This acetylene containing deuterium was used in two runs using water of normal deuterium concentration. An accident prevented an accurate determination of the exchange in the case of one of these experiments but in the other run the deuterium concentration in the water rose to over 30%. Assuming that the deuterium content of the acetylene was the same as the deuterium content of the water from which it was formed, the equilibrium constants were calculated as before. The results were as follows: $K_1 = 0.629$, $K_2 = 0.441$, $K_3 = 2.05$, $K_4 = 1.44$ and $K_5 = 0.904$. The assumption made is probably not the correct one and a change to 96 from 97% deuterium in the acetylene gives values for the constants which check the average values given in Table II very well. It seems very likely from other considerations as well as from experimental work that the deuterium concentration of the acetylene might well be less than the deuterium concentration in the water from which it was made. The results however are in sufficiently good agreement to establish the fact that equilibrium had been reached.

Discussion

The system under consideration is invariant at equilibrium and the amounts of the six molecular species will determine the equilibrium constants. Experimentally the amounts of H, D and C_2X_2 are determined, X of C_2X_2 being either H or D. Using this information together with the constants for equilibria (6) and (7) the above values were calculated. However an examination of the system shows that

$$(1) = {}^1/_2\,[(5) - (6) + (7)]$$
$$(2) = {}^1/_2\,[(5) - (6) - (7)]$$
$$(3) = {}^1/_2[(5) + (6) + (7)]$$
$$(4) = {}^1/_2\,[(5) + (6) - (7)]$$

If therefore the equilibrium constant of (5) were known in addition to the constants of (6) and (7) it would be possible to calculate the other four constants. From the above linear combinations we find that

$$K_1 = \sqrt{\frac{K_5 \times K_7}{K_6}} \qquad K_2 = \sqrt{\frac{K_5}{K_6 \times K_7}}$$
$$K_3 = \sqrt{K_5 \times K_6 \times K_7} \qquad K_4 = \sqrt{\frac{K_5 \times K_6}{K_7}}$$

It is of course possible to develop similar expressions using combinations of other constants.

The equilibrium constants are given to three places just as they came out in the calculations. We are not justified from the experimental technique in using constants to more than two decimal places. Taking the average value to two decimal places we have for the constants $K_1 = 0.60$, $K_2 = 0.42$, $K_3 = 1.95$, $K_4 = 1.37$ and $K_5 = 0.82$.

Summary

The equilibrium constants for the reactions between H_2O, HDO, D_2O, C_2H_2, C_2HD and C_2D_2 have been determined experimentally at 25°.

MINNEAPOLIS, MINNESOTA

RECEIVED DECEMBER 12, 1935

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Composition of Fatty Acid Films on Water Containing Calcium or Barium Salts

BY IRVING LANGMUIR AND VINCENT J. SCHAEFER

Dr. Katharine Blodgett[1] has shown that successive layers of fatty acids and fatty acid soaps can be transferred to glass or metal surfaces by raising and lowering these surfaces through the surface of water on which monomolecular fatty acid films have been spread. The ease in which such multimolecular films may be built up and the properties of the resulting films depend greatly on the *p*H of the water, the temperature, and particularly upon the presence of salts of divalent metals.

Very low concentrations of calcium and barium salts in alkaline water are sufficient to make the stearic acid films on the water solid. Dr. Blodgett has shown that the films skimmed off alkaline water containing calcium and barium leave a white solid residue when heated above 100°, whereas the stearic acid films skimmed off water containing no metallic salts melt at about 70°.

It is thus evident that the monomolecular films of fatty acids on water containing salts of alkaline earth metals contain these metals as constituents and that the multimolecular films transferred to solids are, under these conditions, essentially metallic soaps.

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[1] Blodgett, THIS JOURNAL, **57**, 1007 (1935).

We have undertaken to determine the chemical composition of the films that may be skimmed off water containing barium or calcium salts for different values of *p*H.

Experimental

A large brass tray 50 × 80 cm. and 2 cm. deep was lined with glass on the bottom and sides; this was done by coating the tray with molten hard paraffin which was used as a cement to hold the glass in place. When the brass tray was merely lined with paraffin, the film that was skimmed off always contained perceptible traces of copper, as was shown by its leaving a colored ash. It is usually customary to fill such a tray to the brim with water and use metal strips coated with paraffin as barriers to confine surface films. With such barriers to skim off the film, it is found that the film crumples and extends over the edge of the tray, and thus some of it is lost. It is found much better to fill the tray only within 5 mm. of its rim and to use plate-glass barriers with their plane vertical. Across the tray near one end was a vertical barrier of glass having a gap of about 15 cm. in the center, in which a surface-force balance was mounted. The floating barrier of this balance was attached at its ends to the rigid barrier by light paraffined silk threads floating on the water which prevented the escape of the monomolecular film around the ends of the movable barrier.

A sufficient number of drops of a dilute solution of stearic acid in benzene were placed on the water in the tray to cover nearly the whole surface with a monomolecular film. A movable glass barrier was then advanced until the spreading force amounted to 3.0 dynes/cm. The area occupied by the film was then measured. A movable glass barrier which is called a skim-bar, having its lower edge ground to an acute angle, was lowered into the water within a few millimeters of the glass barrier at the end of the tray which contained the surface balance. The skim-bar was then moved in a direction parallel to the length of the tray so as to skim the monomolecular film. This film crumpled up and was finally forced into a narrow space about 1.5 cm. wide, with length equal to the width of the tray. A scoop of thin platinum foil was then run slowly down the length of this trough, so as to skim off the crumpled film. The tray was thus skimmed about ten times and the total skim collected, which weighed 6–8 mg., was transferred to a light platinum foil boat which was then dried to constant weight at 100° and weighed. A small amount of concentrated sulfuric acid was then added, and the skim was heated until all carbonaceous matter had been burnt off. It was assumed that the residue then consisted of calcium or barium sulfate. Care was taken not to heat this residue to a temperature that would cause decomposition of calcium sulfate. The method was checked by making some runs with pure calcium carbonate and stearic acid treated in the same manner with sulfuric acid.

When pure distilled water was used, it was found that the skim left no measurable ash. The total amount of stearic acid in the skim was only a few per cent. less than the amount that had been placed on the tray.

In studying the films on water containing calcium solutions, the tray was filled with doubly distilled water to which a calcium bicarbonate solution was added in amount sufficient to give a concentration 10^{-4} molar with respect to calcium carbonate (10 mg. of calcium carbonate per liter). The *p*H value was then adjusted by adding sodium hydroxide, sodium bicarbonate, or hydrochloric acid, and the *p*H was determined on samples of water removed from the tray from time to time by LaMotte indicators.

In the studies of films obtained with barium salts in the water, a barium hydroxide solution was added until the concentration was 10^{-4} molar, in terms of barium carbonate (19.7 mg. of barium carbonate per liter). The *p*H was then adjusted by adding either ammonium hydroxide or hydrochloric acid.

Results

The data are recorded in the table. The total weight in mg. of the stearic acid which was applied to the water is given in line 5 of the table. Line 6 contains the area per molecule, when the spreading force is 3 dynes per cm., expressed in square Ångströms. It is to be noted that when the solution is alkaline the film gives an area per molecule closely agreeing with that found for condensed monomolecular films, but as the solution is made more acid, the area increases considerably. The barium films on alkaline water showed an area about 5% less than that of the calcium films.

TABLE I

COMPOSITION OF FILMS

		Calcium					Barium			
1.	Solution	10^{-4} molar $CaCO_3$					10^{-4} molar $BaCO_3$			
2.	Solutions added to adjust *p*H	$NaHCO_3$, NaOH, or HCl					NH_4OH, or HCl			
3.	*p*H	4.5	5.5	6.9	8.5	10.5	4.5	6.9	8.5	10.5
4.	Area of film in square meters	3.36	3.16	2.84	3.35	2.86	4.02	3.19	2.74	2.78
5.	Stearic acid applied, mg.	6.75	6.75	6.70	7.85	6.70	7.35	7.35	6.70	6.70
6.	Area per molecule at $F = 3$ dynes cm.$^{-1}$ in square Ångströms	23.2	21.8	20.0	20.0	20.0	25.6	20.3	18.9	19.2
7.	Dried skim, mg.	6.1	7.0	6.6	8.1	6.7	7.35	7.40	6.8	7.2
8.	Ca or Ba in dry skim, %	1.7	3.8	5.6	7.1	7.5	3.6	12.0	17.8	18.9
9.	Stearic acid recovered in skim, %	89	100	93	93	93	96	89	84	87
10.	% conversion to neutral soap, *f*	24	56	84	108	114	15	56	89	96
11.	Theoretical metal content of neutral soap, %	Ca, 6.60					Ba, 19.51			

The weight of the dried skim is given in the seventh line and the percentage by weight of calcium or barium in this skim is shown in the next line. It is assumed that the skim consists of a neutral barium or calcium soap and free stearic acid. From the barium or calcium content the relative numbers of molecules of soap and of free stearic acid were calculated. The total stearic acid equivalent of the skim was then calculated, and this was compared with the original amount of stearic acid which was applied to the water in the tray, as given in line 5. The ratio between these two amounts gives the fraction of the original stearic acid which was recovered in the skim. These data are shown in line 9. It may be seen that roughly about 90% of the stearic acid was recovered. It is believed that the loss represents monomolecular film which is crumpled up against the glass barriers and that which was lost when the skim-bar was pushed below the surface. The films containing calcium crumpled up into a white, snow-like skim which was much easier to remove than the less rigid barium films. This may account for the smaller recoveries observed with barium films.

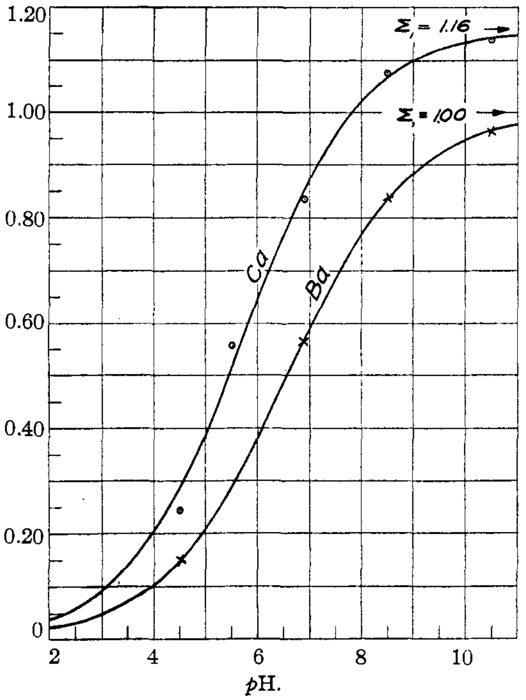


Fig. 1.—Composition of films: crosses and circles denote experimentally determined values, and the curves are calculated by Eq. 1 and Eq. 2. The ordinates represent f, the fractional conversion to neutral soap.

The tenth line gives data on the chemical composition of the skim in terms of f, a quantity which we may call the fractional conversion to neutral soap. This may be defined as the fraction of stearic acid radicals in the skim which may be assumed to be combined with barium or calcium to form neutral soap. The value f in line 10 is expressed as a percentage. The theoretical percentage of metal in neutral soaps of calcium and barium is given in line 11.

The values of f plotted against the pH are given in Fig. 1. As the pH increases, f seems to reach a limiting value of about unity, which means that on sufficiently alkaline solutions the film is approximately pure neutral soap. When the solution becomes acid, the film tends to become pure fatty acid. However, the transition is gradual, so that even if $p\text{H} = 4.5$ the film is roughly 20% neutral soap. It is seen from Fig. 1 that with films containing calcium the limiting calcium content is 1.16 times greater than would be expected for neutral calcium soap. It is, perhaps, possible that this is due to the adsorption of sodium salts upon the under surface of the film, for in these experiments with calcium, sodium salts were used to adjust the pH. This source of error was not possible in the data for barium, for there ammonium salts were used. If we represent the limiting value of f for high values of pH by f_1, then it was found empirically that if we plot $f/(f_1 - f)$ against the pH, the data give approximately a straight line which corresponds to the following empirical equations:

For Ca soap films

$$\log_{10}\{f/(f_1 - f)\} = -2.23 + 0.388\,(p\text{H}) \qquad (1)$$

For Ba soap films

$$\log_{10}\{f/(f_1 - f)\} = -2.41 + 0.367\,(p\text{H}) \qquad (2)$$

The full lines in Fig. 1 have been calculated by these equations. According to these equations, the ratio of the free stearic acid in the film to the combined stearic acid is proportional to the 0.388th power of the hydrogen-ion concentration for the calcium films while in the case of the barium films the exponent is 0.367. Undoubtedly within the experimental error these two values must be considered the same.

Summary

A technique is described for skimming off monomolecular films of fatty acids upon water and analyzing them. When the water contains calcium or barium salts (concentration 10^{-4} molar with respect to carbonate) the films formed by stearic acid are nearly pure neutral soaps when the water

is strongly alkaline, *p*H = 11, and are free fatty acid films when *p*H = 3. Half-conversion to neutral soap occurs at *p*H = 5.1 for calcium and *p*H = 6.6 for barium solutions. These metallic constituents of the films have a profound effect upon the physical properties. They increase the rigidity of the films and affect the ease with which multimolecular films can be formed on metal or glass.

SCHENECTADY, NEW YORK RECEIVED DECEMBER 4, 1935

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE COLLEGE OF LIBERAL ARTS AND SCIENCES OF TEMPLE UNIVERSITY]

The Synthesis of 2-Amino-4-ethylpyrimidine

BY WILLIAM T. CALDWELL AND WILLIAM M. ZIEGLER

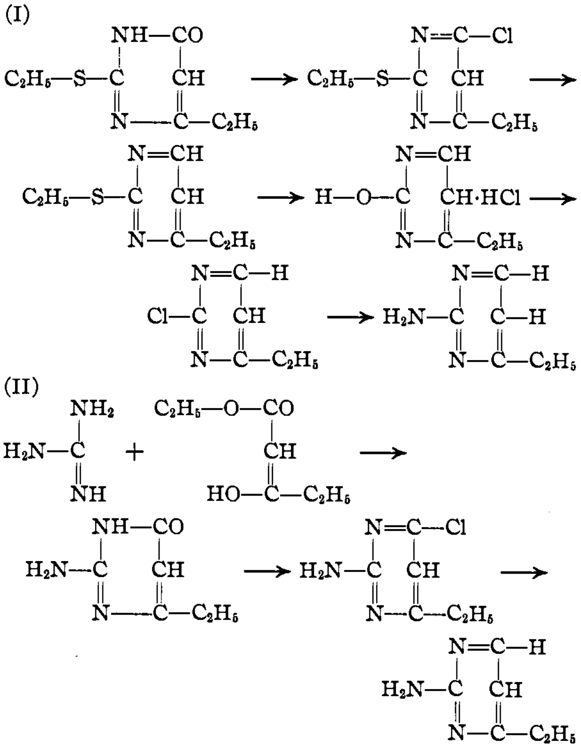
In our synthesis of 6-amino-4-ethylpyrimidine recently reported, one of the steps involved the reduction of 2,6-dichloro-4-ethylpyrimidine by the action of hydriodic acid. In an analogous reaction with 2,6-dichloro-4,5-dimethylpyrimidine, Schlenker[1] reported that the chlorine atom in position 2 was replaced by hydrogen while that in position 6 was exchanged for an hydroxyl group as a result of hydrolysis.

While we believed that this reaction proceeded analogously with 2,6-dichloro-4-ethylpyrimidine, we thought it of interest to prepare 2-amino-4-ethylpyrimidine in order to compare it with the 6-amino compound and to settle more definitely that the reduction had formed 6-oxy-4-ethylpyrimidine.

Furthermore, since the assumption of the presence of 6-amino-4-ethylpyrimidine in vitamin B_1 was based in part upon the nature of absorption bands in related compounds[2] and is still open to question as a result of other work,[3] the synthesis of the isomeric 2-amino-4-ethylpyrimidine may be of interest in connection with the structure of this vitamin.

The synthesis of 2-amino-4-ethylpyrimidine was carried out by two different methods; one starting with 2-ethylmercapto-4-ethyl-6-oxypyrimidine, and the other with 2-amino-4-ethyl-6 oxypyrimidine prepared according to the method described by Jaeger[4] for 2-amino-4-methyl-6-oxypyrimidine.

The syntheses are summarized by the formulas.



Experimental Part

2 - Ethylmercapto - 4 - ethyl - 6 - chloropyrimidine.—This compound was prepared in the usual manner by the action of 77 cc. of phosphorus oxychloride upon 32 g. of 2-ethylmercapto-4-ethyl-6-oxypyrimidine; b. p. 110–112° at 4–5 mm.; yield 24.3 g.

Anal. Calcd. for $C_8H_{11}N_2ClS$: Cl, 17.49. Found: Cl, 17.39.

2 - Ethylmercapto - 4 - ethylpyrimidine.—2 - Ethylmercapto-4-ethyl-6-chloropyrimidine (24 g.) dissolved in 100 cc. of ethanol and 80 cc. of water was reduced by the action of 50 g. of 90% zinc dust; b. p. 105–107° at 4 mm.; yield 16.1 g.

Anal. Calcd. for $C_8H_{12}N_2S$: N, 16.66. Found: N, 16.03.

2-Oxy-4-ethylpyrimidine Hydrochloride.—2-Ethylmercapto-4-ethylpyrimidine (15.8 g.) was hydrolyzed by the action of 50 cc. of concentrated hydrochloric acid. After recrystallizing the product from alcohol it melted at 211–213° with decomposition, having begun to sinter in the neighborhood of 200°; yield 9.9 g.

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(1) Schlenker, *Ber.*, **34**, 2823–2825 (1901).

(2) Williams, Buchman, Ruehle, THIS JOURNAL, **57**, 1093 (1935).

(3) Windaus, Tschesche and Grewe, *Z. physiol. Chem.*, **237**, 100 (1935).

(4) Jaeger, *Ann.*, **262**, 365 (1891).