

## Association Equilibria and Micelle Formation of Fatty Acid Sodium Salts

### I. A Survey of Potentiometric Measurements on Salts with 2—6 Carbon Atoms at High Ionic Strength

PER STENIUS and CLAS-HENRIK ZILLIACUS\*

*Department of Physical Chemistry, Åbo Akademi, Åbo, Finland*

A large quantity of experimental data from potentiometric investigations of the acid-base equilibria in solutions of lower normal fatty acid salts<sup>1-4</sup> has been investigated. The aim of the investigation has been to determine the association equilibria obtained in these solutions. The computer program LETAGROPVRID, written by Sillén and co-workers,<sup>5-7</sup> has been used. The results show that two association processes occur: (i) the formation of aggregates with four anions, irrespective of the hydrocarbon chain length; (ii) the formation of micellar aggregates with aggregation numbers rising rapidly, as the hydrocarbon chain length increases. Hydrophobic bonding seems to be the reason for both types of association.

The hydrolytic equilibria of normal fatty acid salts have been studied systematically at our laboratory for several years. This paper describes comprehensive calculations of the association equilibria in solutions of salts with 2—6 carbon atoms. The experimental procedures and a preliminary treatment of data have been published previously.<sup>1-4</sup> Therefore, a comprehensive description only of fundamental experimental conditions, which are relevant to the interpretation of the results, is given here.

The primary aim of our experiments is to establish, with an accuracy that makes purposeful energetic calculations possible, the association equilibria obtained in solutions of association colloids in addition to the micelle formation. Quite a number of studies of these equilibria have been published. They have been reviewed by Mukerjee.<sup>8</sup> It seems to be quite generally accepted that there is a formation of smaller aggregates below the critical micelle concentration (CMC), but there is considerable disagreement as to the size and structure of these aggregates.

\* Present address: Pargas Kalk Ab, Pargas, Finland.

Most of the papers published concern long-chained salts. This implies that the concentrations below the CMC are low, and that the experimental possibilities are limited. Thus, conductivity measurement is by far the most frequently used method of investigation. Discrepancies between the "normal" 1-1-electrolyte behaviour (according to the Debye-Hückel-Onsager theory) and the observed conductance are interpreted as a consequence of association. However, there is some uncertainty as regards the applicability of the Debye-Hückel-Onsager assumptions even to ion-disperse solutions of long-chain carboxylates.

Danielsson<sup>1</sup> approached the problem in a new way by starting a systematic investigation of the acid-base equilibria of the sodium salts of all lower normal fatty acids. It was expected that a study of the changes in the association processes, as the hydrocarbon chain is increased, would clarify the structural changes in the solutions which, possibly by way of a primary association to smaller aggregates, give rise to the formation of micelles.

## EXPERIMENTAL

*I. Potentiometric titrations.* The structure of water is strongly affected by hydrocarbon chains.<sup>9,10</sup> This makes the applicability of ordinary Debye-Hückel approximations to solutions of fatty acid anions uncertain. At the high concentrations, where association can be expected to be appreciable in solutions of short-chain salts, the approximations are certainly invalid. At these concentrations it is also probable that the formation of larger aggregates leads to a binding of counter-ions to an extent which cannot be ignored.

All investigations in pure solutions of fatty acid salts are hampered by the fact that these effects, which influence the activity of the anions, cannot be separated from the effects of association to polynuclear aggregates, at least if the association is not very extensive.

In their investigations of polynuclear complexes in solutions of inorganic salts, Sillén *et al.*<sup>11,12</sup> have shown that the effects of factors other than association can be diminished by working at a very high ionic strength. The application of this method to our systems has been described in detail in previous papers.<sup>4</sup> We have chosen to work at the ionic strength 3 mol/l, the ionic medium being NaCl. Since all fatty acid anion complexes are weak acids, it is possible to investigate the association equilibria by potentiometric acid-base titrations. These can be made in two ways:

(i) *Volumetrically.* Acid solutions are titrated with alkaline solutions of the following composition:

Alkaline solution: total concentration of fatty acid salt ( $\text{NaB}$ ) =  $C_B$ , concentration of NaCl =  $3 \text{ mol/l} - C_B - C_{\text{OH}}$ , concentration of hydroxide ions =  $C_{\text{OH}}$ .

Acid solution: total concentration of fatty acid salt =  $C_B$ , concentration of NaCl =  $3 \text{ mol/l} - C_B$ , analytical excess of hydrogen ions (free and bound in weak acids) =  $C_H$ .

(ii) *Coulometrically.* Hydroxide ions are added to an acid solution of the same composition as in a volumetric titration by electrolysis of water at a Pt cathode.

The emf is measured for a cell with a glass or a hydrogen electrode as the measuring electrode, and a silver/silver chloride electrode in 3 M NaCl as the reference electrode; the solution in the bridge is a neutral solution with the total fatty acid anion concentration =  $C_B$ , and the concentration of NaCl =  $3 \text{ mol/l} - C_B$ . The cell is calibrated by adding a known excess of hydroxide ions to the solutions investigated, in accordance with the method of Biedermann and Sillén,<sup>11</sup> and the equivalence point is evaluated from a Gran plot.<sup>13</sup> The emf is registered by a digital voltmeter connected to a printer, which measures the emf automatically during a 30 min stabilization period after each addition of hydroxide ions. Volumetric and coulometric additions can be made automatically, the apparatus being connected to a timer which makes it possible to switch automatically between addition of reagent and measurement. The system is stable enough to make titrations lasting several days possible. It has been described in detail in Ref. 14.

In this way, care has been taken to keep the ionic medium as unchanged as possible during a titration. This implies that we think it is possible to make the following two approximations:

- (i) the activity coefficients are constant during a titration;
- (ii) the binding of sodium ions to the complexes is constant and does not affect the association processes to a measurable extent.

The validity of these approximations is discussed below.

*II. Solubilization experiments.* The micelle formation in solutions of sodium pentanoate and hexanoate was investigated by solubilizing methyl cholantrene in solutions at constant ionic strength. The solutions were shaken for 24 h at 25°C with an excess of solid methyl cholantrene. After this, they were filtered, and the concentration of methyl cholantrene in the filtrates was determined by measuring their relative fluorescence at 365 nm in a Beckman DU spectrophotometer with a fluorescence attachment.

*III. Chemicals.* The sodium acetate was *pro analysi* grade from E. Merck.

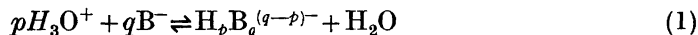
Other fatty acid salts were synthesized by neutralization of the acids (*purissimum* grade from Fluka) with sodium ethylate in dry ethanol. The salts were carefully dried, and their molecular weights then checked by titration with HClO<sub>4</sub> in glacial acetic acid. Only salts with a molecular weight less than 0.25 % from the theoretical weight were accepted.

The sodium chloride was *pro analysi* grade from E. Merck. It was dried before use in a vacuum oven at 110°C.

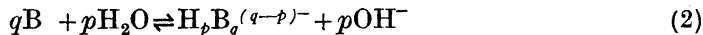
The water was doubly distilled and passed through an ion exchanger (Dowex 50) immediately before use, to eliminate the last traces of CO<sub>2</sub> and other acid and alkaline impurities. Its conductivity was about  $0.5 \times 10^{-6}$  ohm<sup>-1</sup> cm<sup>-1</sup>.

#### TREATMENT OF EXPERIMENTAL DATA

Our approximations imply that it is possible to consider the equilibria under study as simple acid-base equilibria:



Since the electrode system is calibrated with a known excess of OH<sup>-</sup> ions, one will obtain measured values for [OH<sup>-</sup>],  $C_B$  and  $C_H$ . To calculate equilibrium constants for (1) from these, one should know the ionic product of water, the value of which cannot be measured accurately in the ionic medium used. Thus, we prefer to write the equilibria in the following way:



and the stability constants calculated are defined by (charge signs are omitted):

$$\beta_{pq}' = \frac{[H_pB_q][OH]^p}{[B]^q[H_2O]^p} = \beta_{pq}/[H_2O]^p = \beta_{pq}''/K_w^p \quad (3)$$

where  $\beta_{pq}$  is the equilibrium constant for (2) with the water activity included in the constant, and  $\beta_{pq}''$  is the acid constant of (1). Our aim is thus to decide which complexes  $H_pB_q$  that do occur in the solutions, and to evaluate their stability constants  $\beta_{pq}$ .

Our method of calculation follows that of Sillén.<sup>5</sup> Preliminary calculations of the mean composition of the aggregates in solutions of sodium pentanoate and hexanoate have been published earlier.<sup>3,4</sup> The method used to evaluate the complex formation is that used in the computer program LETAGROP-VRID.<sup>6,7</sup> The principle is as follows:

The experimental quantities  $C_H$ ,  $C_B$ ,  $[\text{OH}]$  are used to calculate the quantity

$$Z = \frac{C_H - [\text{H}]}{C_B} \quad (4)$$

which is the number of hydrogen ions bound per carboxylate anion.  $Z$  is a convenient quantity in which the influence of different experimental uncertainties can easily be seen. To calculate  $Z$ , one has to use the ionic product  $K_w$  of water to obtain  $[\text{H}]$ ; in all our titrations  $C_H \gg [\text{H}]$ , and a small error in  $K_w$  is of no consequence. Theoretically,  $Z$  may also be calculated from

$$Z = \frac{\sum p[\text{H}_p\text{B}_q]}{C_B} = \frac{\sum p[\text{OH}]^{-p}[\text{B}]^q \beta_{pq}}{C_B} \quad (5)$$

provided the stability constants  $\beta_{pq}$  of all complexes that occur in the solution are known; the sum is taken over all occurring  $p, q$ -values.  $[\text{B}]$  may be calculated from

$$C_B = [\text{B}] + \sum q[\text{OH}]^{-p}[\text{B}]^q \beta_{pq} \quad (6)$$

LETAGROPVRID utilizes (4)–(6) in the following way. A first guess is made of the complexes occurring in the solutions and their stability constants. This guess and known experimental values of  $C_B$ ,  $[\text{OH}]$  are used to calculate  $[\text{B}]$  and  $Z$  from (6) and (5) for every experimental point. These  $Z$  values are compared to the experimental ones by calculating the error square sum

$$U = \sum_{i=1}^n (Z_{\text{calc}} - Z_{\text{exp}} + \delta Z)^2 \quad (7)$$

where  $n$  is the number of experimental points, and  $\delta Z$  a systematic error in  $Z$ , which may be different for different  $C_B$ 's (*i.e.*, for different titrations).  $U$  is minimized by systematic variation of the  $\beta_{pq}$  and  $\delta Z$ . Other models for the complex formation may be treated in a similar way, and the different minima in  $U$  are then compared. In this way one should, in principle, find a model for complex formation being physically feasible and giving a lower  $U$  value than any other feasible model.

The method implies that a minimum in  $U$  is a correctly chosen indicator of the best possible fit to experimental data. This means that the errors in  $Z$  should have a normal distribution. Of course, there is also always the possibility that other models give a still better conformity. The results should thus be checked through other experiments. Different ways of doing this are discussed below.

## RESULTS

The ( $Z$ ,  $\log[\text{OH}]$ ) values used in the computer calculations on the five salts are given in Tables 1–5. Some of these data have been published before, but it has been considered useful to give a complete presentation, since the values have been chosen from a much larger number of titrations, to shorten the computing time. The tables also contain the difference between the experimentally determined and the theoretically calculated values of  $Z$ , when the “best possible” fit of the finally accepted complex combination was calculated.

Table 1. Hydrolysis of sodium acetate ( $-\log [\text{OH}]$ ,  $Z$ ,  $1000(Z_{\text{calc}} - Z_{\text{exp}} + \delta Z)$ ), 145 experimental points.

Titration 1.  $C_{\text{B}} = 0.300$ ,  $\delta Z = 0.004$ . 6.122, 0.0015, +3; 6.363, 0.0019, +3; 6.508, 0.0023, +3; 6.721, 0.0031, +3; 6.968, 0.0047, +3; 7.185, 0.0071, +3; 7.360, 0.0099, +2; 7.518, 0.0138, +2; 7.699, 0.0203, +2; 7.854, 0.0284, +1; 8.038, 0.0423, 0; 8.175, 0.0570, -2; 8.285, 0.0715, -2; 8.388, 0.0891, -4; 8.500, 0.1119, -5; 8.639, 0.1474, -7; 8.734, 0.1756, -8; 8.825, 0.2066, -8; 8.908, 0.2396, -9; 8.966, 0.2627, -8; 9.080, 0.3146, -8; 9.193, 0.3827, -18; 9.442, 0.5087, -5; 9.688, 0.6378, +4; 9.905, 0.7419, +6; 10.101, 0.8169, +7; 10.299, 0.8738, +8; 10.526, 0.9198, +8; 10.710, 0.9453, +8; 10.871, 0.9617, +6; 11.047, 0.9743, +6; 11.245, 0.9843, +4; 11.435, 0.9920, +2

Titration 2.  $C_{\text{B}} = 0.500$ ,  $\delta Z = -0.004$ . 6.889, 0.0034, -5; 7.247, 0.0071, -5; 7.441, 0.0107, -5; 7.625, 0.0160, -5; 7.792, 0.0229, -5; 7.934, 0.0314, -6; 8.063, 0.0411, -5; 8.160, 0.0506, -5; 8.285, 0.0659, -5; 8.380, 0.0802, -5; 8.486, 0.1002, -5; 8.598, 0.1248, -4; 8.703, 0.1523, -3; 8.794, 0.1814, -2; 8.868, 0.2070, -1; 8.930, 0.2295, +1; 8.994, 0.2561, +2; 9.047, 0.2791, +3; 9.102, 0.3039, +5; 9.155, 0.3289, +7; 9.205, 0.3532, +9; 9.257, 0.3790, +12; 9.301, 0.4022, +13; 9.339, 0.4227, +14

Titration 3.  $C_{\text{B}} = 0.500$ ,  $\delta Z = 0.002$ . 6.564, 0.0018, +1; 7.120, 0.0055, +1; 7.544, 0.0137, +1; 7.857, 0.0274, 0; 7.989, 0.0366, -1; 8.094, 0.0462, -2; 8.206, 0.0586, -2; 8.314, 0.0735, -3; 8.419, 0.0914, -3; 8.524, 0.1130, -4; 8.634, 0.1397, -3; 8.730, 0.1675, -3; 8.813, 0.1947, -3; 8.878, 0.2186, -3; 8.944, 0.2433, -1; 9.004, 0.2681, +1; 9.062, 0.2929, +3; 9.112, 0.3171, +3; 9.167, 0.3418, +7; 9.226, 0.3701, +10

Titration 4.  $C_{\text{B}} = 1.500$ ,  $\delta Z = 0.004$ . 5.180, 0.0001, +4; 6.093, 0.0006, +4; 6.745, 0.0025, +4; 7.149, 0.0060, +3; 7.443, 0.0117, +2; 7.610, 0.0171, +1; 7.818, 0.0269, 0; 7.948, 0.0358, -1; 8.077, 0.0474, -2; 8.194, 0.0606, -3; 8.321, 0.0789, -5; 8.431, 0.0948, -2; 8.567, 0.1258, -4; 8.638, 0.1415, -2

Titration 5.  $C_{\text{B}} = 1.500$ ,  $\delta Z = 0.007$ . 6.180, 0.0032, +4; 7.120, 0.0060, +6; 7.298, 0.0089, +5; 7.419, 0.0117, +5; 7.589, 0.0171, +4; 7.706, 0.0221, +3; 7.869, 0.0314, +2; 8.022, 0.0437, 0; 8.177, 0.0606, -2; 8.306, 0.0788, -4; 8.409, 0.0963, -5; 8.476, 0.1093, -5; 8.528, 0.1203, -5; 8.581, 0.1326, -5; 8.641, 0.1463, -3

Titration 6.  $C_{\text{B}} = 3.000$ ,  $\delta Z = 0.007$ . 7.959, 0.0360, +2; 8.019, 0.0413, +2; 8.067, 0.0459, +1; 8.105, 0.0498, +1; 8.132, 0.0523, +1; 8.158, 0.0556, 0; 8.182, 0.0586, 0; 8.206, 0.0620, 0; 8.227, 0.0647, -1; 8.247, 0.0676, -1; 8.270, 0.0709, -1; 8.294, 0.0743, -1; 8.316, 0.0774, -1; 8.338, 0.0807, -1; 8.356, 0.0836, -1; 8.375, 0.0867, -1; 8.397, 0.0901, -1; 8.418, 0.0930, 0; 8.435, 0.0960, 0; 8.450, 0.0980, +1

Titration 7.  $C_{\text{B}} = 3.000$ ,  $\delta Z = 0.006$ . 4.965, 0.0001, +6; 6.179, 0.0007, +6; 6.642, 0.0020, +6; 6.894, 0.0036, +5; 7.049, 0.0052, +5; 7.157, 0.0067, +5; 7.317, 0.0096, +4; 7.422, 0.0124, +3; 7.505, 0.0149, +3; 7.627, 0.0197, +1; 7.752, 0.0260, 0; 7.859, 0.0332, -2; 7.955, 0.0406, -3; 8.029, 0.0478, -5; 8.094, 0.0545, -6; 8.156, 0.0618, -7; 8.201, 0.0674, -7; 8.251, 0.0741, -8; 8.294, 0.0799, -7

The total concentration  $C_{\text{B}}$  was determined by weighing the salts into measuring flasks; by analysis it was found that the errors in the weighing procedure were considerably less than the uncertainty of  $\pm 0.25\%$  in the molecular weight of the salt. The error in  $C_{\text{B}}$  thus is about  $\pm 0.25\%$ . The error in  $C_{\text{H}}$  is more difficult to establish, since  $C_{\text{H}}$  is calculated from the equivalence point. Usually, it is possible to decide the equivalence point with a Gran plot to an accuracy of about  $\pm 0.1\%$  of the total amount of  $\text{OH}^-$  added, which is also the approximate accuracy of the coulometric and volumetric additions. The error in  $C_{\text{H}}$  thus should be around  $\pm 0.2\%$ . The precision of the  $\log [\text{OH}]$  values is

Table 2. Hydrolysis of sodium propionate ( $-\log [\text{OH}]$ ,  $Z$ ,  $1000(Z_{\text{calc}} - Z_{\text{exp}} + \delta Z)$ ), 122 experimental points.

Titration 1.  $C_{\text{B}} = 0.100$ ,  $\delta Z = 0.002$ . 6.678, 0.0081, -3; 7.013, 0.0116, -3; 7.210, 0.0155, -3; 7.342, 0.0194, -3; 7.603, 0.0298, -2; 7.741, 0.0404, -4; 7.924, 0.0570, -3; 8.064, 0.0754, -3; 8.183, 0.0946, -3; 8.303, 0.1201, -3; 8.467, 0.1625, -1; 8.598, 0.2062, 0; 8.713, 0.2535, 0; 8.845, 0.3126, +2; 8.989, 0.3880, +2; 9.112, 0.4565, +2; 9.234, 0.5232, +6; 9.342, 0.5850, +5; 9.454, 0.6435, +7; 9.564, 0.7005, +6

Titration 2.  $C_{\text{B}} = 0.100$ ,  $\delta Z = 0.004$ . 4.162, 0.0004, +4; 5.650, 0.0015, +3; 6.549, 0.0039, +3; 6.850, 0.0067, +2; 7.072, 0.0100, +2; 7.189, 0.0127, +1; 7.320, 0.0168, +1; 7.427, 0.0207, +1; 7.557, 0.0272, 0; 7.735, 0.0391, -1; 7.866, 0.0512, -1; 7.966, 0.0628, -2; 8.059, 0.0757, -2; 8.147, 0.0900, -2; 8.225, 0.1051, -3; 8.294, 0.1206, -3; 8.352, 0.1334, -2; 8.382, 0.1409, -1; 8.418, 0.1504, -1; 8.453, 0.1605, -1; 8.485, 0.1692, +1; 8.503, 0.1769, -1; 8.531, 0.1839, +1

Titration 3.  $C_{\text{B}} = 1.000$ ,  $\delta Z = 0.005$ . 5.253, 0.0015, +3; 6.424, 0.0034, +3; 6.805, 0.0062, +3; 7.052, 0.0114, +1; 7.256, 0.0146, +2; 7.386, 0.0189, +1; 7.481, 0.0230, +1; 7.650, 0.0326, 0; 7.799, 0.0446, -1; 7.934, 0.0588, -1; 8.049, 0.0714, +1; 8.098, 0.0817, -2; 8.149, 0.0915, -3; 8.220, 0.1043, -2; 8.284, 0.1179, -2; 8.336, 0.1299, -2; 8.377, 0.1404, -2; 8.411, 0.1496, -2; 8.450, 0.1598, 0; 8.478, 0.1689, -1; 8.507, 0.1767, +1; 8.527, 0.1838, 0

Titration 4.  $C_{\text{B}} = 2.000$ ,  $\delta Z = 0.005$ . 4.592, 0.0004, +4; 5.772, 0.0011, +4; 6.343, 0.0023, +4; 6.676, 0.0043, +3; 6.891, 0.0066, +3; 7.084, 0.0099, +3; 7.256, 0.0143, +2; 7.390, 0.0190, +1; 7.523, 0.0253, +1; 7.613, 0.0309, 0; 7.691, 0.0363, -1; 7.746, 0.0410, -1; 7.795, 0.0452, -2; 7.873, 0.0530, -2; 7.931, 0.0600, -3; 7.976, 0.0658, -3; 8.014, 0.0708, -3; 8.044, 0.0753, -4; 8.076, 0.0802, -4; 8.100, 0.0841, -4

Titration 5.  $C_{\text{B}} = 2.000$ ,  $\delta Z = 0.003$ . 3.926, 0.0001, +3; 5.604, 0.0008, +3; 6.154, 0.0016, +2; 6.416, 0.0025, +2; 6.642, 0.0038, +2; 6.877, 0.0061, +2; 7.041, 0.0087, +1; 7.207, 0.0122, +1; 7.371, 0.0176, 0; 7.505, 0.0235, 0; 7.609, 0.0295, -1; 7.699, 0.0344, 0; 7.768, 0.0415, -2; 7.861, 0.0503, -2; 7.917, 0.0570, -3; 7.971, 0.0635, -3; 8.015, 0.0693, -3; 8.046, 0.0736, -3

Titration 6.  $C_{\text{B}} = 3.000$ ,  $\delta Z = 0.003$ . 4.262, 0.0002, +2; 4.981, 0.0006, +2, 5.618, 0.0009, +2; 6.039, 0.0015, +2; 6.260, 0.0020, +2; 6.494, 0.0029, +2; 6.717, 0.0045, +1; 6.886, 0.0063, +1; 7.057, 0.0089, +1; 7.199, 0.0121, +1; 7.344, 0.0165, 0; 7.434, 0.0201, 0; 7.537, 0.0253, -1; 7.615, 0.0297, -1; 7.687, 0.0349, -2; 7.748, 0.0399, -2; 7.789, 0.0437, -3; 7.824, 0.0473, -3; 7.855, 0.0503, -3

dependent on the accuracy with which the emf values can be read and the  $E^\circ$  of the system can be decided. Even if the diffusion potentials are considered, the method used gives the  $E^\circ$  with an accuracy of  $\pm 0.1$  mV<sup>14</sup> and emf readings within  $\pm 0.2$  mV. This gives an error in  $\log [\text{OH}]$  of  $\pm 0.003 \log [\text{OH}]$ -units. The precision of  $Z$  thus can be estimated to be about  $\pm 0.004$ ; the tables show that the differences between experimental data and theoretically calculated values are of this order of magnitude.

The results are also shown in Figs. 1-5. A comparison of these curves immediately shows the increasing association as the length of the hydrocarbon chain increases. At low concentrations, all salts show  $Z$  curves having a position on the  $\log [\text{OH}]$  axis and a shape being independent of  $C_{\text{B}}$ . Moreover, the shape is that to be expected for simple mononuclear equilibria



$$Z = \frac{\beta_{11}}{[\text{OH}] + \beta_{11}}$$

Table 3. Hydrolysis of sodium butyrate ( $-\log [\text{OH}], Z, 1000(Z_{\text{calc}} - Z_{\text{exp}} + \delta Z)$ ), 225 experimental points.

Titration 1.  $C_B = 0.100$ ,  $\delta Z = 0.002$ . 5.692, 0.0014, +1; 6.311, 0.0027, +1; 6.578, 0.0039, +1; 6.747, 0.0049, +1; 6.960, 0.0071, +1; 7.102, 0.0096, +1; 7.261, 0.0132, 0; 7.412, 0.0182, 0; 7.592, 0.0265, 0; 7.742, 0.0362, -1; 7.884, 0.0482, 0; 8.031, 0.0662, -1; 8.158, 0.0857, -1; 8.286, 0.1105, -1; 8.431, 0.1462, -1; 8.564, 0.1861, +1; 8.670, 0.2248, +1; 8.793, 0.2769, +2; 8.915, 0.3353, +2; 9.035, 0.3988, +2; 9.184, 0.5054, -21; 9.348, 0.5884, -11; 9.500, 0.6557, +3; 9.652, 0.7288, +4; 9.813, 0.7942, +4; 9.882, 0.8187, +4; 10.030, 0.8642, +3; 10.226, 0.9065, +5

Titration 2.  $C_B = 0.500$ ,  $\delta Z = -0.001$ . 5.648, 0.0008, -2; 6.366, 0.0021, -2; 6.611, 0.0033, -2; 6.841, 0.0052, -2; 6.997, 0.0072, -2; 7.149, 0.0099, -2; 7.281, 0.0131, -2; 7.392, 0.0171, -2; 7.541, 0.0233, -2; 7.690, 0.0322, -2; 7.817, 0.0422, -1; 7.950, 0.0565, -2; 8.075, 0.0734, -1; 8.173, 0.0901, -1; 8.293, 0.1145, -1; 8.413, 0.1455, -1; 8.515, 0.1753, 0; 8.606, 0.2070, 0; 8.706, 0.2452, +1; 8.731, 0.2554, +1; 8.814, 0.2904, +3; 8.878, 0.3202, +4; 8.907, 0.3334, +5; 8.956, 0.3564, +6; 9.005, 0.3810, +7

Titration 3.  $C_B = 1.000$ ,  $\delta Z = 0.003$ . 4.415, 0.0002, +3; 5.087, 0.0005, +3; 5.555, 0.0008, +2; 5.815, 0.0010, +2; 6.113, 0.0016, +2; 6.282, 0.0021, +2; 6.468, 0.0029, +2; 6.669, 0.0043, +2; 6.841, 0.0062, +2; 7.015, 0.0088, +2; 7.173, 0.0124, +1; 7.372, 0.0191, +1; 7.570, 0.0292, 0; 7.717, 0.0402, 0; 7.852, 0.0534, -1; 7.964, 0.0680, -2; 8.082, 0.0866, -2; 8.210, 0.1117, -3; 8.288, 0.1302, -4; 8.412, 0.1624, -2; 8.491, 0.1871, -2; 8.574, 0.2155, -1; 8.701, 0.2641, +1; 8.794, 0.3047, +2; 8.988, 0.4040, -2; 9.091, 0.4593, -5; 9.115, 0.4691, -2

Titration 4.  $C_B = 1.200$ ,  $\delta Z = 0.001$ . 4.312, 0.0002, 0; 5.458, 0.0006, 0; 5.705, 0.0008, 0; 5.940, 0.0012, 0; 6.047, 0.0013, 0; 6.243, 0.0019, 0; 6.501, 0.0030, 0; 6.697, 0.0045, 0; 6.848, 0.0061, 0; 6.975, 0.0080, 0; 7.100, 0.0104, 0; 7.206, 0.0131, 0; 7.309, 0.0164, 0; 7.412, 0.0204, 0; 7.497, 0.0245, 0; 7.598, 0.0306, 0; 7.696, 0.0377, 0; 7.786, 0.0460, 0; 7.871, 0.0551, 0; 7.980, 0.0667, +2; 8.040, 0.0785, 0; 8.114, 0.0912, 0; 8.190, 0.1066, 0; 8.258, 0.1226, -1; 8.324, 0.1393, 0; 8.386, 0.1563, 0; 8.442, 0.1738, 0; 8.494, 0.1911, 0; 8.540, 0.2073, 0; 8.582, 0.2228, 0; 8.618, 0.2377, -1; 8.650, 0.2497, 0

Titration 5.  $C_B = 1.500$ ,  $\delta Z = 0.001$ . 4.121, 0.0001, 0; 5.448, 0.0006, 0; 5.827, 0.0010, 0; 6.183, 0.0017, 0; 6.412, 0.0026, 0; 6.574, 0.0036, 0; 6.704, 0.0047, 0; 6.807, 0.0059, 0; 6.897, 0.0071, 0; 6.985, 0.0086, 0; 7.078, 0.0105, 0; 7.171, 0.0128, 0; 7.259, 0.0155, 0; 7.345, 0.0187, 0; 7.416, 0.0220, -1; 7.502, 0.0265, -1; 7.580, 0.0312, 0; 7.652, 0.0365, 0; 7.720, 0.0423, 0; 7.784, 0.0485, 0; 7.849, 0.0554, 0; 7.906, 0.0629, 0; 7.967, 0.0714, 0; 8.028, 0.0808, 0; 8.080, 0.0903, 0; 8.138, 0.1009, +1; 8.192, 0.1127, +1; 8.247, 0.1259, +1; 8.300, 0.1396, +1; 8.356, 0.1548, +2; 8.411, 0.1722, +1; 8.464, 0.1901, +1; 8.505, 0.2040, +1

Titration 6.  $C_B = 2.000$ ,  $\delta Z = -0.002$ . 5.453, 0.0003, -2; 5.560, 0.0005, -2; 5.916, 0.0008, -2; 6.146, 0.0015, -2; 6.354, 0.0021, -2; 6.574, 0.0028, -2; 6.719, 0.0042, -2; 6.863, 0.0059, -1; 7.010, 0.0085, -1; 7.154, 0.0121, -1; 7.252, 0.0155, -1; 7.369, 0.0203, -1; 7.482, 0.0262, -1; 7.620, 0.0357, 0; 7.739, 0.0462, 0; 7.850, 0.0591, +1; 7.955, 0.0736, +2; 8.060, 0.0922, +2; 8.119, 0.1041, +3; 8.200, 0.1228, +3; 8.259, 0.1384, +3; 8.324, 0.1574, +3; 8.374, 0.1727, +4

Titration 7.  $C_B = 2.500$ ,  $\delta Z = 0.003$ . 4.028, 0.0001, +2; 4.715, 0.0003, +2; 5.299, 0.0005, +2; 5.714, 0.0009, +2; 6.195, 0.0021, +2; 6.461, 0.0036, +2; 6.650, 0.0054, +2; 6.800, 0.0074, +2; 6.922, 0.0097, +2; 7.029, 0.0122, +2; 7.127, 0.0151, +2; 7.211, 0.0182, +2; 7.287, 0.0214, +2; 7.357, 0.0250, +1; 7.416, 0.0288, +1; 7.478, 0.0329, +1; 7.539, 0.0375, +1; 7.593, 0.0426, 0; 7.649, 0.0482, 0; 7.701, 0.0541, 0; 7.756, 0.0606, -1; 7.811, 0.0681, -1; 7.864, 0.0763, -1; 7.911, 0.0845, -2; 7.960, 0.0937, -3; 8.006, 0.1041, -4; 8.040, 0.1123, -6; 8.070, 0.1193, -6; 8.089, 0.1234, -6

Titration 8.  $C_B = 3.000$ ,  $\delta Z = -0.001$ . 5.964, 0.0014, -1; 6.833, 0.0080, -1; 7.093, 0.0145, -1; 7.330, 0.0247, 0; 7.482, 0.0345, 0; 7.602, 0.0452, 0; 7.730, 0.0598, +1; 7.818, 0.0723, +1; 7.869, 0.0807, 0; 7.916, 0.0892, 0; 7.957, 0.0971, 0; 7.974, 0.1009, 0

Titration 9.  $C_B = 3.000$ ,  $\delta Z = -0.001$ . 5.771, 0.0010, -1; 6.037, 0.0016, -1; 6.261, 0.0024, -1; 6.447, 0.0035, -1; 6.672, 0.0056, -1; 6.865, 0.0085, -1; 7.024, 0.0122, 0; 7.157, 0.0164, 0; 7.252, 0.0202, 0; 7.352, 0.0253, +1; 7.446, 0.0312, +1; 7.524, 0.0373, +1; 7.592, 0.0434, +1; 7.653, 0.0499, +1; 7.707, 0.0562, +1; 7.749, 0.0620, +1

Table 4. Hydrolysis of sodium pentanoate ( $-\log [\text{OH}], Z, 1000(Z_{\text{calc}} - Z_{\text{exp}} + \delta Z)$ ), 198 experimental points.

Titration 1.  $C_B = 0.100$ ,  $\delta Z = 0.006$ . 8.552, 0.2028, -12; 8.263, 0.1178, -8; 8.227, 0.1095, -7; 8.187, 0.0991, -5; 8.102, 0.0784, +1; 8.048, 0.0681, +4; 7.947, 0.0567, +2; 7.856, 0.0473, +2; 7.730, 0.0370, +1; 7.563, 0.0266, +2; 7.479, 0.0225, +2; 7.374, 0.0183, +2; 7.237, 0.0142, +2; 7.042, 0.0100, +3; 6.904, 0.0079, +3; 6.699, 0.0059, +3; 5.966, 0.0028, +3

Titration 2.  $C_B = 0.200$ ,  $\delta Z = 0.004$ . 8.080, 0.0765, -1; 8.004, 0.0661, -1; 7.918, 0.0558, -2; 7.869, 0.0506, -2; 7.815, 0.0454, -2; 7.758, 0.0402, -1; 7.693, 0.0351, -1; 7.612, 0.0299, -1; 7.519, 0.0247, 0; 7.403, 0.0195, 0; 7.245, 0.0143, 0; 7.120, 0.0112, +1; 6.948, 0.0081, +1; 6.774, 0.0060, +1; 6.537, 0.0040, +2; 6.282, 0.0029, +2; 5.717, 0.0019, +2

Titration 3.  $C_B = 0.300$ ,  $\delta Z = 0.003$ . 7.867, 0.0509, -2; 7.812, 0.0440, 0; 7.710, 0.0371, -2; 7.590, 0.0288, -2; 7.533, 0.0260, -2; 7.479, 0.0233, -2; 7.396, 0.0198, -2; 7.301, 0.0164, -1; 7.176, 0.0129, -1; 7.015, 0.0024, +6; 6.882, 0.0074, 0; 6.735, 0.0053, +1; 6.542, 0.0039, +1; 6.194, 0.0025, +1; 5.788, 0.0018, +1; 5.506, 0.0015, +1; 5.078, 0.0012, +1

Titration 4.  $C_B = 0.500$ ,  $\delta Z = -0.001$ . 8.231, 0.1106, +17; 8.141, 0.0928, +11; 8.065, 0.0798, +6; 7.992, 0.0689, +3; 7.916, 0.0590, 0; 7.847, 0.0511, -1; 7.763, 0.0428, -3; 7.681, 0.0361, -3; 7.590, 0.0297, -4; 7.507, 0.0247, -4; 7.424, 0.0208, -4; 7.267, 0.0149, -4; 7.103, 0.0106, -3; 6.916, 0.0072, -3; 6.620, 0.0041, -3; 6.287, 0.0023, -2; 6.038, 0.0016, -2; 5.798, 0.0012, -2; 5.507, 0.0009, -2

Titration 5.  $C_B = 0.750$ ,  $\delta Z = -0.002$ . 8.101, 0.1069, +19; 8.053, 0.0932, +19; 7.994, 0.0805, +16; 7.937, 0.0721, +11; 7.894, 0.0643, +10; 7.842, 0.0574, +7; 7.783, 0.0508, +4; 7.737, 0.0460, +2; 7.686, 0.0411, +1; 7.634, 0.0366, -1; 7.582, 0.0327, -2; 7.517, 0.0285, -3; 7.465, 0.0254, -4; 7.409, 0.0226, -4; 7.353, 0.0201, -4; 7.310, 0.0182, -4; 7.239, 0.0157, -5; 7.186, 0.0140, -4; 7.147, 0.0124, -4; 7.073, 0.0110, -4; 7.024, 0.0099, -4; 6.998, 0.0085, -3; 6.860, 0.0071, -4; 6.765, 0.0059, -4; 6.677, 0.0049, -3; 6.588, 0.0041, -3; 6.483, 0.0034, -3; 6.365, 0.0027, -3; 6.233, 0.0022, -3; 6.133, 0.0019, -3; 6.008, 0.0016, -3; 5.900, 0.0014, -3; 5.678, 0.0011, -2; 5.327, 0.0008, -2; 5.007, 0.0006, -2; 4.676, 0.0004, -2; 4.356, 0.0002, -2

Titration 6.  $C_B = 1.000$ ,  $\delta Z = 0.001$ . 8.131, 0.1960, -23; 8.074, 0.1642, -10; 8.014, 0.1379, -2; 7.959, 0.1147, +5; 7.905, 0.0959, +9; 7.845, 0.0797, +10; 7.778, 0.0653, +10; 7.702, 0.0523, +9; 7.604, 0.0410, +5; 7.477, 0.0306, +1; 7.318, 0.0216, -1; 7.164, 0.0156, -3; 6.958, 0.0102, -3; 6.730, 0.0065, -2; 6.375, 0.0036, -1; 6.020, 0.0022, -1; 5.661, 0.0014, -1

Titration 7.  $C_B = 1.500$ ,  $\delta Z = 0.007$ . 7.954, 0.1937, -13; 7.945, 0.1907, -13; 7.901, 0.1749, -11; 7.845, 0.1568, -10; 7.796, 0.1411, -8; 7.752, 0.1252, -5; 7.692, 0.1104, -5; 7.632, 0.0957, -4; 7.582, 0.0833, -3; 7.531, 0.0724, -2; 7.480, 0.0628, -1; 7.426, 0.0542, -1; 7.370, 0.0465, 0; 7.315, 0.0401, 0; 7.247, 0.0338, 0; 7.183, 0.0286, 0; 7.125, 0.0249, 0; 7.083, 0.0225, 0; 7.027, 0.0198, +1; 6.968, 0.0173, +1; 6.904, 0.0149, +1; 6.826, 0.0124, +2; 6.736, 0.0102, +2; 6.638, 0.0082, +3; 6.547, 0.0068, +4; 6.449, 0.0055, +4; 6.331, 0.0044, +5; 6.272, 0.0039, +5; 6.195, 0.0033, +5; 6.096, 0.0028, +6; 5.940, 0.0021, +6; 5.751, 0.0016, +6; 5.590, 0.0013, +6; 5.438, 0.0010, +7; 5.208, 0.0008, +7; 4.706, 0.0004, +7; 4.402, 0.0002, +7

Titration 8.  $C_B = 2.100$ ,  $\delta Z = 0.002$ . 7.560, 0.1031, +4; 7.461, 0.0814, +2; 7.355, 0.0626, +1; 7.232, 0.0454, 0; 7.088, 0.0320, -2; 6.983, 0.0245, -1; 6.814, 0.0165, -1; 6.505, 0.0079, 0; 6.158, 0.0035, +1

Titration 9.  $C_B = 2.800$ ,  $\delta Z = -0.002$ . 7.727, 0.1777, +10; 7.678, 0.1634, +8; 7.629, 0.1499, +5; 7.580, 0.1365, +2; 7.529, 0.1236, -1; 7.480, 0.1120, -3; 7.414, 0.0977, -5; 7.345, 0.0845, -6; 7.279, 0.0738, -7; 7.211, 0.0638, -8; 7.142, 0.0544, -6; 7.069, 0.0467, -6; 6.987, 0.0387, -4; 6.897, 0.0317, -3; 6.806, 0.0257, -1; 6.716, 0.0211, 0; 6.625, 0.0171, +1; 6.529, 0.0138, +2; 6.424, 0.0110, +3; 6.285, 0.0081, +3; 6.152, 0.0031, +4; 6.015, 0.0046, +3; 5.849, 0.0033, +3; 5.677, 0.0023, +3; 5.464, 0.0016, +2; 5.294, 0.0012, +1; 5.066, 0.0008, +1; 4.657, 0.0004, 0



Table 5. Hydrolysis of sodium hexanoate ( $-\log [\text{OH}], Z, 1000(Z_{\text{calc}} - Z_{\text{exp}} + \delta Z)$ ), 125 experimental points.

Titration 1.  $C_B = 0.100$ ,  $\delta Z = 0.007$ . 6.752, 0.0052, +5; 7.146, 0.0104, +4; 7.349, 0.0155, +3; 7.487, 0.207, +3; 7.657, 0.0311, +1; 7.781, 0.0415, 0; 7.874, 0.0518, -2; 7.956, 0.0622, -2; 7.984, 0.0663, -3; 8.073, 0.0808, -3; 8.142, 0.0933, -3

Titration 2.  $C_B = 0.200$ ,  $\delta Z = -0.002$ . 6.698, 0.0010, 0; 6.228, 0.0021, -4; 6.634, 0.0041, -4; 6.843, 0.0062, -4; 7.145, 0.0114, -4; 7.319, 0.0166, -3; 7.447, 0.0218, 0; 7.458, 0.0269, -5; 7.631, 0.0321, +6; 7.462, 0.0373, -15; 7.766, 0.0425, -15; 7.825, 0.0477, +20

Titration 3.  $C_B = 0.300$ ,  $\delta Z = 0.002$ . 5.152, 0.0018, 0; 5.759, 0.0026, -1; 6.079, 0.0032, -1; 6.337, 0.0041, -1; 6.447, 0.0047, -1; 6.539, 0.0053, -1; 6.627, 0.0061, -1; 6.762, 0.0074, 0; 6.807, 0.0080, 0; 6.931, 0.0092, +1; 7.044, 0.0104, +4

Titration 4.  $C_B = 0.500$ ,  $\delta Z = -0.008$ . 5.768, 0.0008, -8; 6.170, 0.0018, -7; 6.377, 0.0029, -6; 6.609, 0.0049, -4; 6.926, 0.0112, +3; 7.058, 0.0174, +8; 7.237, 0.0360, +12; 7.359, 0.0609, +7; 7.446, 0.0858, -1; 7.486, 0.0982, -4

Titration 5.  $C_B = 0.750$ ,  $\delta Z = -0.002$ . 4.877, 0.0009, -2; 6.185, 0.0066, -2; 6.448, 0.0120, -1; 6.634, 0.0188, 0; 6.745, 0.0251, +1; 6.822, 0.0317, +1; 6.889, 0.0383, +2; 6.948, 0.0458, +1; 7.007, 0.0538, +2; 7.060, 0.0624, +1; 7.105, 0.0705, +1; 7.152, 0.0801, 0; 7.191, 0.0888, -1; 7.237, 0.1005, -3

Titration 6.  $C_B = 1.000$ ,  $\delta Z = 0.008$ . 6.184, 0.0104, +8; 6.385, 0.0165, +7; 6.525, 0.0232, +6; 6.630, 0.0303, +5; 6.711, 0.0378, +4; 6.799, 0.0460, +4; 6.863, 0.0549, +2; 6.929, 0.0645, +1; 6.986, 0.0749, 0; 7.047, 0.0862, 0; 7.106, 0.0986, +1; 7.162, 0.1123, +1; 7.220, 0.1274, +1; 7.274, 0.1442, 0; 7.333, 0.1629, -1; 7.313, 0.1838, -28; 7.450, 0.2080, -13

Titration 7.  $C_B = 1.500$ ,  $\delta Z = 0.003$ . 5.744, 0.0052, +4; 6.098, 0.0113, +4; 6.328, 0.0189, +2; 6.490, 0.0271, +1; 6.633, 0.0373, -2; 6.797, 0.0545, -6; 6.942, 0.0740, -8; 7.162, 0.1079, +4

Titration 8.  $C_B = 2.000$ ,  $\delta Z = 0.004$ . 3.970, 0.0005, +4; 5.100, 0.0013, +5; 5.420, 0.0025, +5; 5.610, 0.0028, +7; 5.800, 0.0063, +6; 6.070, 0.0103, +7; 6.260, 0.0159, +6; 6.460, 0.0252, +5; 6.570, 0.0320, +3; 6.700, 0.0433, 0; 6.820, 0.0561, -3; 6.930, 0.0708, -6; 7.030, 0.0878, -8; 7.130, 0.1080, -8; 7.230, 0.1314, -4; 7.240, 0.1498, -19

Titration 9.  $C_B = 2.500$ ,  $\delta Z = -0.003$ . 5.842, 0.0064, 0; 6.282, 0.0151, +2; 6.521, 0.0250, +2; 6.823, 0.0482, -2; 7.053, 0.0783, -4; 7.255, 0.1185, +3

Titration 10.  $C_B = 2.900$ ,  $\delta Z = -0.003$ . 4.640, 0.0005, -3; 5.068, 0.0011, -3; 5.432, 0.0024, -2; 5.714, 0.0045, -1; 5.908, 0.0068, 0; 6.049, 0.0094, +1; 6.179, 0.0126, +1; 6.292, 0.0160, +2; 6.407, 0.0201, +2; 6.500, 0.0252, 0; 6.613, 0.0311, 0; 6.703, 0.0386, -2; 6.799, 0.0480, -5; 6.911, 0.0600, -7; 7.026, 0.0762, -9; 7.093, 0.0869, -9; 7.196, 0.1060, -7; 7.301, 0.1280, +1; 7.377, 0.1480, +10; 7.467, 0.1710, +28

As the hydrogen ion concentration increases, only free fatty acid is formed in these solutions. Starting from the butyrate, an increase in  $C_B$  leads to a shift of the  $Z$  curves towards lower values of  $p[\text{OH}]$ , which is to be interpreted as the result of a formation of polynuclear aggregates. (5) and (6) show that only when polynuclear aggregates are formed ( $q > 1$ ), the position of the  $Z$  curve depends on  $C_B$ .

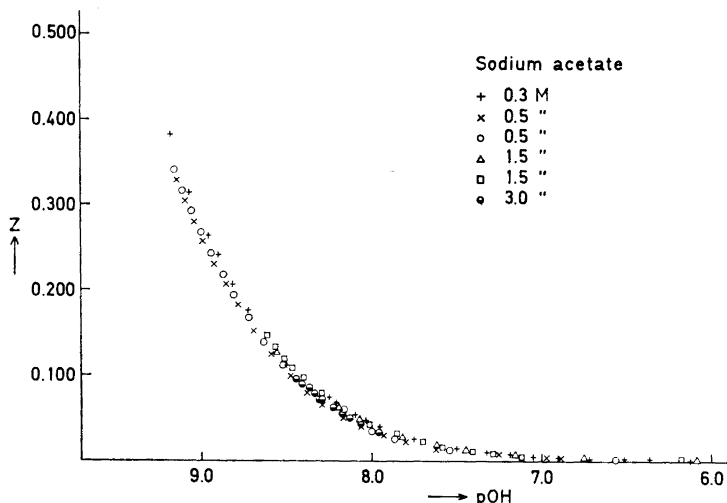


Fig. 1. The hydrolysis of sodium acetate at different concentrations. The quantity  $Z = (C_H - [H])/C_B$  is plotted against  $-\log [OH]$ .

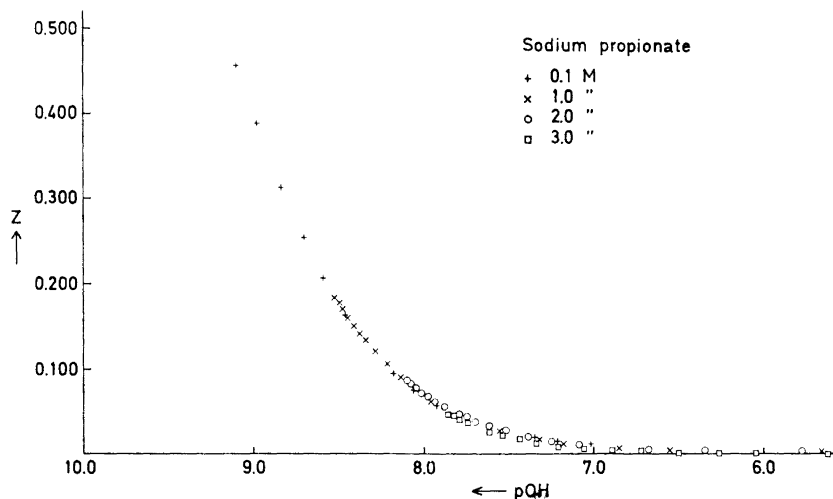


Fig. 2. The hydrolysis of sodium propionate at different concentrations.

The shift of the  $Z$  curves is larger and occurs at lower concentrations, as the hydrocarbon chain increases in length, *i.e.*, the association increases, as the chain length increases.

Remarkable similarities in the curves for different salts can be observed. They all show a concentration region where the shift in the curves is very large, and  $Z$  changes somewhat more steeply with pOH than in other regions.

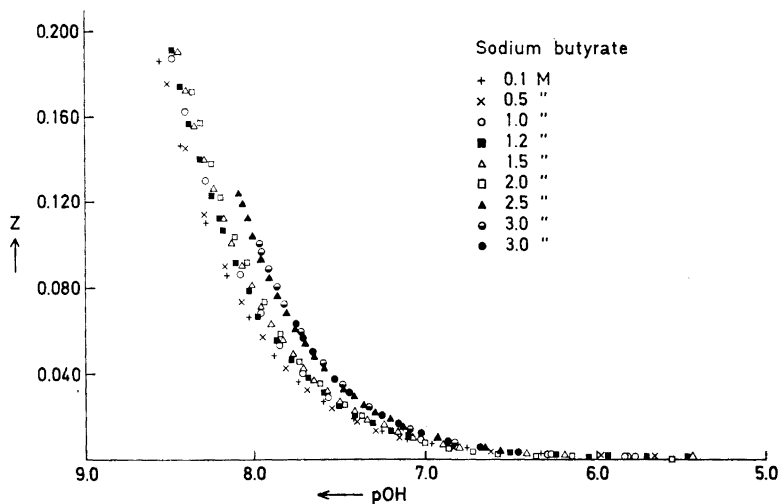


Fig. 3. The hydrolysis of sodium butyrate at different concentrations.

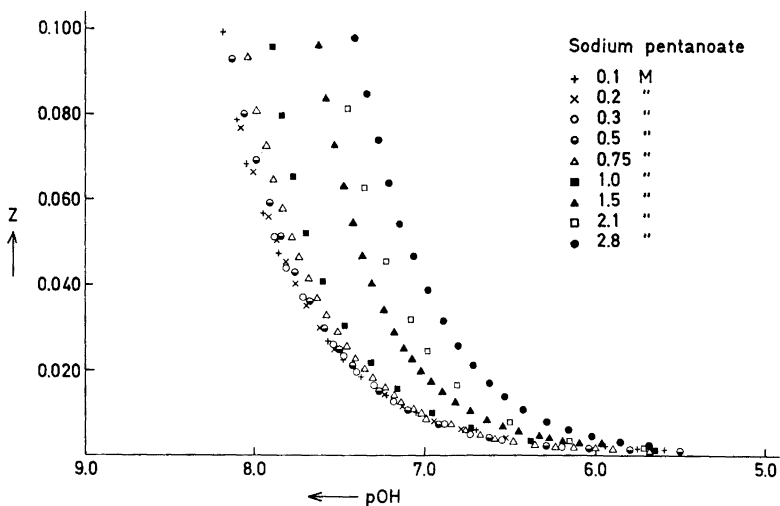


Fig. 4. The hydrolysis of sodium pentanoate at different concentrations.

In pentanoate and hexanoate solutions of very high concentration, a new region is reached where the position and shape of the curves are almost independent of the carboxylate concentration. Moreover, the shape is that for an equilibrium of type (8). The concentration in this region is above the concentration where micelle formation starts to dominate, as indicated by solubilization experiments. This is shown in Fig. 6, which gives the solubilization of methyl cholantrene as a function of the concentration of carboxylate in sodium pentanoate and hexanoate solutions at constant ionic strength.

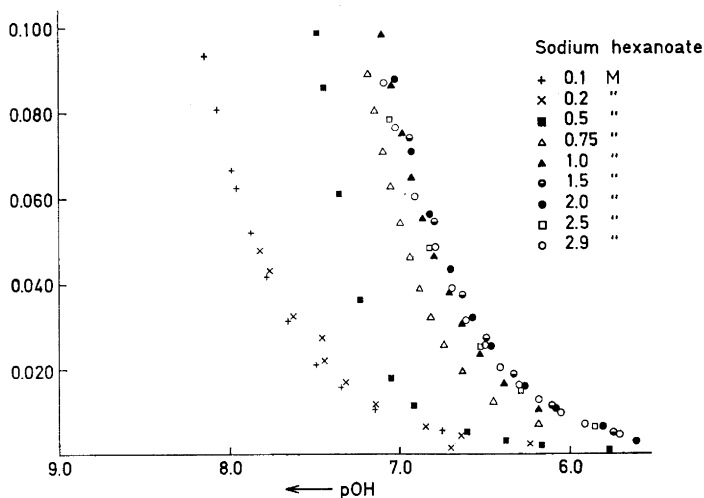
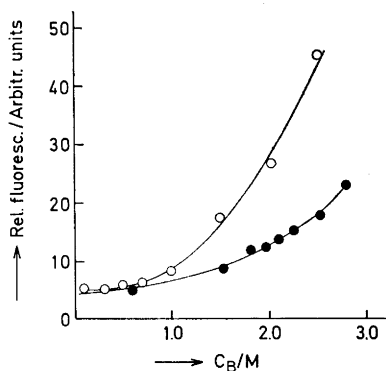


Fig. 5. The hydrolysis of sodium hexanoate at different concentrations.

Fig. 6. The solubilization of methyl cholanthrene in sodium hexanoate (O) and pentanoate (●) solution. Relative fluorescence at 365 nm versus concentration.



Thus there seems to be a formation of aggregates acting as simple monobasic acids at high concentrations; a possible explanation is discussed below.

The calculations done with LETAGROPVRID are summarized in Tables 6–9. The complexes found are given in Table 10. The errors given in this table are the standard deviations of the stability constants obtained in the “best possible” fit of the model, according to eqn. (7). When judging the experimental results, one should consider not these deviations only, since the values of  $U$  and the  $\delta Z$  are of importance, too.

*Sodium acetate.* The curves (Fig. 1) indicate formation of mononuclear acetic acid at all concentrations up to 3 M NaAc. Attempts have been made to introduce formation of double ions (Table 6); addition of the aggregates  $\text{Ac}_2^{2-}$  or  $\text{H}_2\text{Ac}_2$  gave a much worse fit than assumption of HAc only, while the combination  $\text{HAc} + \text{HAc}_2^-$  gave a somewhat better fit than HAc only. As

Table 6. Calculations with LETAGROPVRID on the hydrolysis of sodium acetate and propionate.

		Stability constants ( $-\log \beta_{pq}$ ) of tried complexes ( $p,q$ )		$U$	$\sigma(y)$
		1,1	1,2		
Sodium acetate	I	$9.442 \pm 0.005$	$10.43 \pm 0.07$	0.0033	0.0048
	II	$9.453 \pm 0.005$		0.0021	0.0038
Sodium propionate	I	$9.187 \pm 0.003$	$10.35 \pm 0.04$	0.0007	0.0024
	II	$9.199 \pm 0.002$		0.0001	0.0011

seen from Table 6, the standard deviation in  $Z$  (in accordance with Sillén<sup>7</sup> denoted by  $\sigma(y)$ ) for the model "HAc only" is of the same magnitude as the estimated experimental error in  $Z$ . The improvement in the fit obtained by introduction of  $\text{HAc}_2^-$  thus seems to be lacking in statistical significance. The conclusion is that the association of acetate ions to double ions cannot be confirmed with certainty.

*Sodium propionate.* For sodium propionate (Fig. 2), the argument is exactly similar to that for sodium acetate. It is concluded that the association of propionate ions to double ions cannot be confirmed with certainty.

*Sodium butyrate.* The  $Z$  curves for sodium butyrate (Fig. 3) immediately show association at concentrations larger than 1 M. Calculations with LETAGROPVRID (Table 7) indicate a formation of dimers ( $\text{HB}_2$ ) and tetramers ( $\text{HB}_4$ ,  $\text{H}_2\text{B}_4$ ,  $\text{H}_3\text{B}_4$ ), but no larger aggregates. It has not been possible to intro-

Table 7. Calculations with LETAGROPVRID on the hydrolysis of sodium butyrate.

	Stability constants ( $-\log \beta_{pq}$ ) of tried complexes ( $p,q$ )									$U$	$(y)$	
	1,1	1,2	1,3	1,4	2,3	2,4	2,5	3,4	3,5			
I	$9.213 \pm 0.005$	$9.827 \pm 0.056$				rej. <sup>a</sup>	$19.420 \pm 0.147$	$27.880 \pm 0.133$			0.0020	0.0030
II	$9.212 \pm 0.005$	$10.172 \pm 0.261$	$10.282 \pm 0.152$		$18.797 \pm 0.115$	rej.	rej.	rej.			0.0022	0.0032
III	$9.212 \pm 0.005$	$9.961 \pm 0.082$	$10.357 \pm 0.112$		rej.	rej.	rej.	$27.833 \pm 0.168$	$28.136$ max. $27.766^b$		0.0020	0.0031
IV	$9.216 \pm 0.005$	$9.888 \pm 0.056$		$11.028$ max. $10.760$			$19.171 \pm 0.251$	$27.894 \pm 0.168$			0.0013	0.0025

<sup>a</sup> rej. = rejected. The complex was tried together with the complexes for which stability constants are given in the same row, but the standard deviation came out more than twice as large as the stability constant.

<sup>b</sup> max.: The standard deviation is larger than about 30 % of the stability constant, and instead of a standard deviation, a maximum value for the stability constant is given.

duce complexes free from hydrogen ions into the model, which possibly could be taken as an indication that hydrogen ions are of some decisive importance in the formation of aggregates. However, it is possible that this can be explained by the fact that the investigation of hydrolysis is insensitive to equilibria without hydrogen ions. These equilibria will affect the  $Z$  curves only indirectly.

Table 8. Calculations with LETAGROPVRID on the hydrolysis of sodium pentanoate. See notes to Table 7.

$p, q$	Stability constants ( $-\log \beta_{pq}$ ) of tried complexes ( $p, q$ )					
	I	II	III	IV	V	VI
1,1	9.177 ± 0.009	9.151 ± 0.009	9.179 ± 0.025	9.198 ± 0.034	9.199 ± 0.022	9.199 ± 0.022
1,2		rej.				
1,3	rej.	rej.				
1,4	rej.	rej.				
2,4	17.152 ± 0.076	17.010 ± 0.041	rej.	17.091 ± 0.148	17.075 ± 0.067	17.077 ± 0.077
2,5			17.292 ± 0.080			
3,4	25.847 max. 25.622	rej.		25.954 max. 25.620	25.988 max. 25.724	25.981 max. 25.685
3,5			25.292 ± 0.080			
1,10					rej.	
1,11					12.204 max. 11.975	12.217 max. 12.010
1,12			11.805 ± 0.220	12.792 max. 12.143	rej.	
1,13	rej.	12.669 max. 12.402	rej.			
0,13	rej.	rej.				
$U$	0.0110	0.0087	0.0062	0.0058	0.0055	0.0055
$\sigma (y)$	0.0075	0.0062	0.0054	0.0057	0.0055	0.0055

Sodium pentanoate (Table 8); sodium hexanoate (Table 9). Both salts show a strong shift of the  $Z$  curves as the concentration increases. The pentanoate curve for  $C_B = 2.9$  M is of the same shape as that for a simple monobasic acid, whereas the hexanoate shows this type of curves from 1.2 M upwards. The LETAGROPVRID calculations indicate that tetramers similar to those of the butyrate occur at lower concentrations. Dimers have not been found. There is a formation of large aggregates, which can be thought of as micelles. It should be stressed that the aggregation numbers for the micelles are approximate; the differences in the  $U$  values are not large between as-

Table 9. Calculations with LETAGROPVRID on the hydrolysis of sodium hexanoate. See notes to Table 7.

$p, q$	Stability constants ( $-\log \beta_{pq}$ ) of tried complexes ( $p, q$ )			
	I	II	III	IV
1,1	9.274 ± 0.090	9.274 ± 0.090	9.274 ± 0.090	9.308 ± 0.153
1,2		rej.		
1,3			rej.	
1,4	8.191 max. 7.963	8.083 max. 7.854	rej.	8.162 max. 7.879
1,5			8.014 max. 7.722	
2,3			rej.	
2,4	15.091 ± 0.064	15.078 ± 0.072	15.032 ± 0.071	15.057 ± 0.070
2,5		rej.		
3,4		rej.		
1,16			6.638 max. 7.722	
1,17	6.809 ± 0.227	6.653 ± max. 6.390	rej.	6.571 ± max. 6.311
0,17	0.423 ± 0.208	0.173 max. 0.125	0.064 max. 0.283	0.125 max. 0.216
$U$	0.0079	0.0076	0.0081	0.0049
$\sigma (y)$	0.0078	0.0080	0.0082	0.0066

sumptions of aggregation numbers varying with 3–4 units. The stability constants for the micelle formation are quite uncertain, too. However, it is certain that the stability constant for the hexanoate is several orders of magnitude larger than that for the pentanoate.

In addition to the complexes shown in the tables, attempts have been made with complexes with a large number of protons ( $H_4B_4$ ,  $H_4B_5$ ,  $H_2B_6$ ,  $H_6B_{15}$ , etc.) but these are all rejected immediately in favour of complexes with lower numbers of protons.

#### DISCUSSION AND CONCLUSIONS

Table 10 gives rise to the following comments.

1. The experimental accuracy does not make it possible to decide definitely whether dimers occur in acetate and propionate solutions. To test the reliability of the experiments, Danielsson<sup>15</sup> has measured the water activity at constant ionic strength and varying amounts of sodium acetate and propionate. Considerable changes in the water activities are found, and it is thus necessary

to be careful when drawing conclusions from titrations at high carboxylate concentrations, where there is some uncertainty about the constancy of the activity coefficients. The dimers give a better fit, since the curves at these high concentrations are reproduced better by them than by monobasic acid only. Other workers<sup>16</sup> assert that dimers are formed.

*Table 10.* Hydrolytic equilibria in solutions of short-chain fatty acid sodium salts at high ionic strength (3 M NaCl). The stability constants are given for equilibria of the type  $p\text{H}_2\text{O} + q\text{B} = \text{H}_p\text{B}_q + p\text{OH}$ . The standard deviations are those calculated from the curvefitting with LETAGROPVRID.

	No. of points	Complexes	$-\log\beta_{pq}$	$\sigma(y)$	$U$
Sodium acetate	145	HB	$9.442 \pm 0.005$	0.0048	0.003346
Sodium propionate	122	HB	$9.184 \pm 0.003$	0.0024	0.007143
Sodium butyrate	225	HB HB <sub>2</sub> HB <sub>4</sub> H <sub>2</sub> B <sub>4</sub> H <sub>3</sub> B <sub>4</sub>	$9.216 \pm 0.006$ $9.89 \pm 0.10$ 11.03 max. 10.76 $19.17 \pm 0.25$ $27.89 \pm 0.17$	0.0024	0.001345
Sodium pentanoate	198	HB H <sub>2</sub> B <sub>4</sub> H <sub>3</sub> B <sub>4</sub> HB <sub>11</sub>	$9.199 \pm 0.022$ $17.077 \pm 0.077$ 26.98 max. 25.69 12.22 max. 12.01	0.0052	0.005525
Sodium hexanoate	125	HB HB <sub>4</sub> H <sub>2</sub> B <sub>4</sub> HB <sub>17</sub> B <sub>17</sub>	$9.31 \pm 0.15$ 8.16 max. 7.88 $15.06 \pm 0.07$ 6.57 max. 6.31 0.13 max. -0.22	0.0063	0.004883

Dimers have been found in butyrate solutions, but not in pentanoate and hexanoate solutions. This does not rule out their existence in these solutions either but if they exist, they do so to a measurable extent in a concentration region which is so narrow, that none of our titrations has been made in it.

2. Apart from the aggregates in Tables 7–9, we have tried a large number of complexes with fewer and more protons. Only models giving a more or less reasonable fit have been included in the tables. It is remarkable that a very consistent picture of the lower association is obtained. Butyrate, propionate, and hexanoate, all form tetramers with increasing stability, as the hydrocarbon chain increases. The changes in Gibbs' free energy for complexes of similar composition, as the hydrocarbon chain increases, are compared in Table 11. It is seen that the increase in  $\Delta G^\circ$  per CH<sub>2</sub> group is relatively invariable. The complexes are thus probably formed by association of hydrocarbon chains rather than through hydrogen bonds or rearrangement of solvation



shells around the carboxylic groups. However, this conclusion needs support from other investigations.

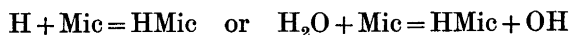
3. It is not possible to introduce small complexes which do not bind hydrogen ions into the models of the association. This is probably so, since the measurement of hydrolysis is insensitive to equilibria without hydrogen ions; all experimental data used in the calculations are taken from solutions with a pH on the acid side of the equivalence point. Activity measurements on the same solutions<sup>15</sup> indicate association in alkaline solutions, too.

Table 11. Changes in Gibbs' energy associated with the formation of complexes in solutions of short-chain fatty acid salts. The energies are given for equilibria of the type  $p\text{H}_2\text{O} + q\text{B} = \text{H}_p\text{B}_q + p\text{OH}$ , where B is the fatty acid anion.

Complex	Sodium carboxylate	Stability constant ( $-\log \beta_{pq}$ )	$\Delta G^\circ$ kcal/mol	Change in $\Delta G^\circ/\text{CH}_2$ group kcal/mol
HB	Acetate	$9.442 \pm 0.005$	$12.88 \pm 0.06$	
	Propionate	$9.184 \pm 0.003$	$12.53 \pm 0.04$	
	Butyrate	$9.216 \pm 0.006$	$12.57 \pm 0.07$	
	Pentanoate	$9.199 \pm 0.022$	$12.55 \pm 0.03$	
	Hexanoate	$9.31 \pm 0.15$	$12.7 \pm 0.2$	
HB <sub>4</sub>	Butyrate	11.03	15.05	
	Pentanoate	—	—	2.0
H <sub>2</sub> B <sub>4</sub>	Hexanoate	8.16	11.13	
	Butyrate	19.17	26.16	
	Pentanoate	17.08	23.31	2.9
H <sub>3</sub> B <sub>4</sub>	Hexanoate	15.06	20.55	2.8
	Butyrate	27.89	38.06	
	Pentanoate	26.98	36.81	1.2
HB <sub>11</sub>	Hexanoate	—	—	
	Pentanoate	12.2	—	
HB <sub>17</sub>	Hexanoate	6.57	8.96	
B <sub>17</sub>	Hexanoate	0.13	0.18	

4. Table 11 shows a qualitative decrease in the free energy of formation of micelles from monomers, as the hydrocarbon chain length increases, *i.e.*, the micelle stability increases. Since it has not been possible to calculate the stability constant for hydrogen ion-free pentanoate micelles, it is not possible to compare association energies without hydrogen ion association.

5. It has been pointed out that *Z* curves at high concentrations have the same shape as that for a simple non-associating monobasic acid; the curves also all coincide, which they should do for such an acid. This can be explained if the micelle is assumed to be a macromolecule with a number of identical carboxylic groups, all with the same dissociation constant, and consequently with identical average degree of dissociation. One thus may assume that protons are associated to the micelle according to



with the stability constant

$$\beta_{\text{mic}}' = \frac{[\text{HMic}][\text{OH}]}{[\text{Mic}][\text{H}_2\text{O}]} = \beta_{\text{mic}}/[\text{H}_2\text{O}] \quad (10)$$

The fraction of the excess of hydrogen ions bound in micelles is given by  $Z_{\text{mic}}$

$$Z_{\text{mic}} = [\text{HMic}]/C_{\text{mic}} \quad (11)$$

where  $C_{\text{mic}}$  is the total concentration of micelles in the solution. If one makes the reasonable assumption that the part of the excess of hydrogen ions which is not bound to the micelles is negligible, one has  $Z_{\text{mic}} \approx Z$ . Further, one may consider the concentration of free hydrogen ions negligible,  $[\text{HMic}] \approx C_{\text{mic}} - C_{\text{H}}$ . Introducing these approximations after combination of (10) and (11) gives

$$\frac{Z}{1-Z} = \frac{\beta_{\text{mic}}}{[\text{OH}]} \quad (12)$$

The position of the  $Z$  curves then is independent of the total concentration of associate, which is in accordance with the experiments.

We consider it proved beyond doubt that there is association in solutions of association colloids below the CMC; this association could be caused by hydrophobic bonding just as the micelle formation. This cannot be definitely established without independent experiments, the methods suggesting themselves being a calorimetric determination of association enthalpies, activity measurements and relaxation time measurements for protons. We continue our investigations in this direction and towards higher homologues.

*Acknowledgements.* We thank Professor Ingvar Danielsson, Åbo Akademi, for aid and advice throughout the work. The late Professor Lars Gunnar Sillén and Dr. Björn Warnqvist, Dept. of Inorg. Chem., Royal Institute of Technology, Stockholm, gave invaluable help with the computer work. Parts of this work were sponsored by *Statens Naturvetenskapliga Kommission*, Helsinki, by *Neste Oy*, Porvoo, and by *Svenska Kulturfonden*, Helsinki, Finland.

#### REFERENCES

1. Danielsson, I. and Suominen, T. *Acta Chem. Scand.* **17** (1963) 979.
2. Danielsson, I. In Overbeek, J. T. G., Ed., *Proc. IV Intern. Congr. Surface Active Substances*, Gordon and Breach, London 1967, Vol. 2 B, p. 555.
3. Danielsson, I., Mäntylä, A., Kreutzman E. and Ritola, P. *Acta Acad. Aboensis, Math. Phys.* **24** (1964) 4.
4. Danielsson, I. and Koivula, T. In Ekwall, P. and Runnström-Reio, V., Eds., *Surface Chemistry*, Munksgaard, Copenhagen 1975, p. 137.
5. Sillén, L. G. *Acta Chem. Scand.* **10** (1956) 186.
6. Sillén, L. G. *Acta Chem. Scand.* **18** (1964) 1085.
7. Sillén, L. G. and Warnqvist, B. *Arkiv Kemi* **31** (1969) 315, 341.
8. Mukerjee, P. *Advan. Coll. Interf. Sci.* **1** (1967) 241.
9. Frank, H. S. and Evans, M. E. *J. Chem. Phys.* **13** (1945) 507.
10. Franks, F. In Franks F., Ed., *Physico-Chemical Processes in Mixed Aqueous Solvents*, Heinemann, London 1967, p. 50.
11. Biedermann, G. and Sillén, L. G. *Arkiv Kemi* **5** (1952) 425.
12. Hietanen, S. and Sillén, L. G. *Acta Chem. Scand.* **13** (1959) 533.

13. Gran, G. *Analyst* **77** (1952) 61.
14. Danielsson, I. *Kemian Teollisuus* **23** (1966) 1081.
15. Danielsson, I. In *Proc. V Intern. Congr. Surface Active Substances*, Ediciones Unidas, Barcelona 1969, Vol. 2 B, p. 869.
16. Rossotti, M. and Rossotti, H. *J. Phys. Chem.* **65** (1961) 926.

Received November 11, 1970.