phatic compounds being 480, 1380, and 1560 cm.⁻¹. If this interpretation is correct, the complex absorption bands observed near 13.4 μ may arise from an outer vibration involving OH and NO₂ groups. Although the spectrum of nitric acid has no direct connection with the nitrites, it was included in the present paper, since it can possibly be interpreted in terms of a related NO₂ group.

Summary

The infrared absorption spectra of sodium ni-

trite and potassium nitrite have been studied between 6 and 16 μ and absorption bands have been observed at 7.6, 8.2, and 13.3 μ . These bands are interpreted as arising from fundamental vibrations of the nitrite group. Force constants and valence angles of the nitrite group are computed by means of the central-force-field approximation. The valence-force-field proves to be an unsatisfactory approximation for the nitrites. The spectrum of nitric acid is discussed.

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[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGill University]

Viscosity Relationships of Aqueous Solutions of Sodium Oleate and Various Phenols

By Ralph G. D. Moore¹

Weichherz and Saechtling^{2.3} in a viscometric investigation of the system sodium oleatephenol-water observed the occurrence of viscosity maxima at certain ratios of sodium oleate to phenol, indicating the formation of complexes between these substances. The authors did not consider them to be definite chemical compounds, but rather a loose association of the soap micelle with the phenol. The present paper presents a more extended study of this phenomenon, with the object of ascertaining how far it is characteristic of phenolic substances.

Attempted verification of some of Weichherz and Saechtling's results showed general qualitative agreement but considerable quantitative discrepancy, the present values for viscosities, especially in the region of lower water content, being without exception higher, sometimes of another order altogether. Comparison of the viscosities of solutions of sodium oleate prepared from oleic acid of varying degrees of purity (cf. Table II, expts. 1, 2, 3, 4) indicates that the cause of this lack of agreement lies in the relative degree of purity of the two specimens of sodium oleate in question, since Weichherz and Saechtling used Kahlbaum "reinst" (I), while the present author used samples (II) prepared from oleic acid which had been purified rigorously by a method analogous to that later described by Brown and Shinowara.⁴ Illustrative of these discrepancies are the following examples.

Solutions of a concentration of 10% or higher in sodium oleate II were found to be metastable at 20°, slowly increasing in viscosity and finally crystallizing, in striking contrast to the reported investigations of Weichherz and Saechtling on solutions containing up to 30% sodium oleate. In a similar manner the viscosities obtained in the present investigation for the ternary system containing phenol were higher than the corresponding values of Weichherz and Saechtling, the former showing, for 90% water content, a maximum of over 1000 cp. at 20°, while in the case of the latter the value was about 17. For the system with 95% water the latter investigators could find no maximum, whereas in the present work the maximum at this concentration was well marked. In addition, the acid soap separation reported by the earlier investigators for this system was not observed, even after keeping the solution for several days. This heterogeneity was only observed (together with the absence of maxima in the viscosity isotherms) when the solutions containing 97% water were examined.

In order to determine whether the ability to cause maxima in the viscosity-concentration isotherms of sodium oleate solutions is a property common to all phenols, the following carefully purified materials have been examined: guaiacol, p-cresol, creosol, catechol, resorcinol, p-hydroxybenzyl alcohol, vanillyl alcohol, o-bromophenol. (4) Brown and Shinowara, THIS JOURNAL, **59**, 6 (1937).

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⁽²⁾ Weichherz and Saechtling. Kolloid Z., 60, 192 (1932).

⁽³⁾ Ibid., pp. 298-306.



oleate.

Fig. 1.—Viscosity isotherms at 30° of sodium oleatephenolic substance-90% water: 1, p-cresol; 2, creosol; 3, guaiacol; 4, phenol; 5, resorcinol; 6, vanillyl alcohol; 7, o-bromophenol; 8, catechol.

In addition, a few measurements were made at critical concentrations on vanillin and p-hydroxybenzaldehyde. The results of this investigation are to be found in Table II. A comparison of the various substances is given in Figs. 1 and 2, in which the 30° isotherms are selected as being more accurate and eliminating to a large extent the difficulty occasionally encountered in obtaining equilibria at 20° within a reasonable time.

Of all the materials examined, p-cresol showed the most marked effect, maximum viscosity at 20° of the system containing 90% water being in the neighborhood of 100–200 poises. As shown by the curves for guaiacol and creosol the effect of introducing a methoxyl group ortho to the hydroxyl was very slight, shifting the position of the maximum slightly to the left of the maximum for the corresponding unmethoxylated phenol, but not affecting the height of the maximum to a very marked extent.

The above four substances produced outstanding effects on the viscosity of sodium oleate solutions containing both 90 and 95% water. In the case of the solutions containing 90% water the effect of catechol was of the same order, but



Percentage by weight of phenolic substance or sodium oleate.

Fig. 2.—Viscosity isotherms at 30° of sodium oleate-phenolic substance-95% water: 1, *p*-cresol; 2, creosol; 3, guaiacol; 4, phenol; 5, catechol; 6, vanillyl alcohol; 7, resorcinol.

the maximum caused by its isomer resorcinol was much smaller, besides being displaced toward the sodium oleate axis. The same was true for obromophenol. At 95% water content, on the other hand, none of these compounds caused a maximum in viscosity.

The other phenols investigated, such as vanillyl alcohol, p-hydroxybenzyl alcohol, vanillin and p-hydroxybenzaldehyde (Table II, expts. 98– 102) showed no sign of a maximum even at 90% water content. It is thus clear that the property under investigation is not common to all substances containing a phenolic hydroxyl group.

Regarding the cause of the maxima, little can be added to the speculations of Weichherz and Saechtling.² An interesting comparison is obtained by an examination of the electrolytic dissociation constants of some of the phenols used, as given in the "International Critical Tables" (Table I). While complete agreement between the order of the constant and the occurrence and size of the viscosity maxima does not exist, it appears that the greater the degree of electrolytic dissociation of the phenol, the less is the effect produced on the viscosity-concentration isotherms of sodium oleate-water systems.

TABLE I

ELECTROLYTIC DISSOCIATION Substance (Order of decreasing effect	CONSTANTS ⁵
Di viscosity isotherms,	1 00 10 10 10
Phenol	1.06×10^{-10}
p-Cresol	1.1×10^{-8}
Catechol	$3.2 imes 10^{-10}$
Resorcinol	6×10^{-7}
(o-Chlorophenol	3.6×10^{-8})
<i>p</i> -Hydroxybenzaldehyde	1.63×10^{-6}
Vanillin	$4.72 imes10^{-6}$

This observation does not support the theory advanced by Weichherz and Saechtling, namely, that the formation of acid soaps, which in the more dilute solutions is preceded by the phenomenon of a maximum viscosity, is a minor cause of the latter. For if the effect produced varies inversely as the acidity of the phenols, other things being equal, the formation of acid soaps cannot be a contributory factor to the occurrence of maxima.

Since this work was carried out, an article has appeared by Angelescu and Ciortan⁶ which describes the effect of the three isomeric cresols on the viscosity of sodium stearate solutions. The phenomena observed were similar to those which form the basis of the present paper, in that all three isomers caused maxima in viscosity which were affected greatly by the temperature. The authors correlate the observed phenomena with the dielectric constants and electric moments of the three cresols.

Experimental

Apparatus.-Few changes were made in the apparatus of Weichherz and Saechtling.³ For the thermostat, manual control of electrolytic heating (1% lead acetate solution, lead electrodes) was used and found very satisfactory. Constancy of temperature to within 0.05° was not difficult to maintain during measurements. The thermometers used were graduated in tenths of degrees and calibrated by the Thüringische Landesamt für Mass und Gewicht (1928). The viscometers were of the Ostwald type, of sufficient range of flow time to permit rapid and accurate measurement of viscosities up to 100 cp.; in the following, all values for viscosity are relative to that of water at 20°. Densities were determined by means of a Westphal balance, the tube containing the solutions being jacketed with an electrically heated water-bath.

Preparation of Materials .- All compounds examined were purified rigorously by redistillation, recrystallization, or other standard procedures. In some cases it was necessary to resort to synthesis to obtain pure materials. A few of the more pertinent details are recorded below.

All oleic acid used was prepared from olive oil by saponification and subsequent partial purification by the lead salt-alcohol method.7 Final purification was effected by repeated crystallization from a 30-40% solution in 95% ethanol at -30° . Raymond⁸ used a similar procedure, and since completion of the present work the suitability of the method has been confirmed by the results of Brown and Shinowara.⁴ After three or four recrystallizations the product was an oil with a very pale yellow tinge, m. p. 12-13°, which yielded on vacuum distillation a water-white material of the same m. p. While undoubtedly not 100%oleic acid,⁹ this product probably was far purer than that used by Weichherz and Saechtling.2.3

The sodium salt, prepared by treating the acid with an equivalent amount of sodium, both first being dissolved in absolute ethanol, was stored in well-stoppered bottles in a desiccator after drying under reduced pressure at 60° over phosphorus pentoxide. Calculated for $C_{17}H_{33}COONa$: Na. 7.56. Found: Na, 7.49.

The p-hydroxybenzyl alcohol was obtained without difficulty from p-hydroxybenzaldehyde by application of the general method of Adams.^{10,11}

Preparation of Solutions and Measurement of Viscosity .- After drying in the Abderhalden pistol under reduced pressure at 60° for at least twelve hours, over phosphorus pentoxide, the sodium oleate was weighed by difference into a stoppered Pyrex flask and dissolved in the calculated amount of air-free, doubly-distilled water at 50°. After the salt had dissolved the calculated amount of a phenol was added and the mixture kept at 50° until equilibrium was attained. Finally the solution, unless perfectly clear, was filtered by air pressure through a prewarmed Jena glass filter, placed in a stoppered flask in the thermostat, and allowed to remain there at 20°.

The usual precautions regarding choice of a viscometer were observed. If accurate filling at 20° was impracticable because of the high viscosity of the solution, it was carried out at 60°, making the necessary correction for difference in density. The mean of five measurements was recorded as the time of flow, except when this was impracticable due to extremely high viscosity. Readings were taken at 20, 30, 40, 60, and 80°, allowing a suitable interval before taking readings for the solution to reach thermal equilibrium. Density measurements were made on the balance of the solution over the same temperature range. To conserve space these values are not recorded with the rest of the data in Table II.

The writer wishes to express his appreciation to Professor H. Hibbert, in whose laboratories this work was carried out, for much helpful advice and criticism, and to acknowledge the assistance

- (7) Skellon, J. Soc. Chem. Ind., 50, 131T (1931).
- (8) Raymond, Chimie & industrie, Special No. Feb. 1929, p. 523.
- (9) Hartsuch, THIS JOURNAL, 61, 1143 (1939).
 (10) Adams and Voorhees, "Organic Syntheses," Coll. Vol. 1. 1932.
- (11) Adams and Carothers, THIS JOURNAL, 46, 1675 (1924).

^{(5) &}quot;International Critical Tables," Vol. VI, 261-302 (1929).

⁽⁶⁾ Angelescu aud Ciortan, Kolloid Z., 82, 164 (1938).

Expt.	Sod. oleate:	-Ratio Phenol:	Water	20°	30°	40°	60°	80°	Remarks
	•			(A) Syster	n: Sodium Olea	te:Phenol:	Water		
1ª	10.00 :	0.00	90.00	15.85	6.24	3.35	1.54	1.02	Metastable 20°
2^a	10.00 :	.00	90.00	17.0	7.64	4.18	1.88	1.21	Metastable 20°
3°	10.00 :	.00 :	90.00	10.0	4.50	2.70	1.43	0.90	
4°	1 0.00 :	. 00	90.00	5.75	3.23	2.17	1.31		
5	9.00 :	1.00	: 90.00	ca. 1000	74.5	13.6	2.22	1.06	Homogeneous
6	8.50 :	1.50	: 90.00	ca. 1500	85.3	14.4	2.22	0.974	Homogeneous
7	8.00 :	2.00	90.00	730–740	52.3	10.5	1.92	. 898	Homogeneous
8	6 .00 :	4.00	: 90.00	3.23	2.08	1.51	0.981	. 665	Homogeneous
9	3.00 :	7.00	90.00	1.66	1.30	1.05	.705	. 557	Homogeneous
10	0.00 :	10.00 :	90.00			(0.808)	. 570	.446	Clear above 40.15°
114	.5.00 :	0.00 :	95.00	1.77	1.41	1.14	.808	.608	Homogeneous
12ª	5.00 :	.00 :	95.00	1.84	1.48	1.20	.839	.625	Homogeneous
13	4.50 :	.50	95.00	2.66	1.45	1.09	.756	. 567	Metastable 20°
14	4.00 :	1.00 :	: 95.00	3.37	1.56	1.10	.724	.543	Metastable 20°
15	3.00 :	2,00 :	: 95.00	1.52	1.17	0.945	.658	. 504	Homogeneous
16	0.00 :	5.00	95.00	1.12	0.886	.725	. 522	.408	Homogeneous
17	3.00 :	0.00	97.00	1.42	1.13	.930	.661	. 505	Homogeneous
18	2.50 :	. 50 :	97.00	(1.34)	(1.06)	(.857)	.612	.472	Heterogeneous
19	2.00 :	1.00	97.00	(1.34)	(1.08)	(.881)	(.600)	.457	below 75
20	1.00 :	2.00	97.00	1.17	0.932	. 704	.047	.407	Homogeneous
21	0.00 ;	3.00	97.00	1.07	.800	.090	. 505	. 590	Romogeneous
				(B) System	: Sodium Oleat	e:p-Cresol:	Water		
22	9.50 :	0.50	: 90.00	95.0	25.3	8.82	2.49	1.32	Homogeneous
23	9.00 :	1.00 :	90.00	1200	122.8	22.6	3.36	1.44	Homogeneous
24	8.50 :	1.50	90.00	ca. 10,000	480	47.5	4.06	1.47	Homogeneous
25	8.00 :	2.00 :	90.00	>10,000	ca. 1500	67.1	4.21	1.40	Homogeneous
26	7.00 :	3.00 :	: 90.00	<i>ca</i> . 10,000	345	35.7	3.32	1.31	Homogeneous
27	6.00 :	4.00	90.00	151	26.5	8.09	2.02	1.12	Homogeneous
28	5.00 :	5.00 :	90.00	13.8	5.90 1.50	3.10	1.35	0.866	Homogeneous
29	4.50 :	0.50	95.00	1.92	1.59	1.22	0.834	.032	elastic 20°
30	4.00 :	1.00 :	95.00	3.70	2.22	1.32	.811	.609	SI. turbid, elastic 20°
31	3.80 :	1.20 :	95.00		2.44	1.41	.808	.605	Homogeneous
32	3.50 :	1.50 :	95.00	4.40	1.98	1.26	.784	. 589	Homogeneous, non-elastic
33	3.00 :	2.00 :	95.00	2.38	1.49	1.10	.745	.569	Homogeneous
34	2.00 :	3.00 :	95.00	1.50	1.18	0.957	.678	. 518	Homogeneous
				(C) System	: Sodium Oleate	:Guaiacol:	Water		
35	9.00 :	1.00 :	90.00	303	56.9	13.2	2.58	1.27	Homogeneous
36	8.00 :	2.00 :	90.00	ca. 2000	90.2	15.5	2.53	1.24	Homogeneous
37	7.50 :	2.50 :	90.00	360	36.5	8.90	1.99	1.09	Homogeneous
38	7.00 :	3.00 :	90.00	59.9	13.3	4.95	1.65	1.05	Homogeneous
39	4.00 :	6.00 :	90.00	1.98	1.56	1.26	0.871	0.645	Homogeneous
40	4.50 :	0.50 :	95.00	1.68	1.37	1.14	.773	.578	Sl. turbid 20°
41	4 .00 :	1.00 :	95.00	2.78	1.67	1.17	.777	. 598	Sl. turbid 20° elastic
42	3.50 :	1.50 :	95.00	2.17	1.42	1.07	.720	. 539	Homogeneous
43	3.00 :	2.00 :	95.00	1.60	1.22	0.985	.687	.516	Homogeneous
44	2.00 :	3.00 :	95.00	1.42	1.12	.913	.650	. 493	Homogeneous
				(D) System	: Sodium Oleat	e:Creosol:V	Water		
45	9.50 :	0.50 :	90.00	73	26.4	9.23	2.54	1.32	Metastable at 20°. elastic
46	9.00 :	1.00 :	90.00	ca. 500	80.0	16.6	2.85	1.30	Clear, metastable
47	8.50 :	1.50 :	90.00	ca. 3000	284	34.4	3.57	1.49	at 20°

Table II Viscosities of Ternary Systems Relative to Water at 20°

		•			•					
Expt.	Sod. oleate: Ph	io ienol:	Water	20°	30°	40°	60°	80°	Remarks	
48	8.00 : 2.	00 :	9 0.00	ca. 10,000	525	46.7	3.83	1.43	Clear, metastable	
49	7.00 : 3.	; 00	90.00	ca. 10,000	294	32.9	3.33	1.30	at 20°	
50	6.00 : 4.	: 00	90.00	180	30.9	9.44	2.16	1.03	Clear	
51	4.00 : 6.	.00 :	90.00	5.86	3.56	2.32	1.24	0.820	Clear	
52	4.50 : 0.	50 :	95.00	1.91	1.54	1.19	0.800	. 595	Clear, non-elastic	
53	4.00 : 1.	.00 ;	95.00	3.12	1.95	1.26	.795	. 598	Turbid, elastic 20°	
54	3.50 : 1.	50 :	95,00	3.69	1.80	1.21	.776	.587	Clear, non-elastic	
55	3.00 : 2.	00 :	95.00	2.25	1.44	1.07	.721	.541	Clear, non-elastic	
56	2.00:3.	00 :	95.00	1.47	1.15	0.941	.662	. 500	Clear, non-elastic	
(E) System: Sodium Oleate: Catechol: Water										
57	9.50 : 0.	50 :	90.00	78	40.5	15.2	4.08	1.87	Opalescent below	
58	9.00 : 1.	: 00	90.00	800-900	226	39.2	5.55	1.99	60°	
59	8.50 : 1.	50 :	90.00		32 6	50				
60	8.00 : 2.	00 :	90.00	ca. 1200	176	19. 2	3.66	1.86	SI. opalescent	
61	7.00 : 3.	00 :	90.00	224	19.8	7.81	2.23	1.28	Sl. opalescent	
62	4.50:0.	50 :	95.00	1.55	1.25	1.04	0.767	0.591	SI, turbid	
63	4.00 : 1.	.00 ;	95.00	1.47	1.20	1.02	.794	.622	Sl. turbid	
64	3.50 : 1.	50 :	95.00	1.59	1.27	1.05	.770	.616	SL turbid	
×.	5100 . 11		(F) System · S	odium Oleate	Resorcing	Water			
6 E	0.75 . 0.	9E .	00.00	F) System: S		Resorcinor:	water	1 14	Matartable 200	
00	9.75 : 0.	20 :	90.00	51.9 70.4	14.7	0.03	2.00	1.14	Metastable 20	
00	9.50 : 0.0	.50 :	90.00	70.4	20.2	7.89	2.29	1.10	Clear	
67	9.00 : 1.	.00 :	90.00	41.1	10.3	7.71	2.45	1.24	Clear	
68	8.00 : 2.	00 :	90.00	5.93	3.82	2.73	1.56	1.01	Heterogeneous over	
69	6.00:4.	00 :	90.00	1.91	1.52	1.24	0.907	0.664	6U°	
70	3.00 : 7.	00 :	90.00	1.46	1.19	1.04	.851	.658	Opalescent 20-80°	
71	0.00 : 10.	00 :	90.00	1.25	0.992	0.812	. 579	. 449	Clear	
72	4.50:0.	50 :	95.00	1.59	1.29	1.08	.754	.571	Opalescent 20-80°	
73	4.00 : 1.	00 :	95.00	1.44	1.17	1.00	.796	.624	Opalescent 20–80°	
7.4	3.00 : 2.	00 :	95.00	1.39	1.13	0. 967	.720	. 538	Opalescent 20–80°	
75	2.00 : 3.	.00 :	95.00	1.32	1.05	.878	. 644	.501	Opalescent 20-80°	
76	0.00 : 5.	00 :	95.00	1.12	0.890	.73 2	. 528	.413	Clear	
		((G) Syst	em: Sodium (Dleate:p-Hyd	roxybenzyl .	Alcohol : Wate	r		
77	9.50 : 0.	50 :	90.00	13.5	6.56	3.76	1.76	1.09	Clear	
78	9.00 : 1.	00 :	90.00	6.86	4.13	2.76	1.52	1.02	Clear	
79	8.50 : 1.	50 :	90.00	4.00	2.80	2.12	1.31	0.935	Clear	
80	8.00 : 2.	: 00	90.00	2.83	2.17	1.73	1.17	0.857	Clear	
			(H)	System: Sodi	um Oleate:Va	anillyl Alcol	101:Water			
81	9.50 : 0.	50 :	90.00	8.59	4.97	3.23	1.69	1.12	Clear	
82	9.00 : 1.	00 :	90.00	4.35	3.10	2.32	1.43	1.04	Clear	
83	8.00 : 2.	00 :	90.00	2.50	1.98	1.61	1.13	0.847	Clear	
84	6.00 : 4.	00 :	9 0.00	(2.02)	1.59	1.29	0.906	. 693	Homogeneous above 20°	
85	3.00 : 7.	00 :	90.00			(1.08)	.745	.571	Homogeneous above 40°	
86	4.50 : 0.	50 :	95.00	1.66	1.30	1.06	.761	. 581	Sl. turbidity below 35°	
87	4.00 : 1.	00 :	95.00	1.62	1.26	1.01	.700	.540	Turbid below 60°	
88	3.00:2.	00 :	95.00	1.48	1.17	0.949	. 659	.501	Turbid below 60°	
89	1.50 : 3.	50 :	95.00	(1.26)	1.00	. 824	. 594	.456	Homogeneous above 30°	
90	0.00 : 5.	00 :	95.00			(.735)	. 530	.416	Homogeneous above 40°	
			(I)	System: Sodi	um Oleate:o-	Bromophene	ol:Water			
91	9.50 : 0.	50 :	90.00	58	30.0	12.8	3.34	1.51	Metastable 20°	
92	9.00 : 1.	00 :	90.00	82	68	25.0	4.99	2.06	Metastable 20°, turbid 20°	
93	8.50 : 1,	50 :	90.00	7.71	6.28	5.38	2.72	1.56	SI. turbidity	

Expt.	Sod, oleate:	-Ratio Phenol:	Water	2 0°	30°	4 0°	6 0°	80°	Remarks
94	8.00 :	2.00 :	90.00	4.32	3.68	3.20	2.47	1.50	SI. turbidity
95	4.50 :	0.50 :	95.00	1.51	1.21	1.01	0.749	0.584	Sl. turbidity
96	4.00 :	1.00 :	95.00	1.9 5	1.58	1.33	1.01	.780	Sl. turbidity
97	3.00 :	2.00 :	95.00	1.62	1.29	1.06	0.764	. 5 9 1	SI. turbidity
			(J) System: S	odium Oleat	e:Vanillin:V	Water		
98	9.00 :	1.00 :	90.00	4.14	3.49	3.03	2.42	2.29	SI. turbid, some ppt.
99	8.00 :	2.00 :	90.00	3.50	2.98	2.68	2.23	1.98	Sl. turbid, some ppt.
100	4.00 :	1.00 :	9 5.00	1.88	1.53	1.29	0,981	0. 84 6	Sl. turbid, some ppt.
			(K) Syster	n: Sodium (Dleate:p-Hyd	lroxybenzal	de hy de:Wate	er	
101	9.00 :	1.00 :	90.00	8.16	7.15	6.43	5.42	4.93	SI. turbid, some
102	8 00 :	2.00:	90.00	2.73	2.31	2.02	1.61	1.41	ppt.

TABLE II (Concluded)

^a Expts. 1, 11 and 2, 12 were made, respectively, with two different lots of sodium oleate prepared from two lots of oleic acid purified by low temperature recrystallization. The material used in expts. 1 and 11 was used throughout Section A and in Section F, expts. 65–70 inclusive. All other expts. were carried out with the material used in expts. 2 and 12. ^b Sodium oleate was prepared from oleic acid purified by the Skellon barium salt method. ^e Sodium oleate was prepared from a sample of commercial acid.

of Mr. Q. P. Peniston in the preparation of some materials used.

Summary

1. Using a more rigorously purified sodium oleate, earlier observations on the occurrence of maxima in the viscosity of sodium oleate:phenol: water systems have been checked qualitatively but not quantitatively, the present results indicating the maxima to be even more pronounced than previously reported.

2. On extending the investigation to other phenolic substances it was found that not all produced such maxima in the viscosity of sodium oleate solutions. The effectiveness of p-cresol, guaiacol and creosol in this regard was of the same order as that of phenol, but in the case of catechol, resorcinol and o-bromophenol the maxima were not so marked or even, at lower concentrations of sodium oleate, non-existent. Vanillyl alcohol, p-hydroxybenzyl alcohol, vanillin and p-hydroxybenzaldehyde did not increase the viscosities of the solutions of sodium oleate examined.

3. Evidence is adduced against Weichherz and Saechtling's² theory that the formation of acid soaps is a minor cause of the observed maxima in viscosity.

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The Degradation of Oriented Cellulose Structures by Polarized Ultraviolet Light

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Introduction

The photochemical changes produced in cellulose have received attention since $Witz^2$ in 1883 reported that cotton when exposed to light was changed, in part at least, to "oxycellulose." Although the exact nature of "oxycellulose" can only be inferred at present, and although some reported experiments may have been complicated by effects other than that of light, nevertheless, it appears that a certain portion of the ultraviolet

(1) Present address: Procter and Gamble Research Laboratory. Ivorydale, Ohio. [Original manuscript received July 26, 1938.] region does produce physico-chemical changes in the cellulose structure.

The structure of cellulose shows very definite differences in properties, depending upon the direction considered. This is indicated macroscopically by its pronounced fibrous nature, microscopically by its strong double refraction, as well as the production of tiny fibrillae by mechanical treatment, and sub-microscopically by the X-ray deduction of its atomic arrangement.

It is reasonable to expect, then, that the anisotropic properties would include the photochemical

⁽²⁾ Witz, Bull. soc. ind. Rouen, II, 190 (1883).