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Association Equilibria and Micelle Formation of Fatty Acid Sodium Salts. IV. A Comparison between the Association of Sodium Pentanoate, Sodium 3-Methylbutyrate and Sodium Trimethylacetate

PER STENIUS

Department of Physical Chemistry, Åbo Akademi, Porthansgatan 3—5, SF-20500 Åbo 50, Finland

A potentiometric investigation of the self-association of sodium 3-methylbutyrate and sodium trimethylacetate has been made in the ionic medium 3 M Na(Cl) at 25°C. The following complexes and stability constants have been found:

Sodium 3-methylbutyrate: (B^- = the 3-methylbutyrate anion)

$B^- + H_2O \rightarrow HB + OH^-$ $\quad -\log \beta_{1,1} = 9.232 \pm 0.016$
$4B^- + H_2O \rightarrow HB_4^{3-} + OH^-$ $\quad -\log \beta_{1,4} = 9.169 \pm 0.052$
$15B^- \rightarrow B_{15}^{15-}$ $\quad -\log \beta_{0,15} = 6.35$ (max. 6.06)

Sodium trimethyl acetate: (B^- = the trimethylacetate anion)

$B^- + H_2O \rightarrow HB + OH^-$ $\quad -\log \beta_{1,1} = 8.8593 \pm 0.0022$
$4B^- + H_2O \rightarrow HB_4^{3-} + OH^-$ $\quad -\log \beta_{1,4} = 9.848 \pm 0.067$
$4B^- + 2\,H_2O \rightarrow H_2B_4^{2-} + OH^-$ $\quad -\log \beta_{2,4} = 17.481 \pm 0.073$

3-Methylbutyrate anions form micelles of about the same size as those of the pentanoate [1] but their stability constant is lower. The compact shape of the trimethyl acetate ions obviously prevents micelle formation, (the increase in mobility of the hydrocarbon part necessary to form stable micelles is not possible), but the small aggregates formed probably are stabilized by hydrophobic bonding.

In a number of investigations,[1–5] it has been shown that straight-chain sodium carboxylates with more than three carbon atoms in the hydrocarbon chain form small aggregates with 4 – 5 anions, and that the smallest carboxylate molecule forming micelles is the pentanoate anion. Thermodynamic [4] as well as spectroscopic [5] results indicate that the attractive forces leading to formation of these aggregates probably are hydrophobic bonding, possibly in conjunction with ion-pair formation, since the sodium ion activity decreases when the association becomes appreciable.[4] This picture is consistent with several previous investigations of the pre-micellar aggregation of surfac-

Table 1. Titration of 0.1 M sodium 3-methylbutyrate at 25°C.

$C_B = 0.1000$ M $\quad E_{OH}° = 342.95$ mV
$C_H° = 0.009678$ M $\quad V = 40.00$ ml

Amount of OH^- added mmol	E mV	pOH	Z_{exp}	$1000(Z_{exp} - Z_{calc})$
0	−146.7	8.277	0.0967	−0.9
0.01865	−145.1	8.250	0.0920	−1.5
0.03731	−143.6	8.225	0.0874	−1.6
0.05596	−142.0	8.198	0.0827	−1.6
0.07462	−140.2	8.167	0.0781	−2.1
0.09327	−138.4	8.137	0.0734	−2.2
0.1119	−136.5	8.105	0.0687	−2.2
0.1305	−134.5	8.071	0.0641	−2.3
0.1492	−132.3	8.034	0.0594	−2.4
0.1678	−129.9	7.993	0.0547	−2.5
0.1865	−127.3	7.949	0.0501	−2.7
0.2052	−124.6	7.904	0.0454	−2.5
0.2238	−121.5	7.851	0.0408	−2.6
0.2425	−118.0	7.792	0.0361	−2.6
0.2611	−114.1	7.726	0.0314	−2.5
0.2798	−109.4	7.647	0.0268	−2.6
0.2984	−103.9	7.554	0.0221	−2.5
0.3171	−97.3	7.442	0.0174	−2.1
0.3357	−88.0	7.285	0.0128	−2.1
0.3544	−74.4	7.055	0.0081	−1.8
0.3731	−44.5	6.550	0.0034	−1.4

Table 2. Titration of 0.5 M sodium 3-methylbutyrate at 25°C.

$C_B = 0.500$ M $\quad E_{OH}° = 348.4$ mV
$C_H° = 0.05530$ M $\quad V = 40.00$ ml

Amount of OH^- added mmol	E mV	pOH	Z_{exp}	$1000(Z_{exp} - Z_{calc})$
0.1865	−147.3	8.380	0.1013	22.3
0.3731	−140.6	8.266	0.0919	7.4
0.5596	−135.7	8.183	0.0826	1.6
0.7462	−131.3	8.109	0.0733	−0.9
0.9327	−126.9	8.035	0.0640	−1.8
1.119	−122.1	7.954	0.0546	−2.1
1.305	−116.8	7.864	0.0453	−1.9
1.492	−110.4	7.766	0.0360	−1.6
1.548	−108.3	7.720	0.0332	−1.4
1.604	−105.9	7.680	0.0304	−1.3
1.660	−103.2	7.634	0.0276	−1.2
1.716	−100.3	7.585	0.0248	−1.1
1.772	−97.2	7.533	0.0220	−0.9
1.828	−93.6	7.472	0.0192	−0.8
1.884	−89.3	7.399	0.0164	−0.7
1.940	−84.3	7.315	0.0136	−0.6
1.996	−77.9	7.206	0.0108	−0.6
2.052	−69.8	7.069	0.0080	−0.6
2.108	−58.0	6.870	0.0052	−0.5

Table 3. Titration of 0.75 M sodium 3-methylbutyrate at 25°C.

$C_B = 0.750$ M $\quad E_{OH}^\circ = 351.8$ mV
$C_H^\circ = 0.07353$ M $\quad V = 40.00$ ml

Amount of OH^- added mmol	E mV	pOH	Z_{exp}	$1000(Z_{exp} - Z_{calc})$
0	−132.2	8.182	0.0980	−4.7
0.1865	−130.4	8.151	0.0918	−3.5
0.3731	−128.2	8.114	0.0856	−3.1
0.5596	−126.0	8.077	0.0794	−2.4
0.7462	−123.6	8.036	0.0731	−1.8
0.9327	−121.0	7.992	0.0669	−1.3
1.119	−118.1	7.943	0.0607	−0.9
1.305	−115.0	7.891	0.0545	−0.5
1.492	−111.5	7.832	0.0483	−0.3
1.678	−107.6	7.766	0.0421	0
1.734	−106.3	7.744	0.0402	0.1
1.790	−105.0	7.722	0.0383	0.3
1.846	−103.5	7.697	0.0365	0.1
1.902	−102.0	7.671	0.0346	0.2
1.958	−100.4	7.644	0.0327	0.2
2.014	−98.8	7.617	0.0309	0.2
2.070	−97.0	7.587	0.0290	0.2
2.126	−95.0	7.553	0.0271	0.1
2.182	−92.9	7.517	0.0253	−0.1
2.238	−90.6	7.479	0.0234	−0.1
2.294	−88.2	7.438	0.0215	−0.2
2.350	−85.4	7.391	0.0197	−0.4
2.405	−82.4	7.340	0.0178	−0.5
2.461	−79.0	7.282	0.0159	−0.6
2.517	−75.0	7.215	0.0141	−0.9
2.573	−70.4	7.137	0.0122	−1.1
2.629	−64.8	7.042	0.0103	−1.3
2.685	−57.7	6.922	0.0085	−1.6
2.741	−47.9	6.757	0.0066	−1.9
2.797	−32.3	6.493	0.0048	−2.2
2.853	3.7	5.884	0.0029	−2.3
2.909	75.2	4.676	0.0010	−1.0

tants with larger hydrophobic moieties.[6–8] Similar considerations[9–10] are generally offered to explain micelle formation in general. A very important contribution to the decrease in Gibbs' energy of the surfactant molecules on micelle formation is the increased mobility of the hydrocarbon chains in the interior of the micelle, as compared to the mobility in water.[6,11] This contribution can hardly be conceived to play any important part in the formation of small aggregates with 2 – 4 ions. It also follows that micelles should not be formed by substances in which the structure of the hydrocarbon portion is such that it cannot increase its mobility on association with other similar molecules.

A method to test this model experimentally is to investigate substances in which the hydrocarbon portions are increasingly branched isomers of the

same compound. This has been done in the present investigation, where the aggregation processes in aqueous solutions of the sodium salts of 3-methylbutyric acid and trimethylacetic acid are compared to the association taking place in aqueous solutions of sodium pentanoate.

LIST OF SYMBOLS

$[B^-]$ = concentration of free carboxylate ions
C_B = total concentration of sodium carboxylate
C_H = analytical excess of hydrogen ions; C_H° = initial excess of hydrogen ions
E = experimental electromotive force; E_{OH} = constant (standard cell potential), E_j = liquid junction potential
K_w = ionic product of water
k = $RTF^{-1}\ln 10$
$\mathbf{k}$ = Boltzmann constant
p, q = number of hydrogen and carboxylate ions
U = error square sum
V = volume of solution
Z_{exp} = $(C_B - [H^+])/C_B$; Z_{calc} = defined by eqn. (6)
$\beta_{p,q}$ = stability constant of complex $H_pB_q^{(q-p)-}$ [defined by eqn. (4)].
$\sigma(y)$ = standard deviation in Z

Table 4. Titration of 1.0 M sodium 3-methylbutyrate at 25°C.

C_B = 1.000 M
C_H° = 0.09205 M
E_{OH}° = 355.2 mV
V = 40.00 ml

Amount of OH^- added mmol	E mV	pOH	Z_{exp}	$1000(Z_{exp} - Z_{calc})$
0	−123.1	8.085	0.0920	−2.3
0.1865	−120.7	8.045	0.0874	−3.5
0.3731	−118.8	8.013	0.0827	−3.1
0.5596	−117.0	7.982	0.0780	−2.3
0.7462	−115.1	7.950	0.0734	−1.7
0.9327	−113.2	7.918	0.0687	−0.8
1.119	−111.3	7.886	0.0640	0.3
1.305	−109.3	7.852	0.0594	1.2
1.492	−106.8	7.810	0.0547	1.6
1.678	−104.5	7.771	0.0500	2.6
1.865	−101.7	7.724	0.0454	2.9
2.052	−98.8	7.675	0.0407	3.5
2.238	−95.4	7.617	0.0361	3.6
2.425	−91.7	7.555	0.0314	3.9
2.611	−87.2	7.478	0.0267	3.8
2.798	−81.8	7.387	0.0221	3.4
2.984	−75.1	7.274	0.0174	2.9
3.171	−66.3	7.125	0.0127	2.2
3.357	−53.1	6.902	0.0081	1.2
3.544	−24.5	6.419	0.0034	−0.2

Table 5. Titration of 1.2 M sodium 3-methylbutyrate at 25°C.

$C_B = 1.200$ M $E_{OH}° = 355.9$ mV
$C_H° = 0.1136$ M $V = 40.00$ ml

Amount of OH^- added mmol	E mV	pOH	Z_{exp}	$1000(Z_{exp} - Z_{calc})$
0.1865	−117.0	7.994	0.0907	−4.0
0.3731	−115.0	7.960	0.0868	−4.4
0.5596	−113.6	7.937	0.0829	−3.4
0.7462	−112.3	7.915	0.0791	−2.1
0.9327	−111.1	7.894	0.0752	−0.6
1.119	−109.8	7.872	0.0713	0.8
1.305	−108.5	7.850	0.0674	2.3
1.492	−107.1	7.827	0.0635	3.7
1.678	−105.6	7.801	0.0596	5.0
1.865	−103.9	7.773	0.0557	6.0
2.052	−102.1	7.742	0.0519	6.7
2.238	−100.1	7.708	0.0480	7.7
2.425	−97.9	7.671	0.0441	8.3
2.611	−95.5	7.631	0.0402	8.7
2.798	−92.8	7.585	0.0363	9.0
2.984	−89.7	7.533	0.0324	9.0
3.171	−86.2	7.474	0.0285	8.8
3.357	−82.1	7.404	0.0246	8.4
3.544	−77.3	7.323	0.0208	7.6
3.731	−71.3	7.222	0.0169	6.6
3.787	−69.4	7.190	0.0157	6.4
3.842	−67.2	7.152	0.0145	6.0
3.898	−64.8	7.112	0.0134	5.5
3.954	−62.1	7.066	0.0122	5.1
4.010	−59.2	7.017	0.0110	4.7
4.066	−55.8	6.960	0.0099	4.0
4.122	−52.0	6.895	0.0087	3.5
4.178	−47.5	6.819	0.0075	2.9
4.234	−41.9	6.725	0.0064	2.1
4.290	−35.1	6.610	0.0052	1.4
4.346	−25.8	6.452	0.0041	0.6
4.402	−11.0	6.202	0.0029	−0.2
4.458	21.3	5.656	0.0017	−0.9
4.514	90.5	4.486	0.0006	−0.6

EXPERIMENTAL

I. Potentiometric titrations. The association of sodium trimethylacetate and sodium 3-methylbutyrate was studied in a series of potentiometric titrations in solutions made 3 M in Na^+ by addition of NaCl. The procedure followed was essentially the same as that described in parts I and III.[1,3] In the titrations, the hydrolysis of trimethylacetic acid and 3-methylbutyric acid, respectively, was studied as a function of the total concentration C_B of the sodium salts. The analytical excess of hydrogen ions, C_B, was varied by coulometric addition of OH^- ions. The concentration of free hydrogen ions was measured with a hydrogen electrode in combination with the reference electrode

Ag|AgCl|3 M NaCl (satd. with AgCl)

Table 6. Titration of 1.5 M sodium 3-methylbutyrate at 25°C.

$C_B = 1.500$ M $\quad E_{OH}^\circ = 362.1$ mV
$C_H^\circ = 0.1594$ M $\quad V = 40.00$ ml

Amount of OH^- added mmol	E mV	pOH	Z_{exp}	$1000(Z_{exp} - Z_{calc})$
0.3731	−103.1	7.864	0.1000	−15.2
0.7462	−101.2	7.832	0.0938	−12.5
1.119	−99.4	7.801	0.0876	−9.5
1.492	−97.7	7.773	0.0814	−6.2
1.865	−95.9	7.742	0.0751	−3.0
2.238	−94.1	7.712	0.0689	0.3
2.611	−92.1	7.678	0.0627	3.3
2.984	−89.8	7.639	0.0565	6.0
3.357	−87.2	7.595	0.0503	8.4
3.731	−84.2	7.544	0.0440	10.5
4.104	−80.6	7.484	0.0378	12.0
4.477	−76.1	7.408	0.0316	12.7
4.850	−70.8	7.318	0.0254	13.0
5.223	−63.5	7.195	0.0192	12.0
5.596	−52.9	7.015	0.0130	9.7
5.969	−35.2	6.716	0.0067	6.1
6.342	62.4	5.066	0.0005	−0.2

and the bridge solution |(3 M − C_B) NaCl, C_B NaB|, where B denotes the carboxylate anion. The complete cell may be written

$$Pt|H_2|H^+ \text{ (in (3 M} - C_B\text{) NaCl, } C_B \text{ NaB)}|\text{bridge}|\text{ref.electr.}$$

and its emf is given by

$$E = E_H^\circ - k \log [H^+] + E_j = E_{OH}^\circ + k \log [OH^-] + E_j \quad (1)$$

where E_j is the liquid junction potential and $k = RTF^{-1} \ln 10$. The constant ionic strength makes it possible to assume that the activity coefficient of $[OH^-]$ and $[H^+]$ may be included in the constants E_{OH}° and E_H°, respectively.[12,13] E_{OH}° was determined by addition of a known excess of OH^- ions and by plotting the quantity $E - k \log [OH^-] = E_{OH}^\circ + E_j$ against this excess. Since E_j is a linear function of $[OH^-]$, E_{OH}° may be determined by extrapolation to zero $[OH^-]$.[12,13] To calculate $[OH^-]$, the equivalence point was determined using a Gran plot.[14] The titrations were performed automatically with a stabilization period of 30 min after each addition of reagent before the final emf value was registered. The emf then generally was stable within ±0.1 mV. The apparatus used has been described in detail in Ref. 15.

The silver/silver chloride electrode was prepared in a procedure slightly modified from that of Brown [16] and conditioned for several days in 3 M NaCl saturated with AgCl before use. The hydrogen electrode was prepared according to Bates.[17] The hydrogen gas used was passed through 10 % KOH, 10 % H_2SO_4, and two solutions of 3 M NaCl and then into the solution, to avoid evaporation of water from the solution.

II. Chemicals. Sodium trimethylacetate and *sodium 3-methylbutyrate* were prepared by neutralization of the corresponding acids (Fluka *purissimum* grade) with 1 M NaOH (Merck "Titrisol"). The salts were dried in a vacuum oven at 110°C. Their molecular weight was checked by titration with perchloric acid in glacial acetic acid and was found to differ less than 0.25 % from the theoretical value. *Sodium chloride.* (Merck *p.a.*) was dried in a vacuum oven at 110°C for a week before use. *Water* was distilled, passed through an ion exchange column, and then redistilled. Its conductivity was about 0.5 μS cm^{-1}. The *solutions* were prepared in volumetric flasks previously calibrated at 25°C.

TREATMENT OF EXPERIMENTAL DATA

From the values of E_{OH}° determined in the experiments one may calculate E_{H}°; using (1), and the relationship

$$E_{H}^{\circ} = E_{OH}^{\circ} + k \log K_{w} \quad (2)$$

If E_{H}° and E_j are known, $[H^+]$ and pH in the solutions can be calculated. In our titrations, E_j was never larger than about 0.2 mV at pOH *ca.* 11. In acid solutions, E_j increases about 20 mV/mol H^+.[18] Since the pH in the solutions in this experiment is never lower than 5, it may safely be assumed that $E_j \approx 0$. However, it is possible that K_w varies somewhat with C_B,[19] and this makes the calculation of pH in the solutions somewhat uncertain. For this reason, the association equilibria are written

$$qB^- + pH_2O \rightleftharpoons H_pB_q^{(q-p)-} + pOH^- \quad (3)$$

and the stability constants are defined by

Table 7. Titration of 2.0 M sodium 3-methylbutyrate at 25°C.

$C_B = 2.000$ M
$C_H^{\circ} = 0.3120$ M
$\delta Z = 0.015 \pm 0.002$

$E_{OH}^{\circ} = 234.2$ mV (369.5 mV) [a]
$V = 40.00$ ml

Amount of OH^- added mmol	E mV	pOH	Z_{exp}	$1000(Z_{exp} - Z_{theor})$
3.731	−209.1	7.470	0.1093	−21.8
4.104	−207.7	7.445	0.1046	−19.3
4.477	−206.2	7.419	0.1000	−16.6
4.850	−204.7	7.394	0.0953	−14.0
5.223	−203.2	7.367	0.0907	−11.4
5.596	−201.6	7.338	0.0860	−8.9
5.969	−199.9	7.308	0.0813	−6.5
6.342	−198.1	7.276	0.0767	−4.1
6.715	−196.2	7.244	0.0720	−1.7
7.088	−194.3	7.210	0.0673	0.3
7.462	−192.3	7.171	0.0627	2.6
7.835	−190.0	7.129	0.0580	4.6
8.208	−187.5	7.083	0.0487	6.3
8.581	−184.8	7.032	0.0440	8.0
8.954	−181.8	6.975	0.0394	9.3
9.327	−178.4	6.912	0.0347	11.3
9.700	−174.7	6.835	0.0300	12.4
10.07	−170.4	6.752	0.0254	12.8
10.44	−165.2	6.640	0.0207	12.9
10.82	−158.6	6.496	0.0160	12.9
11.19	−150.1	6.277	0.0114	12.4
11.56	−137.1	5.839	0.0067	11.8

[a] Since the range of the digital voltmeter was ±230.0 mV, a compensating potential of 135.3 mV was connected in series with the cell in this titration; the E_{OH}° value 369.5 mV is the value without compensating potential.

Table 8. Titration of 3.0 M sodium 3-methylbutyrate at 25°C.

$C_B = 3.000$ M
$C_H^\circ = 0.320$ M
$\delta Z = 0.0049 \pm 0.0006$
$E_{OH}^\circ = 247.6$ mV (382.9) [a]
$V = 40.00$ ml

Amount of OH^- added mmol	E mV	pOH	Z_{exp}	$1000(Z_{ber} - Z_{exp})$
0	−193.6	7.458	0.1066	−9.0
0.3731	−192.3	7.436	0.1035	−8.2
0.7462	−191.0	7.414	0.1004	−7.4
1.119	−190.0	7.397	0.0973	−6.0
1.492	−188.8	7.377	0.0942	−5.1
1.865	−187.6	7.357	0.0911	−4.1
2.238	−186.2	7.333	0.0860	−3.5
2.611	−184.8	7.309	0.0849	−3.0
2.984	−183.3	7.284	0.0817	−2.4
3.357	−181.8	7.259	0.0786	−2.0
3.731	−180.4	7.235	0.0755	−1.4
4.104	−178.9	7.210	0.0724	−1.0
4.477	−177.2	7.181	0.0693	−0.8
4.850	−175.6	7.154	0.0662	−0.5
5.223	−173.9	7.125	0.0631	−0.2
5.596	−172.3	7.098	0.0600	0.3
5.969	−170.7	7.071	0.0569	0.8
6.342	−169.0	7.042	0.0538	1.3
6.715	−167.3	7.014	0.0507	1.8
7.088	−165.5	6.983	0.0475	2.4
7.462	−163.4	6.948	0.0444	2.6
7.835	−161.1	6.909	0.0413	2.6
8.208	−158.6	6.867	0.0382	2.6
8.581	−156.0	6.823	0.0351	2.7
8.954	−153.3	6.777	0.0320	2.9
9.327	−150.3	6.726	0.0289	3.0
9.700	−147.1	6.672	0.0258	3.2
10.07	−143.4	6.610	0.0227	3.3
10.44	−139.3	6.540	0.0196	3.5
10.82	−134.2	6.454	0.0164	3.6
11.19	−127.8	6.346	0.0133	3.5
11.56	−119.8	6.211	0.0102	3.5
11.93	−107.8	6.008	0.0071	3.4
12.31	−86.0	5.639	0.0040	3.3

[a] See note to Table 7.

$$\beta_{p,q} = ([H_pB_q][OH^-]^p)/[B^-]^q \quad (4)$$

The experimental values for C_B, C_H, and $[OH^-]$ are used to calculate the quantity

$$Z_{exp} = (C_H - [H^+])/C_B \quad (5)$$

which is the mean number of protons bound per carboxylate anion. In this equation $[H^+]$ may safely be calculated using K_w for 3 M NaCl, since $C_H \gg [H^+]$ in all titrations and a small error in $[H^+]$ is of no consequence.

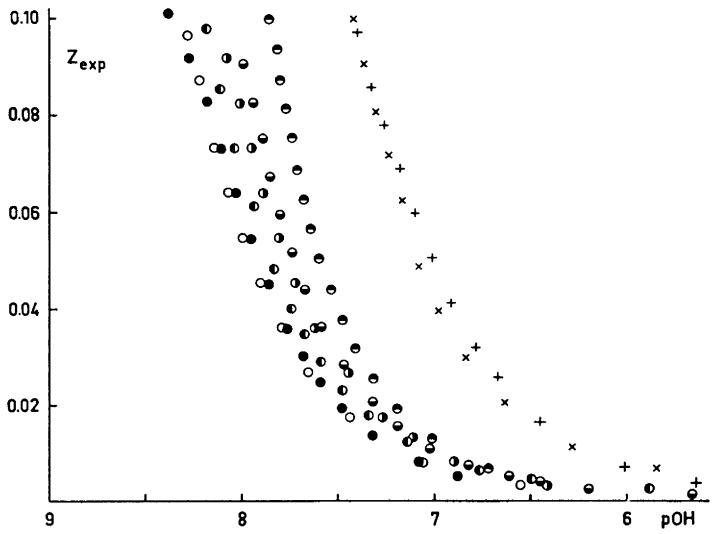

Fig. 1. The hydrolysis of sodium 3-methylbutyrate. $Z_{exp}=(C_H-[H^+])C_B$ plotted against pOH for different total concentrations C_B. Some of the points in Tables 1–8 have been left out. Concentrations of C_B (M): 0.1 ○; 0.5 ●; 0.75 ◐; 1.0 ◑; 1.2 ◒; 1.5 ◓; 2.0 ×; 3.0 +.

If the complexes formed in the solutions and their stability constants are known, a theoretical value for Z can be calculated from [20,21]

$$Z_{calc}=\frac{\sum p[OH^-]^{-p}[B^-]^q\beta_{pq}}{C_B} \tag{6}$$

using experimental values for $[OH^-]$ and values of the free carboxylate ion concentration, $[B^-]$ calculated by solving the equation

$$C_B=[B^-]+\sum q[OH^-]^{-p}[B^-]^q\beta_{pq} \tag{7}$$

the summation being taken over all combinations of p, q defining existing complexes in the solution. The computer program LETAGROPVRID [22] developed by Sillén and co-workers, which has been used in the present work, uses guessed values for p, q, and β_{pq} and experimental values for C_B and OH^- to calculate Z_{calc} for each of the n experimental points and then minimizes the sum of the squares of the errors

$$U=\sum_{i=1}^{n}(Z_{calc,i}-Z_{exp,i}+\delta Z)^2 \tag{8}$$

by adjusting the β_{pq} in (6). Here, δZ is a systematic error in Z_{exp}, which may be different for each titration. As measures of the agreement between Z_{exp} and Z_{calc}, U and the quantity

Table 9. Calculations with LETAGROPVRID on the hydrolysis of sodium 3-methylbutyrate.

	Stability constants ($-\log \beta_{p,q}$) of tried complexes H_pB_q											
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
p,q	Titr. 1–6	Titr. 1–6	Titr. 1–6	Titr. 1–6	All titr.	All titr.	All titr.	All titr.	All titr.	All titr.	All titr.	All titr.
1,1	9.256± 0.017	9.268± 0.020	9.241± 0.015	9.2545± 0.0089	9.255± 0.040	9.270± 0.043	9.290± 0.098	9.290± 0.098	9.290± 0.098	9.290± 0.098	9.290± 0.098	9.252± 0.016
1,2		rej.[b]										
1,3		9.264± 0.045		9.63± 0.16			9.22± 0.015					
2,3		rej.										
1,4	9.50± 0.14	rej.	rej.	9.177± 0.054	9.267± 0.094		9.071± 0.049	9.066± 0.050	9.071± 0.049	9.066± 0.052	9.166± 0.055	9.168± 0.052
2,4	17.73± 0.15	rej.	rej.		rej.	17.85 max 17.60			rej.	rej.		
3,4		rej.	rej.									
1,5			rej.									
2,5			17.491± 0.046	17.71± 0.12			17.79 max 17.56					
1,8					rej.							
0,10									4.64± 0.23			
1,10										rej.		
0,12										rej.		
0,13								5.57± 0.30	rej.	rej.		
1,13							rej.	rej.	rej.			
0,14										5.88[a] max. 5.62	rej.	
0,15											rej.	6.35[a] max. 6.06
1,15											rej.	
1,16											rej.	
1,20								rej.				
U	0.00199	0.00263	0.00214	0.00152	0.01689	0.01573	0.01679	0.01149	0.01212	0.01149	0.01723	0.00748
$\sigma(y)$	0.00377	0.00432	0.00389	0.00328	0.00917	0.00889	0.00919	0.00762	0.00780	0.00758	0.00926	0.00377

[a] max.: the standard deviation is larger than about 20 % of the stability constant and only a maximum value for the constant is given.
[b] rej. = rejected. The complex was tried together with other complexes in the same column, but the standard deviation was larger than 50 % of the stability constant.

Table 10. Titration of 1.00 M sodium trimethylacetate at 25°C.

$C_B = 1.000$ M
$C_H^\circ = 0.05570$ M
$E_{OH}^\circ = 216.3_5$ mV
$V = 40.00$ ml

Amount of OH^- added mmol	E mV	pOH	Z_{exp}	$1000(Z_{calc} - Z_{exp})$
0	−253.3	7.635	0.0557	11.4
0.1865	−232.6	7.589	0.0510	9.5
0.3731	−230.0	7.545	0.0463	8.5
0.5596	−227.2	7.498	0.0417	7.5
0.7462	−224.0	7.444	0.0370	6.4
0.9327	−220.4	7.383	0.0324	5.3
1.119	−216.2	7.312	0.0277	4.3
1.305	−211.2	7.227	0.0230	3.3
1.492	−205.2	7.126	0.0184	2.4
1.678	−197.3	6.993	0.0137	1.5
1.734	−194.7	6.949	0.0123	1.4
1.790	−191.5	6.894	0.0109	1.2
1.846	−188.0	6.835	0.0095	1.0
1.902	−183.9	6.766	0.0081	0.9
1.958	−178.9	6.681	0.0067	0.7
2.014	−172.9	6.580	0.0053	0.5
2.070	−165.0	6.447	0.0039	0.4
2.126	−153.6	6.254	0.0025	0.2
2.182	−132.8	5.902	0.0011	0.1

Table 11. Titration of 1.2 M sodium trimethylacetate at 25°C.

$C_B = 1.200$ M
$C_H^\circ = 0.08425$ M
$E_{OH}^\circ = 219.1$ mV
$V = 40.00$ ml

Amount of OH^- added mmol	E mV	pOH	Z_{exp}	$1000(Z_{calc} - Z_{exp})$
0	−232.4	7.632	0.0702	2.8
0.1865	−231.6	7.619	0.0663	4.6
0.3731	−230.3	7.597	0.0624	5.1
0.5596	−228.5	7.566	0.0585	4.4
0.7462	−226.8	7.538	0.0546	4.4
0.9327	−224.9	7.506	0.0507	4.0
1.119	−222.7	7.468	0.0469	3.3
1.305	−220.4	7.430	0.0430	2.9
1.492	−217.8	7.386	0.0391	2.3
1.678	−214.9	7.337	0.0352	1.7
1.865	−211.5	7.279	0.0313	1.0
2.052	−207.8	7.217	0.0274	0.5
2.238	−203.4	7.142	0.0235	−0.1
2.425	−198.4	7.058	0.0197	−0.5
2.611	−192.3	6.954	0.0158	−0.8
2.798	−184.0	6.814	0.0119	−1.1
2.984	−171.6	6.605	0.0080	−1.4
3.078	−162.0	6.442	0.0061	−1.6
3.096	−159.5	6.400	0.0057	−1.6
3.283	−86.7	5.196	0.0018	−1.6
3.301	−68.9	4.868	0.0014	−1.3
3.320	−50.7	4.561	0.0010	−0.9
3.339	−33.1	4.263	0.0006	−0.6

Table 12. Titration of 1.50 M sodium trimethylacetate at 25°C.

$C_B = 1.500$ M
$C_H^\circ = 0.1108$ M
$E_{OH}^\circ = 223.3$ mV
$V = 40.00$ ml

Amount of OH^- added mmol	E mV	pOH	Z_{exp}	$1000(Z_{calc} - Z_{exp})$
0	−221.3	7.516	0.0738	−6.1
0.1865	−220.5	7.502	0.0707	−5.0
0.3731	−219.9	7.492	0.0676	−3.3
0.5596	−219.3	7.482	0.0645	−1.6
0.7462	−218.2	7.463	0.0614	−1.1
0.9327	−217.0	7.443	0.0583	−0.6
1.119	−215.8	7.423	0.0551	0.1
1.305	−214.3	7.397	0.0520	0.1
1.492	−212.8	7.372	0.0489	0.4
1.678	−211.1	7.343	0.0458	0.5
1.865	−209.4	7.315	0.0427	0.8
2.052	−207.5	7.282	0.0396	0.8
2.238	−205.4	7.247	0.0365	0.9
2.425	−203.0	7.206	0.0334	0.8
2.611	−200.5	7.164	0.0303	0.9
2.798	−197.5	7.113	0.0272	0.7
2.984	−194.2	7.058	0.0241	0.7
3.171	−190.3	6.992	0.0209	0.6
3.357	−185.7	6.914	0.0178	0.5
3.544	−180.0	6.818	0.0147	0.4
3.731	−172.6	6.692	0.0116	0.2
3.197	−162.2	6.517	0.0085	0.2
4.104	−144.9	6.224	0.0054	0.2
4.122	−142.4	6.182	0.0051	0.2
4.141	−139.7	6.136	0.0048	0.2
4.160	−136.7	6.086	0.0045	0.2
4.178	−133.4	6.030	0.0042	0.2
4.197	−129.5	5.964	0.0038	0.3
4.216	−125.0	5.888	0.0035	0.4
4.234	−119.7	5.798	0.0032	0.4
4.253	−113.1	5.687	0.0029	0.4
4.272	−105.0	5.550	0.0026	0.5
4.290	−94.8	5.377	0.0023	0.6
4.309	−82.3	5.166	0.0020	0.7
4.327	−68.2	4.928	0.0017	0.9
4.346	−53.4	4.677	0.0014	1.1
4.365	−37.6	4.410	0.0010	1.5
4.383	−20.5	4.121	0.0007	1.7

$$\sigma(y) = \sqrt{U_0/(n-1)} \tag{9}$$

may be used. Here, U_0 is the value of the minimum in the second-degree surface used to approximate the real U-function by LETAGROPVRID which is defined by the β_{pq}-values that are used to calculate the real U. If the real U in fact is a minimum, the difference between U and U_0 is small, and $\sigma(y)$ defines a standard deviation in Z.

Table 13. Titration of 1.8 M sodium trimethylacetate at 25°C.

$C_B = 1.800$ M
$C_H^\circ = 0.1067$ M
$E_{OH}^\circ = 228.8$ mV
$V = 40.00$ ml

Amount of OH^- added mmol	E mV	pOH	Z_{exp}	$1000(Z_{exp} - Z_{theor})$
0	−208.5	7.392	0.0592	−1.4
0.1865	−207.4	7.374	0.0596	−1.2
0.3731	−206.2	7.353	0.0540	−1.1
0.5596	−205.0	7.333	0.0514	−0.9
0.7462	−203.8	7.313	0.0488	−0.6
0.9327	−202.5	7.291	0.0463	−0.4
1.119	−201.1	7.267	0.0437	−0.3
1.305	−199.6	7.242	0.0411	−0.2
1.492	−198.0	7.215	0.0385	−0.1
1.678	−196.2	7.184	0.0359	−0.1
1.865	−194.3	7.152	0.0333	−0.1
2.052	−192.4	7.120	0.0307	0.1
2.238	−190.2	7.083	0.0281	0.1
2.611	−185.0	6.995	0.0229	0.0
2.984	−178.5	6.885	0.0178	−0.1
3.357	−169.8	6.738	0.0126	−0.1
3.544	−163.8	6.637	0.0100	−0.2
3.600	−161.9	6.605	0.0092	−0.1
3.656	−159.7	6.567	0.0084	−0.1
3.712	−157.3	6.527	0.0077	−0.1
3.768	−154.6	6.481	0.0069	−0.1
3.824	−151.6	6.430	0.0061	−0.1
3.880	−148.1	6.371	0.0053	0.0
3.936	−144.0	6.302	0.0045	0.0
3.992	−139.3	6.223	0.0038	0.0
4.048	−133.4	6.123	0.0030	−0.1
4.104	−125.9	5.996	0.0022	0.0
4.160	−114.7	5.807	0.0014	0.0
4.216	−95.4	5.480	0.0007	0.0

RESULTS AND CALCULATIONS

I. Sodium 3-methylbutyrate. The experimental values for sodium 3-methylbutyrate are listed in Tables 1 – 8, and are summarized in Fig. 1. The titrations were carried out either in duplicate or in triplicate. For each of the concentrations, the titrations agreed within 0.005 units in Z. As discussed in Ref. 1, this is the best agreement that can be expected on the basis of an estimation of experimental errors. One of the titrations only was chosen for the calculations with LETAGROPVRID, to save calculation time. The reported values are those used in the calculations.

The calculations performed with LETAGROPVRID are summarized in Table 9.

(i) In four calculations, the titrations up to 1.5 M 3-methylbutyrate only were used. The reason for this is, that the titrations of $C_B = 2.0$ M and 3.0 M

almost coincide, indicating the dominance of large complexes. It was thus possible to rule out a large number of small complexes in a minimum of computing time. The results indicated the possible complexes H_1B_3, H_1B_4, H_2B_4, and H_2B_5.

(ii) In subsequent titrations, a value for the stability constant of 3-methylbutyric acid was first calculated using only the titration at $C_B = 0.1$ M. The Z curve for this titration very closely coincides with the theoretical curve for a titration in which only a monobasic acid exists in the solution. This value for $\beta_{1,1}$ then was used in subsequent calculations without variation. It was then found, that the small complex giving the "best" values of Z_{calc} was H_1B_4.

(iii) Addition of a larger complex with 10 – 16 anions always decreased U considerably. However, it was very difficult to distinguish between complexes of different size. The LETAGROPVRID procedure selects the complexes that are accepted on the basis of the magnitude of the standard deviations of the stability constants of the tried complexes. Introduction of two large complexes, say, HB_{13} and HB_{14}, invariably resulted in the rejection of both, since the standard deviations were of the same magnitude as the constants themselves. Different complexes then were tried one by one. The uncertainties in the stability constants of the tried complexes then were 20 – 40 %, but the error

Table 14. Titration of 2.0 M sodium trimethylacetate at 25°C.

$C_B = 2.000$ M
$C_H^\circ = 0.1198$ M
$E_{OH}^\circ = 232.5$ mV
$V = 40.00$ ml

Amount of OH^- added mmol	E mV	pOH	Z_{exp}	$1000(Z_{calc} - Z_{exp})$
0	−200.5	7.319	0.0593	−4.7
0.3731	−198.4	7.284	0.0547	−4.3
0.7462	−196.1	7.245	0.0500	−3.9
1.119	−193.7	7.205	0.0453	−3.2
1.492	−191.0	7.159	0.0407	−2.8
1.865	−188.0	7.108	0.0360	−2.3
2.052	−186.3	7.080	0.0337	−2.2
2.238	−184.7	7.053	0.0313	−1.7
2.425	−182.8	7.020	0.0290	−1.6
2.611	−180.7	6.985	0.0267	−1.4
2.798	−178.5	6.948	0.0243	−1.1
2.984	−175.9	6.904	0.0220	−1.1
3.171	−173.1	6.856	0.0197	−1.0
3.357	−169.9	6.802	0.0174	−0.9
3.544	−166.2	6.740	0.0150	−0.8
3.731	−162.0	6.669	0.0127	−0.7
3.917	−156.8	6.581	0.0104	−0.6
4.104	−150.3	6.471	0.0080	−0.4
4.153	−148.3	6.437	0.0074	−0.4
4.340	−138.9	6.278	0.0051	−0.3
4.526	−122.9	6.008	0.0027	−0.1
4.582	−115.4	5.881	0.0020	−0.1
4.638	−104.7	5.700	0.0013	0.0
4.694	−86.1	5.386	0.0006	0.0

Table 15. Titration of 2.5 M sodium trimethylacetate at 25°C.

$C_B = 2.500$ M $\quad E_{OH}^\circ = 239.6$ mV
$C_H^\circ = 0.1474$ M $\quad V = 40.00$ ml

Amount of OH^- added mmol	E mV	pOH	Z_{exp}	$1000(Z_{exp} - Z_{calc})$
0	−185.3	7.183	0.0589	−6.7
0.1865	−184.4	7.167	0.0571	−6.6
0.3731	−183.6	7.154	0.0552	−6.1
0.5596	−182.6	7.137	0.0533	−5.0
0.7962	−181.7	7.122	0.0515	−5.7
0.9372	−180.7	7.105	0.0496	−5.5
1.119	−179.8	7.090	0.0477	−5.0
1.305	−178.8	7.073	0.0459	−4.7
1.492	−177.8	7.056	0.0440	−4.3
1.678	−176.7	7.037	0.0421	−4.1
1.865	−175.6	7.019	0.0403	−3.7
2.052	−174.5	7.000	0.0384	−3.3
2.238	−173.2	6.978	0.0365	−3.1
2.425	−171.9	6.956	0.0347	−2.9
2.611	−170.6	6.934	0.0328	−2.5
2.798	−169.1	6.909	0.0309	−2.3
2.984	−167.5	6.882	0.0291	−2.1
3.171	−165.7	6.851	0.0272	−2.0
3.357	−163.9	6.821	0.0253	−1.8
3.544	−162.0	6.789	0.0235	−1.6
3.731	−159.9	6.753	0.0216	−1.4
3.917	−157.7	6.716	0.0197	−1.2
4.104	−155.1	6.672	0.0179	−1.1
4.290	−152.4	6.627	0.0160	−0.9
4.477	−149.3	6.574	0.0141	−0.7
4.850	−141.6	6.444	0.0104	−0.4
5.223	−130.5	6.256	0.0067	−0.2
5.596	−110.3	5.915	0.0030	−0.0
5.783	−86.9	5.519	0.0011	0.1
5.839	−72.6	5.278	0.0005	0.2

square sum decreased significantly (*cf.* for example, columns VI and IX in Table 9). The lowest U-value was attained with the complex B_{15}, but it should be emphasized that the difference in U between different complexes was quite small (*cf.* for example, columns VIII and X in Table 9).

(iv) Finally, a systematic error δZ was introduced in titrations 7 and 8 to check whether the occurrence of a large complex could not be explained just as well as the result of systematic errors. It was found that this improved the value for $\beta_{0,15}$ and decreased U; the systematic error in titration 7 is 0.015 Z-units (which seems very resonable on inspection of Fig. 1) and the error in titration 8 is insignificant. There is little doubt that on the basis of these potentiometric experiments, micelle-like aggregates are formed by sodium 3-methylbutyrate. The last columns in Tables 1 – 8 show that there is agreement between experimental and theoretical Z values within experimental error (± 0.004 Z units).

Table 16. Titration of 3.0 M sodium trimethylacetate at 25°C.

$C_B = 3.000$ M
$C_H^\circ = 0.2383$ M
$E_{OH}^\circ = 250.0$ mV
$V = 40.00$ ml

Amount of OH^- added mmol	E mV	pOH	Z_{exp}	$1000(Z_{exp} - Z_{calc})$
0	−180.4	7.276	0.0794	−1.5
0.1865	−180.0	7.269	0.0778	−0.9
0.3731	−179.2	7.255	0.0763	−1.4
0.5596	−178.7	7.247	0.0747	−0.9
0.7462	−178.0	7.235	0.0731	−1.0
0.9327	−177.5	7.227	0.0716	−0.6
1.119	−176.9	7.217	0.0700	−0.4
1.305	−176.3	7.206	0.0685	−0.3
1.492	−175.7	7.196	0.0669	0.0
1.678	−175.3	7.189	0.0654	0.6
1.865	−174.8	7.181	0.0638	1.2
2.052	−174.3	7.173	0.0623	1.6
2.238	−173.6	7.161	0.0607	1.8
2.425	−173.0	7.155	0.0592	2.1
2.611	−172.2	7.137	0.0576	2.0
2.798	−171.6	7.127	0.0560	2.4
2.984	−170.9	7.115	0.0545	2.5
3.171	−170.2	7.103	0.0529	2.8
3.357	−169.4	7.090	0.0514	2.9
3.544	−168.6	7.076	0.0498	3.0
3.731	−167.8	7.063	0.0483	3.1
3.917	−167.0	7.049	0.0467	3.3
4.104	−166.1	7.034	0.0452	3.3
4.290	−165.2	7.019	0.0436	3.4
4.477	−164.3	7.004	0.0421	3.5
4.663	−163.4	6.988	0.0405	3.7
4.850	−162.3	6.970	0.0389	3.7
5.036	−161.2	6.951	0.0374	3.5
5.223	−160.0	6.931	0.0358	3.5
5.410	−158.7	6.909	0.0343	3.2
5.596	−157.1	6.882	0.0327	2.8
5.783	−155.7	6.858	0.0312	2.5
5.969	−154.3	6.834	0.0296	2.5
6.156	−152.8	6.809	0.0281	2.3
6.342	−151.2	6.782	0.0265	2.2
6.529	−149.4	6.752	0.0250	2.0
6.715	−147.7	6.723	0.0234	1.9
6.902	−145.9	6.692	0.0218	1.9
7.088	−143.7	6.655	0.0203	1.6
7.275	−141.6	6.620	0.0187	1.6
7.462	−139.2	6.579	0.0172	1.4
7.648	−136.9	6.540	0.0156	1.5
7.835	−134.1	6.493	0.0141	1.3
8.021	−131.0	6.441	0.0125	1.2
8.208	−127.7	6.385	0.0110	1.1
8.394	−123.6	6.316	0.0094	1.0
8.581	−118.9	6.236	0.0079	0.8
8.767	−113.0	6.136	0.0063	0.7
8.954	−105.5	6.010	0.0047	0.5
9.141	−95.0	5.832	0.0032	0.3
9.327	−77.3	5.533	0.0016	0.2

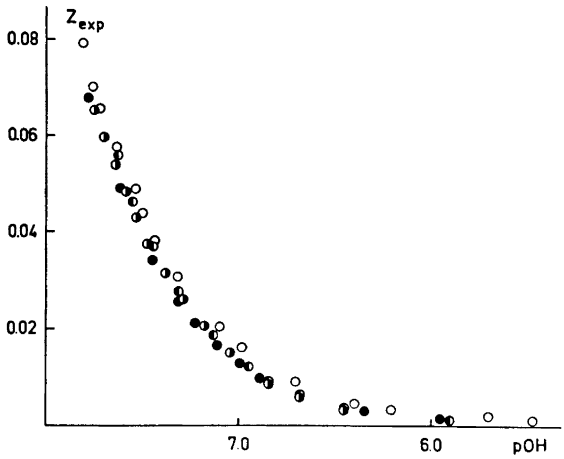

Fig. 2. The hydrolysis of sodium trimethylacetate at low concentrations. Concentrations of C_B (M): 0.1 ○; 0.5 ●; 0.75 ◑; 1.0 ◐.

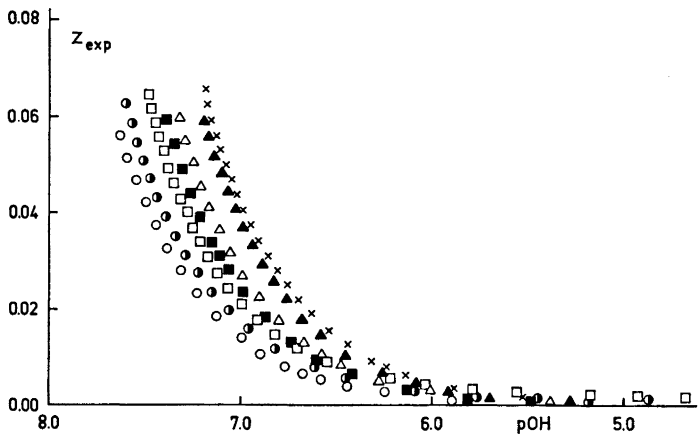

Fig. 3. The hydrolysis of sodium trimethylacetate at higher concentrations. Some of the points in Tables 10–16 have been left out. Concentrations of C_B (M): 1.0 ○; 1.2 ◑; 1.5 □; 1.8 ■; 2.0 △; 2.5 ▲; 3.0 ×.

II. Sodium trimethylacetate. The experimental values for titrations of seven different concentrations of sodium trimethyl acetate are given in Tables 10–16. The experimental results are summarized in Figs. 2 and 3.

The Z curves for all concentrations up to 1.0 M trimethylacetate coincide within experimental error (Fig. 2). Their shape is that of a theoretical normalized curve for a monobasic acid. Obviously, unassociated trimethylacetic

acid only occurs at these concentrations. A value for $\beta_{1,1}$ was calculated with LETAGROPVRID using the four titrations shown in Fig. 2. This value then was used without variation in subsequent calculations. In these, titrations at concentrations above 0.75 M only were utilized.

As Fig. 3 shows, there is a shift of the Z curves indicating complex formation as the concentration exceeds 1 M. Two or three titrations were performed for each concentration and one of these was chosen for use in calculations with LETAGROPVRID on the same grounds as those discussed for sodium 2-methylbutyrate.

The calculations with LETAGROPVRID were fairly straight forward and are summarized in Table 17. The complexes that give the "best" fit to experimental values contain 4 anions. It is seen from the last columns in Tables 10–16 that the agreement between theoretical and experimental values is excellent.

III. Changes in E_{OH}° *with* C_B. Fig. 4 shows the shift in E_{OH}° with C_B for both salts. This linear change is similar to and of the same magnitude (15–16 mV/mol B) as the change found in earlier investigations of straight-chain carboxylates.[1,3,23,24] The reasons for this shift have been discussed elsewhere.[19,25] It is suggested that it is caused by a shift in the standard state energy of OH^- ions as C_B increases. This may cause errors in the complex

Table 17. Calculations with LETAGROPVRID on the hydrolysis of sodium trimethylacetate.

p,q	Stability constants ($-\log \beta_{p,q}$) of tried complexes H_pB_q			
	I	II	III	IV
1,1	8.8593 ± 0.0022	8.8593 ± 0.0022	8.8593 ± 0.0022	8.8593 ± 0.0022
1,2	rej.[a]	rej.		
1,3	rej.	9.488 ± 0.029		
2,3	rej.			
1,4	9.855 ± 0.036			9.848 ± 0.067
2,4	17.460 ± 0.074	17.60 ± 0.14		17.481 ± 0.073
3,4	rej.			
1,5	rej.		10.331 ± 0.0088	
2,5	rej.		17.600 ± 0.057	
1,6				rej.
1,8				rej.
1,10	rej.			
1,12				rej.
U	0.001635	0.002064	0.002661	0.001426
$\sigma(y)$	0.00278	0.00312	0.00354	0.00260

[a] See note [b] to Table 16.

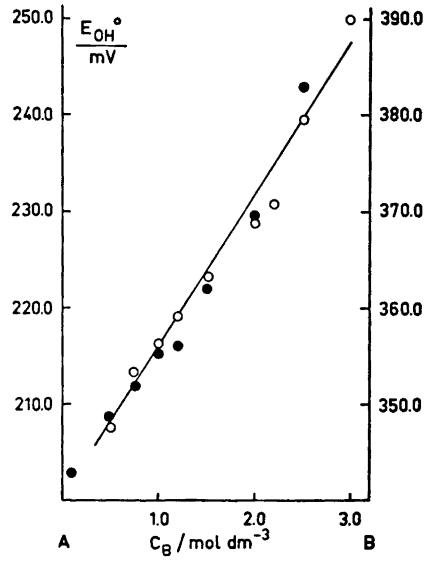

Fig. 4. The variation in standard potential $E_{OH}°$ of the cell used in the study of the hydrolysis of sodium 3-methylbutyrate (B; ●) and trimethylacetate (*A*; ○) as a function of the total carboxylate concentration C_B.

formation found with LETAGROPVRID. It might be concieved that the shift in *Z* curves is caused by a shift in the pOH scale which is dependent on $E_{OH}°$. However, the facts that no shift in the *Z* curves is found for the short-chain salts that do not associate (acetate, propionate [1]) and that there is independent spectroscopic indication that at least butyrate anions do associate [5] seem to make the results given above fairly reliable.

Table 18. A comparison between the complexes formed by different isomers of sodium pentanoate. The stability constants ($-\log \beta_{p,q}$) for the different complexes H_pB_q are given. The values for the pentanoate are taken from Ref. 1.

	$-\log \beta_{1,1}$	$-\log \beta_{1,4}$	$-\log \beta_{2,4}$	$-\log \beta_{1,11}$	$-\log \beta_{0,15}$
Pentanoate $CH_3(CH_2)_3COO^-$	9.199 ± 0.022		17.077 ± 0.077	12.22 max. 12.01[a]	
3-Methylbutyrate $CH_3>CH-CH_2-COO^-$	9.232 ± 0.016	9.168 ± 0.052			6.35 max. 6.06[a]
Trimethylacetate $H_3C-C(CH_3)_2-COO^-$	8.8593 ± 0.0022	9.848 ± 0.067	17.481 ± 0.073		

[a] See note to Table 16.

DISCUSSION

The stability constants of the complexes found for the three pentanoate isomers investigated are compared in Table 18. The following conclusions may be drawn:

(i) All three salts form aggregates with four anions; the difference in stability between these is remarkably small.

(ii) Micellar aggregates are formed by sodium pentanoate and sodium 3-methylbutyrate, with 11 and 15 anions, respectively. As discussed above, not too much significance should be attached to the actual aggregation numbers found, since they represent the best alternative of several almost equal possibilities. Only a crude estimation of the relative stability of the micelles can be made. The stability constant for the proton-free pentanoate micelle, $-\log \beta_{0,11}$, can be roughly estimated by subtracting $\log \beta_{1,1}$ from $\log \beta_{1,11}$; this gives $\log \beta_{11} - \log \beta_{0,11} = 3.0$. This is a considerably larger value than the stability constant found for the 3-methylbutyrate micelles, *i.e.* the micelles of pentanoate are more stable and their concentration becomes appreciable at lower concentrations than the micelles of 3-methylbutyrate.

(iii) Sodium trimethylacetate does not form micelles, but the smaller aggregates formed by this compound are similar to those found for the other isomers, for sodium butyrate and for sodium hexanoate.[1]

These conclusions are remarkably consistent with current concepts of micelle formation and hydrophobic hydration,[10] as discussed in the introduction. On addition of hydrocarbon to an aqueous solution there is "increased structuring" of the water ("cage formation", "iceberg formation", "hydrophobic hydration")[26] which decreases the reorientation time of the water molecules [27] and causes a large entropy decrease. For this reason, hydrocarbon chains are very sparingly soluble in water; if other parts of the molecule are strongly solvated the hydrocarbon chains tend to associate, since this causes a large increase in the entropy of water (hydrophobic bonding).[28] This explains the formation of smaller aggregates of amphiphilic molecules, *e.g.* the compounds in Table 18.

Micelle formation proper takes place if a further increase in entropy can be attained by increasing the mobility of the hydrocarbon chains when they are transferred to a hydrocarbon solvent.[10] In the present case, it is very reasonable to assume that it is possible for the n-pentanoate and 3-methylbutyrate chains to increase their mobility, while the very compact trimethylacetate anion cannot form a sufficiently liquid micellar core. The role of hydrophobic factors in the process of formation of micelles from monomers thus can be divided into two steps:

(i) the formation of smaller aggregates, which decreases the hydrophobic hydration of the hydrocarbon chains,

(ii) the formation of micelles from these aggregates, which increases the mobility of the hydrocarbon chains.

A quantitative indication of the feasibility of this model is given in a recent paper by Lin and Somasundaran,[11] where it is found that the total free energy change per CH_2 group is $-1.39\ \mathbf{k}T$ to $-1.41\ \mathbf{k}T$ for the transfer from aqueous solution to hydrocarbon solution, $-1.10\ \mathbf{k}T$ to $-1.22\ \mathbf{k}T$ for the transfer

from aqueous solution to micelles and -0.61 **k**T to -0.69 **k**T for the transfer from an aqueous solution of ionic surfactants to micelles. The authors suggest that the difference between the two last processes partly might be explained by the fact that the transfer from a solution of ionic surfactants probably takes place from smaller aggregates. The model is also supported by the investigation of the temperature dependence of the stability of sodium butyrate complexes reported in part III,[3] which shows that the formation of small aggregates is accompanied by a large increase in entropy.

In part I,[1] it is reported that the decrease in free energy per CH_2 group on transfer from monomers to aggregates with four anions is about -0.8 **k**T. This would imply an energy of transfer of -0.30 to -0.42 **k**T from small aggregates to micelles, if the values for transfer from aqueous solution to micelle cited above are used. Considering the fact that these are valid for pure aqueous solution, the agreement between these experiments and the values of Lin and Somasundaran is acceptable. This gives some further support to the two-step model of the hydrocarbon chain aggregation suggested above. If it can be assumed that very extensive rearrangement of the solvatation water around the polar end groups does not take place in the transfer from small aggregates to micelles, the increase in internal mobility of the hydrocarbon chain thus causes a decrease in free energy of about $0.3-0.4$ **k**T.

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