linear with respect to pressure between 100 mm. and 760 mm.

The rate of nitrogen adsorption is of the right magnitude to be the slow step in the catalytic synthesis of ammonia.

WASHINGTON, D. C. RECEIVED AUGUST 21, 1933

[CONTRIBUTION FROM THE LABORATORY OF COLLOID SCIENCE, CAMBRIDGE UNIVERSITY, ENGLAND]

Monomolecular Films of the Polyesters

BY SANFORD A. MOSS, JR.

Monolayers of substances of high molecular weight such as derivatives of cellulose and of rubber form either condensed or (apparently) liquid expanded films on various substrates. It has recently been shown that monolayers of proteins on aqueous solutions can exist in three characteristic states: two fluid and one gel-like, compatible with the assumption that polypeptide chains are flexible and extend on the water surface.[1] A transition in the properties of monolayers of simple molecules, such as fatty acids and those of substances which exist normally in the colloidal state, is to be anticipated in films of compounds of large and increasing molecular weight that form true solutions, the eucolloids of Staudinger. It appeared of some interest to examine the properties of films of a typical series of such eucolloids. Thanks to the kindness of Dr. W. H. Carothers of E. I. du Pont de Nemours Company, we were provided with specimens of acidic ethylene succinates.[2] These are identified as follows:

No.	M. p., °C.	Mean mol. wt.	Name	Film formation from chloroform
I	73	1070	Acidic ethylene succinate	Yes
II	82	1380–1400		Yes
III	90	1580–1800		Yes
IV	98	3110–3400		Yes
V	103	3000	Neutral ethylene succinate	Yes
VI	...	15,000		Yes
VII	130	300	Cyclic dimeric ethylene succinate	Does not spread

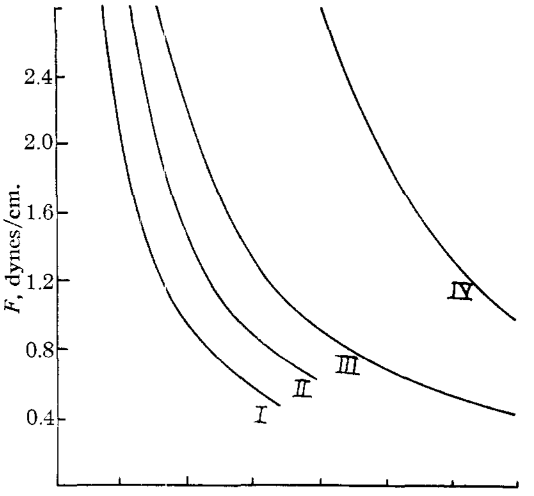

Fig. 1.—Monomolecular films of the polyesters.

The general formula for the first four is

$$HO—OC—(CH_2)_2—CO—[—O—(CH_2)_2—O—OC—(CH_2)_2—CO—]_n—OH$$

where n is 6, 9, 12 and 23, respectively; of V and VI:

$$H—[—O—(CH_2)_2—O—OC—(CH_2)_2—CO—]_n—O—(CH_2)_2—OH$$

where n is 22 and 100, respectively

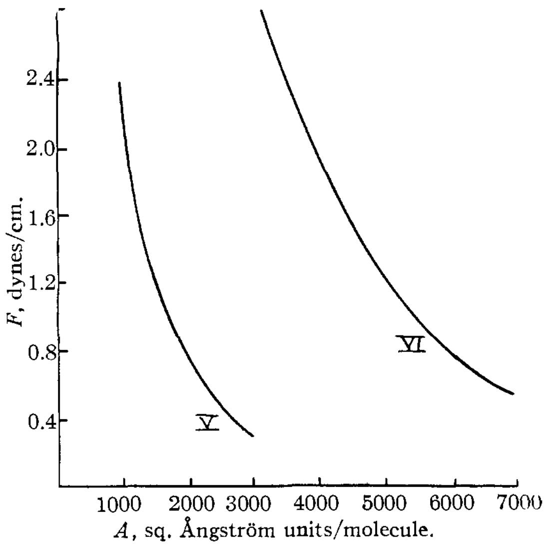

Fig. 2.—Monomolecular films of the polyesters.

With the exception of the cyclic dimeric ethylene succinate, all of the substances when dissolved in chloroform and spread by means of

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(1) Hughes and Rideal, *Proc. Roy. Soc.* (London), **A137**, 62 (1932).

(2) Carothers *et al.*, THIS JOURNAL, **52**, 711 (1930).

an "Agla" micropipet on $N/100$ hydrochloric acid in a Langmuir trough of the type described by N. K. Adam and sensitive to 0.2 dyne per cm. were found to form perfectly reproducible and uniform films.

In the curves are depicted both the force area curves, the force in dynes per cm. and the area in sq. Ångström units per molecule, and the force-weight curve as is usually plotted for uniform films of substances of unknown molecular weight.

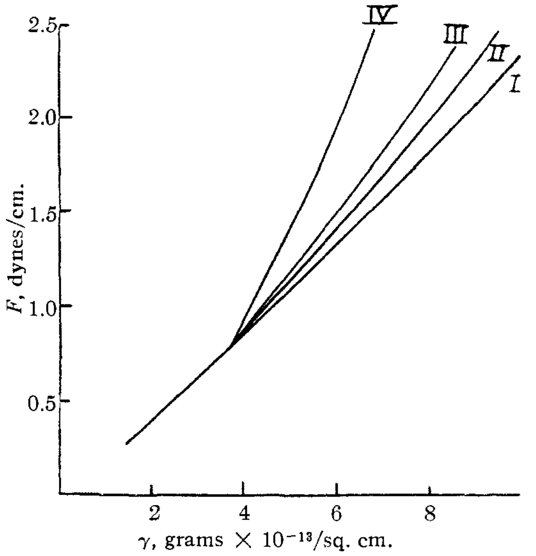
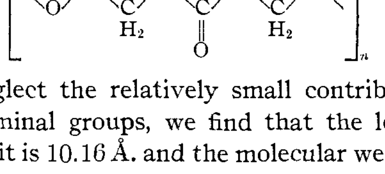


Fig. 3.—Monomolecular films of the polyesters.

It will be observed that the force area curves are similar in character to the vapor expanded films of ethyl myristate, while from Fig. 3 we note that the first four compounds possess identical force-weight curves up to a surface concentration of $\gamma = 4.0 \times 10^{-13}$ g./sq. cm. and a pressure of 0.85 dyne/cm. If we assume that these substances consist entirely of chains of units of composition



and neglect the relatively small contribution of the terminal groups, we find that the length of each unit is 10.16 Å. and the molecular weight 144. With the critical value of $\gamma = 4.0 \times 10^{-13}$ g./sq. cm. derived from the curve we find that to accommodate these units the chains must be flexible and packed parallel and distant from each other by 5.85 Å. In the crystalline state the spacing between the chains is found by x-ray examination to be 5.25 Å.; our thanks are due to J. P. Bernal for this value. As in the polypeptide chains of the proteins, the closeness of approach in closely packed homalic monolayers approaches the values obtained in the crystalline state, but is never quite as small. The great flexibility of these molecular chains is thus evident. On further compression of the film, beyond this limiting area, it appears that the chains are partly pushed into the substrate, the longer chains exerting the greater resistance to this solution, a fact quite consistent with the diminishing bulk solubility in water with increase in chain length. Buckings of the chain or tilting of the molecules into the air would be expected to involve less work for the longer chains, *i. e.*, a smaller value for $\Delta E/\Delta\gamma$.

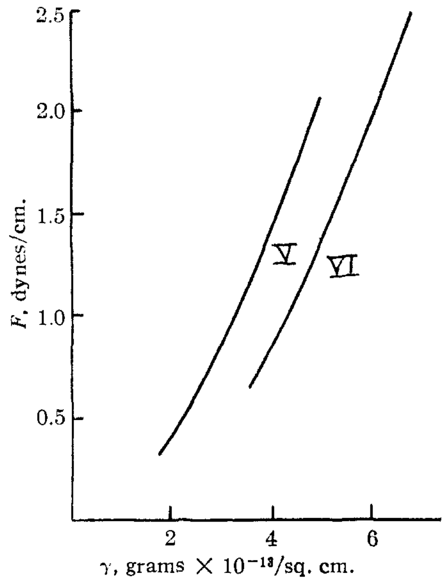


Fig. 4.—Monomolecular films of the polyesters.

The equation of state of these fluid films has not as yet been satisfactorily explored, the two important factors being naturally the cohesion of the chains for one another and the ease of immersion, a factor dependent on the chain length and the relative depth of immersion. Up to the limiting weight of $\gamma = 4.0 \times 10^{-13}$ g./sq. cm., the process of compression is not complicated by this second factor and the equation of state can be represented by the simple form

$$(F + 0.15) = K\gamma \text{ or } (F + 0.15)\,A = K$$

where 0.15 dyne/cm. represents the cohesional force between the chains. Beyond this limiting compression the arbitrary equations found to fit these curves are

$$(F + 0.15)\ (A + 36.6) = 452 \qquad \text{(I)}$$
$$(F + 0.15)\ (A - 32.2) = 556 \qquad \text{(II)}$$
$$(F + 0.15)\ (A - 41.2) = 771 \qquad \text{(III)}$$
$$(F + 0.15)\ (A - 510) = 925 \qquad \text{(IV)}$$
$$(F + 0.15)\ (A - 540) = 1210 \qquad \text{(V)}$$
$$(F + 0.15)\ (A - 2350) = 3470 \qquad \text{(VI)}$$

From the "b" term in these two dimensional van der Waals equations we note that the ease of partial immersion of the chains varies inversely as the chain length, whereas the ease of immersion is about equal for the acid and neutral succinates (IV and V) of nearly the same chain length. The maximum pressure withstood by the films before collapse sets in does not vary appreciably with the chain length and is in the neighborhood of 2.5 dyne/cm.

This work was carried out in the Laboratory of Colloid Science, The University, Cambridge, England, under the direction of Professor E. K. Rideal, to whom the author is greatly indebted.

Summary

It is shown that the polymeric acid and neutral ethylene succinates form a regular series of stable unimolecular films on dilute acid substrates. The films are similar to vapor expanded films of fatty acid esters. Evidence is presented for the assumption that the molecular chains are flexible and can be closely packed before immersion on compression occurs. The closeness of approach is found to be 5.85 Å. units comparable with the value 5.25 Å. obtained from x-ray data.

RIDLEY PARK, PA. RECEIVED AUGUST 21, 1933

[CONTRIBUTION FROM THE LABORATORIES OF THE COLUMBIA DIVISION OF THE PITTSBURGH PLATE GLASS COMPANY AND OF NEW YORK UNIVERSITY]

Aqueous Solubility of Salts at High Temperatures. II. The Ternary System Na_2CO_3–$NaHCO_3$–H_2O from 100 to 200°

BY WILLIAM F. WALDECK,[1] GEORGE LYNN[2] AND ARTHUR E. HILL

An earlier publication[3] from these laboratories gave measurements of the solubility of sodium carbonate in water up to 348°. The present investigation introduces a third component, sodium bicarbonate, up to temperatures of 200°, beyond which the work could not be carried with accuracy because of the very high pressures involved, causing large loss of carbon dioxide in amounts which could not be estimated exactly.

Apparatus and Methods

The solubility measurements were made in bombs of Allegheny metal as shown in Fig. 1, having a capacity of 135 cc. These bombs differ in construction from those used previously[3] in having the sampler set in from the top, which makes the apparatus less unwieldy and permits the insertion of several in the thermostat at one time; they also lack the relief valves of the earlier construction. The details as to threading, springs, washers, etc., may be had from the earlier paper, as also the details of the air thermostat used. The salts used were of the highest commercial grade, the bicarbonate, however, always containing a small percentage of normal carbonate which was determined by analysis and allowed for in the calculations; the two salts and water were weighed into the bomb by the method of difference, so that the exact composition of the complex could be used as one of the necessary two points for determining the composition of the solid phase by the method of extrapolation.[4] After equilibrium had been attained at the temperature of the thermostat and time had been allowed for the settling of the solid, a sample of solution was allowed to enter the sampler by opening its needle valve. After the system had reached room temperature the sampler was removed and weighed, the contents washed out and analyzed for total alkali by titration with methyl orange and xylene cyanole FF as indicator and for carbon dioxide by absorption in soda lime, which gave data for calculation of the complete composition. A small but noticeable amount of iron was leached from the bombs at 190° and above, appearing at first as a bluish opalescence; on exposure to the air this became oxidized and precipitated as what was apparently ferric hydroxide; where the amounts made it advisable, this was filtered off before the analysis. The presence of small amounts of chromium in the samples was mentioned in the earlier publication.

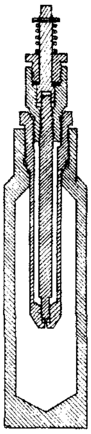


Fig. 1.

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[1] The experimental work of this paper is from the thesis of Mr. Waldeck, presented in partial fulfilment of the requirements for the degree of Ph.D. at New York University, June, 1933.

[2] Mr. Lynn coöperated throughout the completion of this work, which has been written up since his death.

[3] Waldeck, Lynn and Hill, THIS JOURNAL, **54**, 928 (1932).

[4] Schreinemakers, *Z. physik. Chem.*, **11**, 81 (1893); Bancroft, *J. Phys. Chem.*, **6**, 178 (1902); for the algebraic method see Hill and Ricci, THIS JOURNAL, **53**, 4305 (1931).