used different principles for the evaluation of scattering in other materials.)

The investigation of small angle scattering of many different cellulose fibers by the writer showed the following new facts:

1. Different Angle of Scattering in Different Cellulose Fibers.—The angle of scattering of various cellulose fibers proved to vary considerably. In all cases—with the exposure time used—the scattering was very intense within a small angle from the primary beam, causing almost complete blackening of the film, and decreasing quickly within a short distance at the end of the spot (compare photographs). Therefore the extent of the scattering was sufficiently well defined to be easily measured. For illustration, the angle of intense scattering of some of the fibers investigated is given in the order of smaller angles.

Fiber	Hemp	Flax	Jute	Ramie	Viscose	Merc. Cotton	Cotton
Maximum scattering angle	2°	1°42′	1°35′	1°18′	1°9′	51′	36′
Smallest period in Å.	22	26	27	34	38	51, 5	73
Average period in Å. as calculated from mid-point of scattering	44	51, 5	55	68	73	95	146

Accepting Kratky's assumption regarding the validity of the principle of Bragg's law on scattering of compact structures, the angles given would be related with the minimum size and intermicellar distance of the micelles in these fibers. As a preliminary approximation of the *average* size, the identity period is also calculated from the angle at the midpoint of the scattering zone.

Anyway on the basis of this or other principles[11-14] and in connection with other considerations, the data obtained can be explained by the presence of smaller micelles and probably smaller intermicellar distances in hemp, flax and jute, larger micelles and small distances in ramie and cotton and probably small micelles and large intermicellar distances in viscose (faint scattering).

2. Relation with Orientation of Micelles.—The present studies were carried out by using a pin-hole beam instead of a slit, as used in most of the low angle studies by others. This resulted in a scattering image consisting of a horizontal line on the equator of a definite length on both sides of the primary beam in the case of hemp, jute and flax, the line having the same width over its total length, tapering only somewhat at the end. This can be explained by an orientation of the micelles completely parallel to the long axis of these fibers.

In addition fibers were studied where the fibrils and the micellar axis form an angle with the long axis of the fiber. Fibers were selected with decreasing pitch of the fibrils, namely, of *Sanseviera guinensis*, *Agave heterocantha*, and *Cocos nucifera* (and others). The interesting fact was observed that in all these cases the low angle picture consisted of two lines intersecting at the center of the diagram (primary beam), forming a "*cross*" at an angle, presumably identical with the double angle between the micellar and fiber axis. In *Sanseviera* the angle was about 20°, in *Agave* 45° and in *Cocos* (coir, in which the fibrils make an angle of 45° with the long axis) the two scattering lines intersect at exactly 90° (compare photographs).

This fact is the more remarkable as the "*wide*" angle diffraction pattern in these cases shows a *continuous* 002 arc of increasing extent, without any complete interruption. The low angle picture does not show any such smooth transition or continuity between the intersecting lines of the "cross" and appears to represent only the angle formed by opposite parts of the fibrillar spiral at points where the radius is parallel to the X-ray beam.

Therefore, such small angle studies allow a *direct* clear measurement of micellar orientation in fibers. A full explanation of the phenomenon of "cross formation," as described above, might lead moreover to a deeper insight of the micellar structure of fibers.

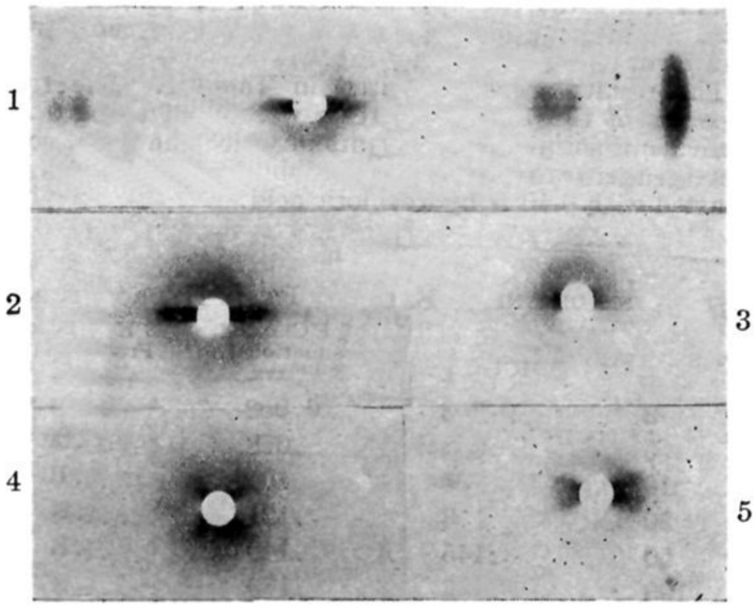

Fig. 1.—Small angle scattering and equatorial wide angle interferences of (1) ramie; (2) jute; (3) mercerized cotton; (4) coir; (5) *Agave heterocantha.* Exposure time, amount of material and distance are the same for all samples.

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Hydrolysis Regeneration of an Anion Exchange Resin

BY HUGO P. KORTSCHAK AND JOHN H. PAYNE

No quantitative examination of the regeneration of anion exchange resins by water without the use of the usual alkaline regenerating agents has appeared in the literature, although it has been mentioned[1,2] that some hydrolysis occurs.

In the course of investigations on the sodium hydroxide regeneration of Amberlite IR-4B, in which the resin was exhausted with hydrochloric acid, then rinsed and backwashed with a total of 24 volumes of water, it was found that the hydrolysis was by no means negligible, amounting to 20% of the total capacity. This was therefore studied more closely.

Experimental

A sample of Amberlite IR-4B was freed of particles smaller than 30 mesh by wet screening, and placed in a 1/2 in. o. d. pyrex tube, supported on a platinum screen. Regenerated, backwashed, settled and drained, the volume of resin was 105 ml. This had been exhausted with hydrochloric acid and regenerated with sodium hydroxide about 25 times before the test run.

Hydrochloric acid, 0.100 *N*, was run through the resin until the effluent concentration was also 0.100 *N*. Water was then run at 25 ml./min., the first 100 ml. being discarded as representing the volume of liquid in the column. The water was purified by ion exchange, and had a *p*H of 6.5. The effluent was collected in convenient increments, and titrated against 0.10 *N* sodium hydroxide, with phenolphthalein indicator. The run was continued until the titration values were found to approach that of the blank, 0.08 ml./100 ml.

This volume of water was not run without interruption. It was found, however, that standing overnight did not increase the acid concentration measurably, if this concentration was below 0.01 *N*. This indicates that under the conditions used, the approach to equilibrium was very close, and interruption of the flow would cause no significant error (compare Kunin,[3] Fig. 6).

The results are summarized in Table I. The total capacity of the 105 ml. of resin was found to be 0.270 equivalents in other experiments in which the resin, completely regenerated by 0.25 *N* sodium hydroxide, was exhausted with 0.10 *N* hydrochloric acid.

TABLE I

HYDROLYSIS OF ANION EXCHANGE RESIN HYDROCHLORIDE

Volume water, liters	Σ HCl removed, equivs.	Σ HCl calcd. Equation 1, equivs.	Σ HCl calcd. Freundlich, equivs.
2	0.053	0.052	0.019
5	.075	.078	.069
10	.095	.100	.100
20	.118	.121	.126
50	.145	.149	.155
100	.168	.170	.173
200	.189	.191	.188

Discussion

Table I gives the total volume of water used, V, in column 1, and the amount of hydrochloric acid removed from the resin, Σ HCl, in column 2. The third column was calculated from the empirical equation

$$\Sigma \text{HCl} = 0.07 \log V + 0.03 \qquad (1)$$

Column 4 was calculated from the Freundlich adsorption isotherm. The result agrees with the conclusion of Kunin and Myers in their study of acid adsorption[1,3] that the Freundlich equation can be applied at acid concentrations below 0.01 *N*. The data of Table I cannot be described in terms of the Donnan equilibrium, lending support to the hypothesis that the mechanism of acid removal by this resin is one of adsorption, and not of ion exchange.

HAWAIIAN SUGAR PLANTERS' ASSOCIATION AND
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[1] R. Kunin and R. J. Myers, THIS JOURNAL, **69**, 2874 (1947).

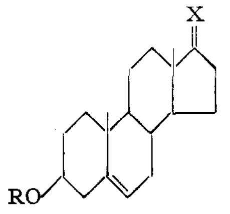
[2] P. Smit, U. S. Patent Application No. 359,575 (Oct. 3, 1940).

[3] R. Kunin and R. J. Myers, *J. Phys. Chem.*, **51**, 1111 (1947).

Dimercaptols of Dehydroisoandrosterone

BY ROBERT H. LEVIN AND J. L. THOMPSON

A recent publication[1] reports the reaction of dehydroisoandrosterone acetate (I) with benzylmercaptan and ethylmercaptan to give the corresponding dimercaptols (II, III). Saponification of II led to the hydroxy compound IV.



I R = CH_3CO, X = O
II R = CH_3CO, X = $(SCH_2C_6H_5)_2$
III R = CH_3CO, X = $(SCH_2CH_3)_2$
IV R = H, X = $(SCH_2C_6H_5)_2$
V R = H, X = $(SCH_2CO_2H)_2$

We had independently prepared the dibenzylmercaptol (IV) in 65% yield by directly condensing dehydroisoandrosterone with benzylmercaptan in the presence of zinc chloride and sodium acetate. Acetylation with acetic anhydride in pyridine at room temperature gave the acetate (II) of dehydroisoandrosterone dibenzylmercaptol in 94% yield.

In the same manner dehydroisoandrosterone has been condensed with thioglycolic acid to give the dimercaptol (V) in 73% yield. The sodium salt of this interesting compound is water soluble.

Experimental

Dibenzylmercaptol of Dehydroisoandrosterone (IV).—To a mixture of 2.8 g. of freshly fused and pulverized zinc chloride, 5 g. of anhydrous sodium sulfate, and 2.88 g. (0.01 mole) of dehydroisoandrosterone was added 25 ml. of benzyl mercaptan. After standing at room temperature for fifteen minutes the mixture was placed in the refrigerator for twenty hours, then allowed to warm up to room temperature and poured into 500 ml. of ice-water. The mixture was extracted with three 125-ml. portions of ether and the ether washed with 5% sodium hydroxide solution and with water and dried over anhydrous sodium sulfate. The ether solution was concentrated on the steam-bath and the excess benzyl mercaptan distilled at 1–5 mm. The residue was crystallized from hexane, giving 4.09 g. (79%) of product, m. p. 150–154°. which, after several recrystallizations from hexane, melted at 184–186°. The yield of pure material was 65% of the theoretical.

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[1] Norymberska, Norymberski and Olalde, THIS JOURNAL, **70**, 1256 (1948).