Further work along these lines with liquids known to give contact angles with certain similar solids is planned.

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SURFACE PRESSURES AND POTENTIALS OF MONOMOLECULAR FILMS OF LONG MOLECULES: POLYMERS OF ω-HYDROXYDECANOIC ACID

Sir:

Remarkable relations are exhibited by films of linear polymers of the formula $HO[(CH_2)_9COO]_xH$ with molecular weights as high as 25,200 and values of x to 148 as obtained from Drs. W. H. Carothers, E. O. Kraemer and F. J. Van Natta [Kraemer and Van Natta, *J. Phys. Chem.*, **36**, 3175 (1932); Carothers and Van Natta, THIS JOURNAL, **55**, 4714 (1933)].

The most prominent characteristics are listed with specific values which refer to condensed films under a pressure of 3 dynes per cm. unless otherwise stated.

1. Thickness of films from 4.0 to 5.0 Å.
2. Distance between centers of adjacent chains 4.0 to 4.8 Å.
3. Apparent vertical cross section of molecule 19.4 to 19.9 sq. Å., or nearly the same as the horizontal cross section (20.5) of molecules, such as stearic acid, oriented vertically.
4. The area (a) per molecule in condensed films is nearly proportional to the molecular weight at any given film pressure (f).

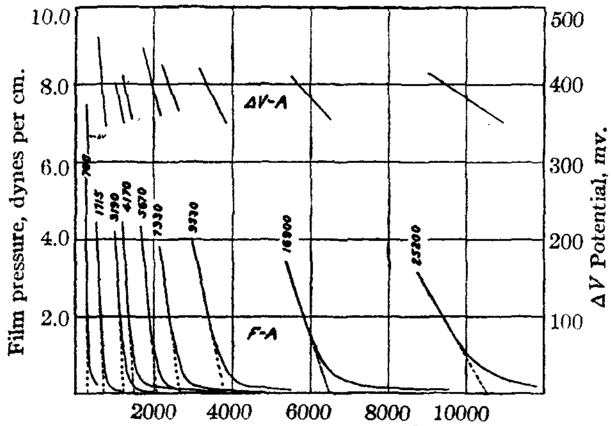

Fig. 1.—Film pressures and surface potentials for linear polymers of ω-hydroxydecanoic acid.

5. The compressibility is very large, since the value of $[(a_0 - a_1)/a_0]/(f_1 - f_0)$ lies between 0.040 and 0.053, and is almost independent of molecular size. Similar values for vertically oriented molecules are in general only one-tenth to one-sixtieth as large.

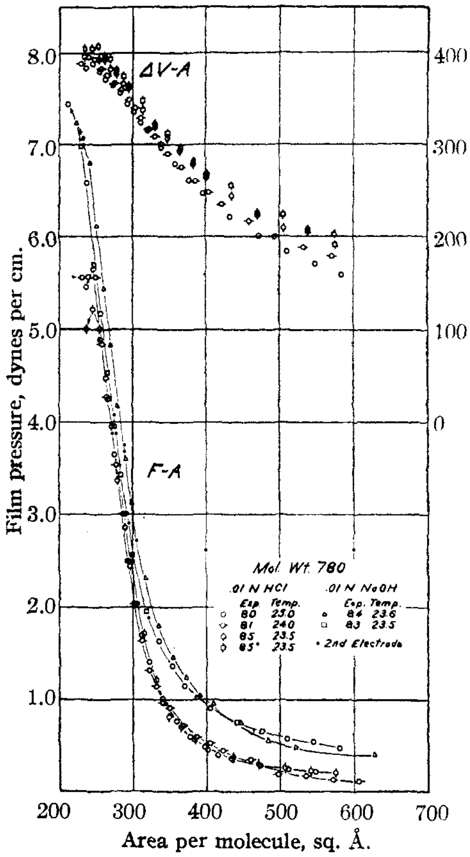

Fig. 2.—Values for polymer of molecular weight 780.

6. The pressure of collapse on 0.01 M hydrochloric acid increases from 3.2 to 5.7 dynes as the molecule becomes shorter, and after collapse the pressure decreases rapidly for a time. On 0.01 M sodium hydroxide the pressure of collapse is higher.
7. At pressures below 1.3 to 2 dynes the films are "expanded," with considerably higher molecular areas if spread on a base than if on an acid aqueous solution.
8. The surface potential (ΔV) of any one of the condensed films increases about 13% less rapidly than the surface density of the film. Thus the surface potential seems to increase with and nearly as the number of polar groups per unit area. However, the mutual effect of the dipoles is such as to decrease the potential.
9. At low pressures the expanded films become non-homogeneous, since the surface potential varies with the location on the surface. This island effect is much more prominent for polymers of high than for those of low molecular weight.
10. The molecular area of the compound of molecular weight 25,200 is 10,400 sq. Å. for zero pressure, or 8800 sq. Å. at 3 dynes per cm. pressure. This is the largest area thus far found for any molecule.

TABLE I

FILMS OF POLYMERS OF ω-HYDROXYDECANOIC ACID ON WATER

Mean values at temperatures from 21.5 to 26.0°. Concentration of hydrogen chloride in the water 0.01 *M*
Columns 2 and 3 are taken mostly from the paper of Carothers and Van Natta

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Mol. wt.	Density $d^{25}{}_4$	Length of molecule in Å.	Vol. of molecule in cu. Å.	Area per molecule at a film pressure			Maximum force	t = thickness of film at a film pressure			d = width of molecular space at			$f \times d$ molecular cross sect. at 3 dynes in sq. Å.	Compressibility of
				$f=0$	$f=3$	$f=$ max.	f_m	$f=0$	$f=3.0$	$f=$ max.	$f=0$	$f=3.0$	$f=$ max.		$f=0$
780	1.0957	60	1170	330	290	246	5.7	3.6	4.0	4.8	5.5	4.8	4.1	19.5	0.040
1715	1.0935	133	2590	700	604	556	4.5	3.7	4.3	4.7	5.3	4.5	4.2	19.4	.046
3190	1.0877	248	4840	1260	1080	970	4.2	3.9	4.5	5.0	5.1	4.4	3.9	19.6	.048
4170	1.0814	324	6360	1490	1300	1130	4.5	4.3	4.9	5.6	4.6	4.0	3.5	19.6	.043
5670	1.0751	440	8700	2050	1800	1688	4.4	4.2	4.8	5.2	4.7	4.1	3.8	19.7	.041
7330	1.0715	570	11330	2670	2277	2180	3.8	4.2	5.0	5.2	4.7	4.0	3.8	19.9	.049
9330	1.0668	730	14450	3800	3200	3000	4.0	3.8	4.5	4.8	5.2	4.4	4.1	19.8	.053
16900	1.0627	1320	26200	6440	5510	5270	3.4	4.1	4.8	5.0	4.9	4.2	4.0	19.9	.048
25200	1.0621	1970	39100	10430	8800	8700	3.2	3.8	4.4	4.5	5.3	4.5	4.4	19.9	.052

These relations, particularly 1, 2, 3, 4, 5 and 10, show conclusively that the molecules of these polymers lie flat on the surface. The molecules are anchored in this position by the polar groups at the ends and at every tenth carbon atom. Thus the molecule acts as a type of centipede, with as many as 149 regions of attachment.

The general relations are exhibited by Table I and Figs. 1, 2 and 3.

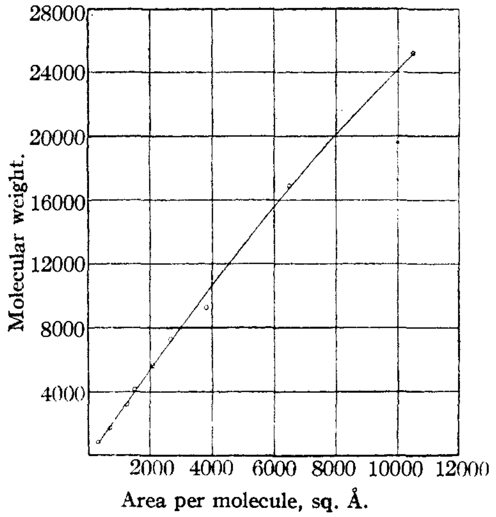

Fig. 3.—Surface area as a nearly linear function of the molecular weight.

The work given here was begun in this Laboratory by Dr. E. H. Fischer.

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RECEIVED MARCH 4, 1935

d-GULO-METHYLOSE (6-DESOXY-*d*-GULOSE) AND ITS RELATION TO A REPORTED INVERSION PRODUCT OF *l*-RHAMNOSE

Sir:

We wish to report the synthesis of a new methyl pentose, *d*-gulo-methylose (6-desoxy-*d*-gulose) by use of the cyanhydrin reaction on *d*-xylo-methylose (5-desoxy-*d*-xylose) [Levene and Compton, *Science*, **81,** 156 (1935)], followed by reduction of the lactone with Na-Hg amalgam in the usual manner. The physical constants of this substance along with several derivatives are recorded below.

Substance	M. p., °C.	$[\alpha]_D$	Solvent
(1) *d*-Gulo-methylose	Glassy solid	−35.7° (constant)	water
a (substance of Muskat	amorphous solid *ca.* 65	+14° → −14°	water)
(2) *p*-Bromophenylhydrazone of (1)	135	−16.1° → +9.2°	ethanol
a (substance of Muskat [1a]	162	− 6.1 → +13°	ethanol)
(3) *p*-Bromophenylosazone of (1)	195–196	±0.00° → 15.3°	pyridine–ethanol 3:2
(4) *d*-Gulo-methylonic lactone	180–181	−68.0°	water
(5) *p*-Bromophenylhydrazide of (4)	132–133	+8.83°	water
(6) *d*-Gulo-methylonic acid	—	−5.00°	water
(7) Sodium salt of (6)	—	+11.03°	water

The synthesis was undertaken for the purpose of testing the claim of Dr. I. E. Muskat [THIS JOURNAL, **56,** 2653 (1934) (this article, although published as a contribution from the Laboratories of the Rockefeller Institute for Medical Research, was never seen prior to publication by the senior author of this Communication)] that a Walden inversion occurred during the alkaline hydrolysis