[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

MONOMOLECULAR FILMS BETWEEN LIQUIDS: BUTYRIC ACID BETWEEN WATER AND HEXANE, AND ACETIC ACID BETWEEN WATER AND BENZENE

BY WILLIAM D. HARKINS AND H. M. McLAUGHLIN

RECEIVED MARCH 21, 1925 PUBLISHED JUNE 5, 1925

Introduction. Number of Molecules per Unit Area in Interfacial Films

The only earlier investigation of the number of molecules in an interfacial film between two liquids is that of Harkins and King,[1] who found that there are 2.78×10^{14} molecules per sq. cm. in the monomolecular film of butyric acid between water and benzene, while between water and air (plus saturated vapor) the number of molecules is almost exactly the same, 2.77×10^{14}. The data of the present paper show that between water and hexane the number is 2.78×10^{14}. Thus, it is evident that the number of molecules in unit area of the film depends upon the dimensions of the molecules as they lie oriented in the film, with the carboxyl groups toward the water and the hydrocarbon groups toward the air, the benzene or the hexane.

The area occupied by a molecule in any one of the three butyric acid films is 32 sq. Å. (32×10^{-16} sq. cm.). Table I gives the number of molecules and the area per molecule for acids that contain from 1 to 10 carbon atoms as determined by Harkins, King and Clark.

TABLE I

AREAS PER MOLECULE IN MONOMOLECULAR FILMS OF NORMAL ALIPHATIC ACIDS ON WATER

(Butyric acid: 2.77×10^{14} molecules per sq. cm.)

No. of C atoms...............	1	2	3	4	7	9	10
Area per mol., sq. Å...........	57	50	39	36	34	32	31

While the films of butyric acid are closely packed, it is evident that this is not true of a film of acetic acid on water, in which the area per molecule is 39% greater than with the C_4 acid. It is of interest to determine the effect of a second liquid phase upon the packing of such an expanded or loosely packed film. Table II presents the data used in the calculation of the number of molecules in the monomolecular film of acetic acid between water and benzene, which is found to be 2.58×10^{14} per sq. cm., or an area of 38.7 Å.^{2} per molecule. Thus, between the two liquids the film is not so highly expanded as when it lies upon the surface of water alone. Marcelin considered that a film such as that of acetic acid on water possesses the characteristics which would be expected in a two-dimensional gas. This indicates that a part of the area occupied by the molecules is due to a two-dimensional pressure. However, if a second liquid phase is

---

[1] Harkins and King, THIS JOURNAL, **41,** 970 (1919).

above the film, the freedom of motion of the acetic acid molecules in the film is greatly reduced, so the decrease of 23% in the area per molecule produced by the presence of benzene as the upper phase is an effect in the expected direction. Thus, the upper liquid phase reduces the area per molecule in the expanded film, but has no effect upon this area in condensed or closely packed films.

Interfacial Tension and Distribution in the Two-Phase Systems: Acetic Acid-Benzene-Water, and Butyric Acid-Hexane-Water

Tables II and III and Fig. 1 give the interfacial tensions for systems in which acetic acid is distributed between water and benzene, and butyric acid between water and hexane. The tables give the densities of both phases, and the distribution of the solute is represented in each case by the values for the concentration ratios C_W/C_B and C_W^2/C_B, or C_W/C_H and C_W^2/C_H. The values of C_W^2/C_H are nearly constant, which indicates that in the hexane the average association of the butyric acid is equivalent to the formation of double molecules. With acetic acid as distributed between water and benzene, C_W/C_B decreases, and C_W^2/C_B increases greatly as the concentration of the butyric acid increases. Thus, the degree of association is less for acetic acid in benzene than for butyric acid in hexane.

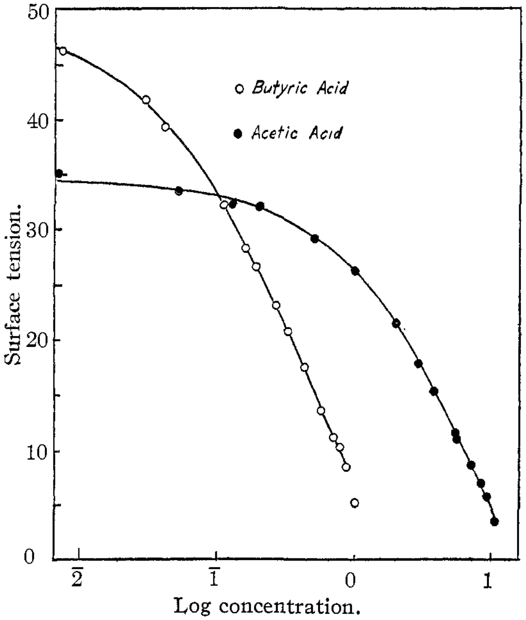

Fig. 1.—Interfacial tension between water and hexane with butyric acid, and between water and benzol with acetic acid.

In the case of a few solutions the distribution of the acid between the two phases did not represent exactly equilibrium conditions, and in such the ratio of the concentrations is given in parentheses. The surface tensions of such solutions are listed in the table, for it has been found that the surface-tension values determined thus, represent equilibrium conditions, since the interfacial tension depends only upon the concentrations very close to the interface on the drop, and this layer reaches a condition extremely close to that of equilibrium.

TABLE II

INTERFACIAL TENSIONS AT THE PHASE BOUNDARY, WATER-BENZENE, WITH ACETIC ACID AS A SOLUTE

C_A Moles per liter	C_W Moles per 1000 g. of water	Water layer density at 20°	C_B Moles per 1000 g. of benzene	Benzene layer density at 20°	C_W/C_B	C^2_W/C_B	Surface tension
0.0	0.0	.....	.....	.....	...	...	35.05
.05094	.05117	0.9987	0.00082	0.8782	62.16	3.181	33.52
.1286	.12983	.9993	.002765	.8785	(46.957)	6.096	32.48
.2027	.20515	1.00003	.003103	.87923	66.120	13.564	32.3
.5020	.5162	1.00264	.009092	.87937	56.787	29.317	29.30
.9929	1.0482	1.00677	.03274	.8794	32.764	34.344	26.29
1.956	2.1802	1.0145	.1027	.8797	21.22	46.263	21.56
2.897	3.417	1.0216	.2275	.8804	15.027	51.346	18.04
3.798	4.7445	1.0285	.3321	.88124	14.288	67.79	15.56
5.394	7.547	1.0383	.6320	.88310	11.941	92.22	11.79
5.619	8.010	1.0387	.6812	.88321	11.757	95.045	11.30
7.241	11.780	1.0496	1.1923	.8863	(9.880)	116.4	8.31
8.486	15.619	1.0525	1.453	.88766	10.735	167.9	7.08
9.221	18.603	1.0549	1.8365	.8903	10.117	188.34	5.87
10.759	26.24	1.0555	3.376	.8964	7.772	203.9	3.55

Radius of tip used = 0.27440 mm. 1 mole = 1 formula weight.

TABLE III

INTERFACIAL TENSIONS AND DISTRIBUTION FOR THE TWO-PHASE SYSTEM BUTYRIC ACID-HEXANE-WATER

Moles per liter	Moles per 1000 g. of water	Water layer density at 20°	Moles per 100 g. of hexane	Hexane layer density at 20°	C^2_W/C_H	$C/{}^2_W C_H$	Surface tension
0.00	0.0	0.9982	.....	0.67555	...	...	49.677
.00731	.00733	.9983	0.00100	.67574	7.317	0.053	46.28
.03015	.03029	.9984	.00434	.67574	7.134	.216	41.806
.03986	.04007	.9984	.00695	.67625	5.761	.230	39.33
.10975	.11096	.9988	.04442	.67697	2.498	.277	32.161
.15818	.16059	.99891	.08974	.67826	1.790	.287	28.446
.19494	.19853	.99899	.1036	.67834	(1.916)	(.380)	26.668
.26430	.27074	.9994	.2440	.67975	1.110	.300	23.18
.32776	.32384	.9997	.36453	.6829	0.916	.305	20.803
.4305	.44737	1.0002	.6533	.68766	.684	.306	17.695
.5818	.6148	1.0008	1.4515	.6970	(.423)	(.260)	13.51
.6905	.7342	1.0013	1.8084	.70503	.406	.298	11.304
.7921	.850	1.00165	2.4272	.71333	.350	.297	10.505
.8581	.9261	1.0021	3.0624	.71997	.302	.279	8.577
1.013	1.109	1.00250	5.1787	.74023	.214	.237	5.366

Purification of Substances and Experimental Methods

Acetic Acid.—Kahlbaum's pure acetic acid was twice recrystallized before making up the solution of 11 normal acid from which all the other solutions were made.

The concentration of the acetic acid was determined by titrating with standard sodium hydroxide solution, using phenolphthalein as an indicator. The sodium hydroxide solution was standardized with hydrochloric acid which had been standardized by precipitation of silver chloride. In titrating the benzene phase a relatively large quantity of water was shaken vigorously with the benzene-acid layer. Weight burets were used for all titrations.

Equilibrium between the water-acid phase and the benzene-acid phase was attained by shaking in the thermostat at 20° for four to six hours. When equilibrium was reached, the two layers were separated while the containing vessel still remained in the thermostat, by forcing the liquid in each case through an inverted U-tube into a clean, dry bottle. The compressed air used in separating the layers was twice filtered through cotton to remove all dust particles. In each case 150 cc. of the acetic acid solution was shaken with 150 cc. of benzene.

Hexane.—The hexane was prepared from ligroin boiling at 30–80°. The ligroin was washed with c. p. concd. sulfuric acid until, after several hours and occasional shaking, the acid showed no coloration. This product was then washed with dil. sodium hydroxide solution, and finally with distilled water, and dried over calcium chloride. The ligroin thus purified was redistilled, using a fractionating column until about 1.5 liters was obtained which had a boiling point of 65–75°.

Butyric Acid.—Kahlbaum's pure acid was used. The acid was redistilled and the fraction boiling at 162–163° was taken.

Summary

1. The number of molecules in a monomolecular film of butyric acid between water and hexane is found to be 2.78×10^{14} per sq. cm., which corresponds to an area of 32 sq. Ångström units per molecule. This is exactly the area previously found for this acid between water and benzene and between water and vapor. This is a tightly packed film, and it seems evident that the number of molecules per unit area depends upon the dimensions of the molecules and their orientation. It should be kept in mind that neither this work nor any other work on surface films gives the slightest evidence as to the direction of orientation of the molecules in the film. Such *evidence* is, however, given by the values for the adhesional and cohesional energies at interfaces as determined in this Laboratory, and indicates that the carboxyl groups orient toward the aqueous phase, and the hydrocarbon chains toward the organic phase, as accords with the *hypothesis* based upon ideas concerning solubility.

2. On water, acetic acid forms an expanded film with an area of 50 sq. Ångström units (10^{-16} sq. cm.) per molecule. With benzene as the upper phase this area is reduced to 38.7 sq. Å.

3. The tables give the interfacial tensions of the system water-hexane with butyric acid as a solute, and of water-benzene with acetic acid as a solute.

CHICAGO, ILLINOIS