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The Absorption Spectra of Nitrocellulose.

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On account of the lack of a suitable solvent it has been hard to obtain the ultraviolet absorption spectra of nitrocellulose. B. Rassow and W. Aehnelt[1] used ether-alcohol as the solvent, but the maximum concentration was only 2 g. in 1000 c.c., namely, 7.94×10^{-3} mol as regards the dinitroglucose unit. Therefore, the characteristic absorption of nitrocellulose remains yet undiscovered, and the linear end-absorption has not been interpreted. Considered from the author's previous consideration, the selective absorption might be observed at a higher concentration or with a thicker layer. A good result has been obtained by using clear films of nitrocellulose prepared with a suitable solvent, instead of solutions, which appeared extremely difficultly to be raised to a concentration higher than Rassow's case. By the film method it was easy to obtain two absorptions (3300–2500 Å and below 2500 Å) which may be reasonably attributed to the nitro-groups as the case of nitroglycerine.[2]

Experimental. The preparation of good films depends chiefly on the selection of the solvent and on the technique of evaporation. Since the solvent remains in films in amounts of a few percent, it must not absorb above 2200 Å. The author used ether-alcohol (80 g. ether and 40 g. alcohol for 2 g. of nitrocellulose) or acetone as the solvent. The mixture of nitrocellulose and the solvent was frequently stirred or shaken so as to bring the suspended nitrocellulose into solution. After standing overnight, 10 c.c. of the filtered solution was spread over the surface of mercury. The liquid film was gradually evaporated to a clear solid film by evacuation in the course of a few days. Different numbers of films of about 1/100 mm. thickness were placed between two quartz plates. From the weight, the area, and the density (1.65), of the films, the thickness was computed. The experiments were carried out in the same way as in the case of nitroglycerine except that exposure time was 7 minutes. In the accompanying figure the logarithm of relative thickness is plotted against the wave number. From the figure, it is established that there are two absorptions.

(1) *Cellulosechem.*, **10** (1929), 163.
(2) This Bulletin, **11** (1936), 712.

Table 1 (Curve 1). Films prepared with acetone. Ilford Special Rapid Panchromatic Plates.

Thickness d (mm.)	log d	log of relative thickness* log D	Wave length (Å)	Wave number (mm.$^{-1}$)
0.246	$\bar{1}$.389	3.506	3185	3139
0.223	$\bar{1}$.348	3.465	3125	3199
0.200	$\bar{1}$.301	3.418	3075	3251
0.161	$\bar{1}$.207	3.324	3000	3332
0.104	$\bar{1}$.017	3.134	2869	3482
0.060	$\bar{2}$.778	2.895	2745	3642
0.051	$\bar{2}$.708	2.825	2647	3777
0.046	$\bar{2}$.663	2.780	2603	3841
0.023	$\bar{2}$.362	2.479	2460	4070

Table 2 (Curve 2). Films prepared with ether-alcohol. Ilford Special Rapid Panchromatic Plates.

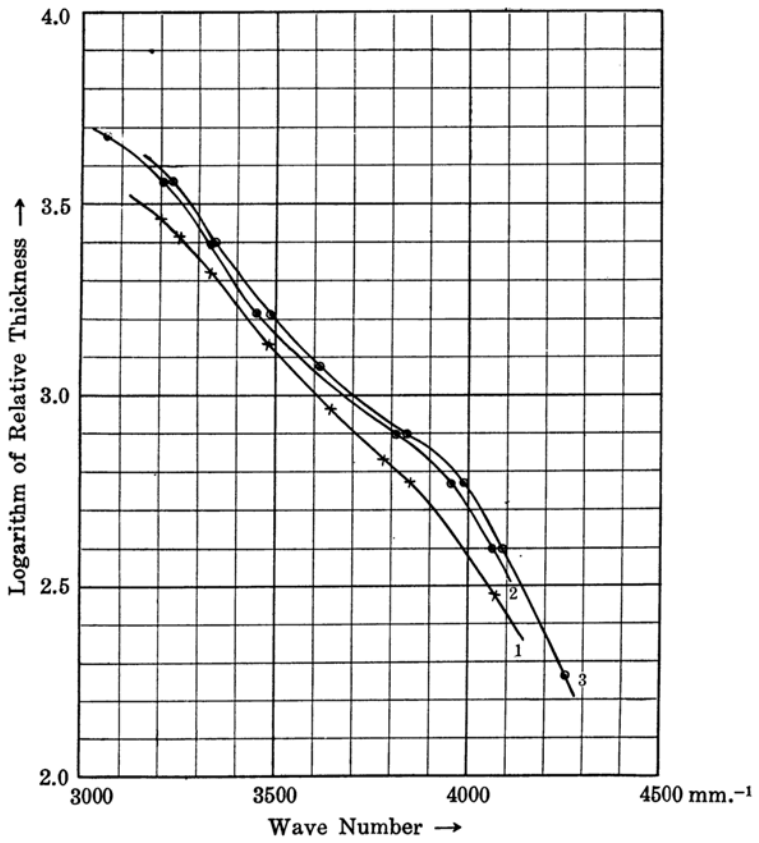
0.549	$\bar{1}$.740	3.857	—	—
0.450	$\bar{1}$.653	3.770	3754	2663
0.359	$\bar{1}$.555	3.672	3265	3062
0.273	$\bar{1}$.436	3.553	3101	3224
0.130	$\bar{1}$.279	3.396	2994	3339
0.124	$\bar{1}$.093	3.210	2891	3458
0.060	$\bar{2}$.778	2.895	2630	3816
0.030	$\bar{2}$.477	2.594	2459	4066

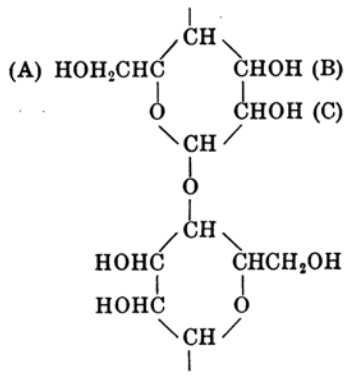
Table 3 (Curve 3). Films prepared with ether-alcohol. Ilford Schumann Plates.

0.273	$\bar{1}$.436	3.553	3089	3236
0.190	$\bar{1}$.279	3.396	2992	3341
0.124	$\bar{1}$.093	3.210	2867	3487
0.090	$\bar{2}$.954	3.072	2765	3616
0.060	$\bar{2}$.778	2.895	2660	3845
0.045	$\bar{2}$.653	2.771	2512	3980
0.030	$\bar{2}$.477	2.594	2444	4090
0.014	$\bar{2}$.146	2.263	2348	4258

* The equivalent thickness of N/2000 of the dinitroglucose unit, calculated from Beer's law. ($\log D = \log d + 4.117$)

Discussion. Considered from the molecular structure it is obvious that these absorptions of nitrocellulose must be attributed to the nitro-groups. When the molecular weight of nitroglucose unit in nitrocellulose divided by the number of nitro-groups is taken as one gram mol, the absorption intensity of nitrocellulose ($\log \varepsilon = 1.1$)[2] is very nearly coincident with the cases of the other nitro-esters and nitro-compounds. If the hydroxyl-groups in the glucose structure considered as the unit of cellulose are marked A, B, and C, as shown in the formula, the combination of AB or of AC may be the most possible for the positions of two nitro-groups in the case of nitrocellulose containing 11%





nitrogen, because a structure with a considerable distance between the two nitro-groups is probably more stable on account of a small interaction between them. It is, therefore, reasonable that the experiments are in excellent agreement with the values calculated for the absorption due to nitro-groups.

In the case of the nitrocellulose of a higher nitrogen content, the absorption seems to remain unchanged as in the case of nitroglycerine, because each of nitro-groups combines indirectly with a different carbon atom by a bridge of an oxygen atom and moreover may also maintain mutually a considerable distance in order to minimize the interaction.

The general discussion will be given later.