in the very high *p*H ranges. A chlorine atom on the carbon next to the carboxyl affects the fungistatic properties of the acid, whereas the same substituent on the beta carbon atom has no effect. Constitutional factors are therefore of considerable significance on the biological effect of fatty acids.

Langmuir[2] pointed out that halogen substitution had an appreciable effect on the dissociation constant of a fatty acid. The theory[3] is rather widely held that the biological activity of an acid is dependent on the dissociation constant; that is, the less ionized the acid, the more powerful its biological effect. The relative fungistatic properties of acetic and monochloroacetic, and of propionic and α-chloropropionic acids, when compared with their respective dissociation constants are in agreement with this theory. In the case of propionic and β-chloropropionic acids, however, the fungistatic properties are not so closely related to the dissociation constants. Propionic acid has a dissociation constant of 1.33×10^{-5}, and β-chloropropionic acid 8.59×10^{-5},[2] but the two acids have essentially identical fungistatic properties.

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(2) Langmuir, *Chem. Rev.*, **6**, 465 (1929).

(3) (a) Tekelenburg, *Nederland. Tijdschr. Hyg. Microbiol. Serol.*, **2**, 176 (1927); (b) Bach, *Bull. sci. pharmacol.*, **39**, 7 (1932).

WARD BAKING COMPANY
NEW YORK, N. Y.
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The Preparation of Aurin Tricarboxylic Acid*

BY DUNCAN A. HOLADAY

Recent work in this Laboratory required the use of pure aurin tricarboxylic acid. Several methods of preparing this compound were tried, including those of Scherrer and Smith,[1] Heisig and Lauer,[2] and Caro.[3] A product satisfactory for use in the determination of aluminum was obtained by each of these methods, but in no instance did the product contain more than 70% aurin tricarboxylic acid based on the air-dried material. The content of dye was determined by titration with titanium trichloride solution.[4]

In the course of the work it was observed that the material prepared by Caro's method would undergo a further reaction on treatment with a second portion of the oxidizing mixture (sodium nitrite–sulfuric acid solution). A study of this reaction developed the following modification of Caro's procedure which has several advantages over previously described preparations and yields a product of high purity. The methods of Heisig and Lauer, and of Scherrer and Smith, require that the temperature be kept below 5°. In the following procedure the reaction is not highly exothermic, and therefore no rigid temperature control is necessary. Caro recommends a purification with sodium bisulfite, which is difficult to perform and in the author's hands does not yield a pure product. In the modified procedure no purification of the reaction product is necessary except the removal of inorganic salts.

Experimental Part

Five grams of finely powdered sodium nitrite was added slowly and with vigorous stirring to 36 cc. of sulfuric acid, avoiding evolution of oxides of nitrogen. To this solution an intimate mixture of 10 g. of methylene-disalicylic acid[5] and 5 g. of salicylic acid was added in small portions with vigorous stirring. After addition of all of the solid material, the mixture was allowed to stand for an hour with occasional stirring. It was then poured into a solution of 5 g. of sodium nitrite in 36 cc. of sulfuric acid, stirred, and allowed to stand overnight. The reaction mixture was added slowly to one liter of cold water, allowed to stand for an hour, and filtered on a Büchner funnel. The precipitate was suspended in one liter of warm water (50°) and filtered. This suspension and filtration was repeated, the free water removed by drawing air through the funnel, and drying was completed in a vacuum oven at 70°. The yield of dry product was 10.5 g. It titrated 97% aurin tricarboxylic acid.

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* Not copyrighted.

(1) Scherrer and Smith, Bureau of Standards Res. Paper RP1118.

(2) Heisig and Lauer, *Org. Syntheses*, **9**, 8 (1929).

(3) Caro, *Ber.*, **25**, 941 (1892).

(4) Evenson and Nagel, *J. Ind. Eng. Chem.*, *Anal. Ed.*, **3**, 167 (1931).

(5) Vanino, "Präparative Chemie," Vol. II, 1937, p. 585.

FOOD DIVISION
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Type III Surface Tension Curves with Minimum in Dilute Solution in Pure Hydrocarbons

BY M. E. L. MCBAIN AND L. H. PERRY

Many properties of colloid systems in water are usually explained in terms of free ions, so that it becomes interesting to examine non-ionizing solvents to see in how far similar behavior is to be found where free ions are almost or quite lacking. One very striking property of many colloidal electrolytes in water is that in very dilute solution they lower the surface tension to about one-third that of water. The surface tension is then at a minimum and thereupon rises to a flat maximum in slightly less dilution. Some non-electrolytic detergents likewise similarly lower the surface tension of water to an almost equal extent in very dilute solution, but it then remains constant on further concentration. The existence of these type III curves has been thoroughly established[1] and they are of special interest because the positive adsorption actually observed by a number of methods does not accord with the requirements of the Gibbs theorem as ordinarily applied to surface tension measurements.

Using hydrocarbons as solvents, we have found that type III curves with minima do actually occur in non-ionizing media. This is shown in Fig. 1 for pure lauryl sulfonic acid dissolved in (a) Nujol, (b) mineral oil, and, in Fig. 2, (c) hydrogenated tetraisobutylene. The results were obtained with the DuNoüy ring tensiometer at 27°, first sweeping the surface to remove contamination. These solutions unlike most of the others to be mentioned leave a film within the ring.

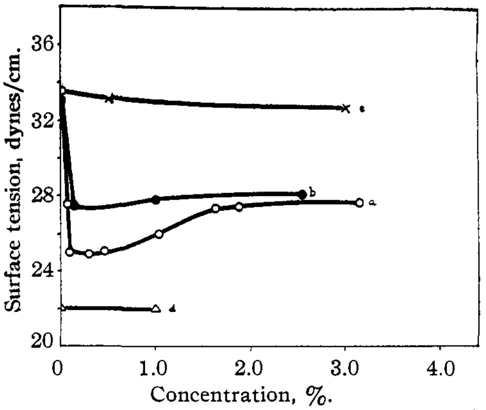

Fig. 1.—Surface tension curves in hydrocarbon solutions: Type III curves for lauryl sulfonic acid in (a) Nujol and (b) mineral oil; Type I curves for (d) lauryl sulfonic acid in n-heptane and (e) butyric acid in Nujol.

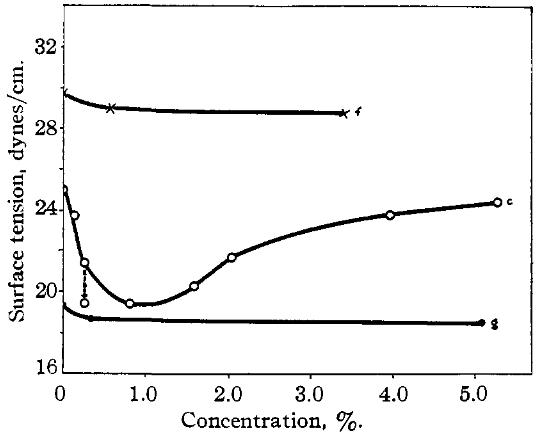

Fig. 2.—Surface tension curves in hydrocarbon solutions of lauryl sulfonic acid: Type I curves for (f) benzene and (g) iso-octane; Type III curve for (c) hydrogenated tetraisobutylene, showing with vertical dashed line the time effect in lowering of surface tension in very dilute solutions only.

On the other hand, lauryl sulfonic acid in solvents such as iso-octane, xylene, benzene and heptane scarcely lowers the surface tension. For iso-octane the value 19.3 dynes/cm. falls steadily with concentration to 18.5 in 5% solution (type I curve). For benzene the value 29.7 of the pure solvent becomes 28.7 for 3.4%, and for n-heptane the value of 22.2 is not changed when 1% of acid is added. These results are summarized in Table I.

TABLE I

SOLUTIONS OF $C_{12}H_{25}SO_3H$ IN HYDROCARBONS SHOWING SURFACE TENSION OF SOLVENT, σ_0; OF 1% SOLUTION, σ_1; AT MINIMUM, $\sigma_{\text{min.}}$, IF ANY; AND TYPE OF SURFACE TENSION CURVE

Solvent	σ_0	σ_1	$\sigma_{\text{min.}}$	Type
Nujol	33.5	25.9	24.8 at 0.2%	III
Mineral oil	33.0	27.8	27.4 at 0.18%	III
Benzene	29.7	29.3	none	I
Xylene	27.8	27.3	none	I
Tetraisobutylene	25.3	22.5	22.3 at 0.15%	III
Hydrogenated tetraisobutylene	25.0	19.5	19.4 at 0.8%	III
Decane	23.7	22.3	none (?)	I, III (?)
Heptane	22.2	22.2	none	...
Iso-octane	19.5	19.2	none	I

It is interesting to compare a surface tension curve in Nujol and in the similar mineral oil with that in water,[1] where the surface tension at the minimum is the same in all three cases, though that of water is as high as 72 dynes. The first thought, that solvents whose own surface tension is already as low as this minimum could not be lowered, is negatived by the result in hydrogenated tetraisobutylene, where it drops from 25 dynes to 19.4. However, the two intervening solvents, benzene and xylene, are not similarly affected by lauryl sulfonic acid. They are lowered but slightly and yield no minimum, showing that surface tension of the solvent is no sufficient guide.[2] Decane appears to be on the borderline among saturated hydrocarbons.

Polar compounds are not enough. For example, nonyl glucoside and another excellent detergent, a polyethylene oxide derivative, scarcely

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(1) McBain and Mills, Reports on Progress in Physics, **5**, 30 (1939); McBain, Vinograd and Wilson, THIS JOURNAL, **62**, 244 (1940); McBain and Wood, *Proc. Roy. Soc.*, **174A**, in press (1940); McBain, Mills and Ford, THIS JOURNAL, **62** in press (1940).

(2) Interesting contrasts between spreading behavior of hexane and benzene on mica surfaces have been reported by Bangham, Mosallam and Saweris, *Trans. Faraday Soc.*, **34**, 554 (1938); *Nature*, **140**, 237 (1937).

lower the surface tension of Nujol or hydrogenated tetraisobutylene. The measurements are hampered, however, by low solubility and a tendency to separate on cooling. In water, Woo's unpublished measurements show that they lower the surface tension from 72 to 31 dynes in extreme dilution, namely, 0.02 and 0.2% solutions, respectively, thereafter remaining constant up to 1% solution.

The sulfated sodium naphthenic or petroleum soaps supplied by the Sherwood Petroleum Company are oil-soluble, not water-soluble. They actually raise the surface tension of *n*-hexane from the value 20.2 to 20.4 or 20.5 for 10% solution and to 22.3 for 50% solution, thus giving a type II curve.

A number of especially interesting solutes of different types could not be tested on account of their insolubility, but a non-electrolytic detergent showed no appreciable lowering in Nujol although 14 and 24% solutions gave the small lowerings of 0.5 and 2.0 dynes. Butyric acid likewise is ineffective, the lowering being 0.5, 0.9 and 2.0 dynes for 1, 9 and 20% solutions, respectively. Lauric acid in 3% solution gave the distinctly greater lowering of 2 dynes. Triethanolamine oleate in 0.5 and 9% gave a lowering of 1 dyne and 2 dynes; thymotic acid in 1% solution 0.8 dynes; and stearic acid gave 1 dyne lowering for 0.7%. Calcium and zinc stearates have practically no effect.

It is evident that appreciable lowering and the production of a type III curve in these hydrocarbons require such a degree of polarity that the solute forms a strong electrolyte or colloidal electrolyte in water.

The only explanation to account for the minimum found in a type III curve is that put forward by McBain[3] based upon the electrical double layer. Now in the present non-ionizing solvents this would have to be a condensed Helmholtz double layer of the classical type instead of the partly diffuse type existing in water. However, the Helmholtz double layer is adequate for explaining lowering of surface or interfacial tension.

These novel observations evidently should suggest many other approaches and experiments to investigators in this field and are significant as a guide to other phenomena in hydrocarbon systems.

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[3] McBain, Ford and Wilson, *Kolloid. Z.*, **78**, 1 (1937).

Alkanolamines. VIII. Reaction of Ethanolamines on *p*-Nitrobenzoic Acid

BY M. MELTSNER, DANIEL GREENFIELD AND HARRY ROSENZWEIG

In some of the previous papers of this series[1,2,3,4] it was shown that alkanolamines, but not their salts, may reduce an aromatic nitro group and that the unreduced and reduced compounds may form addition compounds with the alkanolamines. This is now confirmed by the following experiment on the action of ethanolamines on *p*-nitrobenzoic acid.

Experiment I.—One mole of ethanolamine and one mole of *p*-nitrobenzoic acid were heated at 100° for four hours. The brown solid residue, after extraction with ether and chloroform, was crystallized from alcohol. A white compound of m. p. 168° was obtained. An ether extraction of this substance from dilute hydrochloric acid yielded *p*-nitrobenzoic acid while the hydrochloric acid layer on evaporation gave a white solid, m. p. 82°, corresponding to ethanolamine hydrochloride. The white compound was therefore an addition product, $NO_2C_6H_4COOH\cdot NH_2CH_2CH_2OH$.

Similarly diethanolamine yielded $NO_2C_6H_4COOH\cdot NH(CH_2CH_2OH)_2$, m. p. 138°, and triethanolamine yielded $NO_2C_6H_4COOH\cdot N(CH_2CH_2OH)_3$, m. p. 116°.

Experiment II.—One mole of ethanolamine was refluxed with one mole of *p*-nitrobenzoic acid in an oil-bath for two hours. The reaction mixture was treated several times with cold water and filtered. The filtrate was evaporated to dryness on the water-bath and the residue extracted with alcohol. Evaporation of the alcohol gave a solid identified as *p*-aminobenzoic acid by its positive test for the amino group, its melting point (186°) and the melting point of the dinitrobenzoate (195°). The dry residue, insoluble in alcohol, was recrystallized from hot water and gave $NO_2C_6H_4COOH\cdot NH_2CH_2CH_2OH$.

The residue, insoluble in cold water, was extracted with chloroform to isolate some more *p*-aminobenzoic acid and then recrystallized from hot water. There was obtained in large amounts a pale yellow compound, m. p. 130°, which was identified as the addition product of two moles of ethanolamine and one mole of azoxybenzoic acid: N calcd., 13.72; found, 13.64. The compound can be reduced to yield *p*-aminobenzoic acid. Hydrolysis of the compound with alkali gave *p*,*p'*-azoxybenzoic acid which was identified by means of its ethyl ester. Hydrolysis of the compound with hydrochloric acid yielded monoethanolamine hydrochloride.

Experiment III.—Four moles of diethanolamine and one mole of *p*-nitrobenzoic acid were heated for two hours at 180°. The reaction mixture was washed with chloroform, extracted with hot water and filtered. On cooling, yellow crystals are obtained and identified as *p*-aminobenzoic acid.

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[1] Meltsner, *et al.*, THIS JOURNAL, **57**, 2554 (1935).

[2] Kremer, *ibid.*, **59**, 1681 (1937).

[3] Kremer and Kress, *ibid.*, **60**, 1031 (1938).

[4] Meltsner, *et al.*, *ibid.*, **60**, 1236 (1938).