

## The Ionization Constant, Solubility Product and Solubility of Lauric and Myristic Acid

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The ionization constant ( $K_s$ ), solubility product ( $K_L$ ) and solubility of lauric and myristic acid at 20°C have been determined simultaneously from potentiometric titrations of their aqueous sodium salt solutions according to the method of Back and Steenberg. Measurements were carried out at soap anion concentrations ranging from below the concentration of limited ion association to above the critical concentration for micelle formation. The data obtained support the conception of Ekwall that limited soap anion association starts at a well defined concentration.

Below this concentration of limited ion association the following electrolytic constants were obtained. For lauric acid:  $pK_s = 5.3$ ;  $pK_L = 10.0$ , and  $L$ , the solubility of unionized acid,  $= 2.3 \times 10^{-5}$  moles/litre. For myristic acid:  $pK_s \leq 6.3$ ;  $pK_L = 11.5$ , and  $L \leq 0.6 \times 10^{-5}$  moles/litre.

Data published on the ionization constant and the solubility in water of higher fatty acids are scarce and of insufficient mutual agreement. This is due to experimental difficulties arising in consequence of both the low solubility of these acids and the low concentration at which their anions start to associate.

Ionization constants of fatty acids have been obtained by extrapolation from lower, more soluble homologues<sup>1,2</sup>, by recalculation of pH measurements in water-ethanole mixtures<sup>3,4</sup> and by pH measurements in dilute solutions of neutral sodium salts<sup>5</sup>. In a recent review Ekwall<sup>6</sup>, referring to unpublished measurements, has indicated the apparent change in the ionization constant of lauric acid with soap concentration due to ion association and thereupon following micelle formation. Reported solubilities of fatty acids have been determined using conductivity measurements<sup>7</sup> or conductometric titration<sup>8,9</sup> of fatty acids in saturated water solutions.

Here the method of Back and Steenberg<sup>10</sup> for simultaneous determination of both the ionization constant, the solubility product and the solubility of the unionized protolyte by single potentiometric titrations has been used. Measurements were carried out with sodium laurate and sodium myristate

solutions at concentrations ranging from above the critical concentration for micelle formation (CMC) to below the concentration of limited ion association (LAC).

### EXPERIMENTAL

Purissimum Lauric acid (of St. Just) with a melting point of 42.4°C and myristic acid (of Eastman Kodak) with a melting point of 52.5°C have been used. Sodium salt solutions were prepared by dissolving the acid under nitrogen atmosphere in 0.1 N sodium hydroxide, added in an excess of about 3–5 %. Distilled water and sodium hydroxide solutions had been freed from carbon dioxide by passing a weak anion exchange resin column. After dilution the soap solutions were titrated with 0.02 and 0.002 N hydrochloric acid under nitrogen atmosphere using a magnetic stirrer and a low alkaline error glass electrode, a saturated calomel electrode and a vacuum tube voltmeter. The pH meter was calibrated at pH values 4.00, 6.88 and 9.22 using freshly prepared standard buffers of respectively, potassium hydrogen phthalate<sup>11</sup>, an equimolar mixture of monopotassium phosphate- and disodium phosphate<sup>12</sup> and sodium tetraborate<sup>13</sup>. All titrations were carried forward beyond the second equivalence point. To prevent interference of carbon dioxide, the soap solutions prepared had to be transferred rapidly into the titration vessel. Thus, it was decided to determine the total amount of sodium soap titrated from the two equivalence points of the titration curve. These equivalence points were determined using the method of Gran<sup>14</sup>. At checking points during the titration, at which a fresh liquid junction was desirable at the saturated potassium chloride and the soap solution interface, the calomel electrode was removed before releasing some potassium chloride. Measurements were performed at 20° ± 1°C.

Activity coefficients of soap anions were estimated according to the simplified Debye-Hückel equation, and were used in the calculation of ionization constants and solubility products. For calculation of the ionization constant only titration points down to a pH value corresponding to the solubility limit of unionized acid were employed. A few titration points close to the equivalence point also were disregarded because of the very low buffering capacity at these points. Yet within a single titration there appeared a slight downward trend in the ionization constants calculated, when carrying forward the titration with hydrochloric acid. Thus in Figs. 1 and 2 most titrations are represented by a line connecting the lowest and highest value of the ionization constant calculated.

At very low soap concentrations the accuracy of the titration method naturally falls off. Thus only soap solutions exceeding 0.0004 M were employed. At concentrations considerably exceeding the critical concentration for micelle formation, the equilibrium pH was reached extremely slowly, thus lowering the accuracy of the results.

### RESULTS

The ionization constant,  $K_s$ , the solubility product,  $K_L$ , and the solubility of unionized acid,  $L$ , all are calculated according to the method of Back and Steenberg<sup>10</sup> assuming the simple equilibrium conditions

$$K_s = \frac{a_{\text{H}_3\text{O}^+} \cdot a_{\text{A}^-}}{a_{\text{HA}}} \quad (1)$$

and

$$K_L = a_{\text{H}_3\text{O}^+} \cdot a_{\text{A}^-} \quad (2)$$

to be valid. The fatty acid anion activity  $a_{\text{A}^-} = f_{\text{A}^-} c_{\text{A}^-}$  is calculated from the total concentration,  $c_a$ , of titrand HA and  $\text{A}^-$  and from the concentration of titrator added in excess of the neutralization point,  $c_s$ , according to

$$c_{\text{A}^-} = c_a + c_{\text{H}_3\text{O}^+} - c_s - c_{\text{OH}^-} \quad (3)$$

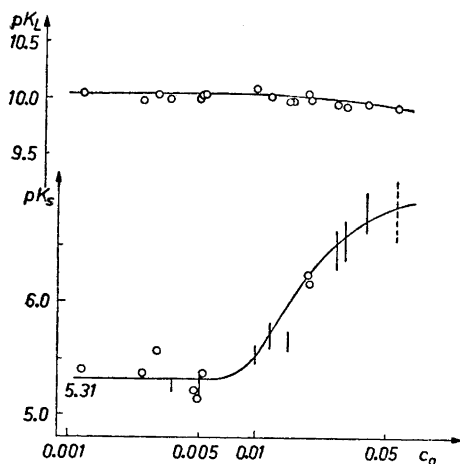


Fig. 1.  $pK_s$  and  $pK_L$  of lauric acid at 20°C versus the total titrand (soap) concentration  $c_a$  in moles/litre at the neutralization point.

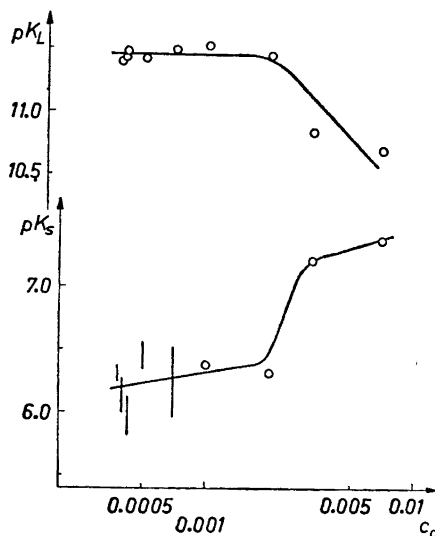


Fig. 2.  $pK_s$  and  $pK_L$  of myristic acid at 20°C versus the total titrand (soap) concentration  $c_a$  in moles/litre at the neutralization point.

Correspondingly  $c_{HA}$  is obtained as

$$c_{HA} = c_s + c_{OH^-} - c_{H_3O^+} \quad (4)$$

If due to formation of micelles or associated ions eqns. (3) and (4) or eqn. (2) are not valid, the constants calculated naturally represent pseudoconstants only.

*Ionization constants.* The lower part of Figs. 1 and 2 presents the  $pK_s$  values versus the total titrand concentration  $c_a$  at the neutralization point, using a logarithmic scale.

A general agreement exists between these results for fatty acids and those of Ekwall, Rosendal and Löfman for bile acids<sup>15</sup> as well as the preliminary data of Ekwall for lauric acid<sup>6</sup>. As obvious from the data in Fig. 1 for lauric acid, the  $pK_s$  values are independent of the total titrand concentration at the neutralization point as long as this concentration is low enough. The slight upward trend in  $pK_s$  within a single titration, which might indicate complex formation between fatty acid anion, and unionized fatty acid here also appears negligible. It seems justifiable to consider the corresponding  $pK_s$  value of 5.3 as given in Table 1 with its 90% confidence range, as the true ionization constant for lauric acid. For myristic acid it was not possible to perform reliable potentiometric titrations at concentrations low enough to finally secure this true ionization constant. Only a lower limit for the ionization constant, *i.e.*  $pK_s \leq 6.3$ , appears from the measurements.

At an intermediate concentration range, within which Ekwall and coworkers by the use of several other methods have demonstrated a limited association

Table 1. Ionization constants of some fatty acids in water.

Fatty Acid	Temp. °C	$pK_s$ with 90 % confidence range	Method
Lauric	20°	$5.31 \pm 0.08$ $\leq 6.3$	pH measurements, titration in water, (this work)
Myristic	20°		
Lauric	20°	4.9–5.0	(3) pH measurements
Myristic	20°	4.9–5.0	(3) in
Palmitic	25°	5.06	(4) water-ethanol
Oleic	25°	5.02	(4) mixture
Lauric	25°	4.8	(5) pH measurements in sodium soap water solutions
Myristic	25°	5.7	
Lauric	20°	5.5	(6) measurements in water *
Lauric	25°	4.82	(2) extrapolated from lower homologues

\* extrapolated from data presented.

of laurate ions<sup>16,17,18</sup>, the  $pK_s$  values calculated increase with total titrand concentration, again levelling off to constant values at the critical concentration for micelle formation. This change in the apparent ionization constants is to be interpreted as a decrease in activity  $a_{HA}$  of unionized acid due to complex formation and provides another indication of beginning ion association.

At higher concentrations the corresponding pseudoconstant again shows up as mainly concentration independent, indicating the size of the micelles to be essentially constant.

Table 1 gives a comparison between the true  $pK_s$  values obtained here and those obtained by other methods. Obviously the direct method as used in this work gives higher  $pK_s$  values, *i.e.* lower ionization constants, than an extrapolation from lower fatty acid homologues or a recalculation from titrations in water-ethanol mixtures.

*Solubility products.* When the potentiometric titration of the soap solution is carried forward at low titrand concentrations, the free fatty acid is precipitated and coagulated near the neutralization point, as expected. If ion association would not occur this precipitation point should move towards the neutralization point at higher titrand concentrations. But obviously this is not the case. Fig. 3 shows a titration starting with a total titrand concentration at the neutralization point of 0.019 moles/litre. When adding hydrochloric acid after this point, the solution slowly turns slightly turbid. Yet precipitation does not occur until late in the titration curve, in connection with a pronounced discontinuity in this curve. The upper part of Fig. 3 presents the solubility product calculated assuming eqns. (2) and (3) to be valid all over the titration curve. Obviously only after the precipitation point has been reached, a constant  $pK_L$ -value occurs, indicating a solubility product to be valid within the later part of the titration curve. This means that a solid phase of unionized acid here seems to exist, while in the earlier part of the titration curve unionized

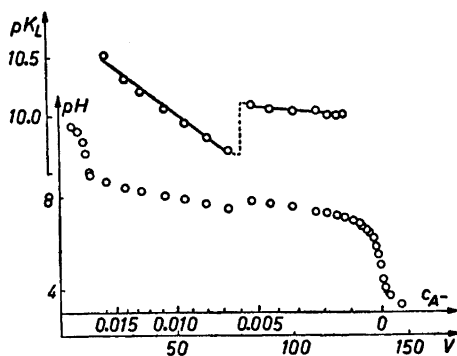


Fig. 3. Titration curve for a 0.019 M sodium laurate solution and the corresponding  $pK_L$  values calculated. Abscissa expressed in  $V$  ml 0.0216 N HCl added in excess of the neutralization point as well as in overall concentration of untitrated laurate anions,  $c_{A^-}$ , in moles/litre.

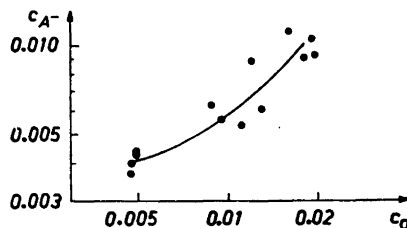


Fig. 4. Overall concentration  $c_{A^-}$  of laurate anion at the titration curve discontinuity point, versus the corresponding total titrand concentration,  $c_a$ , both in moles/litre.

fatty acid is associated to fatty acid anions and thus held in solution. When checking these results by a retitration from the acid to the alkaline side, the discontinuity in the titration curve was less obvious but the change in  $pK_L$ , as shown in Fig. 3 still was apparent.

The upper part of Figs. 1 and 2 presents the solubility product obtained versus the total titrand concentration at the neutralization point. It is obvious from these data that a true solubility product exists at low total titrand concentrations, and that this solubility product is valid also above the concentration of limited ion association (LAC) as soon as a solid phase of free acid has formed. The solubility products with their 90 % confidence range thus obtained are:

for lauric acid  $9.98 \pm 0.03$ ; for myristic acid  $11.45 \pm 0.01$

Ekwall and coworkers have pointed out that within the concentration range of limited ion association unionized fatty acid molecules are associated with fatty acid anions. This is evident also from the data in Fig. 3 typical for this concentration range, showing the precipitation of free fatty acid to be delayed. Further proof is given in Fig. 4 showing that the residual concentration of untitrated fatty acid anions at the point of precipitation is approximately equal to this concentration of limited ion association. The slight upward trend of residual anion concentration with increasing total titrand concentration at the neutralization point indicates that after the precipitation point and the formation of a solid fatty acid phase, residual fatty acid anions still occur to some extent in associated form.

*Solubility of unionized fatty acid and total solubility.* According to the method of Back and Steenberg<sup>10</sup> the solubility of unionized fatty acid,  $L$ , is obtained as the quotient of the solubility product and the corresponding ionization

Table 2. Solubility of some fatty acids in water.

Fatty acid	Temp. °C	Solubility of unionized acid		Total solubility		Reference
		in moles/ litre $\times 10^5$	in mg/ litre	in moles/ litre $\times 10^5$	in mg/ litre	
Lauric (90 % confi- dence range)	20°	2.3	4.6	3.4	6.8	This Work
		1.8 – 3.0	3.6 – 5.9	2.6 – 4.4	5.2 – 8.8	
Myristic	20°	$\leq 0.6$	$\leq 1.4$	$\leq 0.8$	$\leq 1.8$	
Lauric	25°	1.19	2.4	2.4	4.8	John and Mc Bain <sup>7</sup>
	50°	3.5	7.0	5.5	11.0	
	40°	—	—	3.9	7.8	Eggenberger <i>et al.</i> <sup>8</sup>
	50°	—	—	4.6	9.2	
Myristic	25°	0.09–0.11	0.21–0.25	0.42–0.51	1.0–1.2	John and Mc Bain <sup>7</sup>
	50°	0.34	0.78	0.97	2.2	
	50°	—	—	1.84	4.2	Eggenberger <i>et al.</i> <sup>8</sup>

constant. Table 2 gives the data thus obtained together with their 90 % confidence limits. Also given are the total solubilities of these fatty acids in a saturated water solution, *i.e.* the total solubilities at the acid equivalence point, at which  $\alpha_{\text{H}_3\text{O}^+} = \alpha_{\text{A}^-}$ . For comparison other published data also are given. The total solubilities established in this work are lower than those of Eggenberger *et al.*<sup>8</sup> obtained by conductometric titration of with fatty acid saturated water solutions when rechecking earlier data of their own.

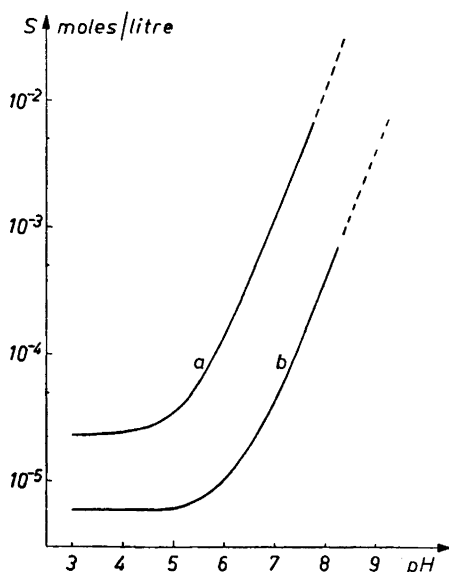


Fig. 5. Total solubility,  $S$ , in moles/litre as a function of pH, for a) lauric acid, b) myristic acid.

On the other hand our data are in reasonable agreement with those of John and Mc Bain<sup>7</sup>, obtained from conductivity measurements using earlier data on the equivalence conductance of soap ions and selecting as the ionization constant for these fatty acids, the one of acetic acid.

To give a complete picture of the solubility of these fatty acids, Fig. 5 shows our values for the total solubility as a function of the pH, (adding the solubility of unionized acid to that of the fatty acid anion determined by the solubility product). Naturally, this solubility product is valid only as long as the fatty acid anion concentration does not exceed the LAC. After the LAC is reached the total solubility increases more rapidly due to solubilization of fatty acid by fatty acid anions. The dotted lines in Fig. 5 within this later region thus present a minimum total solubility only. Naturally, in mixtures of fatty acid the total solubility as calculated for each fatty acid separately, will be exceeded when mixed associate soap anions or mixed micelles begin to form.

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