in 365, by far the greatest relative difference produced in the atomic weight of an element. The atomic weights were obtained by determining in quartz flasks the ratio of the weights of highly purified silver to extremely pure silver chloride. The method involved no transfer of silver or silver chloride from one vessel to another, since in each determination all of the significant operations and all of the weighings were carried out with one quartz flask.

2. The above results refer to the ninth cut of 2. In order to compare the relative efficiencies of the different sets of apparatus used, three determinations were made by the density method of Harkins and Hayes after the sixth cut of 2. These showed atomic-weight lowerings of 0.036, 0.034 and 0.029 for the three independently obtained samples.

CHICAGO, ILLINOIS

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

INTERFACIAL TENSION AND EMULSIFICATION. I. THE EFFECTS OF BASES, SALTS, AND ACIDS UPON THE INTERFACIAL TENSION BETWEEN AQUEOUS SODIUM OLEATE SOLUTIONS AND BENZENE. II. EXTREMELY SMALL INTERFACIAL TENSIONS PRODUCED BY SOLUTES[1]

BY WILLIAM D. HARKINS AND HENRIETTA ZOLLMAN

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Introduction

It has long been recognized that stable emulsions of oils in water form readily if solutes which greatly lower the interfacial tension are present.[2] According to Gibbs[3] such solutes are highly adsorbed at the interface, and the importance of the films thus formed in stabilizing emulsions has been pointed out by Bancroft.[4] It is obvious that the interfacial tension and the extent to which interfacial films are formed are not entirely independent variables, so a comprehensive theory of emulsions should take account of these two factors. The interfacial tension is affected by the electrical charges at the interface, and these electrical charges undoubtedly play an important role in emulsification.

Attainment of Equilibrium

Measurements were made of the interfacial tension at the phase boundary between benzene and aqueous solutions of sodium oleate alone or plus

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[1] An abstract of this paper was presented to the Second Annual Colloid Symposium, June, 1924. "Colloid Symposium Monograph," **2**, 172 (paragraph 9).

[2] Quincke, *Pogg. Ann.*, **139**, 1 (1870); *Wied. Ann.*, **35**, 571 (1888).

[3] Gibbs, "Scientific Papers," Longmans & Co., Vol. **1**, **1906**.

[4] Bancroft, *J. Phys. Chem.*, **17**, 514 (1913); **19**, **275** (1915).

various solutes. Equilibrium was attained by rotating gently the bottles containing the two phases around their longitudinal axes. Table I and Fig. 1 illustrate the variation of interfacial tension which may be found if a soap solution is dropped into benzene without rotation or mixing. The aqueous solution was 0.001 *N* with respect to sodium oleate (NaOl) and 0.005 *N* with respect to sodium hydroxide. The points in the figure represent the mean interfacial tension for each 10 drops, dropped at the rate of about one drop per minute. The tension decreases rapidly with the number of drops both immediately after the two phases have been put in contact (first day) and on the second day, ***but on the second day all of the interfacial tensions are much higher.*** In this experiment sodium hydroxide was used to repress the hydrolysis of the soap. If it is not used the hydrolysis is much greater and the benzene phase extracts much more of the oleic acid, so the aqueous solution becomes more basic, which serves to lower the interfacial tension.

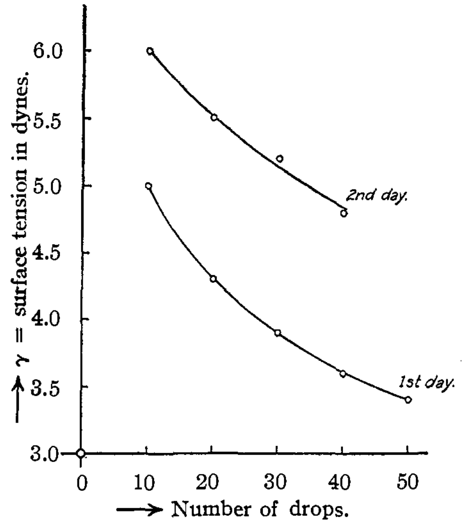

Fig. 1.—Change in interfacial tension as solutions approach equilibrium. Interface: NaOl = 0.001 *N*, NaOH = 0.005 *N* against benzene. Not rotated.

TABLE I

CHANGE OF INTERFACIAL TENSION AS SOLUTIONS REACH EQUILIBRIUM

Interface: 0.001 *N* sodium oleate, 0.005 *N* sodium hydroxide against benzene. Not rotated.

Drops	1st 10	2nd 10	3rd 10	4th 10	5th 10
γ	5.0	4.3	3.9	3.6	3.4
γ after standing 24 hours	6.0	5.5	5.2	4.8	...

Effect of Time of Adsorption

It has long been known that the "dynamic" and "static" surface tensions of certain solutions are different, and with surface active substances the latter is lower. This is especially marked in the case of highly dilute solutions and is due to the fact that if a tightly packed monomolecular, or a thicker film is formed the amount of material in the film is so large that it materially lowers the concentration of the solution for some distance. Harkins and King[5] have shown that this time is sufficiently large so that the surface tension of a 0.001 *N* nonylic acid solution lowers mod-

[5] Harkins and King, *Kansas State Agr. Coll. Publications*, **1920.**

erately rapidly for the first half hour. Du Nouy finds that the surface tension of a sodium oleate solution of about 0.003 N concentration is lowered 30 dynes in two hours, and that the lowering follows the equation $\gamma = \gamma_0 e^{-kt^{1/2}}$.

Fig. 2 illustrates the effect of time on the interfacial tension of the phase boundary 0.001 N aqueous sodium oleate in benzene. The first four points in the lower part of the figure should be on a straight line if this equation holds. However, in the upper part of the figure it is seen that the surface tension is almost linear when plotted against the first power of the time, so it would be simple to obtain other equations which would fit as well.

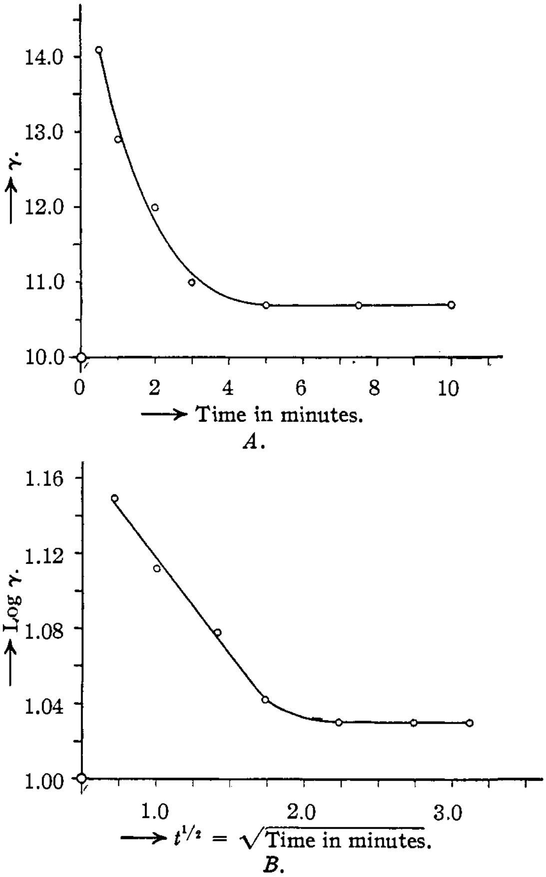

Fig. 2.—Decrease of interfacial tension with time drop hangs before falling. Interface: NaOl = 0.001 N against benzene. Rotated.

In the case of some of the solutions, especially those which are very dilute, *the surface tension passes through a minimum when plotted against the time.*

Wilson and Ries observed this effect in solutions of saponin and sodium palmitate.[6]

In order to permit diffusion into the interface the following amounts of time were allowed for the drops to remain almost fully formed before they are allowed to fall from the tip.

Concn. of NaOl soln., N	0.0001	0.00025	0.0005	0.001	0.0025	0.005	0.01 or more
Time, min.	30.	15.	10.	5.	3.	2.	1.

Interfacial Tensions under Non-Equilibrium Conditions

Table II and Figs. 3 and 4 present results on the interfacial tension of various solutions containing sodium oleate against benzene, which were obtained as quickly as possible after placing the two phases together, and without rotating the solutions. Strange as it may seem, quite definite values were obtained in this way.

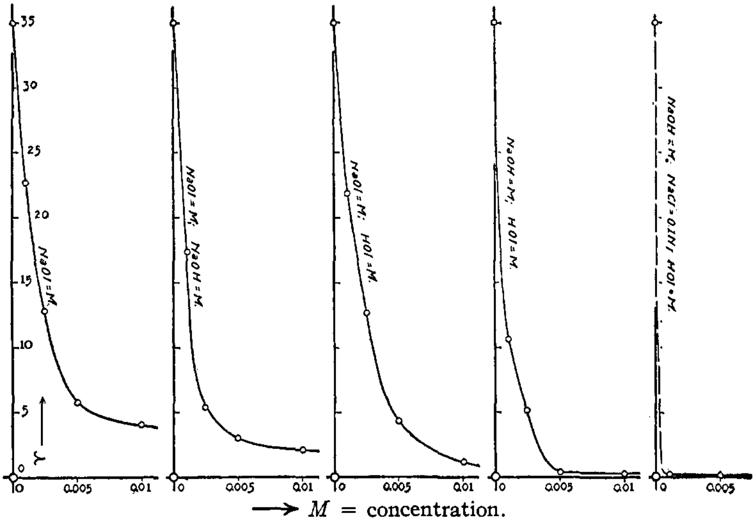

Fig. 3.—Interfacial tensions of non-rotated solutions.

TABLE II

THE INTERFACIAL TENSIONS OF "NON-ROTATED" SOLUTIONS AGAINST BENZENE OR BENZENE SOLUTIONS OF OLEIC ACID

M = concn.	Interfacial tension, dynes/cm. NaOl = M	NaOl = M NaOH = M	NaOl = M HOl = M	NaOH = M HOl = M	NaOH = M NaCl = 0.1 N HOl = M	NaOl = 0.001 NaOH = M	NaOl = 0.001 HOl = M
0.0000	35.0	35.0	35.0	35.0	..	22.7	22.7
.001	22.7	17.4	21.9	13.1	0.19	17.4	21.8
.0025	12.8	5.41	12.8	5.08	..	8.6	19.1
.005	5.83	2.96	4.27	0.38	..	4.79	17.3
.01	4.01	2.10	1.12	0.31	.09	2.52	15.7
.1	2.64	1.23	0.17	0.16	.04	1.19	18.6

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[6] Wilson and Ries, "Colloid Symposium Monograph," **1**, 163 (1923).

The results are of considerable interest. The interfacial tension between water and benzene at 20° is 35.0 dynes per cm. This is lowered to 2.64 by 0.1 *N* sodium oleate alone (Fig. 3). If 0.1 *N* sodium hydroxide is also present this value is lowered by more than 50%; with 0.1 *N* oleic acid in the benzene, by nearly 95% to 0.17, and with both 0.1 *N* sodium hydroxide and sodium chloride in the aqueous phase and 0.1 *N* oleic acid in the benzene, the interfacial tension falls to 0.04 dyne per cm., or to only about one thousandth of the initial interfacial tension.

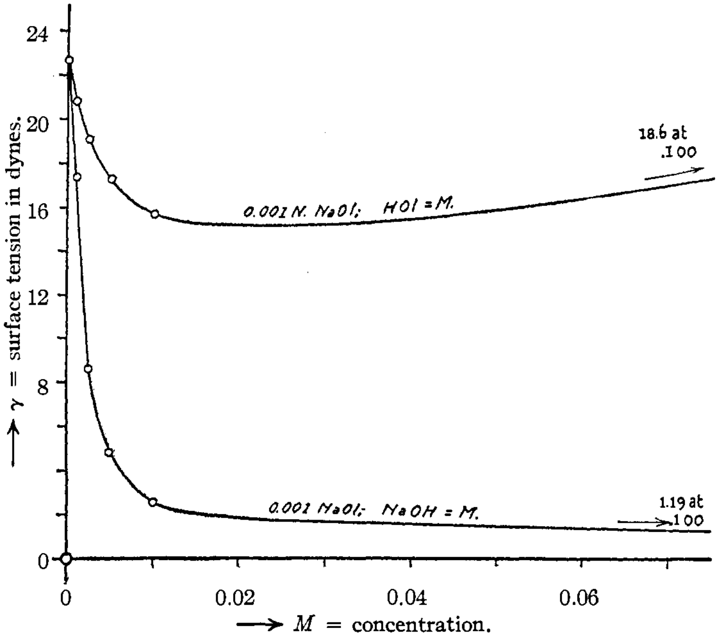


Fig. 4.—Lowering of interfacial tension by acid and base. Not rotated.

Fig. 4 and Cols. 7 and 8 of Table II show that with very dilute sodium oleate (0.001 *N*), which does not produce by itself great lowering of the tension (only to 22.7), the lowering is made extremely large (to 1.19) if 0.1 *N* sodium hydroxide is also present. On the other hand, the presence of oleic acid in the benzene intensifies only slightly the lowering produced by sodium oleate alone.

Interfacial Tensions under Equilibrium Conditions

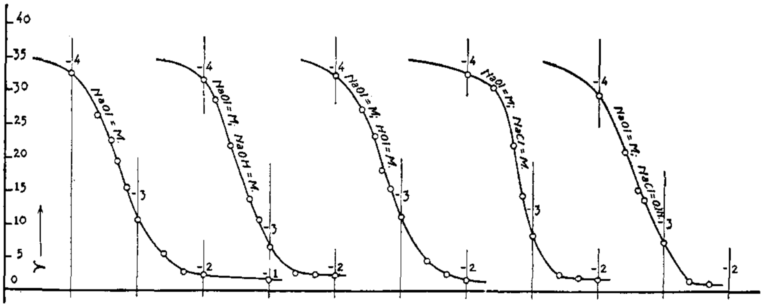
Table III and Fig. 5 exhibit the interfacial tensions found under equilibrium conditions. It is obvious that it is impossible to test here the interesting case of oleic acid in the benzene phase and sodium hydroxide in the aqueous phase. Also, the attainment of equilibrium resulted in the emulsification of the benzene in the aqueous phase of the 0.1 *N* sodium oleate solutions when either sodium hydroxide, oleic acid or sodium chloride

TABLE III

THE INTERFACIAL TENSIONS OF "ROTATED" SOLUTIONS AGAINST BENZENE OR BENZENE SOLUTIONS OF OLEIC ACID

	Interfacial tension, dynes/cm.				
M = concn.	NaOl = M	NaOl = M NaOH = M	NaOl = M HOl = M	NaOl = M NaCl = M	NaOl = M NaCl = 0.1
0.0000	35.0				
.0001	32.6	31.7	32.2	32.4	29.4
.00015	...	28.7	...	...	...
.00025	26.2	21.9	27.2	30.4	21.0
.0004	22.6	...	23.1	...	15.2
.0005	19.5	13.9	18.1	22.0	13.9
.0007	15.5	10.8	15.4	14.5	...
.001	10.8	6.6	11.1	8.4	7.5
.0025	5.37	2.61	4.50	2.28	1.43
.005	2.76	2.39	2.14	2.04	0.98
.01	2.29	2.16	1.57	1.86	Emulsified
.1	1.46	Emulsified	Emulsified	Emulsified	Emulsified

was present in addition. The interfacial tension of sodium oleate alone at 0.1 N concentration is 45% lower under equilibrium than under the non-equilibrium initial condition.



⟶ Log M = log of concentration.

Fig. 5.—Interfacial tensions of rotated solutions.

On the whole, the general order of the effects under the two conditions is the same except that with sodium oleate the lowering effect of sodium chloride is slight, while with sodium hydroxide and oleic acid in different phases it is very large. Thus in the latter case 0.1 N sodium chloride reduces the value found for 0.001 N sodium hydroxide and oleic acid from 13.1 to 0.19, or to one sixty-ninth of the former value.

Effects of Addition of Base or Acid

The Effect of Sodium Hydroxide upon the Interfacial Tension.—Sodium hydroxide of any of the concentrations used lowers the interfacial tension of a benzene-aqueous sodium oleate phase boundary. In accordance with this an emulsion of benzene is much more easily produced, that is by less rolling or shaking, when the base is present than when it is absent. The effect is specially noticeable when the solutions have not been rotated, and have been kept as still as possible. Even under these conditions an emulsion often forms. The lowering of the interfacial tension is most marked at concentrations of the soap at which the interface is *saturated,* that is, when with the soap in the absence of the base the tension is independent of the concentration.

An attempt was made to measure the interfacial tensions of solutions containing 0.1 *N* sodium hydroxide but only very small amounts of sodium oleate (from 0.0001 *N* to 0.001 *N*), but this was unsuccessful on account of their peculiar behavior. The drop is at first large, but decreases in size very rapidly with time, until it has practically vanished. If a drop is formed and the apparatus arranged so that no more liquid may run into it, the drop falls in a short time, and then a second and a third form and fall from the liquid left hanging on the tip after the first one has fallen. *There is a decrease of 30 dynes or more in about a quarter of an hour in the interfacial tension between these liquids and benzene.*

The Effect of Acid on the Sodium Oleate Solution—Benzene Interface under Non-equilibrium Conditions.—As is the case with sodium hydroxide, oleic acid (in the benzene phase) causes a lowering in interfacial tension. However, the presence of oleic acid at 0.01 *N* concentration lowers the interfacial tension of 0.001 *N* sodium oleate (not rotated) only 7 dynes while the same concentration of sodium hydroxide lowers it 20 dynes. Also, the interface 0.001 *N* sodium oleate, water-0.1 *N* oleic acid, benzene has a somewhat higher tension than 0.001 *N* sodium oleate, water-0.01 *N* oleic acid, benzene. The lowering caused by the presence of oleic acid in the benzene phase is far more evident at high concentrations of sodium oleate than at low. From a comparison of Fig. 3a with 3c, it is seen that the interfacial tensions of solutions of sodium oleate against benzene, and against oleic acid of the same concentrations in benzene are almost identical for concentrations less than 0.0025 *N*, but for solutions more concentrated than this, the acid causes a considerable lowering.

The same relation is seen in the case of the rotated solutions. Figs. 5a and 5c are almost identical until 0.005 *N* is reached, and then the one for the acid falls below the other. In fact, it was impossible to measure the equilibrium value of the interface 0.1 *N* sodium oleate, water-0.1 *N* oleic acid, benzene because the solutions emulsified so easily; aqueous 0.1 *N* sodium oleate emulsifies benzene also, but not nearly as readily.

These moderately concentrated solutions of sodium oleate against oleic acid solutions give the smallest interfacial tensions that we have been able to obtain for *equilibrium* conditions. If the interfacial tension is less than about one dyne, emulsification takes place readily and the two layers cannot be separated.

The Effect of Salts on the Interface Sodium Oleate Solution-Benzene.—If a sodium chloride solution of a moderate concentration is added to a sodium oleate solution, a cloudiness appears, which may amount almost to a curd at times. On dilution, the curd dissolves, but the solution remains milky. Sodium hydroxide produces only a slight cloudiness. Potassium iodide has the same effect as sodium chloride. Calcium chloride, even in rather dilute solution, produces insoluble calcium oleate. It is, therefore, impossible to study the effect of calcium chloride alone on the interfacial tension of sodium oleate solutions.

Sodium chloride (0.1 N) lowers the interfacial tension of 0.001 N sodium oleate (non-rotated) from 22.7 to 17.4 dynes, and 0.1 N potassium iodide lowers it to 16.6 dynes. At equilibrium these values become 7.5 for 0.1 N sodium chloride and 4.0 dynes for 0.1 N potassium iodide, as contrasted with 10.8 for sodium oleate alone.

Purification of Reagents

The oleic acid used was prepared by extracting the lead salts of U.S.P. oleic acid with ether, liberating the acid with hydrogen chloride, and distilling the ether. The soap was then prepared by dissolving a slight excess of sodium hydroxide in absolute alcohol, filtering to remove possible carbonate, then adding the acid and refluxing for an hour. The hot solution was filtered again through a hot water funnel and then the soap allowed to crystallize. This was easily drained, washed with absolute alcohol and ether and dried. A 0.001 N solution of this soap in water gave the same interfacial tension against benzene that is reported by Harkins, Davies and Clark,[7] who prepared their acid in a quite different manner. The benzene used was Kahlbaum's, "free from thiophene, recrystallized." This was recrystallized again and was used for all except some of the concentrated solutions, where a benzene containing thiophene was used. The two were checked against each other in several cases, and no difference could be found which could be ascribed to the presence of thiophene. Sodium hydroxide solutions were made up by washing away about two-thirds of the sticks with water, dissolving the remainder in conductivity water and titrating against a standard acid, using phenolphthalein. They were, therefore, not entirely free from carbonate. The sodium chloride solutions were made from a fresh bottle of Kahlbaum's fused salt, "for analysis." Conductivity water was used for the preparation of all solutions. As some change in the interfacial tension of these solutions was found on standing, they were measured the day on which they were prepared. The temperature was in all cases (except for those with a very small interfacial tension) 20°.

Tips for Dropping

The tips were similar to those described by Harkins and Humphery[8] in their paper on the water-benzene interface. The four tips used had radii of 0.4745, 0.2745, 0.1089, and 0.04035 cm., respectively. The smallest tip was made by drawing out a piece of Pyrex capillary tubing until its outside diameter had decreased to less than 1 mm. It was cut off where the diameter had this value. The cut end was then embedded in a block of Wood's metal whose face was perpendicular to the direction of the tube. The capillary was filled with beeswax and the Wood's metal and the tube were ground off

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[7] Harkins, Davies and Clark, THIS JOURNAL, **39**, 541 (1917).

[8] Harkins and Humphery, *ibid.*, **38**, 228 (1916).

together. This gave a perfectly sharp edge of glass after the Wood's metal was melted. The mean radius was that given above. The different diameters varied by a maximum of 4%. All of the other tips were of a circular cross section.

Extremely Small Interfacial Tensions between Benzene and Aqueous Solutions

Measurements were made with this small tip of the interfacial tensions of sodium hydroxide in water against oleic acid in benzene. The tensions were found to be extremely small: 0.38 dyne for 0.005 *N*, 0.31 for 0.01 *N*, and 0.6 for 0.1 *N* solutions in both phases.

Table IV presents results on the interfacial tension between water and an oil, with sodium hydroxide in the aqueous, and oleic acid in the nonaqueous phase. The data are taken from an unpublished paper by Harkins and Thomas, and put into quantitative form the qualitative observations of Clowes.[9] It may be noted that for any of the concentrations listed, an amount of calcium chloride equal to a hundredth of the sodium chloride present, more than overcomes the extremely great lowering of interfacial tension produced by the latter. The effect is of considerable interest, since sea urchins will live in distilled water, but not in water which contains a moderate concentration of sodium chloride alone. However, if the water also contains calcium chloride of one eightieth the concentration of the sodium chloride, the sea urchins thrive much better than in water alone.

Table IV

Effects of Salts upon the Interfacial Tension between Water and Oil with a Film of Sodium Oleate Produced by Chemical Action

Base or salt added to aqueous phase			Surface tension in dynes/sq. cm.	
NaOH, *N*	NaCl, *N*	$CaCl_2$, *N*	Olive oil	Paraffin oil
...	..	....	....	40.6
			[With 0.001 *N* oleic acid in oil.]	
...	..	....	24.11	31.05
0.001	..	....	7.3	7.2
.001	0.15	....	0.002	0.00
.001	..	0.0015	9.88	9.65
.001	0.15	.0015	6.88	7.48
.001	.30	.0030	6.36	7.12
.001	.45	.45	6.70	7.36
.001	.60	.0060	7.31	8.20

The lowest interfacial tension found in the work of the writers is 0.04 dyne per cm. at the interface between benzene containing 0.1 *N* oleic acid and an aqueous solution 0.1 *N* with respect to both sodium chloride and sodium hydroxide. In this case a solid film forms, and this causes the drops to hang longer than usual, but the minute value of the tension indicates that the tensile strength of this film is very low.

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[9] Clowes, *J. Phys. Chem.*, **20**, 408 (1916).

Data

The data from which the interfacial tensions given in this paper are calculated are presented in Tables V and VI. The inclusion of these data is essential, since it is possible that more accurate values of the function ϕ in the equation $\gamma = mg\phi/2\pi r$ may be determined in the future, although the values used, those of Harkins and Brown, are presumably accurate to 0.1%.

TABLE V

DATA FOR PHASES OF WATER AND BENZENE BEFORE MIXING, OR UNDER INITIAL NON-EQUILIBRIUM CONDITIONS

Sodium oleate and sodium chloride are put in the aqueous phase, oleic acid in the benzene. Temperature = 20°.

Concn., = *M*	Volume of one drop, cc.	Density of aqueous phase	Density of benzene phase	Radius of tip, cm.
Solute, NaOl = *M*				
0.0001	0.328	0.9982	0.8788	0.2745
.00025	.260	.9982	.8788	.2745
.0004	.226	.9982	.8788	.2745
.0005	.189	.9982	.8788	.2745
.0007	.147	.9982	.8788	.2745
.001	.0995	.9983	.8788	.2745
.0025	.0215	.9983	.8788	.1089
.005	.0245	.9983	.8788	.2745
.01	.00858	.9984	.8788	.1089
.1	.00527	.9989	.8788	.1089
Solute, NaOl = *M*. NaOH = *M*				
0.0001	0.313	0.9982	0.8788	0.2745
.00015	.286	.9982	.8788	.2745
.00025	.214	.9982	.8788	.2745
.0005	.131	.9982	.8788	.2745
.0007	.0993	.9982	.8788	.2745
.001	.0588	.9983	.8788	.2745
.0025	.00996	.9985	.8788	.1089
.005	.00895	.9986	.8788	.1089
.01	.00803	.9987	.8788	.1089
.1	Emulsified			
Solute, NaOl = *M*. HOl = *M*				
0.0001	0.513	0.9982	0.8788	0.2745
.00025	.271	.9982	.8788	.2745
.0004	.227	.9982	.8788	.2745
.0005	.175	.9982	.8788	.2745
.0007	.147	.9982	.8788	.2745
.001	.102	.9983	.8788	.2745
.0025	.0178	.9983	.8788	.1089
.005	.00795	.9983	.8788	.1089
.01	.00572	.9984	.8788	.1089
.1	Emulsified			
Solute, NaOl = *M*. NaCl = *M*				
0.0001	0.326	0.9982	0.8788	0.2745
.00025	.304	.9982	.8788	.2745
.0005	.215	.9982	.8788	.2745
.0007	.137	.9982	.8788	.2745
.001	.0348	.9983	.8788	.1089
.0025	.00851	.9984	.8788	.1089
.005	.00756	.9985	.8788	.1089
.01	.00682	.9987	.8788	.1089
.1	Emulsified			
Solute, NaOl = *M*. NaCl = 0.1				
0.0001	0.290	0.9997	0.8788	0.2745
.00025	.201	1.0000	.8788	.2745
.0004	.142	1.0002	.8788	.2745
.0005	.129	1.0004	.8788	.2745
.001	.0301	1.0008	.8788	.1089
.0025	.00507	1.0011	.8788	.1089
.005	.00338	1.0014	.8788	.1089
.01	Emulsified			
.1	Emulsified			

Adsorption of Sodium Oleate at the Interface

Gibbs' equation for adsorption may be put into a form suitable for use with electrolytes. If sodium oleate alone were present, without hydrolysis

TABLE VI

DATA FOR PHASES OF WATER AND BENZENE (EQUAL VOLUMES) UNDER EQUILIBRIUM CONDITIONS

Concentrations of solutes give the normality for the solute in one phase only. Temperature = 20°.

Concn. = *M*	Volume of one drop, cc.	Density of aqueous phase	Density of benzene phase	Radius of tip, cm.
Solute, NaOl = 0.001. NaOH = *M*				
0.001	0.167	0.9982	0.8788	0.2745
.0025	.0355	.9985	.8788	.1089
	.0427			.2745
.005		.9985	.8788	
	.0192			.1089
.01	.0095	.9988	.8788	.1089
.1	.00391	1.0029	.8788	.1089
Solute, NaOl = 0.001. HOl = *M*				
0.001	0.214	0.9983	0.8788	0.2745
.0025	.185	.9983	.8788	.2745
.005	.166	.9983	.8788	.2745
.01	.149	.9983	.8788	.2745
.1	.179	.9983	.8788	.2745
Solute, NaOl = *M*				
0.001	0.222	0.9983	0.8788	0.2745
.0025	.120	.9983	.8788	.2745
.005	.0516	.9983	.8788	.2745
.01	.0157	.9984	.8788	.1089
.1	.100	.9989	.8788	.1089
Solute, NaOl = *M*. NaOH = *M*				
0.001	0.167	0.9982	0.8788	0.2745
.0025	.0220	.9985	.8788	.1089
.005	.0113	.9986	.8788	.1089
.01	.00803	.9987	.8788	.1089
.1	.00182	1.0030	.8788	.04035
Solute, NaOH = *M*. HOl = *M*				
0.001	0.123	0.9983	0.8788	0.2745
.0025	.0202	.9985	.8788	.1089
.005	.000536	.9985	.8788	.04035
.01	.000426	.9989	.8788	.04035
.1	.000219	1.0029	.8788	.04035
Solute, NaOl = *M*. HOl = *M*				
0.001	0.214	0.9983	0.8788	0.2745
.0025	.119	.9983	.8788	.2745
.005	.0377	.9983	.8788	.2745
.01	.00400	.9984	.8788	.1089
.1	.000225	.9989	.8788	.04035
Solute, NaOH = *M*. NaCl = 0.1. HOl = *M*				
0.001	0.000257	1.0000	0.8788	0.04035
	.000103			.04035
.01	.0000597	1.0014	.8788	.0194
	.0000565			.04035
.1	.0000173	1.0058	.8788	.0194

and without colloidal material, the equation could be used in the form: $\mu = -[\alpha c/2RT].[\partial\gamma/\partial(\alpha c)]$, where α is the activity coefficient of the salt.

If calculated in this way it is found that the area in the monomolecular film per molecule of sodium oleate is 47×10^{-16} (47 Å.) if sodium oleate alone is present and, using the requisite more complicated equation, 40 Å. if sodium chloride of the same concentration is also present. The corresponding area for butyric acid in the monomolecular film between water and benzene is 36 Å. while for oleic acid on water it is 20 Å. The hydrolysis and the presence of colloidal material in the solutions of sodium oleate make the results for this substance less close to the actual areas than for such acids as butyric acid. However, the amount of colloidal material in these dilute solutions is small.

Summary

1. The interfacial tension between phases of water and benzene has been determined in the presence of different concentrations of sodium oleate alone, or with sodium hydroxide, sodium chloride or oleic acid in addition. The determinations were made both under equilibrium, and

under non-equilibrium initial conditions. The interfacial tension between water and benzene is 35.0 dynes per cm. at 20°. If the aqueous phase is 0.1 *N* with respect to sodium hydroxide, and the benzene phase contains the same concentration of oleic acid, the interfacial tenison is reduced to $^1/_{219}$ of its former value. This suggests that the energy of chemical union between the base and the acid may be used directly to aid in the formation of the surface. If sodium chloride of 0.1 *N* concentration is also present in the aqueous phase, the tension is reduced to a thousandth of the former value or to 0.04 dyne per cm. This lowering is exceedingly remarkable. The lowering of interfacial tension produced by sodium oleate is increased by the addition of sodium hydroxide, or sodium chloride, and particularly by a mixture of the two, and also by oleic acid.

2. Under initial non-equilibrium conditions 0.001 *N* aqueous sodium oleate has an interfacial tension against benzene of 22.7. If 0.001 *N* sodium hydroxide is in the aqueous phase and oleic acid of the same concentration in the benzene, the value is only 13.1. If the aqueous phase is in addition 0.1 *N* with respect to sodium chloride the tension falls greatly, to 0.19. Addition of calcium chloride to the aqueous phase to the extent of one fiftieth of the amount of the sodium chloride, raises the tension to 11.1 dynes per cm. or nearly to the value found when neither salt is present. Thus the calcium chloride largely overcomes the effect of the sodium chloride even though it is fifty times more dilute.

3. A calculation of the area per molecule in the constant film of sodium oleate gives about 47 Å. when sodium oleate alone is present, but sodium chloride of the same concentration reduces the area to 40 Å.

4. It was observed that when the interfacial tension was below 10 dynes per cm. the benzene emulsified easily in the aqueous phase, while when below 1 *dyne it appeared to emulsify spontaneously. A later paper from* this Laboratory will show that extremely vigorous beating forms emulsions stable for years with systems in which the interfacial tension is about 10 dynes per cm.

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