers recommended that the mixture be kept for three days before using, and said that it would retain its reactivity for several weeks. Heuser and Jorgensen, on the other hand, reported that the mixture must be used within a few days (60). If undegraded products with lower nitrogen contents are desired, it has been found that diluting the reagent with phosphoric acid will effect this (61).

The Chemical Heterogeneity of Cellulose Nitrate

Most definitive texts (14)(27)(62) on cellulose state that no appreciable variation in degree of substitution has been found in cellulose nitrates prepared by the usual methods. Yet, on studying the literature, there seems to be much evidence that this is not generally true. Abadie (63) in discussing this problem, quotes Champetier as concluding, from a study of a series of papers by other workers, that fractional precipitation does not produce fractions of different nitrogen content. Other authors use work by Brunswig (64) and Kumichel (65) as evidence that cellulose nitrate is chemically homogeneous. Berl and Hefter (35) and Craik and Miles (66), on the other hand, found a definite heterogeneity on fractional solution of cellulose nitrates. Miles (41) also cited work by Atsuki and Ishiwara which produced variations in nitrogen content. In addition, Craik and Miles reported that the viscosity seemed to increase with the nitrogen content. Many other investigations have been concerned with this particular phenomenon. Brown (67) found a spread in nitrogen content

from 13.69% to 13.95%, and Glegg (68) from 13.16% to 13.85%, both using nitrated cotton linters. Two sets of fractionations on technical nitrates were reported by Scherer and Rouse (69) and Scherer and Masuelli (70). The first paper showed a nitrogen range of 11.80% to 12.14% and the second 11.87% to 11.93%, and the authors concluded that there was no appreciable fractionation according to D.S. In these last four papers, which were fractional precipitation studies, the D.S. increased with the D.P. This type of dependency of the two variables was also reported by Zapf (71) and Munster (72). However, Timell (73) illustrated that the variation in D.S. was affected by the sort of cellulose used, since he showed that the decrease in D.S. with D.P. was much less with nitrated ramie than with nitrated linters.

Several workers have indicated, on the other hand, that the two variables, D.S. and D.P., may not show corresponding changes throughout the fractionation. Wilson and Miles (74) reported on a fractional solution of cellulose nitrate (prepared with gaseous nitric acid and a limited reaction time) using aqueous acetone, which gave complex results (See Table I).

Scherer and Thompson (75) carried out a fractionation of a commercial cellulose acetate in which the D.S. increased with decreasing D.P. Timell and Purves (76) listed several other workers who found complex D.S.-D.P. relationships on fractionating such derivatives as methylcellulose and cellulose xanthate diethylacetamide. They studied the fractionation of methylcellulose having a low degree of substitution by means of their nitrated derivatives, since the methylcelluloses themselves were not sufficiently soluble. Using fractional precipitation, they found a general inverse relationship between D.P. and D.S., which is illustrated in Figure 2.

TABLE I

Fractional Extraction of an Incompletely Nitrated Cellulose (74)

Fraction No.	Weight, %	Viscosity	Nitrogen, %
1	2.93	43	12.70
2	2.46	48	12.80
3	19.42	58	13.35
4	56.87	46	13.10
5	4.28	--	10.70
6	0.61	--	-
Residue	16.74	--	10.70

The D.P. at which the D.S. leveled off increased with the increase in D.S. of the original material. Fractional solution of the same materials gave similar results, but seemed to show a definite tendency toward producing low D.P. fractions with higher D.S. values than the other method. The authors discussed this with reference to Jorgensen's concept of fractional solution, which will be described in the next section.

Much light has been provided by Rosenthal and White (77) on the marked effect of the chemical nature of the participants in solvent fractionation. They were able to reverse the order of variation in D.S. by changing the non-solvent used in fractional precipitation of a cellulose acetate. With water, the fractions showed D.S. decreasing with D.P.; with heptane, the D.S. increased as the D.P. decreased. With this established, they evolved the idea of "crossfractionation". Each fraction was first obtained using water and then refractionated using heptane (or

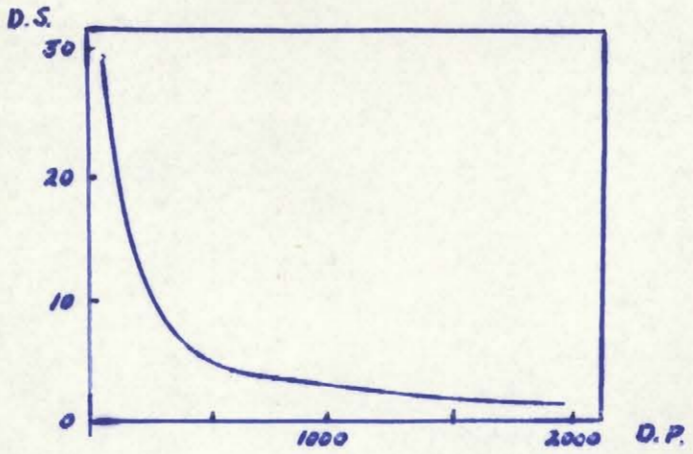

FIGURE 2

D.S.-D.P. Relationship Obtained by Fractionation of Nitrated Methylcelluloses (76)

pentane). This was repeated until each fraction showed a relatively narrow distribution of both D.S. and D.P., and the resolution was much better than could be obtained using the conventional precipitation technique. Timell has suggested (73) that this practise could be applied to fractionation of cellulose nitrates, using the same solvents. A parallel observation of the dependency on the chemical nature of the solvent system was made by Scherer and Lou (78), who described the necessity of altering the solvent system according to the D.S. of the material, in order to achieve successful fractionation of cellulose nitrates.

Carboxymethylcellulose was found by Timell (79) to be very susceptible to fractionation according to D.S. Even fractional precipitation resulted in a sequence of fractions in which both the D.S. and the

D.P. showed complex changes. Fractional solution seemed to increase the dependency of the fractionation on the D.S.

Abadie (63) gives some preliminary data taken from work in progress on industrial nitrocellulose, some of which show definite variations in nitrogen content. Ellefson (80) indicated that fractions obtained in a study of nitrated wood pulps had variable nitrogen contents. Mathieu (81), nitrating with N_2O_5, found non-uniformity most evident if the reaction was stopped after a limited time. Emery and Cohen (82) severely criticized several published papers on the grounds that neglecting the variation in nitrogen content led to large errors in viscosity measurements. They submitted data showing how wide the variation in degree of substitution could get and to what extent it influenced the determination of chain-length distribution. Page (83), however, found no variations in D.S. on fractionation of nitrates and several other papers on fractionation do not mention the degree of substitution of the fractions at all (84)(85)(86).

Fractionation According to D.S.

Generally, most early work using fractional precipitation failed to show any appreciable variation in chemical content between the fractions (87). As technique improved, however, and especially in cases where the investigators were specifically interested in distribution of the groups, distinct differences in D.S. were found (76)(82). The influence of the D.P. on the order of fractionation was probably considerable in all these cases. In contrast, the record of fractional solution shows that it has nearly always resulted in a fractionation according to D.S. as well as D.P. According to Scott (88), theoretical considerations based on solution

thermodynamics definitely indicate that any appreciable heterogeneity will strongly influence the course of either type of fractionation. According to Jorgensen (89), the factor of accessibility is superimposed on the other determinants in fractional solution. When an incompletely substituted derivative is fractionally extracted, the first low D.P. fractions will not include all the material in that D.P. range, but only the short chains in the disordered, most easily accessible regions.

A variety of solvent systems has been used in the past for fractional solution of cellulose nitrates, namely acetone-water (66)(90), ethyl ether-ethanol (35), alcohol-water (91), alcohol-acetone (92), etc. An ethyl acetate-ethanol system was first used by Atchison (93) and subsequently by others (84)(89), but nowhere was the nitrogen content of the fractions determined.

Wilson and Miles (74) published data of a fractional solution (See Table I), but made no comment on the anomalous D.S. distribution. Cherubin (94) performed a simple fractionation, dividing his samples into acetone-soluble and -insoluble portions, in a study of the early stages of nitration with a weak technical mixture. His fractions showed very great differences in D.S. Recently, and after the present work was terminated, Smith (92) published a fractional solution study of D.S. and D.P. distributions of low D.P. cellulose nitrates, having average nitrogen contents between 11.5% and 12.5%. These were prepared by the equilibrium method of Lindsley and Frank (61); i.e., diluting the nitric acid-phosphoric acid-phosphorus pentoxide mixture with excess phosphoric acid. Smith's results indicate a non-uniform distribution of nitrogen content for sulfite pulp derivatives, but not for cotton linters.

The important fact that the viscosity of a cellulose nitrate is

dependent on its degree of substitution was only recently recognized. Wannow (95) was the first to study this phenomenon in 1943 and his empirical relationships were subsequently used by several workers. Lindsley and Frank (61) have recently derived an empirical equation which provides a correction factor for viscosity values at any nitrogen level, the increase in viscosity with increasing D.S. being mostly due to the simultaneous increase in degree of solvation, i.e., in effective hydrodynamic volume of the molecular coils.

EXPERIMENTAL PROCEDURE

Nitration of Cotton Linters

The Preparation of the Nitrating Mixture

Reagent grade fuming nitric acid was available which had a distinct yellow color, indicating the presence of dissolved oxides of nitrogen. Since the latter would be expected to cause some degradation of the cellulose, it was considered desirable to remove them by a method used industrially; nitrogen gas being passed first through concentrated sulfuric acid and then through the nitric acid to be cleaned. The colorless acid was titrated with standard alkali and assayed a 92.5% acid content. It could be stored in the dark at 5°C. indefinitely without any noticeable reappearance of a yellow color.

The components of the nitrating mixture used were those prescribed by Alexander and Mitchell (59). Fuming nitric acid was mixed with phosphorus pentoxide in the weight ratio of 1000 g. of acid to 404 g. of the latter. The nitric acid was placed in a flask having a wide ground glass joint and cooled in a brine bath at -15°C. The flask was then taken out of the cold bath and scoops of reagent grade phosphorus pentoxide added while the mixture was swirled by hand. After cooling in the brine bath, this procedure was repeated until the required amount of anhydride had been added. The mixture was then placed in the dark for about twenty-four hours at 15°C. with intermittent shaking to dissolve the remaining solid matter. It was then stored in the dark at 5°C. and could be used as long as it remained homogeneous and comparatively uncolored, which usually was within the next three days. After this time, crystalline material would precipitate out and the mixture became progressively more

yellow. The precipitation could be inhibited by keeping the mixture at a higher temperature but this accelerated the color formation. Nitrations using highly colored reagent gave very poorly nitrated products.

Preparation of the Cotton Linters

Acetate grade cotton linters obtained through the courtesy of the Hercules Powder Company, Wilmington, Del. were extracted in a Soxhlet apparatus with a 2:1 benzene:ethanol mixture for 24 hours, after which the de-waxed linters were air-dried and stored in closed bottles. Before nitration they were dried over-night in a desiccator over phosphorus pentoxide.

Equilibrium Nitration

Sample No. 1: - Ten g. of dried linters was added to 1,000 g. of nitrating mixture and allowed to stand for four hours at 5°C. The excess acid was removed by means of a suction funnel, and the fibrous material dropped piecemeal into a large amount of 50% aqueous methanol which was immersed in a brine bath set at -15°C. A mechanical stirrer continually agitated the methanol bath and the fibers were kept there for thirty minutes. They were then washed twice with fresh 50% methanol and subsequently refluxed for five minutes three times with this aqueous methanol. Finally, they were steeped in methanol for two hours, filtered off with suction, and then dried in a vacuum oven at 60°C. for two hours. The dry fibers were then stored in an evacuated desiccator over phosphorus pentoxide.

Sample No. 2: - The above procedure was repeated on another ten g. of material. The only deviation was the use of a five hour reaction time instead of four.

Sample No. 3: - Another ten g. was nitrated with the following alterations in procedure: the reaction time was only ninety minutes, the product was stabilized first dropping the fibers into cold dilute acetic acid, and the final drying was from water.

Sample No. 4: - Another ten g. was nitrated for five hours, stabilized with 50% aqueous methanol but finally dried from water.

The analytical data for these four samples are listed in Table III.

Samples Nos. 5, 6, 7, 8: - In order to obtain derivatives prepared under equilibrium conditions with lower average nitrogen contents, the standard nitrating mixture was diluted with the following proportions of 85% phosphoric acid (61): respectively; 50%, 40%, 35%, and 30% by volume. The nitrations were carried out for four hours at 5°C. and the products stabilized with 50% aqueous methanol as before and dried from water. The results are shown in Table IV.

Rate Controlled Nitration

A Dewar flask containing methanol was used as a cooling bath and dry ice added to obtain the required low temperatures. The reaction flask containing the nitrating mixture was placed in the cold bath and time allowed for equilibrium with the surrounding liquid to be reached. The mixture was in every case the full strength reagent used previously for complete nitration, and the temperature was determined by means of an alcohol thermometer placed directly in the reaction flask. Dried cotton linters were dropped into the nitrating mixture and the thermometer used to stir the mixture to a uniform slurry, after which it was removed and the flask stoppered for the rest of the run. After the required reaction time the content of the flask was quickly poured into a large excess of

vigorously stirred ice water. The nitrated product was then stabilized with 50% aqueous methanol as previously. In all nitrations the acid:cellulose weight ratio was maintained at 100:1.

At first a series of exploratory nitrations at different times and temperatures were run, in order to gain some information on the effect of these variables. The conditions used and the nitrogen contents of the products are given in Table V. Some of these nitrates proved useful for fractionation studies.

Since the temperature seemed to strongly influence the rate of nitration, additional time studies were carried out on a small scale (15 g. of acid and 150 mg. of cellulose) to determine the optimum temperature for rate-controlled nitration (Table VI).

A reaction temperature of -32°C. seemed to be best suited for producing material with nitrogen contents between 10%-14%. Two 7.5 g. samples were accordingly nitrated at this temperature with the following unexpected results:

15 min. reaction time . . . . . 13.94% N

18 " " " . . . . . 13.99% N

The reaction seemed to be proceeding more rapidly than could be expected, considering the results obtained in the small-scale nitrations at this temperature. An additional series of nitrations using 5 g. samples confirmed this accelerated rate phenomenon (Table VII).

The following series of samples was accordingly obtained for fractionation studies:

Sample No.	Nitrogen, %
9	9.70 (used only for solubility tests)
10	12.05
11	12.56
12	13.12
13	13.62

Analytical Procedures

Determination of Nitrogen Content

The semi-micro Kjeldahl method used for determination of nitrogen content throughout this investigation was evolved from the standard procedure as described by Gunning (96). Continuous use over the years in these laboratories has produced a modification which is well adapted to handling cellulose nitrate samples.

The cellulose nitrate samples were dried for at least twenty-four hours in a desiccator at 0.01 mm. pressure over phosphorus pentoxide. A one inch square of white cigarette paper was weighed on a balance to 0.00005 g. The sample was then placed on the paper and weighed as quickly as possible, the weight being kept between 10 and 25 mg. Both paper and sample were then transferred to a 30 ml. Kjeldahl digestion flask and 2.5 ml. was added of a solution containing 35 g. of salicylic acid dissolved in 500 ml. of concentrated sulfuric acid. This solution tended to turn a dark amber color when left standing in the light, but could be kept colorless in the dark.

The sample dissolved in the acid after $\frac{1}{2}$-2 hr., depending on how much it was shaken and the age of the acid mixture, the result being an amber colored clear solution. (If any kind of violent reaction took place when the acid was added to the sample, the latter contained some entrained liquid and the analysis was invalid). Approximately 300 mg. of sodium thiosulfate crystals were then added and the flask gently swirled to produce a uniform mixture. After standing for at least ten minutes, the flask was placed on the digestion rack and heated with a low flame until white fumes reached halfway up the neck of the flask. The heat was then removed and the flask allowed to cool somewhat, after which 600 mg. of

anhydrous potassium sulfate was added. The mixture was then completely digested, starting with a low flame and gradually increasing the heat to avoid excessive bumping. The digestion was complete when the mixture became a clear, colorless solution. Bradstreet (97) listed several workers who recommend an "afterboil" to insure complete conversion to ammonia, but no evidence could be evinced here that this was necessary. After digestion was complete, the flask was cooled. At this point the acid solution should be clear, viscous and colorless. If it changed to an opaque solid, the presence of too high a concentration of potassium sulfate was indicated, which, according to many workers (97)(98), might cause decomposition of the ammonium sulfate in the course of high temperature digestion.

The cooled, digested mixture was diluted with 8 ml. of distilled water and then transferred to a steam distillation apparatus. The digestion flask was washed four times with distilled water to bring about a complete transfer to the distillation unit. A solution of 40% sodium hydroxide (10 ml.) was added to the mixture and the distillation started. The distillate was absorbed in 25 ml. of a 1.0% boric acid solution which contained some methyl purple, and which was just on the violet side of this indicator. The distillation was continued until the contents of the flask had increased to 60 ml. The green solution was then titrated against standard hydrochloric acid in a 10 ml. burette, calibrated to 1/20 ml. Blank determinations used 0.10 ml. of the acid and the calculation for per cent nitrogen was:

$$\%N = \frac{[\text{Vol. of Acid} - 0.1 \text{ ml.}]\,[\text{N acid}]\,[1400]}{[\text{Weight of Sample}]\,[1000]}$$

Once the technique was established, the precision of the method came to $\pm$ 0.03% nitrogen. The hydrochloric acid was internally standardized by running several analyses on potassium nitrate which had been recrystall-

ized twice from ethanol and dried at 105°C. This compound contained 13.86% nitrogen, and when this figure was inserted in the above equation, the normality of the acid was determined.

Viscosity Measurements

In general, all viscosity measurements were done with reagent grade anhydrous ethyl acetate. A standard Cannon-Fenske viscometer was used and all measurements were carried out in a constant temperature water bath maintained at 25 ± 0.02°C. From 5 to 15 mg. of each sample was weighed directly into a 50 ml. volumetric flask, about 25 ml. of solvent was added, and the flask shaken until all the material had dissolved. More solvent was added up to the 50 ml. mark and the solution allowed to stand for at least one hour. A 10 ml. aliquot was then introduced into the viscometer and the time of flow checked until three values agreed within ± 0.1 sec.

The specific viscosity was calculated from t, the time of flow of the solution, and t_o, the time of flow of the solvent:

$$\eta_{sp.} = \frac{t}{t_o} - 1$$

It was then corrected for loss of kinetic energy by means of the following equation:

$$\eta_{sp.corr.} = \eta_{sp.}\left[1 + \frac{t_o + t}{t} \cdot \frac{F_o}{1 - F_o}\right]$$

F_o was a factor peculiar to any one viscometer and was found from the expression:

$$F_o = \frac{d_o V}{8\pi t_o \eta_o L}$$

where: d_o = density of the solvent

V = volume of the viscometer bulb in ml.

t_o = solvent time of flow

η_o = viscosity of solvent in poise

L = length of the viscometer capillary in cm.

For the viscometer used in this investigation, ethyl acetate produced a factor:

$$F_o = 0.0311$$

The intrinsic viscosity was calculated by the use of Martin's empirical equation (99):

$$\log [\eta] = \log \eta_{sp.}/c - K[\eta]c$$

where: c = concentration in g./100 ml.

K = constant = 0.20.

The intrinsic viscosity was in all cases corrected for the deviation in nitrogen content from the trinitrate. This was done by means of the equation derived by Lindsley and Frank (61):

$$\log \frac{[\eta]_T}{[\eta]} = \log (1.833 - 0.0589\ N) + (14.15 - N)0.114$$

where: $[\eta]_T$ = intrinsic viscosity adjusted to the trinitrate

$[\eta]$ = uncorrected intrinsic viscosity

N = nitrogen content in per cent.

This equation was reproduced graphically, with the quantity $\frac{[\eta]_T}{[\eta]}$ plotted against percentage of nitrogen, and the correction factor for any particular nitrogen content could thus be read off directly from this graph (Figure 3).

$$\text{LOG}\ \frac{[\eta]_T}{[\eta]} = \text{LOG}\,(1.833 - 0.589\,[\%N]) + (14.15 - [\%N])\,0.114$$

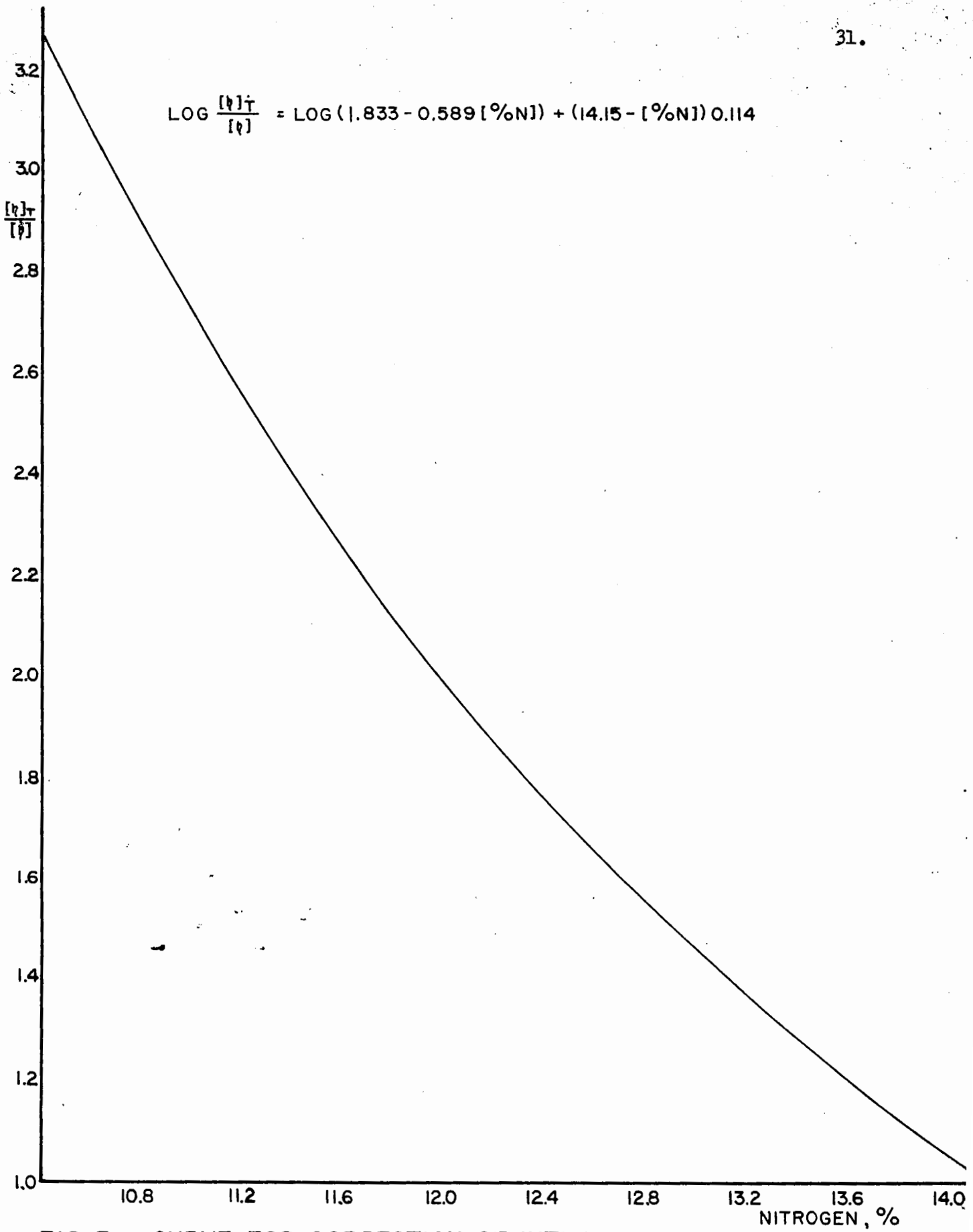

FIG. 3: CURVE FOR CORRECTION OF INTRINSIC VISCOSITY FOR DEVIATION FROM THEORETICAL TRINITRATE.

Fractional Precipitation

In order to have a relative basis of comparison for fractional solution, Sample No. 1 was fractionated by a conventional precipitation method, using acetone as the solvent and water as the precipitant (73). This revealed the overall chain length distribution for the cellulose material (Figure 4), and also indicated some chemical heterogeneity among the shorter molecules (Table VIII).

Fractional Solution

The Fractionation Mixtures

The solvent mixtures were composed of U.S.P. ethanol (95%) and reagent grade anhydrous ethyl acetate, according to the schedule in Table II.

TABLE II

Mixed Solvent System for Fractional Solution

Mixture No.	Ratio:ethanol/ethyl acetate	Ethanol, %
I	10/9	52.7
II	10/10	50.0
III	10/11	47.6
IV	10/12	45.4
V	10/13	43.5
VI	10/14	41.7
VII	10/15	40.0
VIII	10/16	38.5
IX	10/17	37.1
X	10/18	35.7
XI	10/19	34.5
XII	10/20	33.3
XIII	10/21	32.3
XIV	10/22	31.3

Fractionation of "Completely" Nitrated Cellulose

First attempt:- Five g. of cellulose nitrate No. 2 was placed in a 1-liter flask with 500 ml. of mixture No. IV. The flask was shaken for two hours and the supernatant liquid removed by passing it through a coarse sintered glass filter into a suction flask. The extraction was repeated with another 500 ml. of the same mixture and the extracts combined. The total solution was placed in a large dish and evaporated almost to dryness over a steam bath. The remaining solution was then transferred to a tared small evaporating dish and kept in a vacuum oven at 60°C. for at least four hr., after which it was finally dried over phosphorus pentoxide in an evacuated desiccator for 24 hr. and then weighed. The fibrous undissolved material which remained on the filter was returned directly to the extraction flask and the next solvent mixture, No. V, added. This procedure was repeated until the undissolved material became swollen and lost its fibrous nature, which in this case occurred when mixture No. XIV was used. The weights of the fractions obtained by this method are shown in Table IX. They were, in all cases, obtained as brittle, slightly discolored films, and the sum of their weights considerably exceeded the original one, as is shown in the table. In addition, attempts to determine the nitrogen contents produced results both erratic and low.

The recovery of dissolved cellulose nitrate:- The effect of recovering the fractions by evaporation of the solvent was studied with regard to both temperature and the overall efficiency of the solvent removal. Two samples of nitrate No. 2, containing 13.88% nitrogen, were weighed and then dissolved by shaking for six hours in a mixture of 20 ml. of ethanol plus 100 ml. of ethyl acetate. Sample A was evaporated to dryness at room temperature, while Sample B was similarly treated but the evaporation hastened

by means of a steam bath, as in the previous experiment. Both samples were then dried in a vacuum oven at 60°C. for 14 hr., with their weights determined after 2, 4, and 14 hours of drying. They were then stored overnight in a vacuum desiccator over phosphorus pentoxide and their nitrogen contents determined. The results are shown in Table X, and indicate the inefficacy of this method of isolation.

The use of precipitation for removing the cellulose nitrate from solution was investigated, first with 5:1 ethyl acetate:ethanol as the solvent and mixtures of ethanol and water as the precipitant. A weighed quantity of nitrate No. 2 was dissolved in the solvent mixture and then precipitated by slowly pouring the solution into an excess of precipitant. The precipitated fibers were separated on a coarse sintered-glass filter and dried as previously. The results of three runs are shown in Table XI.

In a parallel study, the solvent composition was altered by increasing the proportion of ethanol. Samples were dissolved in 3.5:1 and 2.5:1 ethyl acetate:ethanol mixtures and precipitated in identical manners. The comparative recoveries and nitrogen contents are found in Table XII. Since the latter solvent mixture did not dissolve all the material, an additional comparison was made to account for the apparent low recovery. This time the mixed solvent after solution was evaporated at room temperature and replaced by reagent grade acetone. The acetone solution was then poured into water and the precipitated fibers dried as usual. The results of this technique are also recorded in Table XII.

Since solution of Sample No. 2 caused a decrease in nitrogen content on precipitating, comparative experiments were run on nitrates No. 3 and No. 4. The results, in Table XIII, all involved precipitation of acetone solutions into water.

First Modification of the Procedure:- Extractions on Sample No. 2 were carried out as before, except that an additional solvent mixture, No. II, was introduced into the series before No. IV. The fractions were isolated by first concentrating the solutions at room temperature to approximately 100 ml., and then precipitating into a 33% aqueous ethanol bath, after which the fibers were collected on tared sintered glass filters and dried. This experiment was carried out in duplicate to assess the reproducibility of the procedure, although it should be noted that the room temperature during the second run was noticeably lower than in the first one. The comparative weights, viscosities and nitrogen contents are summarized in Tables XIV-A and XIV-B.

After the extraction with mixture No. XIV, the residual material, which was somewhat swollen, was extracted with acetone. In both cases, not all the material would dissolve. The insoluble portion was separated by filtration and the dissolved part precipitated into water. The data for both are included in Tables XIV-A and XIV-B. To obtain an equivalent residue without carrying out the stepwise fractionation, a sample of nitrate No. 2 was extracted with mixture No. XIV, and the residue dissolved in acetone. In This case no insoluble portion was found, as is shown in Table XV.

Final Modification of the Procedure:- Since it was strongly suspected that temperature differences would influence the fractional solution, all subsequent fractionations were carried out at a constant temperature. A wide-necked flask was placed in a water bath set at 25 $\pm$ 0.02°C., and agitation supplied by a glass stirrer introduced through a mercury seal. A single extraction with 500 ml. of solvent for three hours was used for each fraction. Isolation of the extract was performed in a

rotary evaporator, which allowed rapid removal of a solvent under vacuum at a controlled temperature. By this means each fractionation solvent was quickly removed (in about 15 min.), and the solid matter could be easily redissolved in acetone and then precipitated into water.

Duplicate fractionations were attempted on nitrate No. 3 (13.80% N), and showed quite conclusively that it had distinctly different solubility characteristics as compared to No. 2. Only a few fractions could be obtained before the material swelled, and the weight proportions were excessively non-uniform. The results indicated, however, an encouraging reproducibility (Table XVI).

Another preliminary experiment was carried out with Sample No. 4, which contained 13.95% nitrogen. In concordance with the previous results, it was found to yield much smaller fractions initially, and to be strongly resistant to swelling. It was therefore inferred that small differences in average nitrogen content could not be ignored in carrying out fractional solutions of these types of nitrates.

As a means of decreasing the solvent power of the mixtures for use with nitrate No. 3, water was added to make up 5% of each solvent mixture, and a small-scale fractionation using 2 g. of material was performed. As a control measure, a similar fractionation using the original mixtures was also carried out. The comparative results are given in Table XVII, and illustrated in Figure 5. It was evident that the water depressed the dissolving and swelling power of the mixtures, the swelling beginning after 30%-40% of the material had been removed.

A full-scale duplicate fractionation was then carried out on nitrate No. 3, using the diluted mixtures. The complete data are recorded in Tables XVIII-A and XVIII-B. A single fractionation was also performed on Sample No. 4, using undiluted solvents, in this case. The results are

listed in Table XIX.

Solubility Tests

The solubility properties of the incompletely nitrated derivatives differed markedly from those which were substituted to a higher degree. This was evident as soon as an attempt to fractionate Nitrate No. 11 (12.56% N) was made, using the unmodified solvent mixtures. The data (in Table XX) indicated an excessive solubility in the early phase of the fractionation and a sudden insolubility in the later stage.

In order to obtain more information about the nature of these incomplete nitrates, the most extreme case, No. 9 (9.70% N), was studied. Its solubility in four solvent mixtures, having ethanol contents from 20.0% to 28.6%, was determined by shaking individual samples for twenty-four hours in each mixture. The insoluble residue was then filtered off and weighed:

ethyl acetate:ethanol - 2.5:1 . . . . . 63% insoluble
" " : " - 3.0:1 . . . . . 70% "
" " : " - 3.5:1 . . . . . 68% "
" " : " - 4.0:1 . . . . . 65% "

Since modification of the solvent in this way seemed to have little effect on the relative insolubility of the material, the study of this sample was not continued. However, the nitrogen contents of both soluble and insoluble portions were determined and averaged:

Soluble - 12.50% N Insoluble - 7.40% N

The solubility of nitrate No. 11 was studied further by viscosity measurements. Seven samples of this derivative were weighed into 50 ml. volumetric flasks and viscosity determinations were carried out, using as solvents the following series:

(1) 90% ethyl acetate - 10% ethanol

(2) 85% " " - 15% "

(3) 80% " " - 20% "

(4) 75% " " - 25% "

(5) 70% " " - 30% "

(6) 65% " " - 35% "

(7) 60% " " - 40% "

All seven samples were incompletely soluble. The specific viscosity of each soluble portion was calculated with respect to the time of flow of its solvent, and a comparative intrinsic viscosity found by dividing by the weight of the original sample. This final value was relatively uniform for all seven solvent systems, indicating that the ethanol content had no effect on the dissolving power in this range.

The effect of diluting a known solvent mixture with limited amounts of water was studied, using a reprecipitated sample containing 12.84% nitrogen (The first fraction obtained in the experiment described in Table XX). A mixture of ethyl acetate and ethanol (2.5/1) was first diluted with enough water to make up 15% of the total volume, and the sample then extracted for 6 hr. The residue was further extracted with a similar mixture containing only 10% water. The extracted portions were:

(a) 15% water solution - 11% of the sample

(b) 10% " " - 39% " " "

Since this sample was 39.2% of the original material, the above sub-fractions were: (a) 4.3% and (b) 15.3% of the total derivative.

Fractionation of The Products of Rate-Controlled Nitration

Sample No. 13:- A first attempt to fractionate nitrate No. 13 (13.62% N) yielded a somewhat unexpected result. Considering that Sample No. 3 required a 5% aqueous dilution of solvents to prevent excessively large early fractions, it was expected that a similar dilution would suffice for No. 13, which had a nitrogen content only slightly lower than the former. However, when No. 13 was fractionated with these solvents, only 20.0% of the sample could be extracted using the complete range of solvent mixtures. In fact, almost the entire extraction was accomplished early in the fractionation, with mixture No. II. The residue was partially soluble in acetone. Actually, only three fractions were obtained:

Soluble in mixture II - 20%

" " acetone - 69%

Insoluble - 11%

Since the nitrate showed such surprisingly high resistance to fractionation, it was decided to fractionate it with the original undiluted mixtures. This produced a successful separation into 11 fractions, including a residue which was again partially soluble in acetone. The results are tabulated in Table XXI.

Sample No. 12:- This nitrate was fractionated into 9 fractions by means of mixtures diluted to 2% water content. The results are given in Table XXII.

Sample No. 11:- This nitrate produced 17 fractions when treated with solvent mixtures containing 5% water. The results are given in Table XXIII.

Sample No. 10:- This nitrate produced 16 fractions when treated with solvent mixtures containing 10% water. The results are given in Table XXIV.

Renitration of Residues:- Some of the insoluble residues from the above fractionations were renitrated in order to make them soluble for viscosity determinations. The standard non-degradative nitration mixture was used and the samples were treated for 24 hr. at 5°C. These viscosities are included in the appropriate tables of fractionation data.

Fractionation of Incomplete Nitrates Prepared Under Equilibrium

Sample No. 7:- This sample could only be divided into three fractions, the data for which are given in Table XXV. The residue was insoluble in ethyl acetate and acetone.

Sample No. 6:- This sample could not be fractionated into more than two components under any of the conditions applied. It separated into soluble and insoluble portions which were consistent as to per cent weight and nitrogen content when any of the following solvents were used: mixture I (5% aqueous dilution), mixture I (undiluted), mixture XIV (5% aqueous dilution). The insoluble portion was completely resistant to further extraction by mixture XIV (undiluted), ethyl acetate, acetone, ether/ethanol (2/1), ethanol, and ethanol/ethyl acetate mixtures (10/7, 10/6). The data for the two fractions are given in Table XXVI.

Sample No. 5:- This sample showed a strong tendency toward swelling and it was necessary to use fractionating mixtures which contained 15% water. Even so, only five fractions could be obtained, as shown in Table XXVII.

Fractionation of Regenerated Cellulose Nitrates

Sample No. 13:- Three g. of this sample was dissolved quickly in 1500 ml. of acetone with the aid of a Waring Blendor. Not all the material was soluble, however, and the mixture, on centrifuging, separated into a

clear supernatant liquid and a swollen gel. The former was poured into a large excess of water to precipitate it, and dried as usual. The gel was also poured into water and could be recovered as a loose, fibrous material. The two products had the following characteristics:

Soluble portion (88.5%); Nitrogen content: 13.58%, $[\eta]_T$:26.0

Insoluble " (11.5%); " " : 12.93%

The soluble portion was fractionated in the same manner as Sample No. 13 had been. In this case, the undissolved material became swollen and each fraction had to be separated by centrifuging instead of filtering. The entire sample was divided into 8 fractions, as shown in Table XXVIII.

Sample No. 3:- Three g. of this sample was treated in the same manner. The sample was completely soluble in this case, and the fractionation could be carried out on the entire sample after it had been precipitated. The precipitated material had the following characteristics:

Nitrogen Content: 13.51%, $[\eta]_T = 26.3$

On fractionating, it produced 10 fractions (Table XXIX).

EXPERIMENTAL RESULTS

TABLE III

Nitration of Cellulose Under Equilibrium Conditions

Sample No.	Nitrogen, %	$[\eta]_T$, dl./g.(a)
1	13.82	25.0
2	13.88	26.1
3	13.80	22.9
4	13.95	25.4

(a) All values are intrinsic viscosities in ethyl acetate corrected for deviation from the trinitrate value, 14.14% N.

TABLE IV

Preparation of Partial Nitrates Under Equilibrium Conditions

Sample No.	Phosphoric Acid Dilution of Nitrating Acid, %	Nitrogen, %	$[\eta]_T$, dl./g.
5	50(a)	11.51	23.6
6	40	12.43	(Insoluble)
7	35	13.28	(partially) (insoluble)
8	30	13.79	22.8

(a) by volume

TABLE V

Results of Varying Time and Temperature of Nitration
(750 g. of nitrating acid and 7.5 g. of cellulose)

Temp., °C.	Time, min.	Nitrogen, %
-38	10.0	9.70
-38	17.5	10.95
-36	15.0	11.17
-36	20.0	12.05
-34	15.0	12.56
-34	20.0	13.62

TABLE VI

Rates of Nitration at Three Low Temperatures
(15 g. of nitrating acid and 150 mg. of cellulose)

Temp., °C.	Time, min.	Nitrogen, %
-35	15	10.70
"	20	10.72
"	25	10.78
"	30	11.33
-32	5	10.07
"	10	11.86
"	15	13.00
"	23	13.56
"	25	13.80
"	30	13.85
"	40	13.87
-30	20	12.66
"	27	13.60

TABLE VII

Rate Of Nitration at -32°C.
(500 g. of nitrating acid and 5 g. of cellulose)

Reaction Time, min.	Nitrogen, %
5	10.37
8	13.12
10	13.74
15	13.91

TABLE VIII

Fractional Precipitation of Sample No. 1
(Nitrogen Content: 13.82%; $[\eta]_T$ 25.0)

Fraction No.	Weight, %	$[\eta]$ (a)	Nitrogen, %	$[\eta]_T$	D.P.
1	2.0	18.0	13.60	21.4	1800
2	4.6	29.8	13.72	33.9	2850
3	8.3	24.6	13.68	28.5	2400
4	12.1	22.8	13.65	26.6	2240
5	8.4	22.2	13.64	26.1	2190
6	11.9	21.1	13.71	24.2	2030
7	8.7	19.9	13.58	23.7	1990
8	6.8	19.6	13.62	23.1	1940
9	9.2	17.3	13.69	20.0	1680
10	9.3	14.3	13.72	16.3	1370
11	7.7	10.8	13.48	12.7	1070
12	4.5	7.2	13.20	9.7	815
13	6.5	3.1	10.55	9.6	805

(a) Measured in acetone

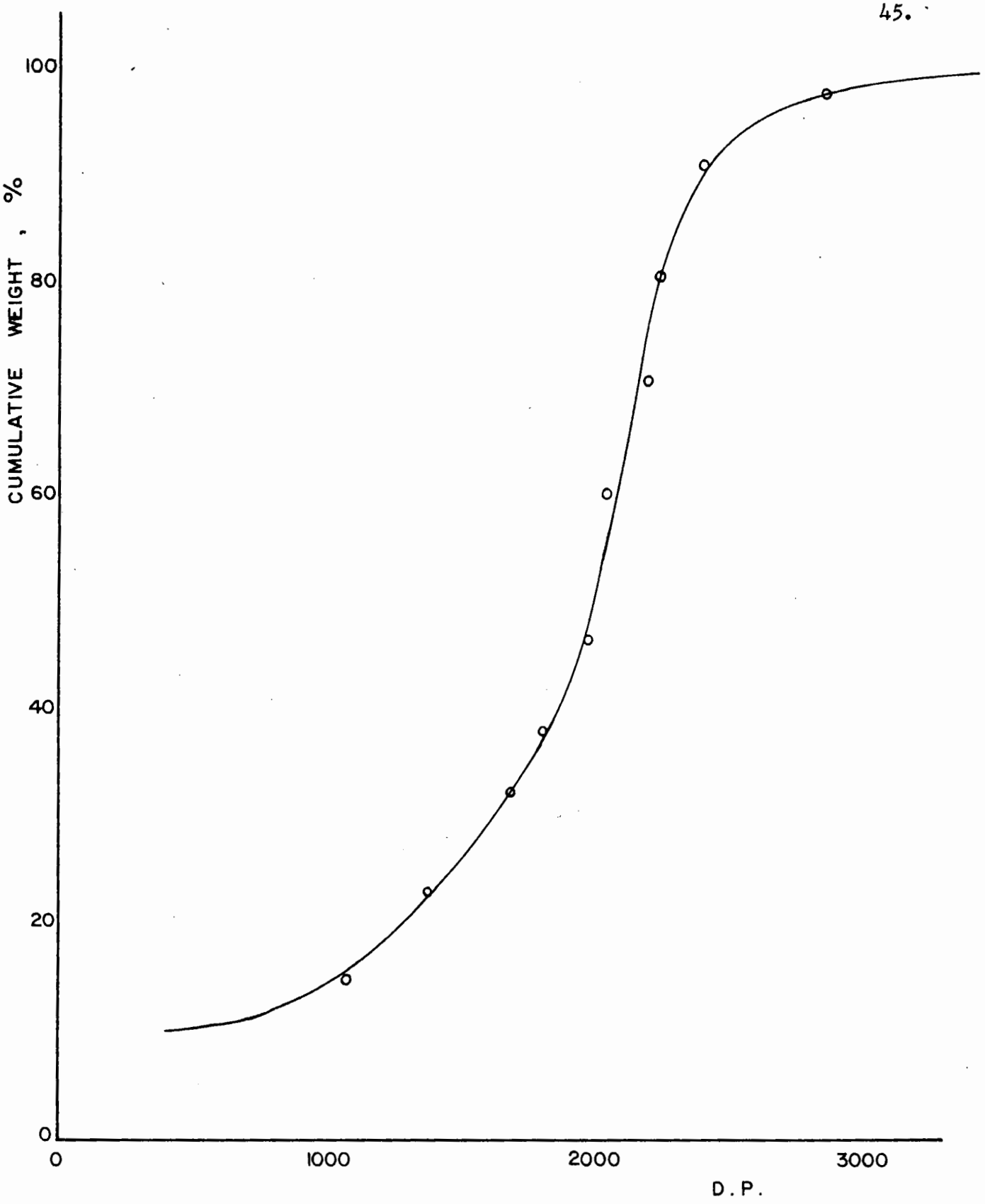

FIG. 4 : CHAIN LENGTH DISTRIBUTION OBTAINED BY FRACTIONAL PRECIPITATION OF SAMPLE NO. 1.

TABLE IX

First Fractionation of Sample No. 2

Solvent Mixture	Weight of Fraction, g.	Percentage of Total
IV	0.4576	9.15
V	0.1677	3.35
VI	0.0591	1.18
VII	0.4232	8.46
VIII	0.2288	4.58
IX	0.1858	3.72
X	0.2618	5.24
XI	0.2500	5.00
XII	0.1590	3.18
XIII	0.1377	2.75
XIV	0.1985	3.97
RESIDUE(a)	2.8595	57.19
TOTALS	5.3887	107.77

(a) Washed with water and dried

TABLE X

Removal of Solvent From Cellulose Nitrate by Evaporation
(Nitrate No. 2 - 13.88% Nitrogen)

Drying Time in Oven at 60°C., Hr.	Per Cent Weight of Original		Nitrogen Content After Drying %	
	(A)(a)	(B)(a)	(A)(a)	(B)(a)
2	113.0	105.5	-	-
4	112.0	104.5	-	-
14	109.0	103.0	8.76	12.74

(a) (A) - solvent evaporated off at room temperature
(B) - " " " over steam

TABLE XI

Recovery of Cellulose Nitrate by Precipitating from an Ethyl Acetate-Ethanol Mixture[a]

Recovered, %[b]	Nitrogen, %	$[\eta]_T$, dl./g.
98.7	13.63[c]	24.8[c]
98.7	13.63	24.7
96.3	13.73	27.7

(a) The solvent was 5/1 ethyl acetate/ethanol.
(b) The precipitating agent was 2/1 water/ethanol for the first two, and 5/1 for the third.
(c) The original values were: 13.88% Nitrogen and $[\eta]_T = 26.5$.

TABLE XII

The Effect of Solvent Composition on the Precipitation of Cellulose Nitrate

Solvent	Recoveries, %		Nitrogen, %	
	Soluble	Insoluble	Soluble	Insoluble
ethyl acetate/ethanol; 3.5/1	100.0[a]	-	13.75	-
" " / " ; 2.5/1	58.3[a]	32.1	13.85	13.26
Acetone[b]	66.7[c]	32.1	13.87	13.24

(a) Precipitant was 3/1 water/ethanol.
(b) Used as replacement solvent for soluble portion of the previous run.
(c) Precipitant was water.

TABLE XIII

Changes on Precipitating Cellulose Nitrate[a]

Sample No.	Nitrogen, %		$[\eta]_T$, dl./g.	
	Original	Final	Original	Final
3	13.80	13.51	22.9	26.3
4	13.95	13.71	25.4	-

(a) Solvent:acetone; Precipitant:water.

TABLES XIV-A, XIV-B

Fractional Extractions of Sample No. 2[a]
(Nitrogen Content: 13.88%; $[\eta]_T$: 26.5 dl./g.)

XIV-A

Fraction No.	Solvent Mixture	Weight of Fraction, g.	Weight of Fraction, %	Cumulative Weight %	Nitrogen Content, %	Weighted Nitrogen Content, %	$[\eta]_T$, dl./g.	Weighted $[\eta]_T$ dl./g.
1	II	0.4890	9.87	9.87	12.83	1.266	13.5	1.332
2	IV	0.3837	7.75	17.62	12.88	0.998	17.7	1.371
3	V	0.2049	4.14	21.76	13.05	0.540	19.3	0.799
4	VI	0.2008	4.05	25.81	13.16	0.533	18.7	0.757
5	VII	0.1667	3.37	29.18	13.26	0.447	19.8	0.667
6	VIII	0.1251	2.53	31.71	12.55	0.318	24.6	0.662
7	IX	0.0966	1.95	33.66	13.44	0.262	21.4	0.417
8	X	0.1709	3.45	37.11	13.68	0.472	19.7	0.680
9	XI	0.3548	7.16	44.27	13.43	0.962	23.7	1.697
10	XII	0.2296	4.64	48.91	13.51	0.627	22.1	1.025
11	XIII	0.1464	2.96	51.87	13.42	0.397	23.3	0.690
12	XIV	0.3165	6.39	58.26	13.68	0.874	24.3	1.553
13	R_S[b]	1.8612	37.58	95.84	13.76	5.171	30.3	11.387
14	R_I[b]	0.2068	4.18	100.02	9.42	.394	—	—
TOTALS		4.953				13.261		

(a) Fractions obtained by extracting 5 g. of material twice with each solvent mixture. Fractions were recovered by precipitation into 33% aqueous ethanol.
(b) For treatment of residues, see procedure section.

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Fractional Extractions of Sample No. 2[a] (continued)

(Nitrogen Content: 13.88%; $[\eta]_T$: 26.5 dl./g.)

XIV-B

Fraction No.	Solvent Mixture	Weight of Fraction, g.	Weight of Fraction, %	Cumulative Weight, %	Nitrogen Content, %	Weighted Nitrogen Content, %	$[\eta]_T$, dl./g.	Weighted $[\eta]_T$, dl./g.
1	II	0.2560	5.28	5.28	13.04	0.689	13.0	0.684
2	IV	0.2089	4.31	9.59	13.27	0.572	16.4	0.707
3	V	0.1462	3.01	12.60	13.37	0.402	19.8	0.596
4	VI	0.1969	4.06	16.66	13.59	0.552	17.2	0.698
5	VII	0.1670	3.44	20.10	13.47	0.463	20.7	0.712
6	VIII	0.1581	3.26	23.36	13.32	0.434	20.1	0.655
7	IX	0.1289	2.66	26.02	12.76	0.339	24.6	0.654
8	X	0.1826	3.76	29.78	13.44	0.505	21.3	0.801
9	XI	0.2247	4.63	34.41	13.60	0.630	22.7	1.051
10	XII	0.2217	4.57	38.98	13.68	0.625	23.8	1.088
11	XIII	0.1791	3.69	42.67	13.52	0.499	24.4	0.900
12	XIV	0.2392	4.93	47.60	13.54	0.668	25.8	1.272
13	R_S [b]	2.4266	50.01	97.61	13.81	6.906	23.8	11.902
14	R_I [b]	0.1159	2.39	100.00	9.50	0.227	—	—
TOTALS		4.852				13.511		

(a) Fractions obtained by extracting 5 g. of material twice with each solvent mixture. Fractions were recovered by precipitation into 33% aqueous ethanol.

(b) For treatment of residues, see procedure section.

TABLE XV

One Step Fractionation of Sample No. 2

	Weight, %	Nitrogen, %	$[\eta]_T$, dl./g.
Soluble in Mixture XIV	54.0	13.36	23.6
Residue - Soluble in Acetone	46.0	13.30	32.9

TABLE XVI

Trial Fractionations on Nitrate No. 3

Mixture No.	Weight, % Exp. (1)	Exp. (2)
II	8.40	8.32
IV	0.15	0.21
V	0.28	0.37
VI	17.90	18.86
VII (Swelling)	8.84	7.78
TOTALS	35.57	35.54

TABLE XVII

Small Scale Fractionations of Sample No. 3

(Anhydrous Solvents)

Mixture No.	Fraction Weight	
	g.	%
I	0.1163	5.99
II	0.0428	2.21
IV (Swelling)	0.6939	35.77
V	0.0548	2.82
VI	0.0143	0.73
VII	—	—
VIII	0.0294	1.51
IX	0.1408	7.26
R_s	0.8481	43.72
	1.9404	100.01

(Solvents Containing 5% of Water)

Mixture No.	Fraction Weight	
	g.	%
I	0.0028	0.14
II	—	—
IV	0.1820	9.08
V	0.0218	1.09
VI	—	—
VII	—	—
VIII	0.0107	0.53
IX	0.0670	3.34
X	0.0538	2.68
XI	0.0504	2.51
XII	0.0802	4.00
XIII (Swelling)	0.2715	13.55
R_s	1.2638	63.06
	2.0050	99.98

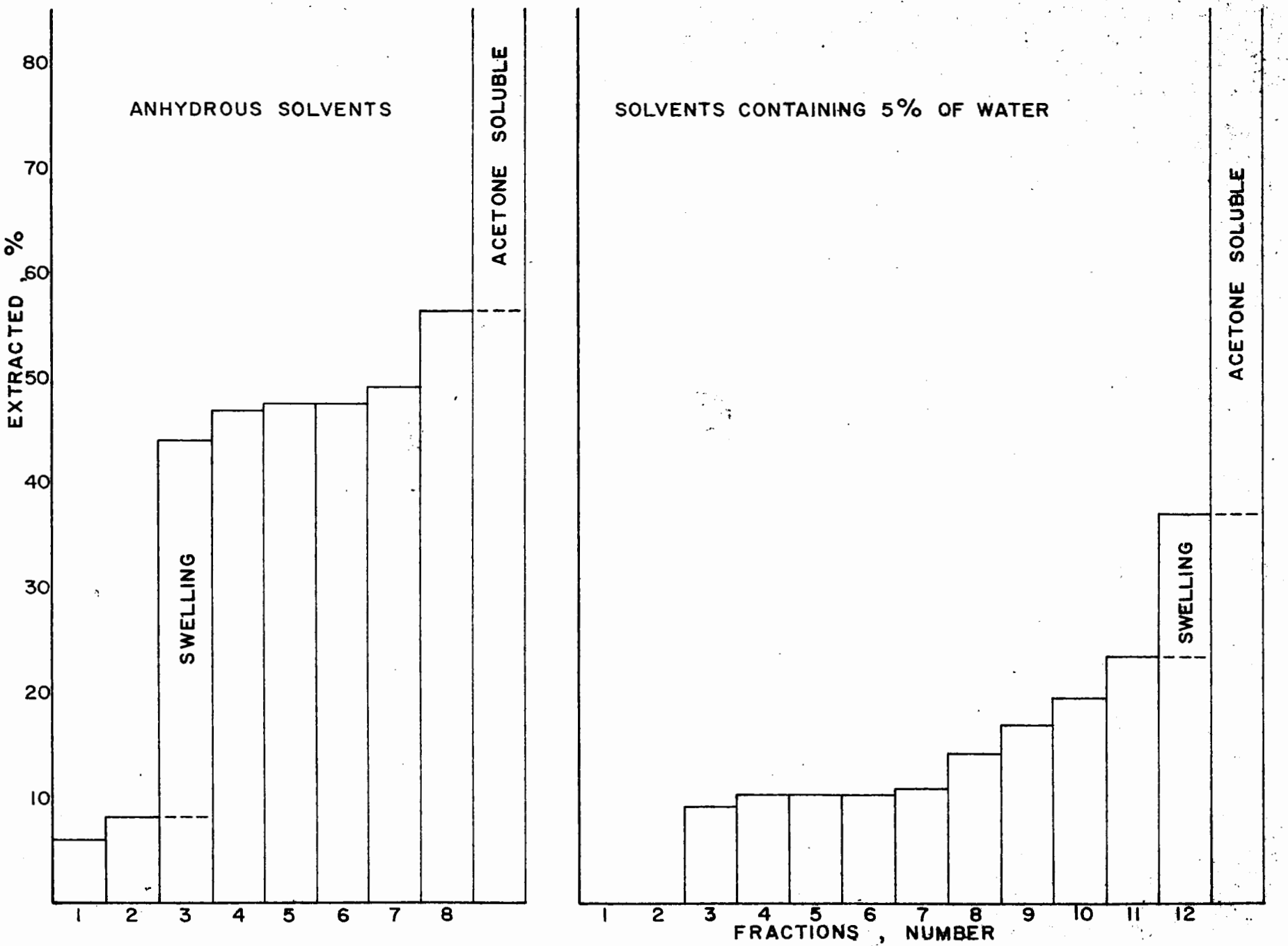

FIG. 5 : EFFECT OF DILUTING THE SOLVENT MIXTURES ON FRACTIONAL EXTRACTION OF SAMPLE NO. 3.

TABLES XVIII-A, XVIII-B

Fractional Extractions of Sample No. 3
(Nitrogen Content: 13.80%; $[\eta]_T$: 22.9 dl./g.)

XVIII-A

Fraction No.	Solvent Mixture	Weight of Fraction, g.	Weight of Fraction, %	Cumulative Weight, %	Nitrogen Content, %	Weighted Nitrogen Content, %	$[\eta]_T$, dl./g.	Weighted $[\eta]_T$, dl./g.
1	I	0.0105	0.21	0.21	-	-	-	-
2	II	0.0516	1.04	1.25	12.84	0.135	15.4	0.160
3	III	0.0449	0.90	2.15	13.84	0.116	17.3	0.156
4	IV	0.1024	2.06	4.21	13.55	0.279	15.4	0.317
5	V	0.1694	3.40	7.61	12.99	0.442	18.8	0.639
6	VI	0.0752	1.51	9.12	12.99	0.196	19.1	0.288
7	VII	0.2299	4.62	13.74	13.46	0.622	18.9	0.873
8	VIII	0.0381	0.77	14.51	13.39	0.103	20.4	0.157
9	IX	0.0320	0.64	15.15	12.60	0.081	24.1	0.154
10	X	0.1065	2.14	17.29	13.63	0.292	18.8	0.402
11	XI	0.0655	1.32	18.61	13.24	0.175	21.8	0.288
12	XII	0.1499	3.01	21.62	13.29	0.400	23.7	0.713
13	XIII	0.2583	5.19	26.81	13.49	0.700	20.6	1.069
14	XIV	0.1872	3.76	30.57	13.39	0.503	23.5	0.884
15	R_s[a]	3.4540	69.43	100.00	13.81	9.588	25.0	17.358
TOTALS		4.975[b]				13.632		23.46

(a) Residue was completely soluble in acetone.
(b) Initial sample weighed 5 g.

. . . .

Fractional Extractions of Sample No. 3 (continued)
(Nitrogen Content: 13.80%; $[\eta]_T$: 22.9 dl./g.)

XVIII-B

Fraction No.	Solvent Mixture	Weight of Fraction, g.	Weight of Fraction, %	Cumulative Weight %	Nitrogen Content, %	Weighted Nitrogen Content, %	$[\eta]_T$, dl./g.	Weighted $[\eta]_T$, dl./g.
1	I	0.0075	0.15	0.15	-	-	-	-
2	II	0.0244	0.49	0.64	12.93	0.063	15.1	0.074
3	III	0.0149	0.30	0.94	12.59	0.038	18.7	0.056
4	IV	0.1212	2.43	3.37	12.97	0.315	18.9	0.459
5	V	0.0699	1.40	4.77	13.26	0.186	17.3	0.242
6	VI	0.2111	4.23	9.00	13.55	0.573	17.4	0.736
7	VII	0.2290	4.59	13.59	13.50	0.620	19.4	0.890
8	VIII	0.0314	0.63	14.22	13.22	0.083	19.7	0.124
9	IX	0.0217	0.44	14.66	13.20	0.058	20.5	0.090
10	X	0.0704	1.41	16.07	13.22	0.186	21.4	0.302
11	XI	0.0298	0.60	16.67	12.97	0.078	22.1	0.133
12	XII	0.3316	6.65	23.32	13.59	0.904	21.5	1.430
13	XIII	0.0965	1.94	25.26	13.52	0.262	23.3	0.452
14	XIV	0.4142	8.31	33.57	13.30	1.105	26.1	2.169
15	R_s (a)	3.3120	66.43	100.00	13.81	9.174	26.9	17.870
TOTALS		4.986 (b)				13.645		25.03

(a) Residue was completely soluble in acetone.
(b) Initial sample weighed 5 g.

TABLE XIX

Fractional Extraction of Sample No. 4
(Nitrogen Content: 13.95%; $[\eta]_T$: 25.0 dl./g.)

Fraction No.	Solvent Mixture	Weight of Fraction, g.	Weight of Fraction, %	Cumulative Weight %	Nitrogen Content, %	Weighted Nitrogen Content, %	$[\eta]_T$, dl./g.	Weighted $[\eta]_T$, dl./g.
1	II	0.1443	2.86	2.86	12.77	0.365	14.6	0.418
2	IV	0.0915	1.81	4.67	12.98	0.235	19.7	0.357
3	V	0.0797	1.58	6.25	12.80	0.202	23.5	0.371
4	VI	0.1153	2.29	8.54	13.24	0.303	21.0	0.481
5	VII	0.4590	9.10	17.64	13.60	1.238	22.1	2.011
6	VIII	0.0803	1.59	19.23	13.31	0.212	20.9	0.332
7	IX	0.0274	0.54	19.77	13.06	0.071	25.3	0.137
8	X	0.0768	1.52	21.29	13.22	0.201	28.4	0.432
9	XI	0.2077	4.12	25.41	13.78	0.568	23.1	0.952
10	XII	0.3024	5.99	31.40	13.78	0.825	23.6	1.414
11	XIII	0.4269	8.46	39.86	13.85	1.172	22.9	1.937
12	XIV	0.3328	6.60	46.46	13.86	0.915	24.4	1.610
13	R_s	2.7020	53.55	100.01	13.88	7.433	28.6	15.315
TOTALS		5.046				13.740		25.77

TABLE XX

Fractional Solution on Sample No. 11 Using Undiluted Mixtures

Mixture No.	Weight, %	Nitrogen, %
II	39.2	12.84
IV	5.4	12.98
V	3.0	12.77
XIV	6.8	13.41
RESIDUE(a)	45.6	11.32

(a) Completely insoluble in acetone.

TABLE XXI

Fractional Extraction of Sample No. 13
(Nitrogen Content: 13.62%; $[\eta]_T$: 23.0-24.5 dl./g.[a])

Fraction No.	Solvent Mixture	Weight of Fraction, g.	Weight of Fraction, %	Cumulative Weight %	Nitrogen Content, %	Weighted Nitrogen Content, %	$[\eta]_T$, dl./g.	Weighted $[\eta]_T$, dl./g.
1	I	0.1141	3.73	3.73	12.97	0.484	18.9	0.705
2	II	0.0297	0.97	4.70	12.90	0.125	19.5	0.189
3	III	0.1717	5.61	10.31	13.40	0.752	22.8	1.279
4	IV	0.0606	1.98	12.29	13.26	0.263	22.5	0.446
5	V	0.2136	6.97	19.26	13.63	0.950	24.7	1.722
6	VI	0.1649	5.38	24.64	13.43	0.723	20.3	1.092
7	VII	0.2335	7.62	32.26	13.52	1.030	26.2	1.996
8	VIII	0.2007	6.55	38.81	13.73	0.899	22.8	1.490
9	IX	0.3062	10.00	48.81	13.69	1.369	24.2	2.420
10	R_s	1.2157	39.69	88.50	13.82	5.485	26.2	10.399
11	R_I	0.3522	11.50	100.00	13.04	1.500	21.3[c]	2.450
TOTALS		3.0629[b]				13.580		24.19

(a) This material was not completely soluble and the viscosity was corrected for 88.5% solubility.
(b) The initial sample weighed 3 g.
(c) Renitrated for viscosity determination.

TABLE XXII

Fractional Extraction of Sample No. 12
(Nitrogen Content: 13.12%)

Fraction No.	Solvent Mixture	Weight of Fraction, g.	Weight of Fraction, %	Cumulative Weight %	Nitrogen Content, %	Weighted Nitrogen Content, %	$[\eta]_T$, dl./g.
1	I	0.3799	12.55	12.55	12.70	1.594	
2	II	0.1897	6.27	18.82	13.15	0.825	
3	III	0.1957	6.46	25.28	13.14	0.849	
4	IV	0.1915	6.32	31.60	13.12	0.829	
5	V	0.0962	3.18	34.78	13.08	0.416	
6	VI	0.2380	7.86	42.64	13.16	1.034	
7	VII	0.1828	6.04	48.68	13.23	0.799	
8	R_s	0.6674	22.04	70.72	13.59	2.995	24.3
9	R_I	0.8866	29.28	100.00	12.55	3.675	
TOTALS		3.0278(a)				13.016	

(a) Initial sample weighed 3 g.

TABLE XXIII

Fractional Extraction of Sample No. 11
(Nitrogen Content: 12.56%).

Fraction No.	Solvent Mixture	Weight of Fraction, g.	Weight of Fraction, %	Cumulative Weight %	Nitrogen Content, %	Weighted Nitrogen Content, %	$[\eta]_T$, dl./g.
1	I	0.3697	12.33	12.33	12.38	1.526	
2	II	0.0847	2.83	15.16	12.25	0.347	
3	III	0.1065	3.55	18.71	12.84	0.456	
4	IV	0.0673	2.25	20.96	12.45	0.280	
5	V	0.0595	1.98	22.94	12.65	0.250	
6	VI	0.0916	3.06	26.00	12.91	0.395	
7	VII	0.0643	2.15	28.15	12.83	0.276	
8	VIII	0.0762	2.54	30.69	12.96	0.329	
9	IX	0.0982	3.28	33.97	12.96	0.425	
10	X	0.0446	1.49	35.46	12.71	0.189	
11	XI	0.0929	3.10	38.56	13.00	0.403	
12	XII	0.1266	4.22	42.78	13.45	0.568	
13	XIII	0.0169	0.56	43.34	12.32	0.069	
14	XIV	0.0359	1.20	44.54	13.01	0.156	
15	XIV(a)	0.2947	9.83	54.37	13.47	1.324	24.3
16	R_s	0.0461	1.54	55.91	12.82	0.197	
17	R_I	1.3220	44.10	100.01	11.66	5.142	22.0(c)
TOTALS		2.9977(b)				12.332	

(a) Undiluted mixture XIV used to get additional fraction.
(b) Initial sample weighed 3 g.
(c) Renitrated for viscosity determination.

TABLE XXIV

Fractional Extraction of Sample No. 10
(Nitrogen Content: 12.05%)

Fraction No.	Solvent Mixture	Weight of Fraction, g.	Weight of Fraction, %	Cumulative Weight %	Nitrogen Content, %	Weighted Nitrogen Content, %	$[\eta]_T$, dl./g.
1	I	0.3410	11.33	11.33	12.04	1.364	
2	II	0.0390	1.30	12.63	11.87	0.154	
3	III	0.0743	2.47	15.10	12.16	0.300	
4	IV	0.0339	1.13	16.23	12.19	0.138	
5	V	0.0384	1.28	17.51	12.15	0.156	
6	VI	0.0317	1.05	18.56	12.00	0.126	
7	VII	0.0331	1.10	19.66	11.88	0.131	
8	VIII	0.0201	0.67	20.33	12.05	0.081	
9	IX	0.0317	1.05	21.38	12.23	0.128	
10	X	0.0357	1.19	22.57	12.45	0.148	
11	XI	0.0404	1.34	23.91	12.40	0.166	
12	XII	0.0313	1.04	24.95	12.55	0.131	
13	XIII	0.0307	1.02	25.97	12.25	0.125	
14	XIV[a]	0.0269	0.89	26.86	12.22	0.109	
15	R_S	0.7530	25.01	51.87	13.62	3.406	24.7
16	R_I	1.4490	48.14	100.01	10.70	5.151	23.6[c]
TOTALS		3.0102[b]				11.814	

(a) Material was still unswollen at this point.
(b) Initial sample weighed 3 g.
(c) Renitrated for viscosity determination.

TABLE XXV

Fractional Extraction of Sample No. 7
(Nitrogen Content: 13.28%)

Fraction No.	Solvent Mixture	Weight of Fraction, %	Cumulative Weight, %	Nitrogen Content, %	Weighted Nitrogen Content, %
1	I	81.50	81.50	13.05	10.636
2	III	5.00	86.50	12.20	0.610
3	R_I	13.50	100.00	12.93	1.746
TOTALS					12.992

TABLE XXVI

Fractional Extraction of Sample No. 6
(Nitrogen Content: 12.43%)

Fraction No.	Solvent Mixture	Weight of Fraction, %	Cumulative Weight, %	Nitrogen Content, %	Weighted Nitrogen Content, %
1	(a)	14.00	14.00	12.70	1.778
2	R_I	86.00	100.00	12.22	10.509
TOTALS					12.287

(a) See procedure section for solvents used here.

TABLE XXVII

Fractional Extraction of Sample No. 5
(Nitrogen Content: 11.51%; $[\eta]_T$ = 23.6 dl./g.)

Fraction No.	Solvent Mixture	Weight of Fraction, g.	Weight of Fraction, %	Cumulative Weight %	Nitrogen Content, %	Weighted Nitrogen Content, %
1	I	0.3355	58.56	58.56	11.22	6.570
2	VIII	0.1534	26.78	85.34	11.74	3.144
3	XII	0.0442	7.72	93.06	11.92	0.920
4	Ethyl Acetate	0.0146	2.55	95.61	11.18	0.285
5	R_I	0.0252	4.40	100.01	11.08	0.488
TOTALS		0.5729[a]				11.407

(a) Initial sample weighed 0.6 g.

TABLE XXVIII

Fractional Extraction of a Precipitated Portion of Sample No. 13[a]
(Nitrogen Content: 13.58%; $[\eta]_T$: 26.0 dl./g.)

Fraction No.	Solvent Mixture	Weight of Fraction, g.	Weight of Fraction, %	Cumulative Weight %	Nitrogen Content, %	Weighted Nitrogen Content, %	$[\eta]_T$, dl./g.	Weighted $[\eta]_T$, dl./g.
1	I	0.0779	3.08	3.08	12.56	0.387	16.0	0.493
2	II	0.0805	3.18	6.26	12.95	0.412	17.1	0.544
3	III	0.1017	4.02	10.28	13.01	0.523	19.7	0.792
4	IV	0.5897	23.30	33.58	13.48	3.141	22.0	5.126
5	V	0.1389	5.49	39.07	13.32	0.731	23.0	1.263
6	VI	0.2989	11.81	50.88	13.53	1.598	24.0	2.834
7	VII	1.1859	46.86	97.74	13.39	6.275	32.3	15.136
8	R_s[b]	0.0573	2.26	100.00	12.87	0.291	39.0	0.881
TOTALS		2.5308[c]				13.358		27.069

(a) The insoluble portion (11.5%) was not included in this fractionation.

(b) Completely soluble in acetone.

(c) Initial sample weighed 2.611 g.

TABLE XXIX

Fractional Extraction of Precipitated Sample No. 3
(Nitrogen Content: 13.51%; $[\eta]_T$: 26.3 dl./g.)

Fraction No.	Solvent Mixture	Weight of Fraction, g.	Weight of Fraction, %	Cumulative Weight %	Nitrogen Content, %	Weighted Nitrogen Content, %	$[\eta]_T$, dl./g.	Weighted $[\eta]_T$, dl./g.
1	VI	0.0331	1.14	1.14	12.07	0.138	-	-
2	VII	0.0843	2.91	4.05	12.93	0.376	16.0	0.466
3	VIII	0.0300	1.03	5.08	12.84	0.132	15.7	0.162
4	IX	0.0282	0.97	6.05	12.90	0.125	16.0	0.155
5	X	0.2509	8.65	14.70	13.50	1.168	17.1	1.479
6	XI	0.2493	8.60	23.30	13.55	1.165	19.1	1.643
7	XII	0.1525	5.26	28.56	13.39	0.704	21.5	1.131
8	XIII	0.2731	9.42	37.98	13.28	1.251	23.9	2.251
9	XIV	0.2461	8.49	46.47	13.26	1.126	23.8	2.021
10	XIV(a)	1.5526	53.53	100.00	13.40	7.173	31.4	16.808
TOTALS		2.9001(b)				13.358		26.116

(a) Undiluted mixture XIV was able to dissolve all the remaining material.
(b) Initial sample was 2.904 g.

DISCUSSION OF RESULTS

Nitration of Cellulose Under Rate-Controlled Conditions

The nitration reaction studied here appeared to occur in two stages, as is seen from Figure 6; an initial rapid phase followed by a much slower one. The initial reaction most likely involved a nitration of the surface and outer, more disordered portions of the microfibrils. The latter stage represented the gradual conversion of the inner regions of the fibrils. This is in accord with the ideas of Miles (51), and indicates that nitration is similar in this respect to other cellulose reactions.

It was not practical to vary the temperature used, -32°C., to any extent; a higher temperature resulting in too rapid a reaction and a lower one giving an excessively viscous nitration mixture. As is also seen from Figure 6, the amount of cellulose being nitrated had a definite influence on the rate of reaction, especially on the second, slower phase. Although the weight proportions of cellulose to nitrating reagent were maintained constant at 1:100, the larger amount of material reached the final degree of substitution much sooner than the smaller one. After five minutes of nitration however, both samples had approximately the same nitrogen content. The explanation of this phenomenon is probably that the heat of reaction evolved during the initial stage of the nitration was less efficiently dissipated in the case where the larger amount of material was used.

The substitution reached at the point where the rate curves branch, 10.1% nitrogen, is equivalent to Miles' value for the beginning of what he called the third stage of nitration. From this point on, the

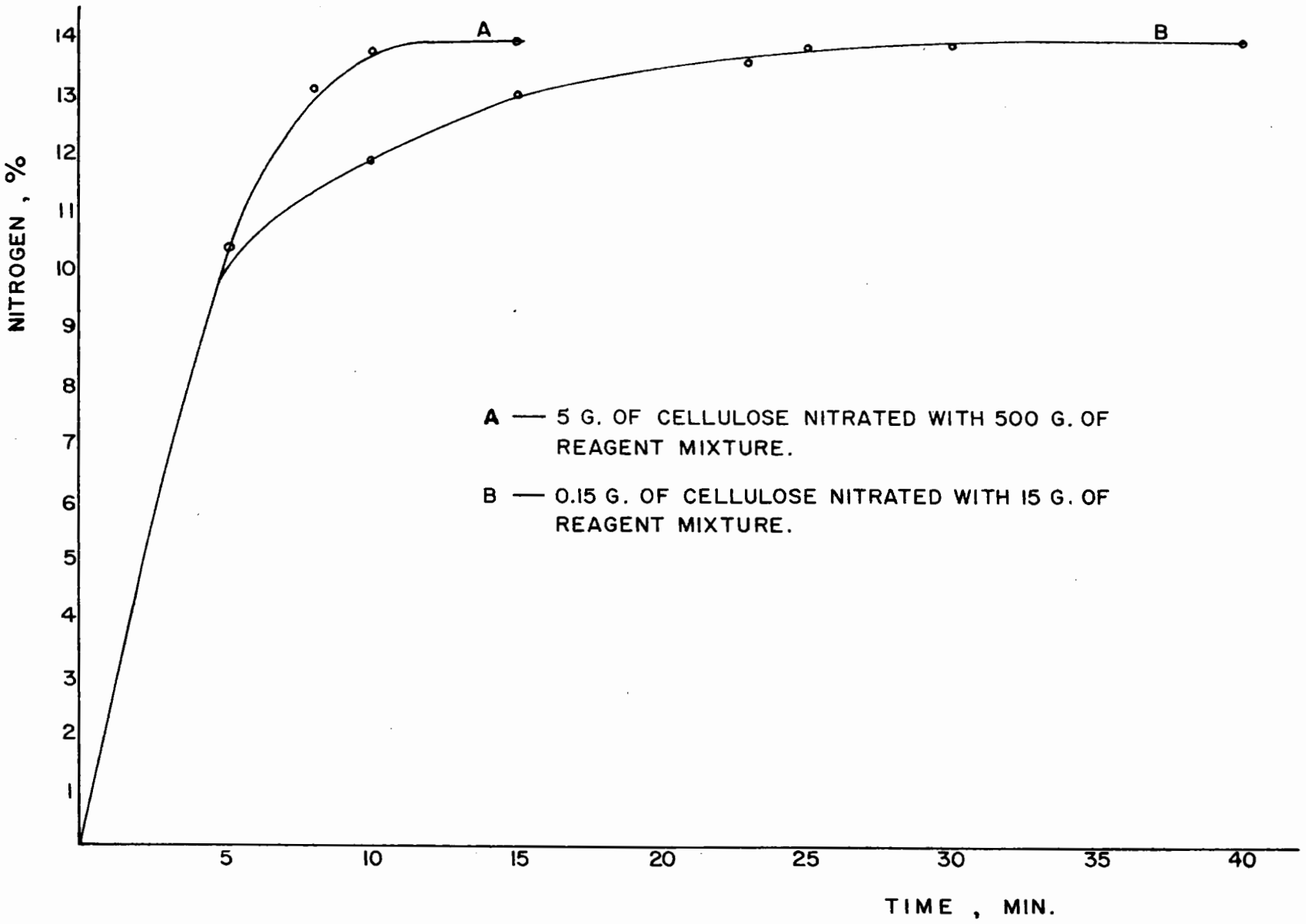

FIG. 6 : THE RATE OF NITRATION.

crystalline pattern of cellulose trinitrate begins to appear, and it is known to be rather resistant to penetration by nitrating mixtures. The rate of reaction in this region will in part be inversely dependent on the number of nitrate groups already present:

(1) $R = \frac{k}{N}$ where R = rate of nitration

N = nitrogen content

A swelling agent which can enter not only crystalline cellulose but also crystalline cellulose nitrate would thus seem to be a prerequisite for complete esterification of the crystalline regions.

Chedin (45) has studied the solubility properties of nitrates obtained after interrupting the nitration reaction during its initial stages. As the reaction time increased, more and more of a soluble portion containing 12.1% to 12.7% nitrogen was produced, while the insoluble parts were found to be barely nitrated at all. Cherubin (94) studied this phenomenon in detail, using a technical nitration mixture, and his results not only agree with the above but seem to indicate the beginning of the transition to the second, more gradual phase of nitration. In Table XXX, Cherubin's data show quite clearly that nitration was restricted to about 35% of the cellulose until this portion contained 12.0% nitrogen, after which more material was nitrated to that level. Finally, a point was reached where even the insoluble portion contained an appreciable amount of nitrogen. The insolubility of the latter was attributed to non-uniform substitution. Although most of the present study was concerned with more highly substituted products, one sample, No. 9, having an average nitrogen content of 9.70%, seemed to be comparable with those used by the above workers. Its solubility and nitrogen contents are included in Table XXX,

TABLE XXX

Solubility of Cellulose Nitrates Obtained After Interrupting the Nitration Reaction

(Mainly from the work of Cherubin (94))

Initial Average N Content, %	Soluble in Acetone		Insoluble in Acetone	
	Weight, %	Nitrogen, %	Weight, %	Nitrogen, %
2.5	35	5.9	65	0.67
3.3	25	9.9	75	1.10
3.4	37	8.0	63	0.69
4.0	31	10.9	69	0.80
4.7	37	11.8	63	0.54
6.4	51	11.9	49	0.54
7.3	58	12.1	42	0.98
11.7	83	12.6	17	7.20
9.7(a)	33(b)	12.5	67(b)	7.40

(a) Sample No. 9 from the present investigation; prepared with a non-degradative acid mixture.

(b) Average values of four different solubility tests. (See experimental section).

where it can be seen that it exhibited the same substitution level for both fractions as the other specimens listed. While it would be improper to attribute any importance to the seemingly fixed level of 7.2%-7.4% nitrogen which the insoluble portion attained at the end of this phase, it seems quite evident that the range 12.0% to 12.7% nitrogen is a characteristic leveling-off value in rate-controlled nitrations. As is seen

from Table XXX the sample investigated here was less soluble in acetone than the corresponding ones studied by Cherubin. This difference can presumably be accounted for by the lower average D.P. of the technical nitrates. That this was so, is also indicated by the fact that Cherubin reported a considerable loss of material when recovering his samples after precipitation of the acetone solutions into water; whereas in this case the recovery was rarely less than 99%, under similar conditions.

Fractionation of Cellulose Nitrates Obtained in Rate-Controlled Reactions

For this study four samples were chosen which would cover the later stage of nitration; i.e. from 12.0% to 13.6% nitrogen. The results of these experiments are shown in Tables XXI-XXIV.

Jorgensen has offered a description of the progress of fractional extraction which was intended to explain why the fractions did not show the expected rate of increase in D.P. (89) "In the earlier part of the fractionation the fibers retain their unswollen state and the extraction solvents are unable to come in contact with those parts of the chains which are located within the highly ordered regions. Thus, the first fractions represent the most easily dissolved material in the accessible regions only." This explanation seems quite plausible and, while it is a detriment to D.P. distribution studies, this fractional extraction procedure could be well suited to following the course of a reaction which also depended on the accessibility of the fiber. The points of interest pertinent to this were the following:

(a) The amount of material that could be extracted without swelling the fibers.

(b) The D.S. and D.P. of the isolated fractions.

(c) The order of extraction with regard to the nitrogen content of the fractions.

(d) The nitrate substitution of the remaining material.

The amount extracted before swelling can be found from the data in Tables XXI-XXIV. Except for Sample No. 10, swelling is indicated in these tables by a termination of extraction with the mixed solvents, and the fraction immediately preceding the residues is therefore the one at which swelling occurred. For No. 10, the material remained intact until treated with acetone, and its swelling point corresponded to (R_s) in Table XXIV. The approximate swelling points were taken as the mid-points of these last fractions, and the values for the four samples are listed in Table XXXI.

TABLE XXXI

The Amount of Material Extracted Before Swelling

Average Nitrogen Content, %	Amount Extracted before Swelling, %	Nitrogen Content of Extracted Portion, %
12.05	39.37	12.83
12.56	49.46	12.87
13.12	45.66	13.03
13.62	43.81	13.51

The proportion of material which could be extracted without destroying the fiber structure seemed to be fixed at approximately 45%. The lowest substituted sample appeared to have a somewhat premature swelling point which may be indicative of the loosening of structure which

is said to take place during the intermediate nitration period (41). However, this difference may be fortuitous, since the excessive size of the swelling fraction, i.e. 25%, made it difficult to establish the actual swelling point. Table XXXI shows quite definitely that this point was not dependent on the nitrogen content.

The distribution of nitrate groups for these samples can best be shown graphically. Figure 7 gives the integral distribution curves in which, for each of the three lower nitrates, a fraction with an extremely low D.S. appears, consisting of the insoluble residues, which could not be further fractionated. These curves were used for the production of the differential, or frequency distribution curves shown in Figure 8. Sample No. 11 evidently had a distribution somewhat different from the other three, which exhibited fairly random distributions about their respective average nitrogen contents - broadening with decreasing D.S.

The sequence of fractionation is also best seen in graphical form. In this case, a type of bar graph was used (Fig. 9, 10), and, in order to show clearly how the nitration proceeded, the average nitrogen content for each sample was indicated by a broken line. This value was obtained by averaging the weighted values for each fraction.*

The fractions isolated, which were all obtained before swelling occurred, and which thus represented the more accessible portion of the fiber, evidently had a lower D.S. than most of the remainder of the material

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* It has been well established that any prolonged time in solution will cause a certain amount of denitration, for derivatives prepared in this manner (92). In most fractionations performed in this study, this loss was at most 0.3% of nitrogen for the total sample (See TABLE XIII).

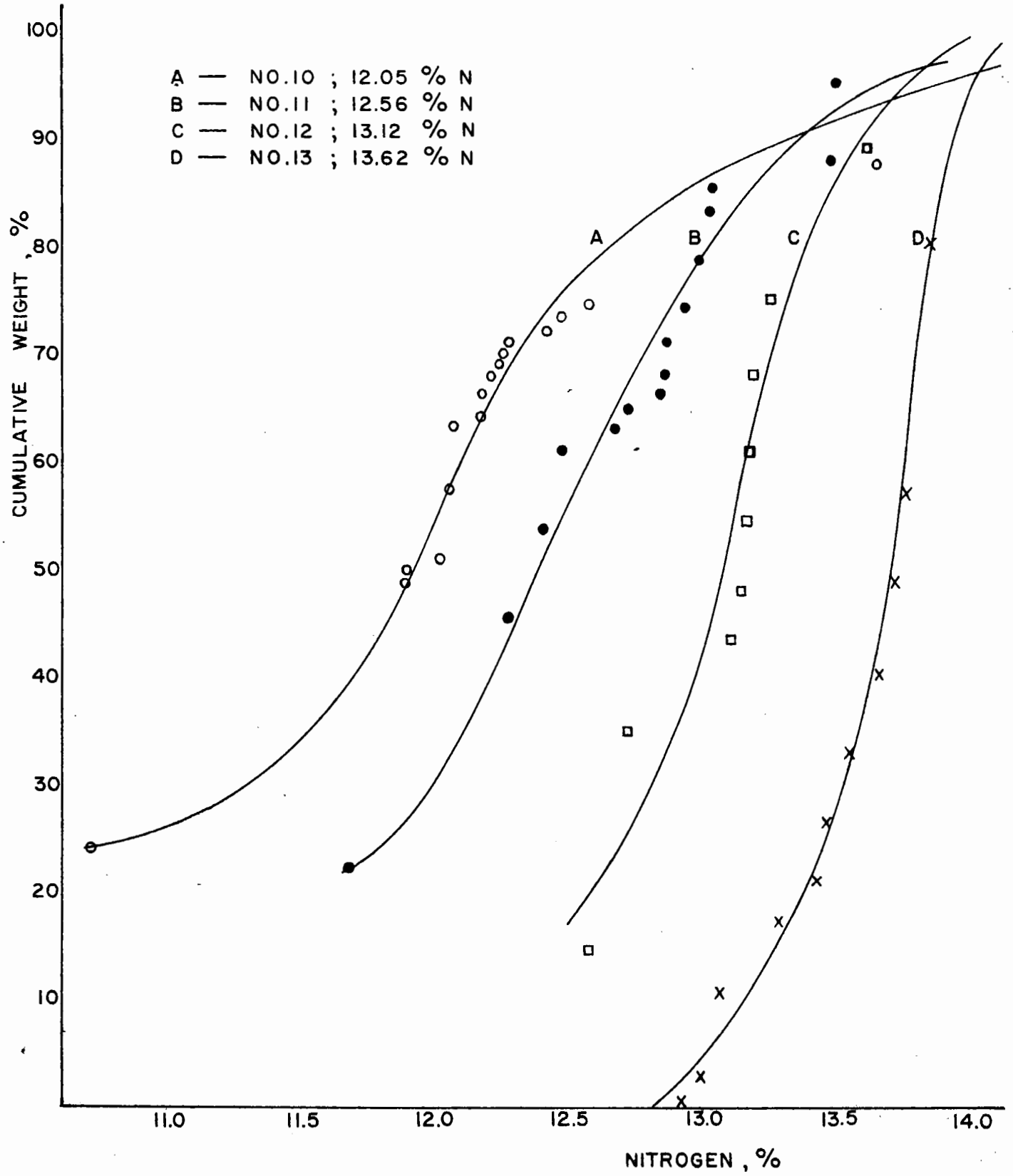

FIG. 7 : INTEGRAL DISTRIBUTION CURVES FOR SAMPLES NOS. 10,11,12,13.

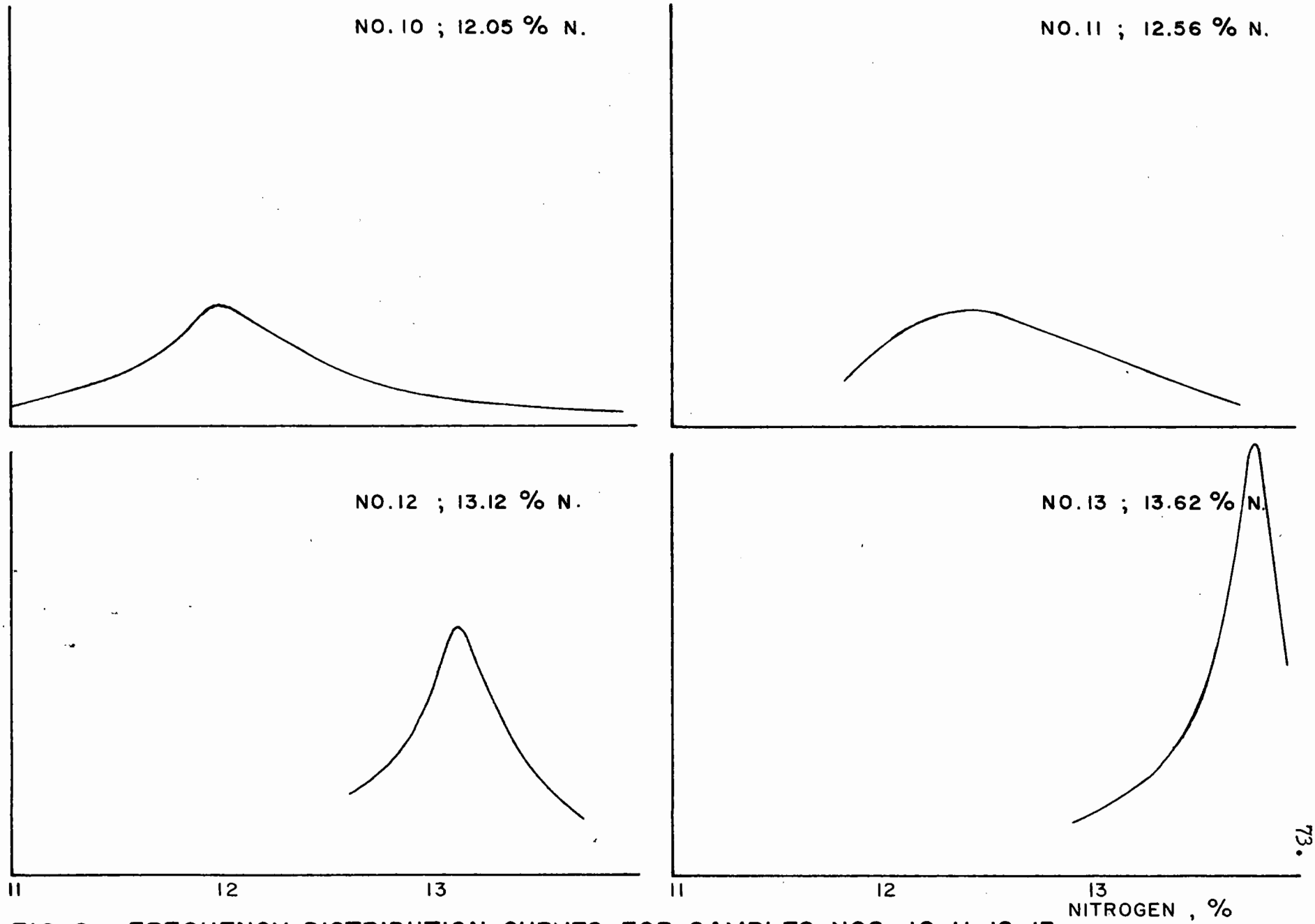

FIG. 8 : FREQUENCY DISTRIBUTION CURVES FOR SAMPLES NOS. 10, 11, 12, 13.

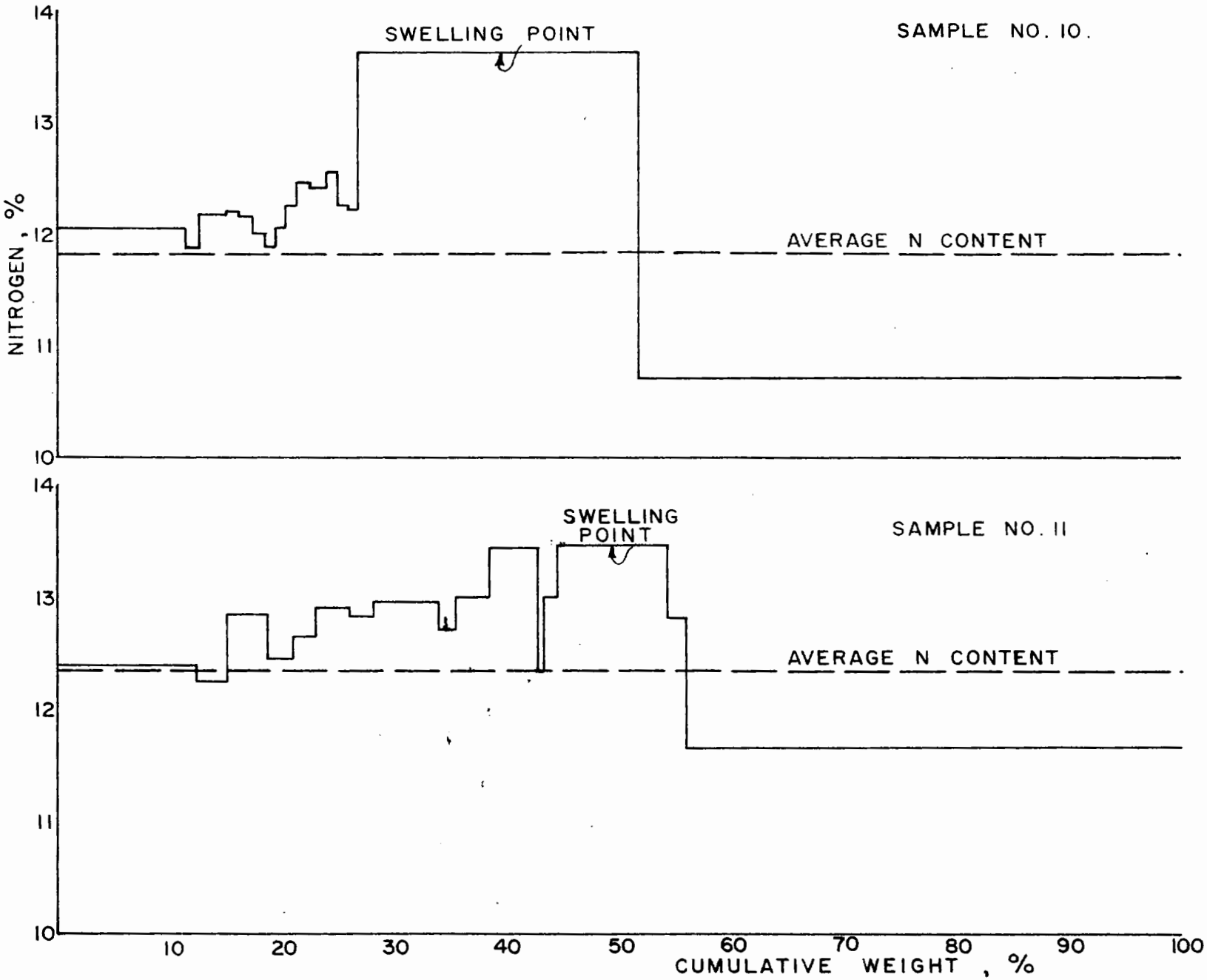

FIG. 9 : BAR GRAPHS SHOWING FRACTIONATION SEQUENCES FOR SAMPLES NOS. 10,11.

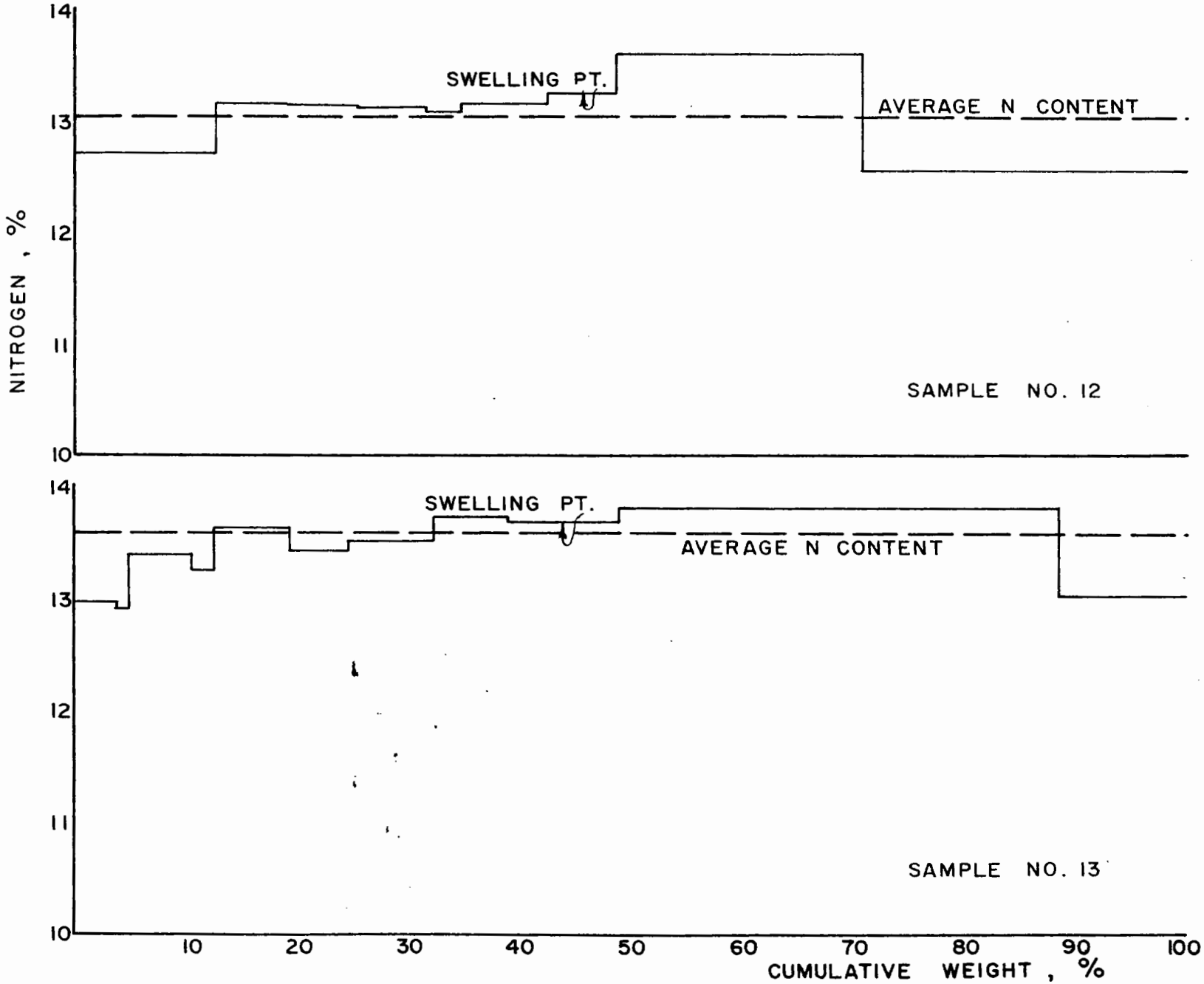

FIG. 10 : BAR GRAPHS SHOWING FRACTIONATION SEQUENCES FOR SAMPLES NOS. 12,13.

As the reaction proceeded, these low-substituted localities gradually became converted until, for the highest nitrated sample, only 5% of this region remained low-substituted. The minor variations in nitrogen content from fraction to fraction did not seem to be significant, and were probably the composite result of chain length deviations, altered solubility caused by localized swelling or crystallization, and experimental errors.

Chedin has postulated that nitration of cellulose is accompanied by preferential diffusion (45) - the complete nitrating bath penetrating the interfibrillar spaces, while only nitric acid (more or less hydrated) enters the highly crystalline regions. This would account for the situation that prevailed for Sample No. 10. Here the accessible region was probably in contact with the complete nitrating bath, and was nitrated to at least 12.0% nitrogen, which has been shown to be the minimum substitution needed to allow nitration to continue into the microfibrils. The latter had been nitrated in part by a much stronger reagent, i.e. nitric acid. However, Chedin's theory must be extended to account for the gradual increase in nitrogen content of the accessible regions. If we imagine that nitration is capable of causing induced crystallinity in the disordered regions, which are thought to be partially crystalline in nature (8), it follows that nitric acid will gradually force out phosphoric acid from this area, with a resultant increase in substitution. This secondary nitration does not go to completion, possibly because of the limited ability of the chains to crystallize. This question will be dealt with later in the discussion of completely nitrated fibers.

The progress of nitration in the relatively inaccessible crystalline regions followed a seemingly conventional pattern. The determining factor for solubility here was not the average nitrogen content, since in

some cases the insoluble portion contained as much nitrogen as a previously dissolved fraction. Instead, it seems quite reasonable to ascribe insolubility to non-uniformly nitrated chains (Spurlin estimates that 1% of unsubstituted material in a chain is enough to cause insolubility (15)). It is of interest to relate the amount of non-uniform nitration - as measured by the percentage of insoluble material - to the average nitrogen content of these insoluble residues. This has been done in Table XXXII, and the corresponding data for Sample No. 9 have also been included.

TABLE XXXII

The Amounts and D.S. of the Insoluble Portions of Rate-Controlled Nitration Products

Sample No.	Total Sample Nitrogen Content, %	Insoluble Residues	
		Weight, %	Nitrogen, %
9	9.70	65.0	7.40
10	12.05	48.1	10.70
11	12.56	44.1	11.66
12	13.12	29.3	12.55
13	13.62	11.5	12.04

When the data are plotted against each other they form a smooth curve, as in Figure 11, which shows how the non-uniformity decreases more and more as the average D.S. increases. This is what could be expected if substitution in this region was the result of a random attack on the chains. In contrast, the soluble residues have a relatively constant value (13.5%-13.8%) in all four cases (Sample No. 9 is not comparable here, not having been fractionated).

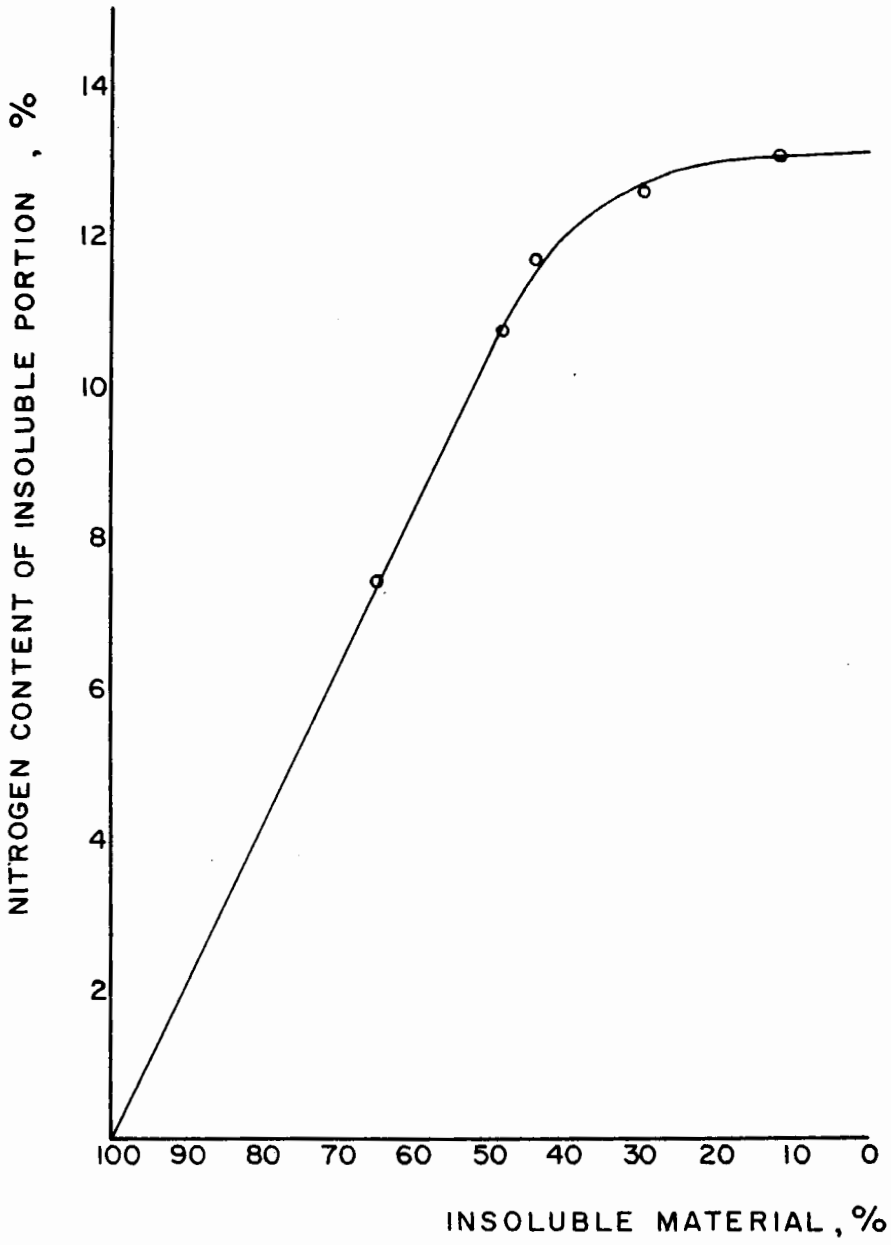

FIG. 11 : VARIATION OF NITROGEN CONTENT WITH AMOUNT OF INSOLUBLE MATERIAL.

If a cellulose nitrate is dissolved and reprecipitated the resulting product will no longer possess the fiber structure of the original material. This elimination of the influence of the native fine structure was effected using Sample No. 13, which was then fractionated. As is seen in Figure 12, the first fractions still exhibited a low D.S., but so did the last one, even though it was eventually soluble - the original insoluble portion having been removed beforehand. The most important change was in the order of the viscosities of the fractions. Table XXVIII shows that fractionation took place more according to the chain length than previously.

The additional peak in the frequency distribution (Fig. 13) is entirely due to the inclusion of the 11.5% of insoluble material (containing 12.93% N). Due to the somewhat altered distribution, as compared to the original data for Sample No. 13, the insoluble portion exerted a more predominant influence on the distribution than before. If we disregarded this fraction, the distribution would be similar to that shown in Figure 8 for Sample No. 13.

Fractionation of Cellulose Nitrates Obtained in Equilibrium-Controlled Reactions

If the mechanism referred to above for the rate-controlled reaction of cellulose is valid, nitrates obtained under conditions of true chemical equilibrium should have different properties and behave differently when fractionated. Three samples, Nos. 5, 6 and 7, were prepared by gradually increasing the amount of phosphoric acid present in the standard nitration mixture, thus lowering the final nitrate substitution.

Sample No. 5 had an average nitrogen content of 11.51% and a

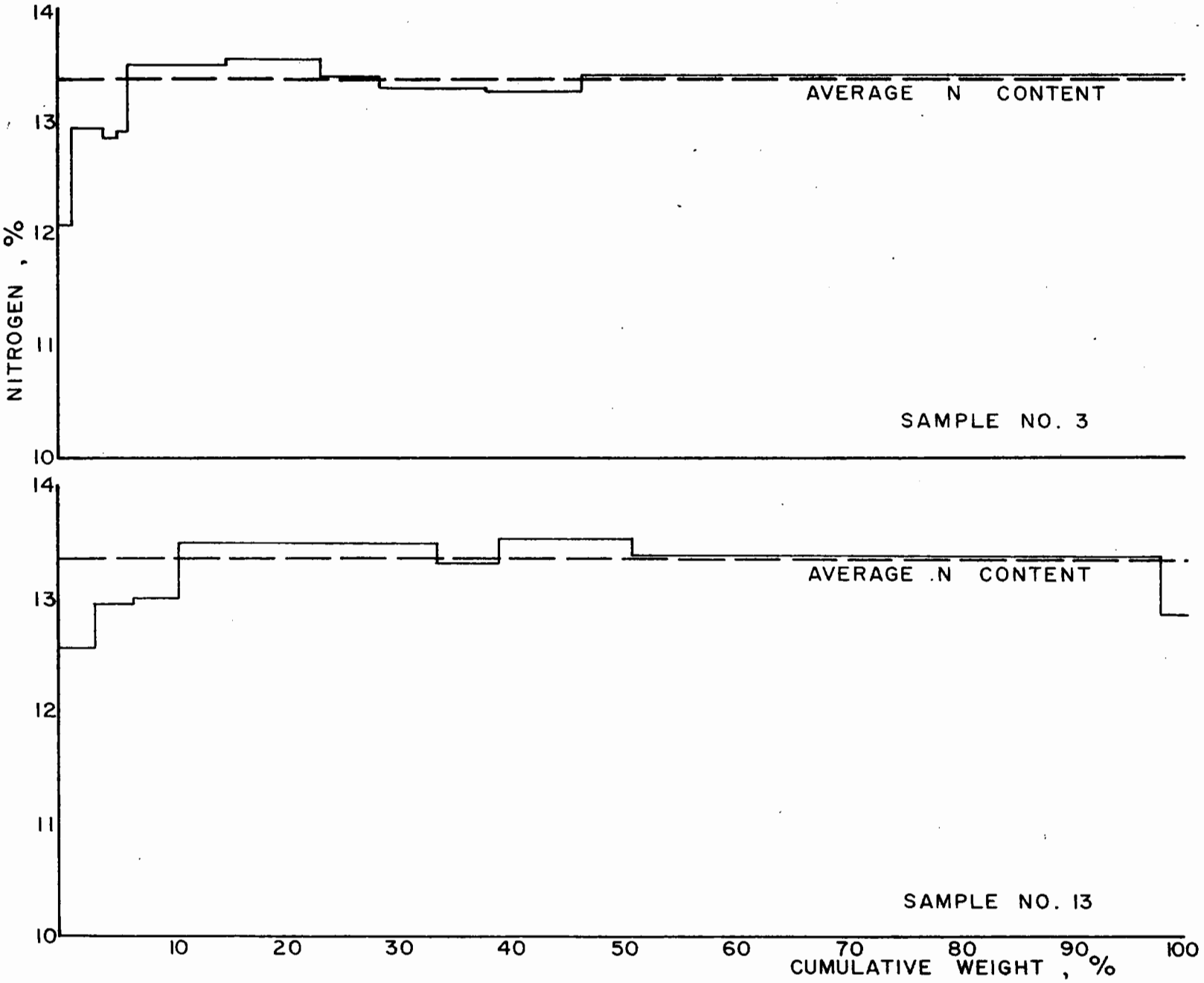

FIG. 12 : FRACTIONATION SEQUENCES FOR REPRECIPITATED SAMPLES NOS. 3 , 13.

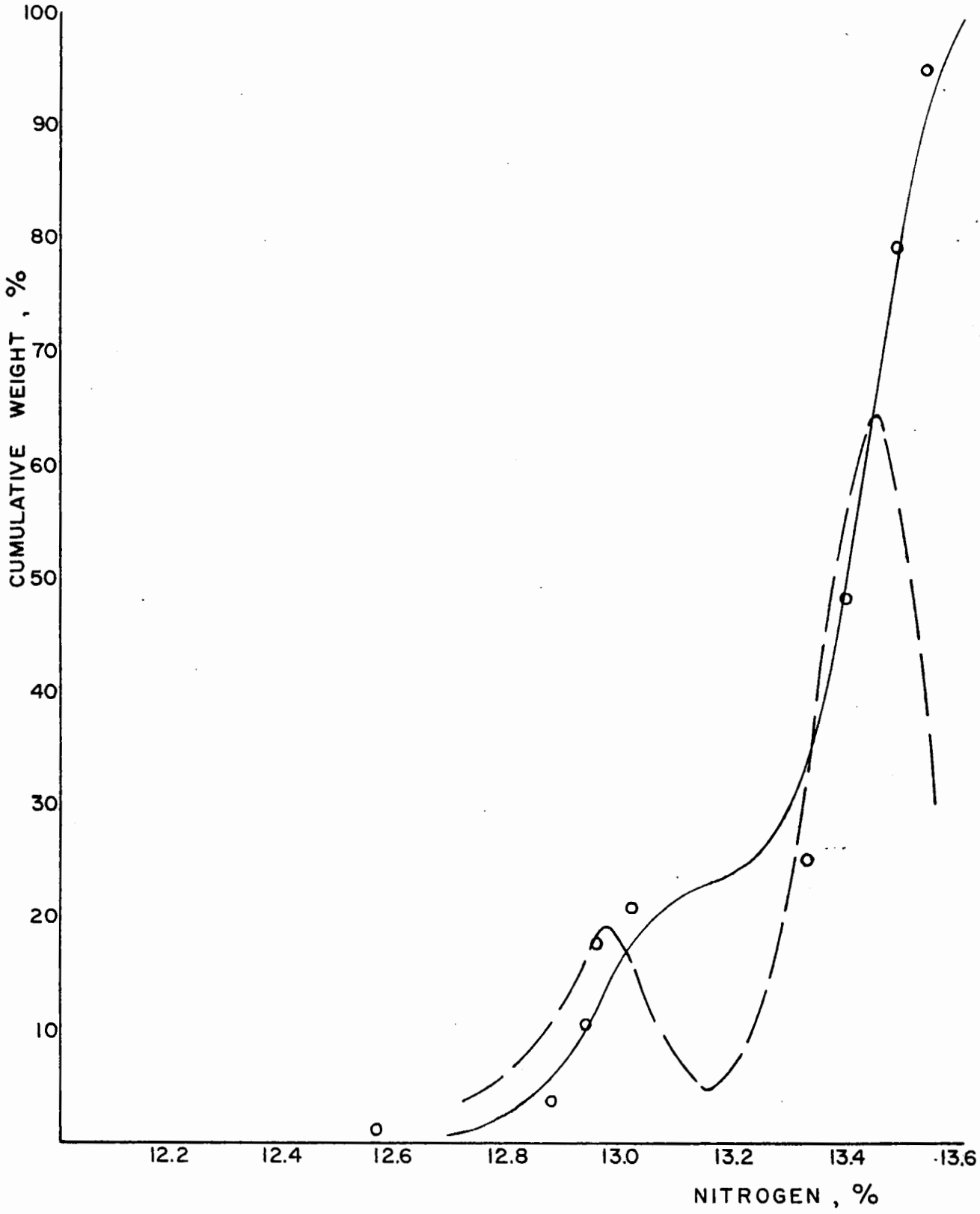

FIG. 13 : INTEGRAL AND FREQUENCY DISTRIBUTION CURVES FOR REPRECIPITATED SAMPLE NO. 13.

viscosity of 23.6, indicating that no appreciable degradation had taken place. However, it proved to be very susceptible to swelling and yielded only five fractions, which exhibited a relatively narrow nitrate distribution, ranging from 11.08% to 11.92% nitrogen (Table XXVII). This was in marked contrast to the behaviour of the rate-controlled nitrates on fractionation. The amount of insoluble material amounted to 4.4%. Sample No. 6 (12.43% nitrogen) was shown to consist of two portions of very rigid proportions; 14.0% being generally soluble under any circumstances, while the remaining 86.0% resisted dissolution by all known solvents. These two portions had respective nitrogen contents of 12.70% and 12.22% (Table XXVI). Sample No. 7 (13.28% nitrogen) exhibited an almost completely reversed behaviour. Most of the material was easily dissolved leaving a small additionally soluble portion of lower nitrogen content plus 13.5% of an insoluble residue (Table XXV).

It is evident that limiting nitration by diluting the bath with phosphoric acid leads to a complex reaction. Another study in this laboratory (100) produced similar results; the nitration products were almost completely soluble around 11.5% and above 13.5% nitrogen, but a condition of partial solubility existed for products with intermediate nitrogen contents. Lindsley and Frank, who introduced this technique, make no mention of any such problem (61). However, on studying their published data, it seems that, for cottons of a comparable average chain length (viscosities of 17 and 39 as compared to 25 for the linters used here), very few samples in this substitution range were tested - and those that were exhibited a lower viscosity than both lower and higher substituted samples. While it is doubtful that these workers would have ignored any considerable insolubility during their viscosity determinations,

their nitrates may have undergone an involuntary pre-fractionation, since all their products were originally dissolved in acetone, filtered, and then precipitated into water.

Smith (92) has also used phosphoric acid as a diluent in obtaining nitrates in the 11.5%-12.5% range, and his fractionation data indicate that the material was practically entirely soluble. The average D.P. of his cellulose was very low, however, the highest being only about 700. It is doubtful whether this material would have retained much of its original fibrous characteristics after such extensive degradation, and there would be little to inhibit rapid uniform diffusion by the nitrating agent. In concordance with this, Smith's fractionation data for nitrated linters show a rather narrow and symmetrical nitrate distribution.

Fractionation of Cellulose Nitrates of a Maximum D.S.

The fractional precipitation data for Sample No. 1 (Table VIII) was primarily obtained to establish the true D.P. distribution of the material, as pictured in Figure 4. However, evidence of under-nitrated material among the shorter chains was also produced.

The fractionation data for Sample No. 2, although obtained by a relatively crude technique, can be useful if allowance is made for the effect of lack of temperature control. In addition, the time of contact with the solvent was longer (4 hr. per fraction as opposed to 3 hr. for all the other experiments). The first experiment was performed at the most elevated temperature (approximately 33°C.), and this probably accounts for the incongruous nature of the data. From Table XIV-A it is seen that there were large early fractions, a low average D.S. for all the fractions, and most significantly, over 4% of an insoluble residue containing only

9.4% nitrogen. While this last phenomenon does not seem remarkable in light of the insoluble residues found for rate-controlled nitration, it is hard to believe that any of this sample could be so poorly nitrated after 4 hours' contact with the nitrating mixture used here. Instead of this, there is strong evidence that this insoluble residue was the result of the fractionation procedure, which caused a slight denitration, accelerated by the relatively high temperature. The low average nitrogen content found after fractionation is additional confirmation for this. The second experiment was performed at a lower temperature, and the results in Table XIV-B are all consistent with a more moderate denitration effect. The early fractions are smaller, the average nitrogen content is higher, and the insoluble residue only 2.39% of the total. The contrast is even more noticeable in Figure 14, where the nitrate distributions are plotted, and in Figure 15, which shows the fractionation sequences. The single-step fractionation shown in Table XV indicated the inherent total solubility of this sample.

Sample No. 3 was fractionated in duplicate, under controlled temperature conditions and with a shorter time of contact between solvent and polymer. The results indicated good duplication as far as nitrate distribution was concerned (Fig. 16), and in both cases no insoluble residue was found (Tables XVIII-A, XVIII-B). However, this sample exhibited some surprising properties. It was quite susceptible to swelling (see Fig. 5 and Table XVII), yielded less material before swelling than even the lowest of the rate-controlled samples, and its nitrate distribution showed a considerable amount of low D.S. material. The somewhat low viscosity of this sample, indicating a previous degradation, might explain these anomalies.

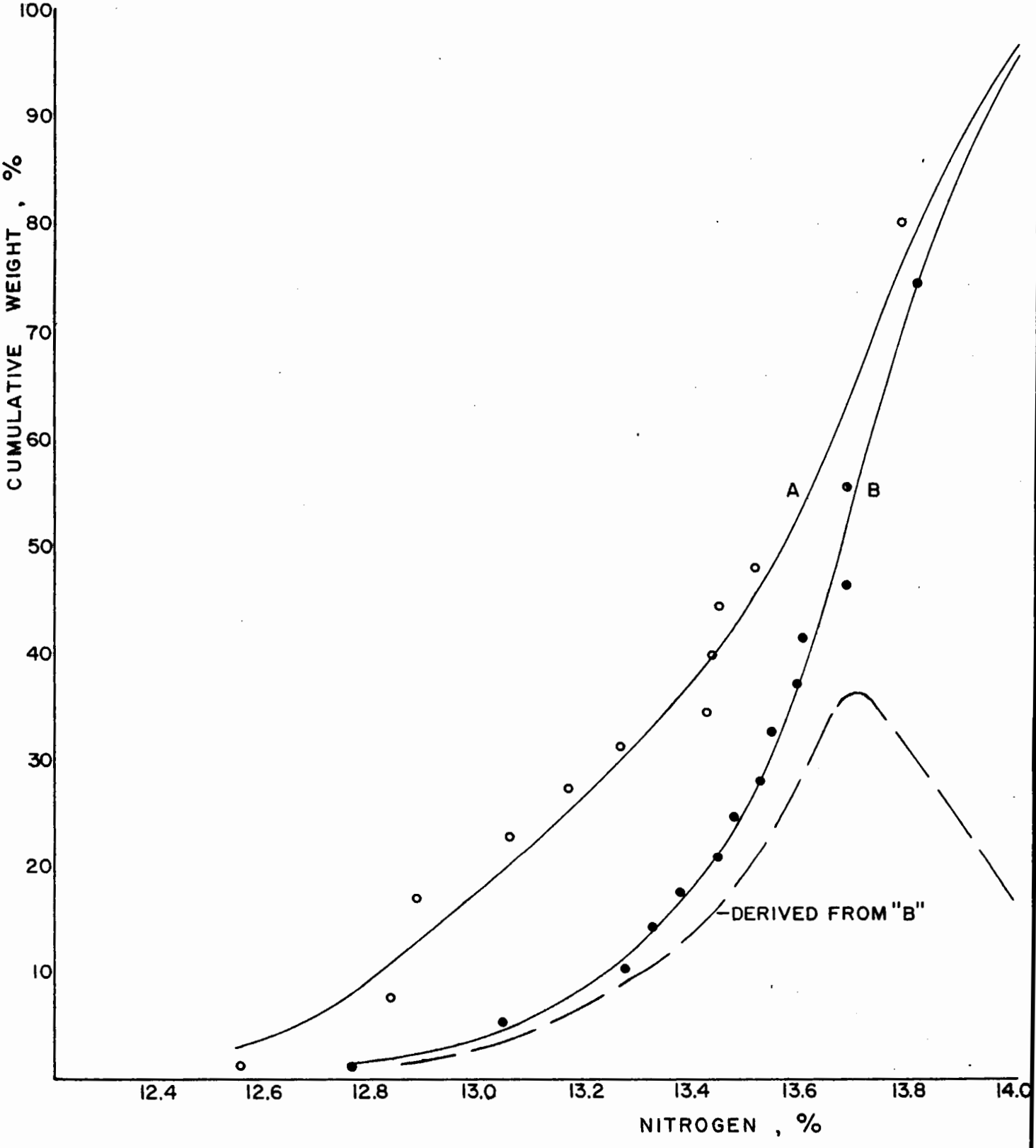

FIG. 14 : INTEGRAL AND FREQUENCY DISTRIBUTION CURVES FOR SAMPLE NO. 2.

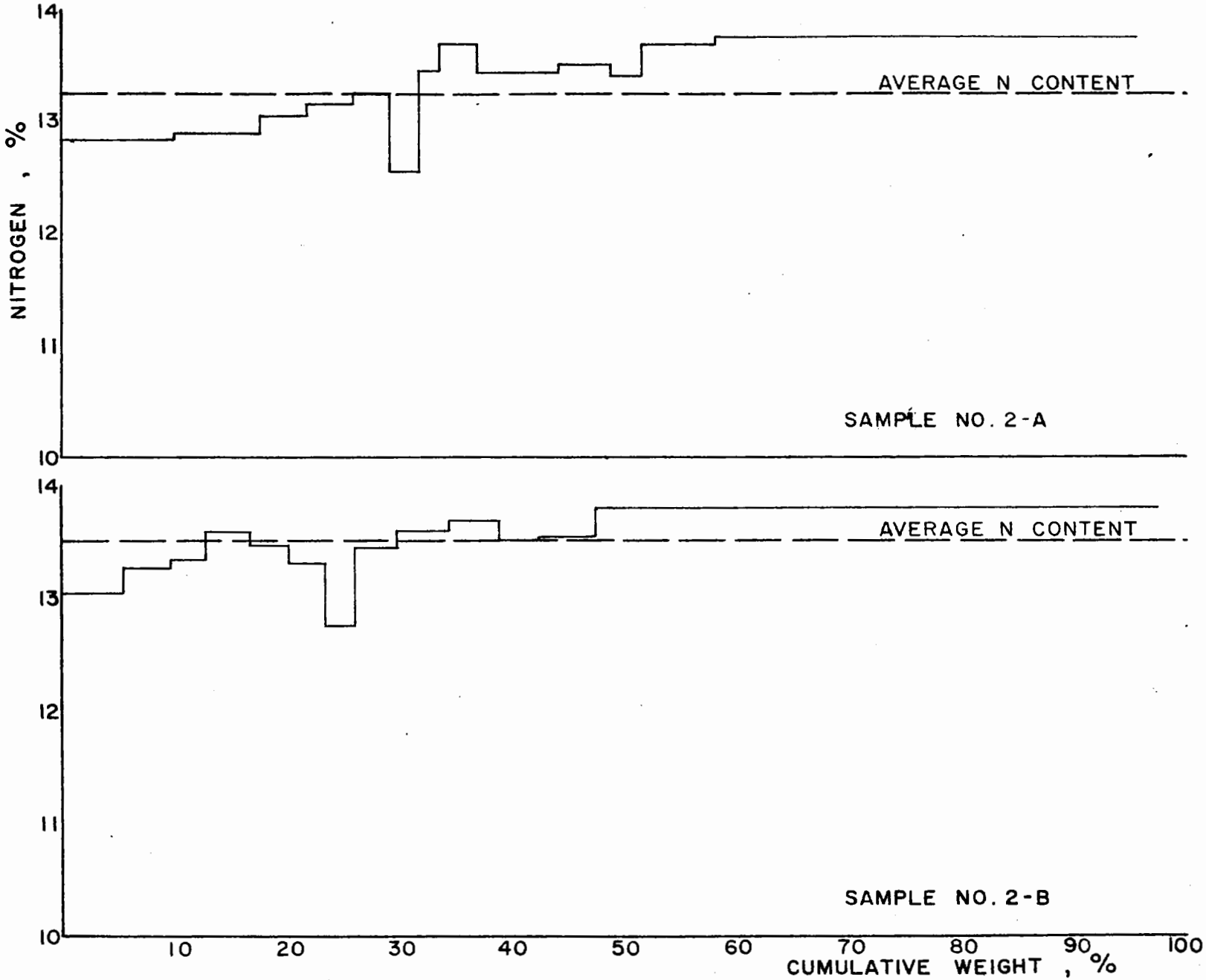

FIG. 15 : FRACTIONATION SEQUENCES FOR SAMPLE NO. 2.

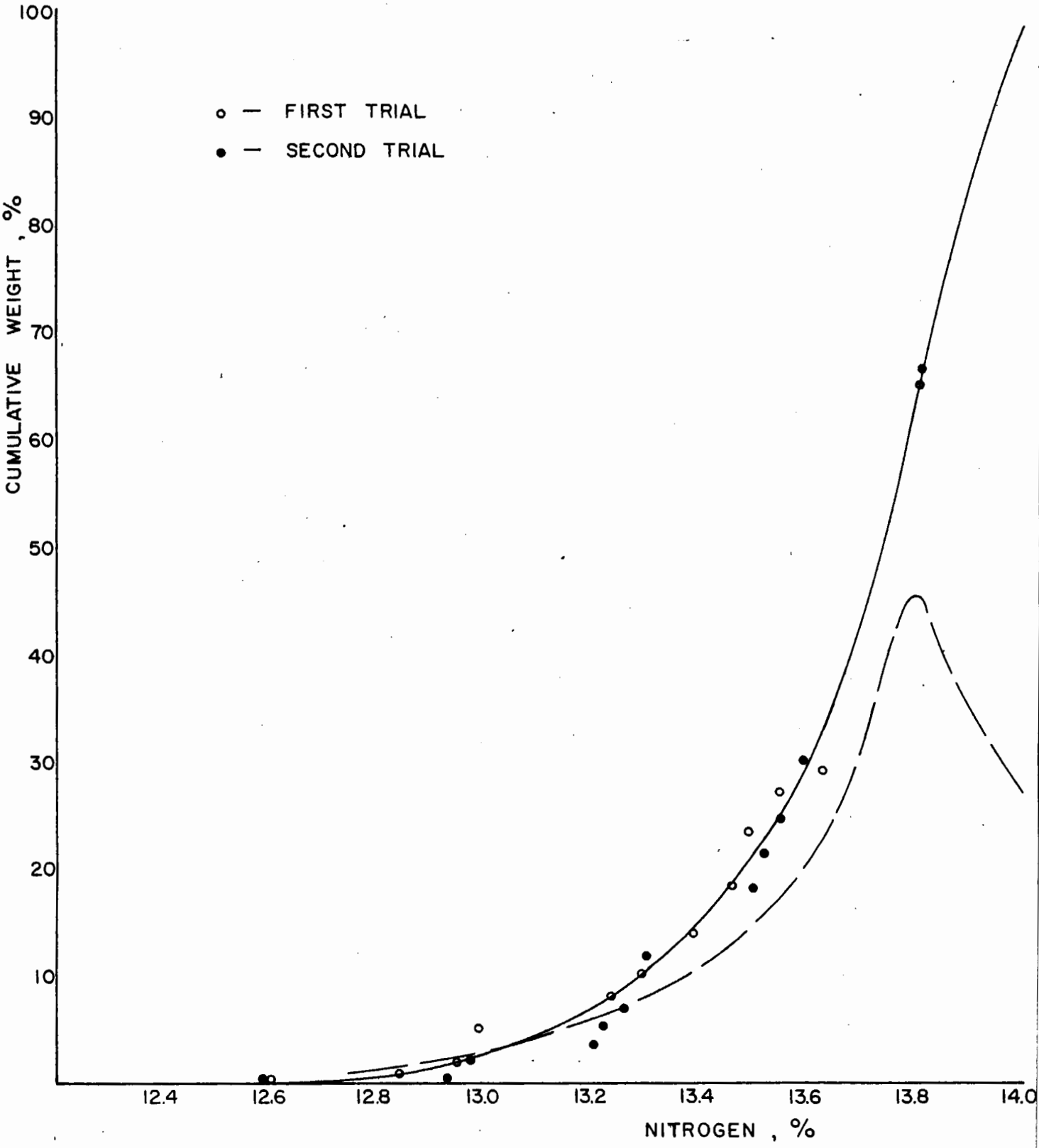

FIG. 16 : INTEGRAL AND FREQUENCY DISTRIBUTION CURVES FOR SAMPLE NO. 3.

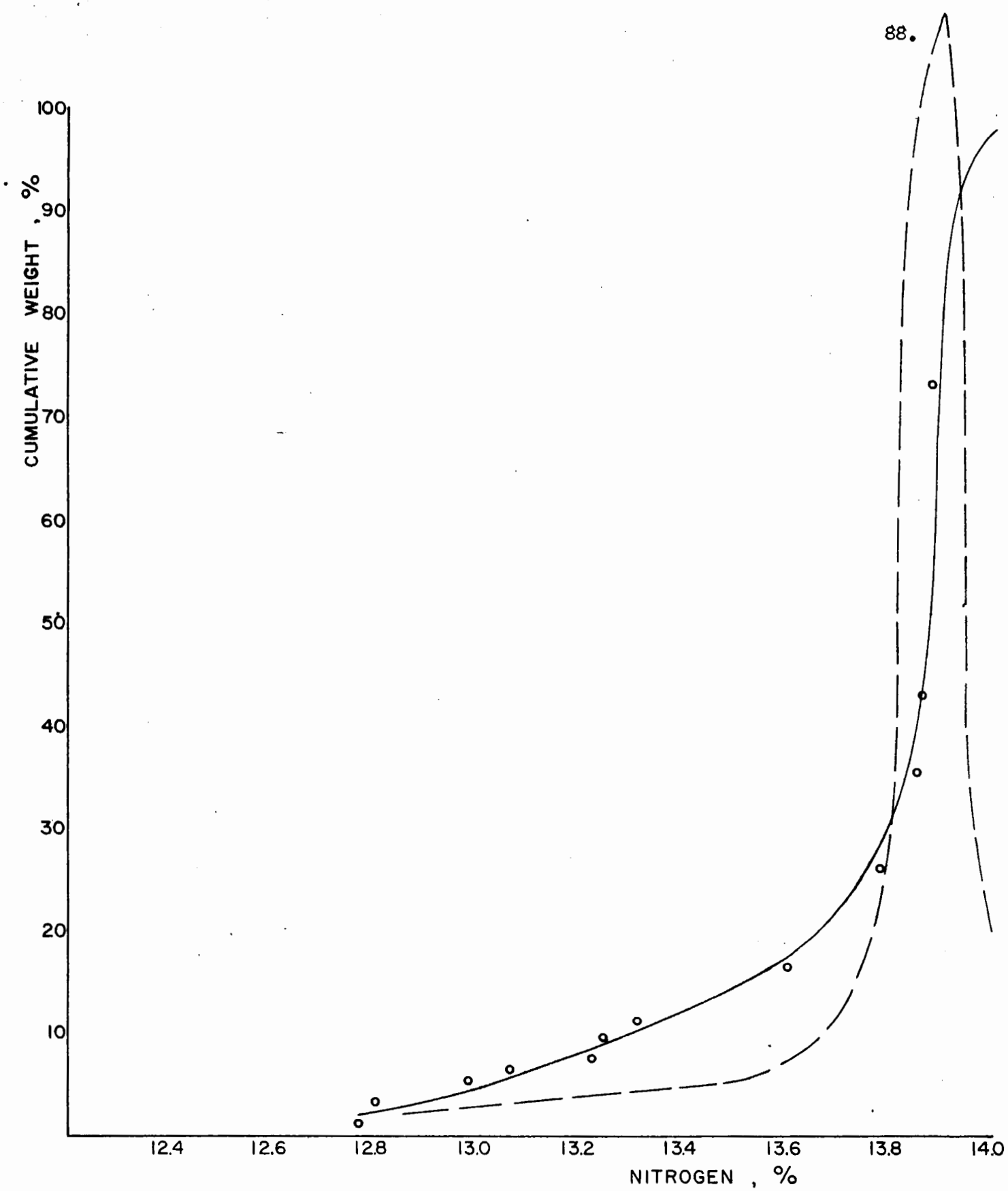

FIG. 17 : INTEGRAL AND FREQUENCY DISTRIBUTION CURVES FOR SAMPLE NO. 4.

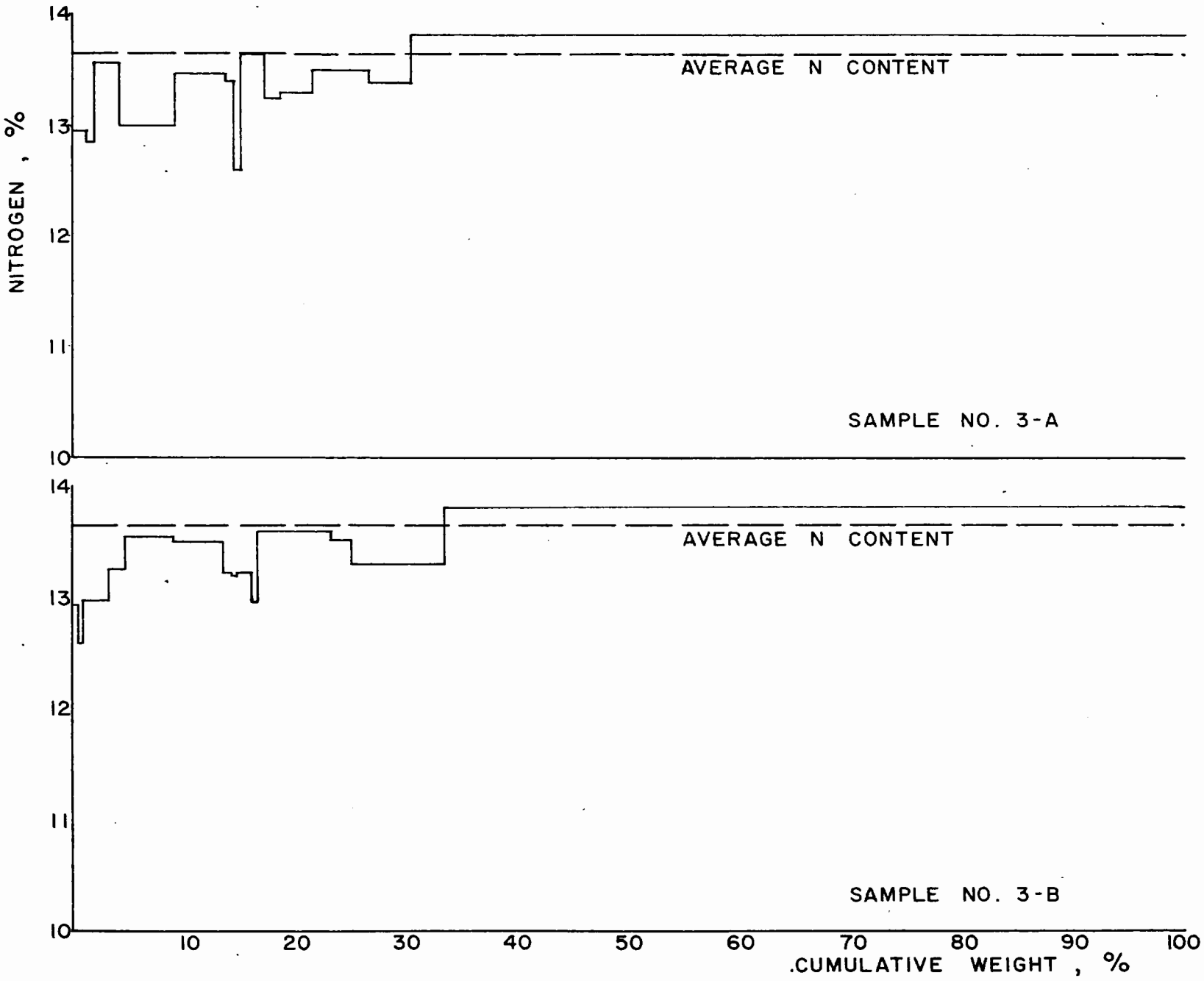

FIG. 18 : FRACTIONATION SEQUENCES FOR SAMPLE NO. 3.

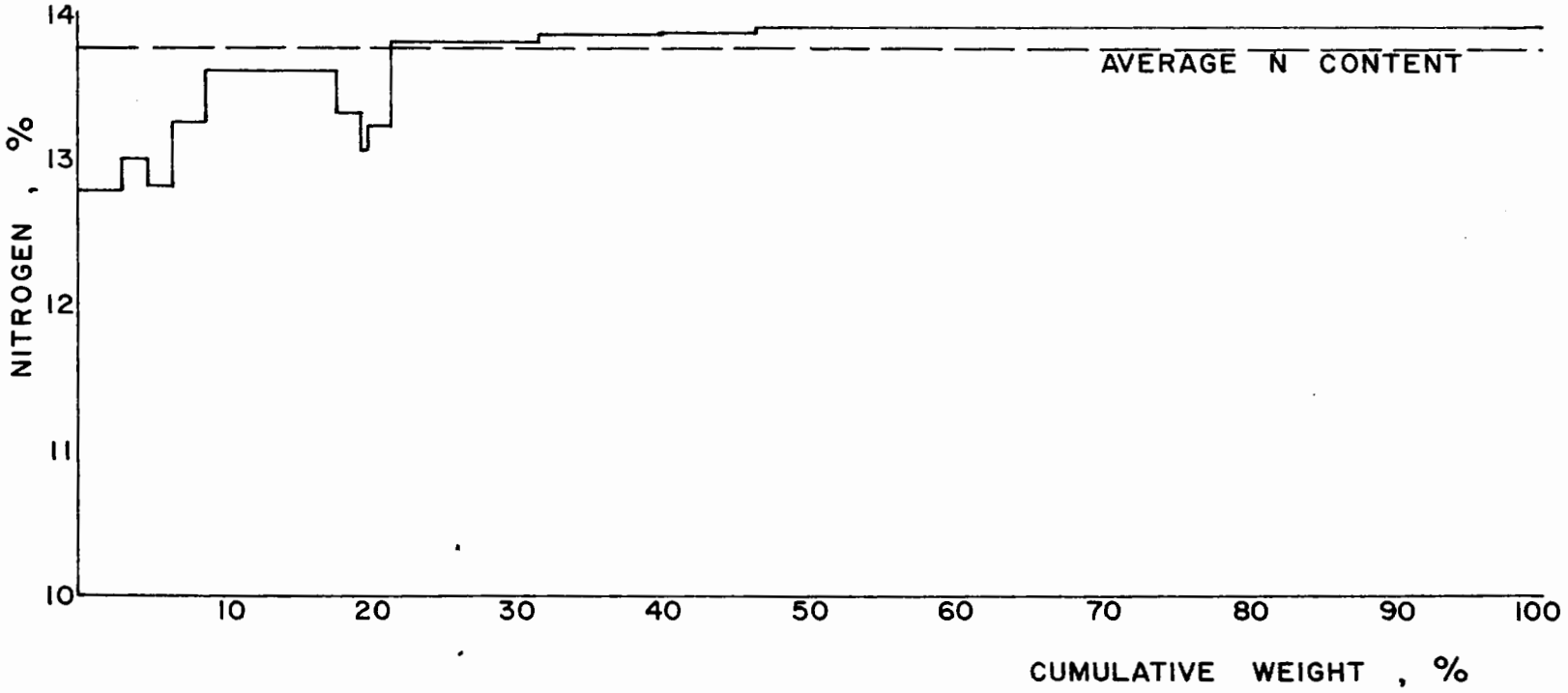

FIG. 19 : FRACTIONATION SEQUENCE FOR SAMPLE NO. 4 .

Sample No. 4 produced the smallest initial fractions, as might be expected from a substance so close to a tri-nitrate. It had only a small amount of material of low nitrogen content (Fig. 17), was not easily swollen, and contained no insoluble residue (Table XIX).

Here we are concerned with the same questions that arose in the fractionation of the rate-controlled products. The latter showed that a seemingly constant amount could be extracted before swelling occurred. If we disregard Sample No. 3, which presumably had undergone some alteration in structure, it is found that Samples Nos. 2 and 4 have swelling points which agree closely, namely at 45.64% and 43.16% respectively (Compare with results in Table XXXI).

The overall nitrate distribution for each of these three samples were consistent with their average D.S. These are reproduced in Figures 14, 16 and 17. Sample No. 2 had the lowest average D.S. and also exhibited the broadest distribution. Sample No. 3 showed a narrower frequency distribution and Sample No. 4 had a very narrow distribution curve, although maintaining a left-hand skewness. The integral curves for all three samples started at a minimum nitrogen content of 12.6%-12.8%. The fractionation sequences (Figs. 15,18,19) exhibited the erratic change in nitrogen content which might be expected considering the potential number of variables that could influence the order of extraction. Approximately 5-10% of less nitrated material still remained, but not all of it appeared in the first fractions. A minimum nitrogen content range seemed to appear after 15%-25% of the sample had been extracted. The cause of this lies evidently in the effect of chain length on solubility. Examining the viscosity values in Tables XIV-A, XIV-B, XVIII-A, XVIII-B, and XIX, it is found that each of these low D.S. regions corresponded to a maximum in the D.P. for the

fraction sequence.

The sequence graphs also confirm the impression given by the fractionation studies on rate-controlled nitrates. The inaccessible regions were still nitrated to a higher degree than the more soluble portions, and the latter included about 5%-10% of low-nitrated material which was composed of both short and long chains. This illustrates the advantage of fractional solution over precipitation for the present purpose. The latter brought out the presence of low D.S. material (Table VIII) but did not give a true picture of the D.S. or D.P. involved. The fixed proportion of 12.6%-13.0% nitrogen found in all the highly nitrated materials (Nos. 2,3,4,13) seems to imply that a final equilibrium has been reached. It is difficult to state what distinguishes this part from the rest of the fiber. It must be highly accessible, not only at the beginning of nitration, but also at the end. As has been mentioned previously, this may be due to an inherent inability to crystallize.

When Sample No. 3 was dissolved and reprecipitated, its fractionation characteristics were altered considerably. The fractions were extracted in order of increasing D.P., and only the first few fractions showed an extremely low D.S. (Table XXIX and Fig. 12). However, the distribution curve was narrower than before (Fig. 20), and some of the low D.S. material may have been present in the later fractions.

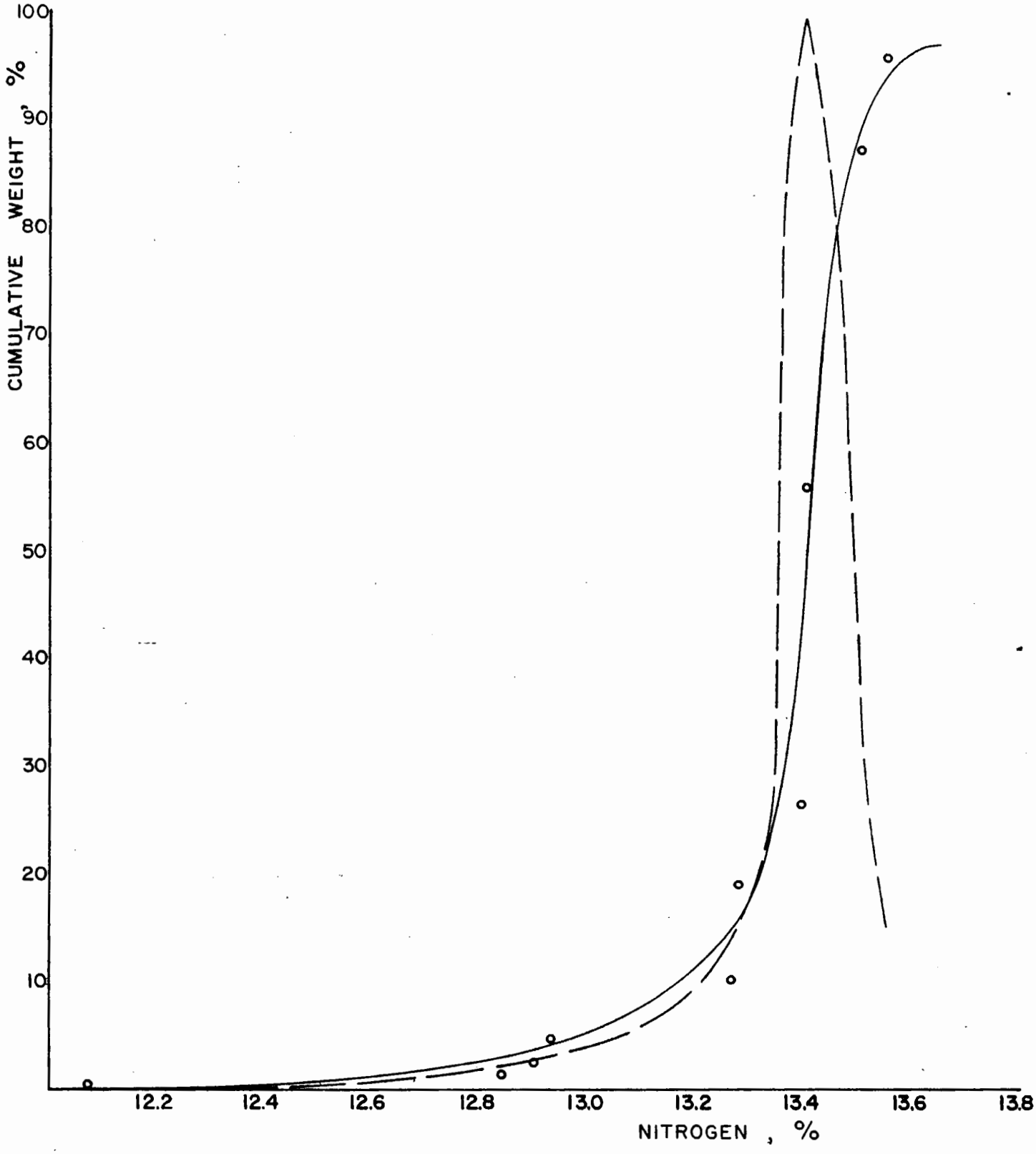

FIG. 20: INTEGRAL AND FREQUENCY DISTRIBUTION CURVES FOR REPRECIPITATED SAMPLE NO. 3.

CONCLUSIONS

The results obtained here indicate clearly the intrinsic difference between the fractional precipitation and the fractional solution methods as applied to polymers like cellulose nitrate. The former procedure effects a subdivision of the material mainly according to the molecular weight differences of the chain molecules. As is evident from Table VIII, however, the nitrate substitution of the chains also has an influence, which can only be eliminated by increasing the degree of substitution to the tri-stage. The variation in nitrogen contents is, apart from the very last fraction, not considerable and reflects the well-known fact that the solubility properties of cellulose derivatives are more influenced by slight changes in the degree of substitution than in the molecular weight.

To the two factors determining the fractional precipitation behavior of cellulose nitrate there is added another one in the case of fractional solution, namely the fine structure of the fiber. It is evident from the results obtained here that all three factors are operating in this case, although to a relative degree depending on external circumstances. With a native cellulose fiber such as the cotton linters used here, fractional extraction will first remove the shortest chains within the accessible regions, i.e. those chains that are located on the surface of the microfibrils. At this stage, however, the extraction media will have a composition favoring solution of nitrates of an intermediate D.S., corresponding to approximately 12.5-13.5% nitrogen, and this effect will be superimposed on the other two. As extraction proceeds, material within the outer sections of the microfibrils will be removed, first those of

short chain length and subsequently those of medium size. The nitrate substitution will still be a factor of primary influence but not quite as great as during the first stage, as the solvent mixtures used will now be able to dissolve material with a wider range in D.S. At this point swelling probably gradually begins and from then on the fiber structure is rapidly destroyed. On further fractionation short and medium sized chains will be extracted from the swollen gel and when finally maximum swelling has occurred chains of all sizes and substitution will be dissolved.

Destruction of the original native fiber structure will, as was mentioned previously, render the influence of the fine structure of the fiber less operative. The results obtained indicate clearly that a regenerated nitrate is more uniform, both chemically and physically than its native counterpart. This fact will, of course, influence its solubility properties and make it more difficult to subdivide into fractions. The difference noticed here between the two modifications was quite considerable and thus furnishes an indirect proof of the great effect of the fiber structure on the course of fractionation.

It is evident from the above that the conditions in fractional solution of partly substituted cellulose nitrates are very complicated and that this method could hardly be expected to be very useful for estimating chain-length distributions. Although formerly enjoying a widespread popularity, the procedure is now never applied for this purpose. Lately, however, this method has been employed with some success for establishing the distribution of substituents in various cellulose derivatives such as mixed cellulose nitrates (76), carboxymethylcelluloses (79) and cellulose nitrates (92). The results in the last-mentioned

investigation, which appeared after the present study was terminated, corroborate on the whole the results noted here.

The well-known fact that nitration of cellulose seems to occur in two steps is fully confirmed by the present results. Figure 6 indicates a rapid nitration until a nitrogen content of 12% has been reached after which the rate of reaction rapidly decreases. The frequency curves in Figure 8 and also those in Figures 14, 16 and 17 show how the nitrate distribution becomes more and more narrow as the average D.S. increases and in this respect nitrates are apparently similar to all other cellulose derivatives, e.g. carboxymethylcellulose (79). Even the highest substituted nitrate investigated here is, however, far from completely homogeneous chemically and a recent contention that cellulose nitrates should be chemically uniform (63) would seem to warrant some modification in view of these results.

All the fractional solution experiments indicate that the nitrates investigated were more highly substituted in the interior of the microfibrils and along the longer chain molecules than on the surface or along the shorter chains. These conditions are exactly opposite to what has been found for other cellulose derivatives such as methylcelluloses (76), cellulose acetates (77), or carboxymethylcelluloses (79), and seem to distinguish nitrates from all other derivatives in this respect. The present results indicate that nitration of native cellulose occurs first on the surface of the microfibrils but that subsequently the interior, crystalline regions are more or less completely nitrated before the now slower conversion of the accessible portions has taken place. This is contrasted to e.g. the methylation or acetylation of cellulose where the accessible localities are rapidly converted to the tri-stage and the

remainder of the material reacts only slowly.

It would be premature to offer an explanation at this stage for this strange phenomenon. Chedin (45) has suggested that in technical nitrations only the planar HNO_3 molecule can enter the crystalline region whereas the disordered parts are nitrated by HNO_3-H_2SO_4 complexes. Provided the water formed in the esterification can diffuse out from the crystalline portion, this should result in a higher degree of nitration in this part than in the accessible one. Similar considerations could presumably be applied in the present case, where planar nitric acid and very bulky phosphoric acid and phosphorus pentoxide molecules were present.

Another problem which seems difficult to explain is the fact that all the short-chain material has such a low nitrogen content. Smith (92), investigating technical nitrates, obtained similar results and tried tentatively to explain this by assuming a stronger hydrolytic degradation and lower degree of nitration of the inner parts of the microfibrils due to dilution of the nitrating acid in this region. This assumption is not corroborated by the present findings, especially as no theory involving shortening of the chain molecules can now be invoked here. If accepted as valid the results would indicate a preponderance of short-chain material on the surface of the microfibrils.

SUMMARY AND CLAIMS TO ORIGINAL RESEARCH

1. A method has been developed for following the nitration of cellulose without accompanying degradation, involving the use of a nitric acid-phosphoric acid-phosphorus pentoxide mixture and a temperature of -32°C.

2. Cellulose nitrates of various degrees of substitution could be divided into approximately fifteen fractions before swelling occurred by using extraction mixtures consisting of ethyl acetates and ethanol, with or without the addition of water.

3. A series of four cellulose nitrates, ranging in nitrogen contents from 12.0 to 13.6% and obtained by interrupting the nitration reaction at various time intervals, were studied by this fractional solution method, and the fractions were analyzed for average degree of substitution and molecular weight (intrinsic viscosity). The fractionation was found to be influenced by both these properties but also, and probably primarily, by the location of the chain molecules within the fiber structure.

4. Similar experiments were carried out with nitrates of various degrees of substitution, obtained in equilibrium-controlled reactions and with non-equilibrium products regenerated from acetone solutions. In the latter case the fiber structure had considerably less influence on the fractionation.

5. In all cases the degree of substitution and molecular weight of the fractions increased with proceeding fractionation, the remaining swollen part exhibiting the highest nitrogen content. This was in marked contrast to the known behavior of other cellulose derivatives under similar conditions.

6. Frequency curves obtained in this way showed how the nitrate distribution became more narrow as the average degree of substitution increased. However, even the highest substituted nitrate was not completely chemically uniform, and recent claims in this direction are probably not valid.

7. Cellulose nitrates formed under equilibrium-controlled conditions or regenerated from solution were found to be more uniform chemically than similar products isolated directly in rate-controlled reactions.

8. The results obtained indicated that native cellulose was nitrated in a two-stage reaction, involving an initial, rapid conversion of the surface and outer regions of the microfibrils. After this stage, the interior of the microfibrils was nitrated more rapidly and more completely than the more accessible portions, which only slowly reached their maximum nitration level. The shorter chains generally contained less nitrate groups than the longer ones, indicating a preferential location of short-chain material within the accessible regions.

REFERENCES

1. Mark, H., In "Cellulose and Cellulose Derivatives", 2nd Edition, ed. by Ott, E. and Spurlin, H.M. Interscience Publishers Inc., New York, Vol. I, 217 (1954).

2. Hermans, P.H., "Physics and Chemistry of Cellulose Fibers." Elsevier, New York. 251 (1949).

3. Ibid., 307.

4. Howsmon, J.A. and Sisson, W.A., In "Cellulose and Cellulose Derivatives", ed. by Ott, E. and Spurlin, H.M. Interscience Publishers Inc., New York, Vol. I, 233 (1954).

5. Mark, H., Chem. Revs. 26:169 (1940).

6. Baker, W.O., Ind. Eng. Chem. 37:246 (1945).

7. Nickerson, R.F. and Habrle, J.A., Ind. Eng. Chem. 37:1115 (1945).

8. Frey-Wissling, A., Science 119 no. 3081:80 (1954).

9. Sen, M.K. and Roy, S.C., Nature 173 no. 4398:298 (1954).

10. Ranby, B.G., Makromol. Chem. 13:40 (1954).

11. Sisson, W.A., Ind. Eng. Chem. 30:530 (1938).

12. Spurlin, H.M., Trans. Electrochem. Soc. 73:95 (1938).

13. Timell, T.E., "Studies on Cellulose Reactions", Stockholm (1950).

14. Barsha, J., In "Cellulose and Cellulose Derivatives", 2nd Edition, ed. by Ott, E. and Spurlin, H.M. Interscience Publishers Inc., New York, Vol. II, 713 (1954).

15. Spurlin, H.M. Ibid., 691.

16. Astbury, W.T. and Woods, H.J. J. Textile Inst. 23:17T (1932).

17. Nickerson, R.F., Ind. Eng. Chem., Anal. Ed. 13:423 (1941).

18. Davidson, G.F., J. Textile Inst. 34:T87 (1943).

19. Battista, O.A. and Coppick, S., Textile Research J. 17:419 (1947).

20. Ranby, B.G., "Fine Structure and Reactions of Native Cellulose", Stockholm (1952).

21. Morehead, F.F., Textile Research J. 20:549 (1950).

22. Hock C.W., J. Polymer Sci. 8:425 (1952).

23. Brown, R.K. and Purves, C.B., Pulp and Paper Mag. of Can. 48:100 (1947).

24. Rosenthal, A. and Brown, R.K., Pulp and Paper Mag. of Can. 51:99 (1950).

25. Rollins, M.L., Anal. Chem. 26:718 (1954).

26. Schur, M.O. and Hoos, B.G., Ind. Eng. Chem. 29:26 (1937).

27. Heuser, E., "The Chemistry of Cellulose", John Wiley & Sons, Inc., New York (1944).

28. Farmer, R.C., J. Soc. Chem. Ind. 50:75T (1931).

29. Hughes, E.D., Ingold, C.K. and Reed, R.I., J. Chem. Soc. 2400 (1950).

30. Westheimer, F.W. and Kharasch, M.S., J. Am. Chem. Soc. 68:1871 (1946).

31. Klein, R. and Mentser, M., J. Am. Chem. Soc. 73:5888 (1951).

32. Chedin, J., Chimie and Industrie 61:571 (1949).

33. Lunge, G., J. Am. Chem. Soc. 23:527 (1901).

34. Schiemann, G. and Kuhne, S., Cellulosechemie. 15:80 (1934).

35. Berl, E. and Hefter, O., Cellulosechemie. 14:65 (1933).

36. Naray-Szabo, S. and von Susich, G., Z. Physik. Chem. 134:264 (1928).

37. Miles, F.D. and Milbourne, M., J. Phys. Chem. 34:2598 (1930).

38. Miles, F.D. and Craik, J., Nature 123:82 (1929).

39. Miles, F.D. and Craik, J., J. Phys. Chem. 34:2607 (1930).

40. Hess, K. and Trogus, C., Z. Physik. Chem. B15:157 (1932).

41. Miles, F.D., Trans. Faraday Soc. 29:110 (1933).

42. Trillat, J.J., Trans. Faraday Soc. 29:85 (1933).

43. Mathieu, M., Trans. Faraday Soc. 29:122 (1933).

44. Chedin, J. and Tribot, A., Chem. Abst. 40:7613 (1946).

45. Chedin, J., Chem. Abst. 40:7614 (1946).

46. Tribot, A. and Chedin, J., Chem. Abst. 42:4746 (1948).

47. Sakurada, I., Cellulosechemie. 15:18 (1934).

48. Rogowin, Z.A. and Tichonow, K., Cellulosechemie 15:104 (1934).

49. Rogowin, Z.A. and Tichonow, K., Cellulosechemie 16:11 (1935).

50. Chedin, J. and Tribot, A., Assoc. Tech. Ind. Papetiere, Bull. 5:435 (1951).

51. Bouchonnet, A., Trombe, F. and Petitpas, G., Bull. Soc. Chim. France 4:894 (1937).

52. Foex, M., Bull. Soc. Chim. France 8:381 (1941).

53. Keays, J.L., Ph.D. Dissertation, McGill Univ. (1949).

54. Berl, E. and Rueff, G., Cellulosechemie 12:53 (1931).

55. Berl, E. and Rueff, G., Cellulosechemie 14:109 (1933).

56. Berl, E., Ind. Eng. Chem., Anal. Ed. 13:322 (1941).

57. Davidson, G.F., J. Textile Inst. 29:T195 (1938).

58. Nicolas, L., Assoc. Tech. Ind. Papetiere, Bull. 5:427 (1951).

59. Alexander, W.J. and Mitchell, R.L., Anal. Chem. 21:1497 (1949).

60. Heuser, E. and Jorgensen, K., Tappi 34:57 (1951).

61. Lindsley, C.H. and Frank, M.B., Ind. Eng. Chem. 45:2491 (1953).

62. Doree, C., "The Methods of Cellulose Chemistry", D. Van Nostrand Co. Inc., New York, 2nd Ed. (1947).

63. Abadie, F.A., Norsk Skogind 7:68 (1953).

64. Brunswig, H., Cellulosechemie 7:118 (1926).

65. Kumichel, W., Kolloid-Beih. 26:161 (1928).

66. Craik, J. and Miles, F.D., Trans. Faraday Soc. 27:756 (1931).

67. Brown, R.K., Ph.D. Dissertation, McGill Univ. (1946).

68. Glegg, R.E., Ph.D. Dissertation, McGill Univ. (1946).

69. Scherer, P.C. and Rouse, B.P., Rayon Textile Monthly 29:55 (1948).

70. Scherer, P.C. and Masuelli, F.J., Rayon Textile Monthly 30:47 (1949).

71. Zapf, F., Makromol. Chem. 10:35 (1953).

72. Munster, A., J. Polymer Sci. 8:633 (1952).

73. Timell, T.E., Svensk Papperstidn. 58:1 (1955).

74. Wilson, G.L. and Miles, F.D., Trans. Faraday Soc. 40:150 (1944).

75. Scherer, P.C. and Thompson, R.B., Rayon and Synthetic Textiles 31 no. 9:69; 31 no. 10:51 (1950).

76. Timell, T.E. and Purves, C.B., Svensk Papperstidn. 54:303 (1951).

77. Rosenthal, A.J. and White, B.B., Ind. Eng. Chem. 44:2693 (1952).

78. Scherer, P.C. and Lou, L.H., Rayon and Synthetic Textiles 33:41 (1952).

79. Timell, T.E., Svensk Papperstidn. 56:311 (1953).

80. Ellefson, Ø., Norsk Skogind 7:405 (1953).

81. Mathieu, M., Assoc. Tech. Ind. Papetiere, Bull. 7:63 (1954).

82. Emery, C. and Cohen, W.E., Australian J. Appl. Sci. 2:474 (1951).

83. Page, E.J., Textile Research J. 23:28 (1953).

84. Heuser, E., Shockley, W. and Kjellgren, R., Tappi 33:101 (1950).

85. Davis, W.E., Ind. Eng. Chem. 43:516 (1951).

86. Roseveare, W.E. and Poore, L., Ind. Eng. Chem. 45:2518 (1953).

87. Cragg, L.H. and Hammerschlag, H., Chem. Revs. 39:93 (1946).

88. Scott, R.L., Ind. Eng. Chem. 45:2532 (1953).

89. Jorgensen, L., "Studies on the Partial Hydrolysis of Cellulose" Oslo, (1950).

90. Yamamoto, S., Chem. Abst. 27:3328 (1933).

91. Clement, L. and Riviere, C., Bull. Soc. Chim. France 1:1075 (1934).

92. Smith, T.H., Norsk Skogind 8:402 (1954).

93. Atchison, J.E., Paper Trade J. 116:243 (1943)

94. Cherubin, G., Bull. Soc. Chim. France 21:192 (1954).

95. Wannow, H.A., Kolloid-Z. 102:29 (1943).

96. Assoc. Offic. Agr. Chemists, "Official Methods of Analysis", 7th Ed., 13, (1950).

97. Bradstreet, R.B., Chem. Revs. 27:331 (1940).

98. Dickinson, W.E., Anal. Chem. 26:777 (1954).

99. Pfeiffer, G.H. and Osborn, R.H., In "Cellulose and Cellulose Derivatives", 1st Edition, ed. by Ott, E. Interscience Publishers Inc., New York, 956 (1943).

100. Timell, T.E., Unpublished results.