Qualitative evidence has been obtained in the course of the isolation and purification of 2-undecenal of the presence of the decomposition mixture of analogs and homologs of this aldehyde. Aldehydes of the type represented by 2-undecenal readily undergo oxidation, reduction, and isomerization thus making it possible to account for many of the end products which have been qualitatively and quantitatively identified in various types of oxidizing fat systems.

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The Hydrolysis of Soap Solutions. II. The Solubilities of Higher Fatty Acids

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IN studying the hydrolysis of soap systems, some investigators state that the fatty acid formed is in excess of its saturation value in certain concentrations; others state that it is always less. The first step is to determine what the saturation values actually are.

In general, there have been few available data for the solubilities of the higher fatty acids though some isolated values are given in the literature. In 1942 Ralston and Hoerr (1) determined the solubilities of the normal saturated fatty acids from C_6-C_{18} in water and in a number of organic solvents at the temperatures 0, 20, 30, 45, and 60°C. Saturated solutions of the acids made with conductivity water were titrated with barium hydroxide, using phenolphthalein as indicator. The authors apparently made no correction for carbon dioxide, neglect of which would lead to high results.

Experimental

The solubilities of capric, lauric, myristic, palmitic, and stearic acids in water were determined at 25° and 50°C., using a conductivity method. Saturated solutions of the pure Kahlbaum acids (except Eastman's capric and some Lepovsky's especially prepared myristic) were prepared by adding crystals of the acids to conductivity water in 100 ml. or 250 ml. Jena glass bottles. They were heated on a water bath to about 60-70°C. for half an hour or longer, with intermittent shaking, then allowed to stand, usually 24 hours or longer. Crystals of capric and lauric acids separated on cooling, leaving the solutions perfectly clear. Excess myristic, palmitic, and stearic acids in finely divided form often remained suspended in the solutions, making them appear cloudy.

The conductivity of these solutions was determined by use of a Grinnell Jones-Dyke type of bridge supplied by Leeds and Northrup, with an oil thermostat at 25°C. ± 0.01° and 50°C. ± 0.05°. Bottles of solution were allowed to come to the desired temperature in the thermostat, then the conductivity cell was filled. The reading was taken after about 15 minutes. The resistance did not remain constant but changed almost continuously even over a period of several hours. The values usually, but not always, increased with time, probably due to sorption of the dissolved acid. The cell was rinsed with acetone to remove any sorbed acid before refilling it for another trial.

The resistance given for the acids in Table I is the average of from 5 to 10 measurements, rounded off to two or three significant figures. Deviation from the mean ranged from 0.7% in the case of capric and lauric acids, to about 7% in the case of stearic and palmitic acids at 25°C. where the solubility is very low.

The equivalent conductivities for the acids at 25° and 50° were obtained from the values of Bunbury and Martin(2) and of Gonick (3). Some of the mobilities were known at 25° and at 90°C., and the values at 50° were calculated by linear interpolation. The equivalent conductivities used at 25 and at 50°C. were the following:

	25°	50°
Hydrogen ion	349.8	478
Capric acid	374.7	519.2
Lauric acid	373.3	517.4
Myristic acid	372.3	516
Palmitic acid	371.4	514.7
Stearic acid	370.7	513.6

The method of calculation was that used by McBain and Taylor (4). The following calculation for the solubility of palmitic acid at 50°C. illustrates the method used for all. The cell constant was 0.02895. The specific conductivity of water at 50° was 1.47×10^{-6} (at 25°, it was 0.72×10^{-6}), and that of the saturated palmitic acid solution at 50°C. was $\frac{0.02895}{13,200} = 2.19 \times 10^{-6}$ mhos. The conductivity of conductivity water is assumed to be due to the H^+ and HCO_3^- from dissolved carbon dioxide. Therefore the dissolved palmitic acid slightly increased the H^+ concentration and decreased the HCO_3^- concentration. The difference between the increased hydrogen ion concentration, C_{H^+}, and the decreased HCO_3^- concentration, $C_{HCO_3^-}$ would be equal to the concentration of the free palmitate ion, C_{P^-}. In the above measurements the conductivity of palmitic acid is $\frac{2.19}{1.47}$ times that of water. If V_1 is the volume in liters containing one mole of acid completely dissociated, and Λ is the equivalent

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conductivity, then $\Lambda \times \frac{1}{V_{cc}}$ = specific conductivity, and $C_{H^+} = \frac{1}{V_1}$.

$$C_{H^+} = \frac{2.19 \times 10^{-6}}{514.7} \times 10^3 = 4.26 \times 10^{-6} \text{ moles per liter}$$

$$C_{P^-} = \left(\frac{2.19}{1.47} - \frac{1.47}{2.19}\right) \frac{1.47 \times 10^{-6}}{514.7} \times 10^3 = 2.35 \times 10^{-6} \text{ M.}$$

In pure water $C_{H^+} = C_{P^-} = \sqrt{4.26 \times 2.35 \times 10^{-12}} = 3.16 \times 10^{-6}$ M. From the ionization equilibrium of the acid we get $\frac{\alpha^2 s}{1-\alpha} = K$, where α is the degree of ionization of the acid, s is the solubility of the acid in moles per liter, and K is the ionization constant of the acid* (1.2×10^{-5} at 25° and 1.13×10^{-5} at 50°). Then $\alpha s = 3.16 \times 10^{-6}$, and solving the above equation for s, we get $s = 4.05 \times 10^{-6}$ M,

$C_{H^+} = 3.16 \times 10^{-6}$ M, the concentration of dissociated acid

$C_{HP} = 0.89 \times 10^{-6}$ M, the concentration of undissociated acid.

This method of correcting for carbon dioxide makes a very slight difference in the case of the more soluble capric and lauric acids but makes a significant difference for palmitic and stearic acids. Total solubility, the concentration of dissociated acid expressed as C_{H^+}, and the concentration of undissociated acid are given in Table 1.

McBain and Taylor (4) found the solubility of palmitic acid at 90°C. to be 1.2×10^{-5} M. C. C. Addison (5) reports the solubility of capric acid as 0.0050% (2.9×10^{-4} M) at 20° by surface tension measurements. McBain and Eaton (6) gave the solubility of lauric acid as 1.88×10^{-5} M, using the same method that is used here. Ralston and Hoerr (1) give the solubility of lauric acid at 20°, determined only by titration, as 0.0055 g. per 100 g. of water (2.7×10^{-4} M), and at 60° 0.0087 g. per 100 g. of water (4.3×10^{-4} M); their values are in general five to ten fold greater than found here, which may be due to their failure to take into account carbon dioxide in their method of analysis.

The concentration of fatty acid present in soap solutions of a range of concentrations was calculated, using pH values to be published in another communication, and found to be always less than the saturation concentration as determined by these experiments.

TABLE I

The Resistance, Specific Conductivity, Total Solubility, Concentration of Dissociated and Undissociated Acid, in Saturated Solutions of Some Fatty Acids at 25° and 50°C.

Acid	Temp. °C.	Resist. (ohms)	Spec. Cond'y x 10^6 mhos	Total Solub'y x 10^6 M	C_{H^+} M	Conc'n Undis. Acid
Capric	25	1280	22.6	359	60	300
	50	810	35.7	500	68.8	431
Lauric	25	6300	4.60	24.0	12.1	11.9
	50	2790	10.4	54.7	19.8	34.9
Myristic						
Kahlbaum	25	21000	1.38	4.2	3.3	0.9
Lepovsky	25	18000	1.61	5.1	3.9	1.2
Kahlbaum	50	9000	3.22	9.7	6.2	3.4
Palmitic	25	24000	1.20	3.2	2.6	0.6
	50	13200	2.19	4.0	3.1	0.89
Stearic	25	27000	1.07	2.1	1.8	0.3
	50	15500	1.86	2.7	2.3	0.44

Summary

The solubilities of capric, lauric, myristic, palmitic, and stearic acids in water at 25° and 50° C. were determined by use of conductivity measurements. Correction was made for carbon dioxide; and total solubilities, together with the concentration of dissociated and of undissociated acid were calculated. Their solubilities range from 359×10^{-6} M for capric acid to 2.1×10^{-6} M for stearic acid at 25°C. The solubility of lauric and myristic is approximately doubled by an increase of temperature from 25° to 50°C., that of capric, palmitic, and stearic acids increases by 25 to 40%.

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* This was deduced from the temperature coefficient of the dissociation constant of acetic acid between 25° and 90°, and from the dissociation constants of the homologous series of fatty acids up to caprylic acid at 25°, where the change with increasing molecular weight has become very small (4). If a more accurate value for the dissociation constant should be supplied (a smaller value; it cannot well be larger), this would increase the values calculated here for the solubility of the fatty acid and render it still less possible for neutral soap solutions to yield enough free fatty acid to saturate the water.