

# Further Studies on the Interaction of Sorbic Acid with an Insoluble Polyamide

By M. B. RODELL, R. BODNAR, W. L. GUESS, and J. AUTIAN

A previous paper reported the sorption and diffusion of sorbic acid in an insoluble polyamide. Further studies have been continued on this project and are reported in this paper. Experimental methods of Browne and Steele have given further evidence that the interaction of sorbic acid with nylon 66 is primarily one of hydrogen bonding at the amide linkage. Application of the Rotinyan-Drozdov equation to the sorption data confirms that the rate-determining step in the sorption process is the diffusion process in the nylon. Diffusion coefficients, calculated by several methods from sorption data, are compared to the diffusion coefficients obtained by the use of the experimental method of Barrer. Finally, X-ray diffraction and infrared spectra studies on the nylon-sorbic acid complex are used to help explain the mechanism of interaction, with emphasis on a possible double hydrogen bond formation.

A PREVIOUS PAPER reported an investigation which concerned the interaction of sorbic acid with an insoluble polyamide, nylon 66 (1). Equilibrium sorption and diffusion studies were conducted to permit the evaluation of a number of constants, such as (a) saturation value of the solute in the plastic, (b) standard affinity of the solute for the plastic, (c) standard heat of sorption, (d) apparent diffusion coefficient of the solute in nylon, and (e) activation energy of diffusion.

In the study referred to, the standard heat of sorption for sorbic acid in nylon 66 was found to approach a value of  $-10.0$  Kcal./mole which suggested that perhaps a double hydrogen bond formation was operative between the acid and the nylon or that some degree of chemical reactivity might be occurring between the sorbic acid and the polymer. Thus, it was decided to continue the interaction study of sorbic acid with nylon 66 to establish, if possible, the mechanism of interaction and to include other data which the authors felt would be pertinent to the sorbic acid-nylon problem. For convenience, the *Experimental* section includes the following studies: (a) determination of the mechanism of interaction, (b) diffusion *versus* rate of interaction, and (c) determination of diffusion coefficient.

## EXPERIMENTAL

### Equipment and Supplies

Beckman DB and Beckman IR-7 spectrophotometers (Beckman Instruments, Fullerton, Calif.); X-ray generator, No. 12045, and a Debye-Scherrer

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diffraction camera (North American Electric Co., Mount Vernon, N. Y.); Weissenberg diffraction camera (Charles Supper Co., Watertown, Mass.); sorbic acid (supplied as Sorbistat by Chas. Pfizer and Co., Inc., Brooklyn, N. Y.); orange I (Allied Chemical and Dye Corp., New York, N. Y.); and nylon 66 (0.01 in. thick), (supplied as Polypenco 101 by the Polymer Corporation of Pennsylvania, Reading, Pa.) were used.

### Determination of the Mechanism of Interaction

#### Sorption Studies of Dye and Sorbic Acid by Nylon.

—Sufficient evidence has been accumulated to demonstrate that acid dye molecules interact with the end amino groups of nylon by an ionic mechanism (2, 3). Since acid dyes are comparatively strong acids, they are primarily in the ionic state even at low pH values and thus will interact with the positively charged end amino groups. Browne and Steele postulated that organic acids may be sorbed by nylon 66 in either of two ways (4): first, the acids may interact with the end amino groups, or second, they may interact with the amide groups along the polymer chain. These investigators concluded that if in a solution containing an organic acid and a dye, the organic acid were to be bound at the end amino groups, the over-all sorption of the dye by the nylon would be decreased. However, should the acid be bound to the amide groups, there would be no decrease in total sorption of the dye. In fact, dye sorption and its diffusion rate would tend to increase, a result of the swelling action of the acid which permits less hindrance to passage of the dye through the plastic.

To detect if sorption of sorbic acid occurred at the end amino groups rather than at the amide linkages, a diffusion experiment was conducted on nylon 66 similar to that of Browne and Steele (4). In this experiment, a solution of 300 ml. of orange I (0.025%) was kept in contact with 6.0 Gm. of nylon 66 and the sorption measured at various time periods up to equilibrium. The data were then used to calculate the apparent diffusion coefficient as reported in a previous paper (1). In this experiment,  $D$  was found to equal  $0.691 \times 10^{-9}$  cm.<sup>2</sup>/second with equilibrium total sorption of 14.7 mg. dye per gram of nylon.

When the same amount of dye was placed in a 0.1% sorbic acid solution, however, and another diffusion study was made, the diffusion coefficient of

dye in the nylon was calculated at  $1.80 \times 10^{-9}$  cm.<sup>2</sup>/second, with equilibrium total sorption now at 22.5 mg. dye per gram of nylon. In each case the temperature chosen was 61°. Following the rationale of Browne and Steele, the conclusion is that sorbic acid must be bound to nylon 66 through hydrogen bonding at the amide linkages.

**X-Ray Diffraction Studies.**—The measurement of the scattering or diffraction of X-rays is used commonly to determine the degree of periodicity or crystallinity of a given material. In a well-crystallized substance, the periodicity in all directions is well defined, so that the scattered X-rays will suffer either destructive interference or reinforcement in accordance with the Bragg law (5)

$$n\lambda = 2d \sin\theta \quad (\text{Eq. 1})$$

A monochromatic X-ray beam (wavelength  $\lambda$ ) is diffracted by a set of parallel equally spaced planes (spacing  $d$ ) within a crystal. Diffraction will occur only in precise directions (angle  $\theta$ ) with respect to the planes for each of several orders of diffraction ( $n$ ). Scattered X-ray beams are confined to narrow angular ranges, predicted by Eq. 1. With crystalline materials, a sharp well-defined scattering curve results. In the case of amorphous materials having almost a complete lack of periodicity, a broad scattering curve would result.

X-ray photography is the most common procedure utilized to record the diffracted radiation. A material containing a relatively high degree of crystallinity will show sharp definite diffraction bands, a degree of higher-order bands, and back reflection bands when examined in a Debye-Scherrer camera. However, a more amorphous material would exhibit broad diffuse bands, with little or no higher-order or back reflection bands. Thus, through the comparison of diffraction bands from several samples of a material, it is possible to determine qualitatively whether a given sample is more ordered and crystalline than another.

The experimental work involved in this portion of the investigation was accomplished through the use of the Debye-Scherrer diffraction camera and the Weissenberg camera. With the Debye-Scherrer technique, one obtains a film strip in which the diffraction bands shown are those through the axis of the diffraction cone. On the other hand, the Weissenberg technique results in a diffraction pattern of the entire diffracted cone.

In each case, X-ray photographs were made of a sample of nylon 66 that had been treated with 0.125% sorbic acid solution at 55°, as well as of nylon 66 exposed only to water at this temperature.

A sliver of the nylon sample was mounted in the camera at right angles to the incident X-ray beam and exposed for 2 hours to  $\text{CuK}\alpha$  radiation (1.54 Å.). The cameras used were a standard Debye-Scherrer camera (radius 57.3 mm.) and a standard Weissenberg camera (radius 28.65 mm.) held in a stationary position. During exposure time, the samples were held stationary within the camera, and the diffracted beams in a continuous cone were recorded on the X-ray film. The films were uniformly developed and fixed, then visually examined to determine any difference in the crystalline structures of the treated and untreated nylon samples. Figures 1 to 4 include representative X-ray results on nylon.



Fig. 1.—Debye-Scherrer X-ray diffraction photograph of nylon 66 treated with sorbic acid.

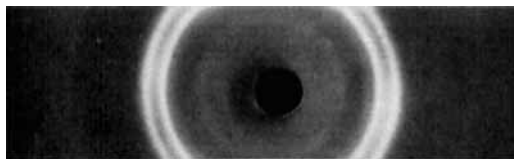


Fig. 2.—Debye-Scherrer X-ray diffraction photograph of nylon 66.

**Infrared Spectrophotometry.**—The instrument chosen for this phase of the investigation was the Beckman IR-7 spectrophotometer. This instrument, equipped with a double beam, enabled a differential analysis to be conducted on nylon 66 treated with 0.125% sorbic acid at 55.0°. The analysis was conducted by mounting a strip of nylon 66 exposed only to water at 55.0° in the path of the rear beam of the instrument and mounting a strip treated with sorbic acid in the path of the front beam. The absorption spectrum thus obtained was an analysis of the difference between the two samples. Figure 5 illustrates an infrared absorption spectrum of sorbic acid, while Fig. 6 is the differential infrared absorption spectrum of the nylon treated with sorbic acid compared with untreated nylon.

**Results and Discussion.**—The sorption studies with the (a) dye and nylon and (b) dye, sorbic acid, and nylon indicate that sorbic acid interacts at the amide linkages rather than at the end amino groups. Since sorbic acid is primarily in the unionized state at pH values below 3.5 (pH of sorption experiments), it is postulated that the interaction must be one of a dipole-dipole type where hydrogen bond formation is taking place between the protonic hydrogen of the acid with the negative site of the carbonyl group in the amide linkages. Secondary valence forces then come into play to stabilize the interaction. Heats of sorption for a group of weak organic acids, such as benzoic acid and salicylic acid, as well as other similar molecules in nylon, have fallen in the range of approximately  $-2$  to  $-4$  Kcal./mole (6, 7) and support the contention that one hydrogen bond has formed. Generally, it is assumed that the energy requirement for one hydrogen bond is in the range of  $-4.0$  to  $-5.0$  Kcal./mole. Since the value for sorbic acid approached  $-10.0$  Kcal./mole, it is suggested that a double hydrogen bond has formed between the acid and the polyamide.

If indeed a double hydrogen bond formation does occur between the sorbic acid and the nylon, it may well be represented as shown in Fig. 7. Here the sorbic acid molecule has taken a position between parallel molecules of the nylon, thereby breaking some of the intermolecular bonds between the polymer chains. The double hydrogen bond then can

take place as shown, where the amide hydrogen of one chain interacts with the carbonyl oxygen in sorbic acid, while the hydroxyl hydrogen of the sorbic acid interacts with the carbonyl oxygen of the adjacent chain.

Figure 5, an infrared absorption spectrum of sorbic acid, indicates a strong absorption band at  $1700\text{ cm}^{-1}$ , corresponding to a carbonyl function. The band seen at a wave number of  $3000\text{ cm}^{-1}$  corresponds to that of a free hydroxyl group. Figure 6 is a spectrum of the differential infrared analysis described earlier and reveals a shift of the carbonyl band to  $1720\text{ cm}^{-1}$ , indicating a slight stretching or twisting of the carbonyl group. The carbonyl function may thus be accommodating or aligning itself for bonding with the amide hydrogen of the polymer chain. The band shown in Fig. 6 at  $2500\text{ cm}^{-1}$  indicates the presence of a bonded hydroxyl group, opposed to the free hydroxyl at  $3000\text{ cm}^{-1}$  shown in Fig. 5. Further comparison of Figs. 5 and 6 shows similarities in the region of  $1000$  to  $850\text{ cm}^{-1}$ , indicating the presence of the remainder of the sorbic acid moiety. Failure to see any absorption bands in Fig. 6 in the region from  $1500$  to  $1100\text{ cm}^{-1}$  is attributed to the high absorption by nylon 66 in this region, thus preventing a tracing on the chart.

Although diffusion mainly occurs through the amorphous zone of the nylon, considered to be less rigidly oriented and more random in its distribution of chains, the line of demarcation is not exact. The amorphous region of plastic materials is considerably less aligned in the arrangement of polymer chains than is the crystalline zone, but random



Fig. 3.—Weissenberg X-ray diffraction photograph of nylon 66 treated with sorbic acid.



Fig. 4.—Weissenberg X-ray diffraction photograph of nylon 66.

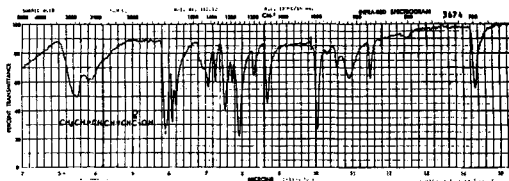


Fig. 5.—Infrared spectrogram of sorbic acid.

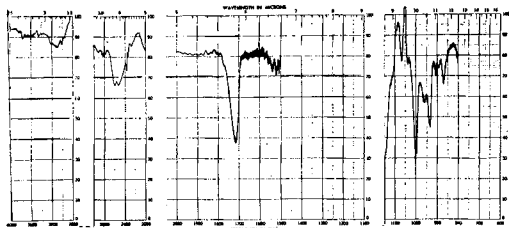


Fig. 6.—Infrared spectrogram of differential analysis of sorbic acid in nylon 66.

overlapping and convolution of chains can, and most likely do, occur.

It is postulated that the phenomenon involved in this interaction is, in fact, the formation of a double hydrogen bond, the sorbic acid being capable of assuming the same geometric plane as the surrounding polymer chains and fitting itself between these chains. Additionally, secondary valence forces probably stabilize the interaction, attracting the nonpolar moieties of the acid and nylon to each other.

Figure 1 is an X-ray diffraction photograph of nylon 66 previously treated with sorbic acid, taken in a Debye-Scherrer camera. Examination of the diffraction bands at the left of the photograph shows them to be relatively more narrow and sharp, opposed to those bands in Fig. 2, a photograph of untreated nylon 66. The presence of these narrower and sharper bands demonstrates that the treated nylon is more ordered and crystalline than the untreated nylon. Barely visible in the center of Fig. 1 is a pair of bands indicative of a higher order of diffraction, while to the right of the same figure the back reflection bands can hardly be seen. The broader and more diffuse bands shown in Fig. 2 lend further support to the double hydrogen bonding concept, since the inclusion of sorbic acid in the nylon tends to realign the polymer chains in the amorphous zone, thus giving more order to the nylon chains. This higher degree of order results in the more crystalline polymer seen in Fig. 1.

Figures 3 and 4 are X-ray diffraction photographs, taken in a Weissenberg camera, of nylon 66 treated with sorbic acid and untreated nylon 66, respectively. Again, the same effect is seen as in Figs. 1 and 2, with Fig. 3 showing the clearer and sharper diffraction bands.

#### Diffusion versus Rate of Interaction

Another point to be considered in the diffusion of sorbic acid into nylon 66 concerns the kinetics of the interaction. Rotinyan and Drozdov developed a basic equation, applicable to such diverse processes as roasting, leaching, washing, or cementation, which

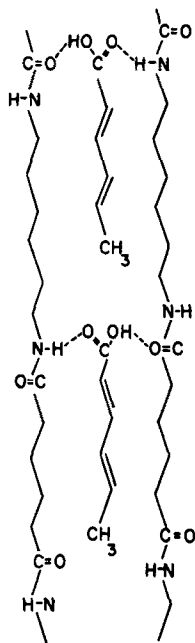


Fig. 7.—Schematic diagram of possible double hydrogen bonding of the sorbic acid-nylon 66 system.

could be used to evaluate the diffusion coefficient and the rate constant for a first-order reaction (8). The equation may be stated as

$$\frac{1}{t} \ln \frac{a}{a-x} - \beta \frac{x}{t} = M \quad (\text{Eq. 2})$$

where  $a$  is the initial concentration of solute in the liquid phase in moles/liter,  $x$  is the concentration of solute in moles/liter reacting in time  $t$  in seconds, and  $\beta$  and  $M$  are constants defined as

$$\beta = \frac{vk}{kva + DSB\mu} \quad (\text{Eq. 3})$$

$$M = \frac{kDSB}{kva + DSB\mu} \quad (\text{Eq. 4})$$

where  $v$  is the volume of solution in contact with the solid phase in liters,  $k$  is the first-order rate constant,  $D$  is the diffusion coefficient in  $\text{cm}^2/\text{second}$ ,  $S$  is the surface area of the solid phase in  $\text{cm}^2$ , and  $\mu$  is a coefficient allowing for the transition from surface to volume concentration. The term  $B$  in Eqs. 3 and 4 is equal to  $xv/SL$ , where  $x$ ,  $v$ , and  $S$  are as previously defined, and  $L$  is the thickness of the growing diffusion zone in the solid. At equilibrium,  $L$  would be equal to the film thickness in centimeters.

Equation 2 is a general equation, applicable to a process where molecules from one phase react at the surface of a second phase, then penetrate and diffuse into successive levels of the second phase as diffusion continues.

If  $(1/t)\ln[a/(a-x)]$  is plotted against  $x/t$ , a straight line should result with a slope of  $\beta$  and an intercept of  $M$ . To test the validity of the equation, plots were made of all diffusion data for the sorbic acid-nylon 66 system. Figure 8 shows one such plot for four concentrations of sorbic acid diffusing into nylon 66 at  $55^\circ$ .

There are two alternatives to the diffusion process under consideration: (a) when the diffusion rate is

higher than the reaction rate and (b) when the diffusion rate is lower than the reaction rate.

In the first case, the process kinetics will be wholly governed by chemical factors, expressed by the following mathematical requirements:

$$D \rightarrow \infty; \beta \rightarrow 0; DSB\mu \gg kva; M \rightarrow k$$

If this were the case, the term  $kva$  may be dropped from Eqs. 3 and 4, and Eq. 2 becomes the usual equation for the velocity of a first-order reaction.

In the second case, however, the reaction rate is determined mainly by the rate at which the reagent is supplied to the reaction zone, and the mathematical requirements are

$$kva \gg DSB\mu; \beta \rightarrow 1/a; M \rightarrow DSB\mu/va$$

Thus, the term  $DSB\mu$  may in effect be dropped from Eqs. 3 and 4. It is important to note that  $\beta$  can only approach  $1/a$ ; should they be equal, the reaction would occur only at the surface of the plastic and the diffusion coefficient would be zero.

Table I presents the values for  $kva$ ,  $DSB\mu$ ,  $\beta$ ,  $1/a$ ,  $M$ , and  $DSB\mu/va$  for all concentrations of sorbic acid employed at each temperature. Since all conditions for the second alternative are met, the Rotinyan and Drozdov equation supports the theory that solute molecules penetrate and diffuse through a plastic material and that the rate-determining step is truly the diffusion process.

Table II presents a comparison of diffusion coefficient values obtained by the Berthier method (9)

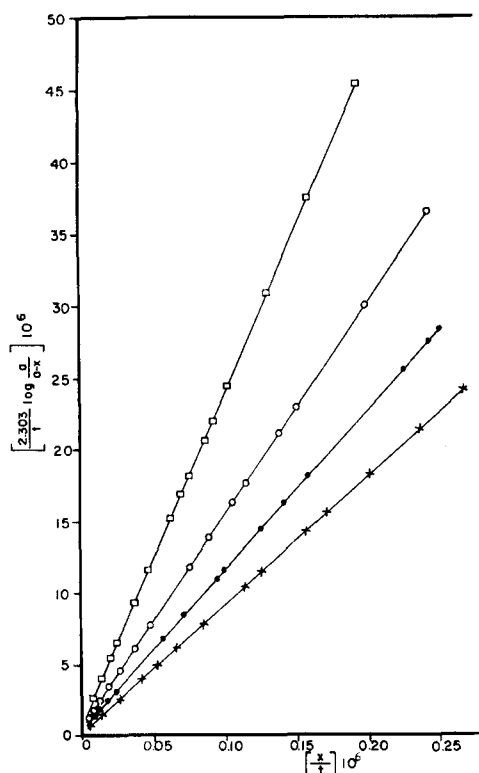


Fig. 8.—Rotinyan-Drozdov equation plot for four concentrations of sorbic acid in nylon 66 at  $55^\circ$ . Key: Sorbic acid solution—X, 0.125%; ●, 0.10%; ○, 0.075%; □, 0.05%.

TABLE I.—VALUES FROM PLOTS OF KINETIC DATA USING ROTINYAN-DROZDOV EQUATION FOR FOUR CONCENTRATIONS OF SORBIC ACID AT THREE TEMPERATURES

Temp., °C.	(a) 10 <sup>8</sup> (M/L)	β (L/M)	1/a (L/M)	(M) 10 <sup>8</sup> (Sec. <sup>-1</sup> )	(DSB <sub>0</sub> /va) 10 <sup>8</sup> (Sec. <sup>-1</sup> )	(kva) 10 <sup>8</sup> (M/Sec.)	(DSB <sub>0</sub> ) 10 <sup>8</sup> (M/Sec.)
67	10.98	90.71	91.07	0.2240	0.2249	0.6162	0.2469
67	8.907	111.3	112.2	0.4839	0.4877	0.5528	0.4344
67	6.731	148.2	148.5	0.9739	0.9760	3.159	0.6569
67	4.535	219.5	220.5	1.525	1.532	1.500	0.6949
61	10.67	93.65	93.72	0.2165	0.2167	3.523	0.2312
61	8.681	115.1	115.2	0.4610	0.4612	8.689	0.4004
61	7.019	141.8	142.4	0.9405	0.9443	1.604	0.6628
61	4.515	220.8	221.4	1.158	1.160	1.972	0.5240
55	11.53	86.71	86.73	0.1941	0.1942	1.290	0.2238
55	9.276	107.6	107.8	0.3999	0.4006	2.028	0.3716
55	6.978	143.1	143.3	0.7439	0.7446	5.179	0.5196
55	4.453	223.4	224.5	0.9204	0.9250	0.8337	0.4119

TABLE II.—COMPARISON OF DIFFUSION COEFFICIENTS OBTAINED BY BERTHIER METHOD AND ROTINYAN-DROZDOV EQUATION FOR SORBIC ACID IN NYLON 66

Temp., °C.	Concn., (M/L) × 10 <sup>8</sup>	Berthier Method (cm. <sup>2</sup> /Sec.) × 10 <sup>8</sup>	Rotinyan-Drozdoz Eq. (cm. <sup>2</sup> /Sec.) × 10 <sup>8</sup>
67	10.98	0.309	1.04
67	8.907	0.542	2.34
67	6.731	1.01	4.69
67	4.535	1.46	7.33
61	10.67	0.285	0.863
61	8.681	0.383	1.82
61	7.019	0.555	3.49
61	4.515	0.729	4.62
55	11.53	0.262	0.662
55	9.276	0.270	1.36
55	6.978	0.295	2.52
55	4.453	0.353	2.98

described in an earlier paper (1) with those obtained from the Rotinyan-Drozdoz equation.

### Time-Lag Method for Determining Diffusion Coefficient

The diffusion data presented in this paper and the previous one have all been obtained from sorption studies of sorbic acid by nylon 66. For purposes of comparison, an experiment was designed to determine the diffusion coefficient of sorbic acid through nylon 66 using permeation cells.

The experimental design involved the use of two 1000-ml. round-bottom, two-necked flasks constructed so that a cylindrical opening was at the side of each. When the two flasks were joined, sealed with O-rings, and clamped together, a water-tight seal was provided. A strip of nylon 66 was placed between the flasks prior to joining.

Following the immersion of the flasks into a water bath, sorbic acid solution at a definite concentration and volume was poured into one flask and an equal volume of distilled water into the other. A mechanical stirrer was placed into each flask to insure complete mixing.

Over a period of time, aliquots were withdrawn from both flasks and the sorbic acid content determined by a spectrophotometric method. A plot of the amount of sorbic acid passing through the nylon *versus* time is shown in Fig. 8. This type of experiment was conducted at four different original concentrations of sorbic acid at 67°.

As shown in Fig. 9, after a steady state has been

reached, a linear relationship follows. If the linear portion of the curve is extrapolated to the time axis, the diffusion coefficient may be calculated easily by using Barrer's equation (10):

$$D = \frac{L^2}{6t} \quad (\text{Eq. 5})$$

where  $D$  is the diffusion coefficient in cm.<sup>2</sup>/second,  $L$  is the thickness of the film (plastic), and  $t$  the time in seconds where the extrapolated intercept occurs (time lag). Table III presents a summary of diffusion coefficients obtained by the time-lag method and by the Berthier method for four original concentrations of sorbic acid at 67.0°. In general, the  $D$  values are comparable, and perhaps are as should be expected using two different methods of finding the diffusion coefficients. Table III does reveal that, by either method, the diffusion coefficient increases as the original sorbic acid concentration in the solution decreases. These results suggest that at higher concentrations of sorbic acid formation of

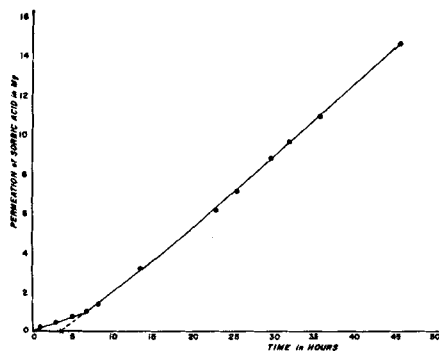


Fig. 9.—Barrer time-lag plot for permeation of 0.1% sorbic acid solution through nylon 66 at 67°.

TABLE III.—COMPARISON OF DIFFUSION COEFFICIENTS OBTAINED BY BERTHIER METHOD AND BARRER TIME-LAG METHOD FOR SORBIC ACID IN NYLON 66 AT 67°

Concn., (M/L) × 10 <sup>8</sup>	Berthier Method (cm. <sup>2</sup> /Sec.) × 10 <sup>8</sup>	Barrer Time-Lag Method (cm. <sup>2</sup> /Sec.) × 10 <sup>8</sup>
10.98	0.309	0.692
8.907	0.542	0.753
6.731	1.01	0.806
4.535	1.46	0.844

aggregates or clusters occurs in the plastic which hinders the over-all migration of individual sorbic acid molecules through the plastic. With more dilute solutions, the mobility of individual molecules increases, and diffusion proceeds at a more rapid rate.

### SUMMARY

Studies on the interaction of sorbic acid by nylon 66 were continued for the purpose of (a) postulating the mechanism of interaction, (b) verifying the rate-determining step in the sorption process, and (c) comparing diffusion coefficients by the time-lag method to a sorption method. Results of the various experiments may be summarized as follows.

Dye-sorption studies indicated that sorbic acid was most likely interacting at the amide linkages in the polymer rather than at the end amino groups.

Differential infrared analysis on samples of untreated and treated (with sorbic acid) nylon suggested a double hydrogen bond formation between the acid and the nylon, confirming that the previously found  $\Delta H^\circ$  of  $-9.77$  was correct.

X-ray diffraction studies on untreated and treated (with sorbic acid) nylon indicated that a greater degree of order results with the sorbic acid molecules acting as the ordering agent.

Application of the Rotinyan-Drozdov equation to kinetic sorption data confirmed that the rate-determining step is the diffusion step in the plastic.

Diffusion coefficients obtained from the time-lag method approximated within experimental errors those determined by a sorption method (Berthier method).

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## Drug Standards

### Calcium Assays for Official Use

By A. Q. BUTLER\*, F. A. MAURINA†, and F. A. MORECOMBE‡

Comments recommending consideration of direct complexometric titration for the assay of the official calcium salts were investigated and the method used was the method chosen for the official compendia ("National Formulary" and "United States Pharmacopoeia"). Selection of an indicator that conformed to requirements of these compendia introduced unexpected problems, and the selection of naphthol green screened murexide for the N.F. XI and U.S.P. XVI monographs represented a compromise between analytical suitability and compendial requirements. Further study of the indicator problem resulted in the selection of hydroxy naphthol blue as the indicator of choice; this indicator will be specified in the N.F. XII and U.S.P. XVII monographs.

**D**URING THE circulation of proof for N.F. X and U.S.P. XV, several reviewers recommended that direct complexometric (EDTA) titration be considered for the assay of the official calcium salts. It was not possible to complete the studies necessary to document the suitability of the method for compendial use before N.F. X

and U.S.P. XV were published, so an investigation of the recommended procedure was postponed until the N.F. XI and U.S.P. XVI were in preparation.

Previous studies performed in the American Pharmaceutical Association Drug Standards Laboratory (1, 2) had shown the suitability of an EDTA back titration procedure for the assay of some calcium salts, but no attempt appears to have been made to include the procedure in the compendia. The number of comments received in favor of the direct EDTA titration method and the advantages claimed for this method over the oxalate-permanganate procedure suggested

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