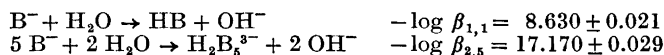


## Association Equilibria and Micelle Formation of Fatty Acid Sodium Salts. III. The Association of Sodium Butyrate at 40° in 3 M Na(Cl)

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A potentiometric investigation has been made of the self-association of sodium butyrate (NaB) at 40°C in the ionic medium 3 M Na(Cl). The following complexes and stability constants ( $\beta$ ) have been found:



The results indicate (i) that the aggregates formed are slightly larger than those formed at 25°C; (ii) that the association is endothermic, the standard enthalpy of association being about 20 kJ/mol butyrate; (iii) that the increase in entropy of the system on association is very large (about 65 J mol<sup>-1</sup> K<sup>-1</sup>), and (iv) that these aggregates probably are formed by hydrophobic bonding.

Parts I and II<sup>1,2</sup> in this series show quite conclusively that small aggregates are formed by sodium alkanoates with more than 3 carbon atoms in the hydrocarbon chain. The aim of the present investigation is to obtain a better understanding of the forces holding the molecules together in these aggregates by investigating the dependence of the aggregation processes in sodium butyrate solutions on temperature. Previous investigations<sup>1-3</sup> indicate that the nature of these forces is similar to those causing micelle formation; the hydrocarbon chains are held together by hydrophobic bonding and the repulsion between the carboxylate end groups is decreased by ion pair formation.

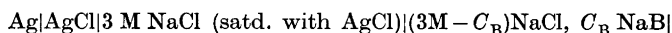
### LIST OF SYMBOLS

[B<sup>-</sup>] = concentration of free butyrate ions  
 $C_B$  = total concentration of sodium butyrate  
 $C_H$  = analytical excess of hydrogen ions;  $C_H^0$  = initial excess of hydrogen ions

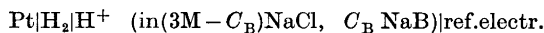
$E$	= experimental electromotive force; $E_{\text{OH}^\ominus}$ , $E_{\text{H}^\oplus}$ = constants (standard cell potentials), $E_j$ = liquid junction potential
$K_w$	= ionic product of water
$k$	= $RTF^{-1} \ln 10$
$p, q$	= number of hydrogen and butyrate ions in complex $\text{H}_p\text{B}_q$
$U$	= error square sum
$V$	= volume of solution
$Z_{\text{exp}}$	= $(C_{\text{H}} - [\text{H}^+])/C_{\text{B}}$ ; $Z_{\text{calc}}$ = defined by eqn. (8)
$\beta_{p,q}$	= stability constant of complex $\text{H}_p\text{B}_q$ (defined by eqn. 15)
$\sigma(y)$	= standard deviation in $Z$
$\ominus$	= standard state

## EXPERIMENTAL

*I. Potentiometric titrations.* The self-association of butyrate anions was studied by investigating the hydrolysis of butyric acid as a function of the total butyrate concentration  $C_{\text{B}}$  in a series of potentiometric titrations. These were all performed in solutions made 3 M in  $\text{Na}^+$  by addition of NaCl, in order to make it possible to use concentrations instead of activities.<sup>9,10</sup>  $C_{\text{B}}$  was kept constant in each titration, the analytical excess of hydrogen ions,  $C_{\text{H}}$ , being varied by coulometric addition of  $\text{OH}^-$  ions. The concentration of free hydrogen ions was measured with a hydrogen electrode in combination with the reference electrode



where NaB denotes sodium butyrate. The bridge solution thus was a neutral solution of similar composition to the solution titrated. The complete cell may be written



and its emf is given by

$$\begin{aligned} E &= E_{\text{H}^\oplus}^\ominus - k \log[\text{H}^+] + E_j \\ &= E_{\text{OH}^\ominus}^\ominus + k \log[\text{OH}^-] + E_j \\ &= E_{\text{OH}^\ominus}^\ominus + k \log K_w - k \log[\text{H}^+] + E_j \end{aligned} \quad (1)$$

where  $E_{\text{H}^\oplus}^\ominus$  and  $E_{\text{OH}^\ominus}^\ominus$  are constant potentials,  $k = RTF^{-1} \ln 10 = 62.132 \text{ mV}$  at  $40^\circ\text{C}$  and  $E_j$  is the liquid junction potential.

The titration vessel and the system used to record the emf have been described in detail elsewhere.<sup>11,12</sup> The titrations were performed automatically. A digital voltmeter with a printout unit was used to measure the emf of the cell for 30 min after each addition of  $\text{OH}^-$ . The voltmeter was then turned off and the coulometer started, electrolytic addition of  $\text{OH}^-$  being performed for 30 min, followed by a new 30 min recording period. The emf values recorded, except for a few points in the immediate vicinity of the equivalence point, were stable within  $\pm 0.1 \text{ mV}$  for 15–20 min; the zero-point drift of the system was less than  $0.2 \text{ mV}/24 \text{ h}$ . The highest currents used in the electrolysis was  $2 \text{ mA}$ . The titration vessel was thermostated at  $40.0 \pm 0.1^\circ\text{C}$ .

*II. Cell calibration and calculation of  $[\text{H}^+]$ .* In each titration,  $E_{\text{OH}^\ominus}^\ominus$  was determined according to the method developed by Biedermann and Sillén.<sup>9</sup> Known excess concentrations of  $\text{OH}^-$  were added and the experimental quantity  $E - k \log[\text{OH}^-] = E_{\text{OH}^\ominus}^\ominus + E_j$  then was plotted against  $\text{OH}^-$  and extrapolated to  $[\text{OH}^-] = 0$ . This procedure invariably yielded straight lines and the intercept was taken as  $E_{\text{OH}^\ominus}^\ominus$ . The equivalence point was determined using Gran plots<sup>13</sup> from the  $E$ -values measured in the alkaline side of the equivalence point.

To calculate  $[\text{H}^+]$  in the acid solutions,  $K_w$  was determined in 3 M NaCl at  $40^\circ\text{C}$  using the method described by Ingri *et al.*<sup>14</sup> A solution 0.05 M in HCl, was titrated in the same way as the butyrate solutions. Since  $[\text{H}^+] = C_{\text{H}}^\ominus$  in this solution,  $E_{\text{H}^\oplus}^\ominus$  may be determined

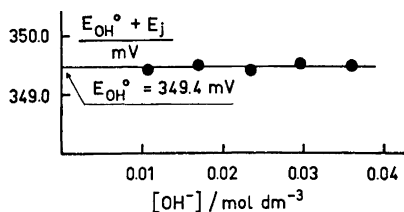


Fig. 1. The potential  $E_{\text{OH}^{\circ}} + E_j$  as a function of  $[\text{OH}^-]$  in the titration of 0.5 M sodium butyrate.

in the same way as  $E_{\text{OH}^{\circ}}$  by plotting  $E + k \log[\text{H}] = E_{\text{H}} + E_j$  against  $[\text{H}^+]$  and extrapolating to  $[\text{H}^+] = 0$ . Then  $K_w$  may be calculated from [eqn. (1)]:

$$\log K_w = (E_{\text{H}}^{\circ} - E_{\text{OH}^{\circ}})/k \quad (2)$$

The value obtained for  $K_w$  in this way was used to calculate  $[\text{H}^+]$  in all solutions at all  $C_B$ .  $E_j$  was found to be negligibly small for all concentrations of  $[\text{H}^+]$  or  $[\text{OH}^-]$  used in our titrations; the slopes of the plots of  $E_{\text{H}}^{\circ} + E_j$  and  $E_{\text{OH}^{\circ}} + E_j$  were found to be zero (see Fig. 1). pOH thus was calculated from the simplified equation

$$\text{pOH} = -\log[\text{OH}^-] = (E - E^{\circ})/k \quad (3)$$

*III. Electrodes.* The Ag/AgCl electrode was prepared by a method slightly modified from that of Brown.<sup>15</sup>

The hydrogen electrode was prepared according to Bates.<sup>16</sup> Commercially available hydrogen was purified by passing it through (i) a platinum catalyst to remove traces of oxygen, (ii) a 10%  $\text{H}_2\text{SO}_4$  solution, (iii) a 10% NaOH solution, (iv) two wash bottles containing 3 M NaCl, and (v) a glass spiral of 1 m length. Vessels (ii)–(v) were all thermostated at 40°C. In this way it was found possible to ensure that (a) the hydrogen gas did not cause temperature changes in the titration vessel, (b) there were no changes in concentration due to evaporation of solvent with the hydrogen gas.

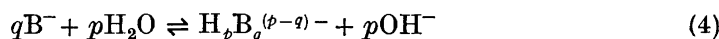
New Ag/AgCl and hydrogen electrodes were prepared for each titration. The stabilizing time for a fresh electrode system was 2–3 h.

The discharge electrode was made of platinum. It had an area of ca 4 cm<sup>2</sup> and was covered with platinum black by electrolysis in aqueous  $\text{K}_2\text{PtCl}_6$ . The anode was a silver plate heavily coated with AgCl and immersed in 3 M NaCl.

*IV. Chemicals.* Sodium butyrate was prepared by neutralization of hot butyric acid (Fluka *puriss.* grade) with 1 M NaOH (Merck *p.a.* grade). The salt was dried in a vacuum oven at 110°C for about a week. The 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. The water was distilled, passed through an ion exchange column and then redistilled. Its conductivity was about 0.5  $\mu\text{S cm}^{-1}$ . The solutions were prepared in volumetric flasks previously calibrated at 40°C.

#### TREATMENT OF EXPERIMENTAL DATA

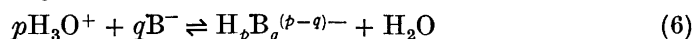
Since the electrode system is calibrated with a known excess of  $\text{OH}^-$  ions, one may calculate  $E_{\text{OH}^{\circ}}$ ,  $[\text{OH}^-]$ , and  $C_{\text{H}}$  directly from the experimental emf values and hydroxide ion additions. To calculate  $[\text{H}^+]$ , the value of  $K_w$  should be known. This cannot be determined in each solution, since the limited solubility of butyric acid does not allow a determination of  $E_{\text{H}}^{\circ}$ . For this reason, it is preferred to write the equilibria studied in the following way



The stability constant for this reaction is given by

$$\beta_{pq}' = \frac{[H_p B_q][OH^-]^p}{[B^-]^q [H_2O]^p} = \frac{\beta_{pq}}{[H_2O]^p} = \frac{\beta_{pq}'' K_w^p}{[H_2O]^p} \quad (5)$$

where  $\beta_{pq}''$  is the stability constant if the reaction is written



Following Sillén,<sup>17</sup> the quantity

$$Z_{\text{exp}} = (C_H - [H^+])/C_B \quad (7)$$

*i.e.* the number of hydrogen ions bound per carboxylate anion, is calculated.  $[H^+]$  can be calculated from (1) if  $K_w$  is known; since  $C_H \gg [H^+]$  in all experiments a small error in  $K_w$  in this case is of no consequence. Theoretically,  $Z$  may also be calculated from, using the law of mass action,

$$Z_{\text{calc}} = (\sum p[OH^-]^{-p}[B^-]^q \beta_{pq})/C_B \quad (8)$$

the sum being taken over the  $p, q$ -values giving all the complexes occurring in the solution.  $[B^-]$  may be calculated by solving the equation

$$C_B = [B^-] + \sum q[OH^-]^{-p}[B^-]^q \beta_{pq} \quad (9)$$

The error square sum minimization procedure LETAGROPVRID<sup>18,19</sup> developed by Sillén and co-workers, has been used in the present work to find values of  $p, q$ , and  $\beta_{pq}$  which give values for  $Z_{\text{calc}}$  that agree within experimental error with  $Z_{\text{exp}}$ . In this procedure, guesses are made for possible values of  $p$  and  $q$ , *i.e.* possible complexes, and the  $\beta_{pq}$ -values are then adjusted to give a minimum in the sum of the squares of the errors

$$U = \sum_{i=1}^n (Z_{\text{calc},i} - Z_{\text{exp},i} + \delta Z)^2 \quad (10)$$

where  $n$  is number of experimental points and  $\delta Z$  is a possible systematic error which may be different for each titration (for example, an error in  $C_B$  or  $C_H$ ). As an indication of the agreement between experiments and the suggested complex formation in the solutions, one may also use the standard deviation

$$\sigma(y) = \sqrt{U_0/(n-1)} \quad (11)$$

which is conveniently compared with the experimental error in  $Z_{\text{exp}}$ . However, the quantity  $U_0$  used in this equation is not the  $U$  value in (10), but the minimum in  $U$  for the second-degree surface which is used to approximate the true  $U$ -function in the search for a minimum. If the found minimum is a good one, the difference between  $U$  and  $U_0$  will be small.

## RESULTS AND CALCULATIONS

The ionic product of water at 40°C.  $K_w$  at 40°C was determined in two titrations of 0.05 M HCl in 3 M NaCl. The values of  $\log K_w$  calculated from (2) were -13.58 and -13.54, respectively. The value  $\log K_w = -13.56$  was used in subsequent calculations of  $Z_{\text{exp}}$ .

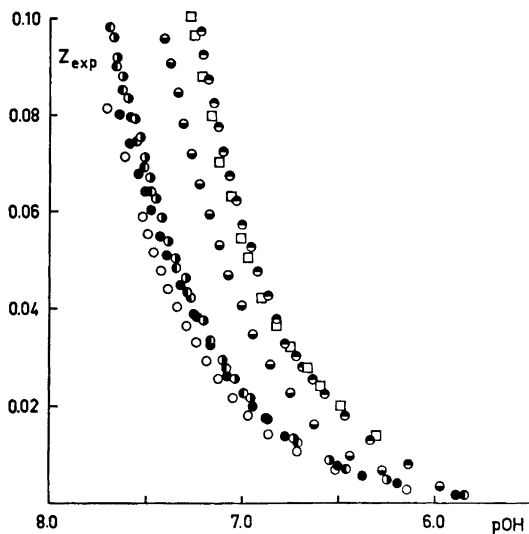


Fig. 2. The hydrolysis of sodium butyrate at different concentrations. The quantity  $Z_{\text{exp}} = (C_{\text{H}} - [\text{H}^+])/C_{\text{B}}$  is plotted against  $-\log [\text{OH}^-]$ . Temperature = 40°C. Some points in Tables 1–7 have been left out. Concentrations of  $C_{\text{B}}$ : ○ 0.5 M; ● 1.0 M; ● 1.2 M; ● 1.5 M; ● 2.0 M; ● 2.5 M; □ 3.0 M.

Table 1. Titration of 0.500 M sodium butyrate at 40°C.

$C_{\text{B}} = 0.500 \text{ M}$   
 $C_{\text{H}}^{\circ} = 0.04025 \text{ M}$   
 $V = 30.00 \text{ ml}$

$\delta Z = 0.0036 \pm 0.0004$   
 $E_{\text{OH}^{\circ}} = 349.4 \text{ mV}$

Amount of OH <sup>-</sup> added mmol	<i>E</i> mV	<i>p</i> OH	<i>Z</i> <sub>exp</sub>	1000( <i>Z</i> <sub>calc</sub> - <i>Z</i> <sub>exp</sub> )
0	-128.7	7.695	0.0837	-2.3
0.1865	-123.7	7.614	0.0712	-2.2
0.3731	-118.1	7.524	0.0588	-1.5
0.4290	-116.1	7.492	0.0551	-1.4
0.4850	-113.9	7.457	0.0513	-1.4
0.5410	-111.6	7.420	0.0476	-1.3
0.5969	-109.2	7.381	0.0439	-1.2
0.6529	-106.5	7.338	0.0402	-1.1
0.7088	-103.7	7.293	0.0364	-0.7
0.7648	-100.5	7.241	0.0327	-0.5
0.8208	-97.0	7.185	0.0290	-0.2
0.8767	-93.0	7.120	0.0252	0.2
0.9327	-88.5	7.048	0.0215	0.5
0.9887	-83.1	6.961	0.0178	0.9
1.044	-76.5	6.855	0.0140	1.5
1.100	-67.8	6.715	0.0103	1.9
1.156	-55.4	6.515	0.0066	2.5
1.212	-32.2	6.142	0.0028	3.1
1.231	-16.1	5.883	0.0016	3.3

*Potentiometric titrations of sodium butyrate.* Seven different concentrations of sodium butyrate were titrated, starting from solutions to which were added HCl to give  $Z_{\text{exp}}$  ca. 0.1. For each concentration, two titrations were performed. These generally gave values for  $Z_{\text{exp}}$  which agreed within  $\pm 0.005$  units in  $Z$ . As discussed in part I, this is the accuracy that may be expected considering the errors inherent in the experimental method. To decrease calculation time, one titration only for each concentration was used in LETAGROPVRID. The additions, emf values,  $Z_{\text{exp}}$ , and  $p\text{OH}$  for these titrations are given in Tables 1–7 and in Fig. 2. The constant  $E_{\text{OH}}^\circ$  for each titration is also given in the tables, and as a function of  $C_{\text{OH}}^\circ$  in Fig. 3. The slope of the straight line defined by these values is 13 mV/mol; at 25°C it is 10 mV/mol.<sup>20</sup>

*Calculations with LETAGROPVRID.* The version of LETAGROPVRID described in Ref. 19, adapted to an UNIVAC 1108 computer, was used to find the values of  $p, q, \delta Z$ , and  $\beta_{pq}$  that were able to explain the experimental results within experimental error. The calculations are summarized in Table 8. The final result, giving a standard deviation in  $Z$  of 0.0067, is that only butyric acid and the complex  $\text{H}_2\text{B}_5$  are formed. It should be emphasized, however that this does not rule out the existence of, for example, the complexes  $\text{H}_1\text{B}_5$

Table 2. Titration of 1.000 M sodium butyrate at 40°C.

$C_{\text{B}} = 1.000 \text{ M}$   
 $C_{\text{H}}^\circ = 0.08013 \text{ M}$   
 $V = 30.00 \text{ ml}$

$\delta Z = 0.0046 \pm 0.0005$   
 $E_{\text{OH}}^\circ = 354.9 \text{ mV}$

Amount of $\text{OH}^-$ added mmol	$E$ mV	$p\text{OH}$	$Z_{\text{exp}}$	$1000(Z_{\text{calc}} - Z_{\text{exp}})$
0	-119.2	7.631	0.0801	3.4
0.1865	-116.2	7.582	0.0739	1.4
0.3731	-113.4	7.537	0.0677	0.7
0.4290	-112.0	7.519	0.0658	-0.0
0.4850	-111.3	7.503	0.0639	-0.3
0.5410	-110.2	7.486	0.0621	-1.0
0.5969	-109.1	7.468	0.0602	-1.4
0.6529	-108.0	7.450	0.0583	-1.7
0.7088	-106.9	7.433	0.0565	-2.0
0.7648	-105.8	7.415	0.0546	-2.2
0.8208	-104.6	7.396	0.0527	-2.4
0.8767	-103.4	7.376	0.0509	-2.7
1.063	-99.6	7.315	0.0447	-2.4
1.249	-95.2	7.244	0.0384	-2.1
1.436	-90.2	7.164	0.0322	-1.5
1.623	-84.1	7.066	0.0260	-0.8
1.809	-76.5	6.943	0.0198	0.2
1.996	-66.1	6.776	0.0136	1.3
2.182	-49.3	6.506	0.0073	2.7
2.238	-41.3	6.377	0.0055	3.1
2.294	-29.9	6.193	0.0036	3.6
2.350	-10.4	5.879	0.0018	4.0

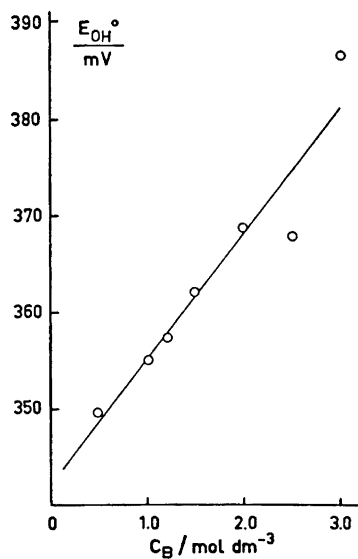


Fig. 3. The change in  $E_{\text{OH}}^0$  with  $C_B$  for sodium butyrate at 40°C.

Table 3. Titration of 1.2 M sodium butyrate at 40°C.

$C_B = 1.200 \text{ M}$   
 $C_{\text{H}^+} = 0.1141 \text{ M}$   
 $V = 30.00 \text{ ml}$

$\delta Z = 0.0022 \pm 0.0006$   
 $E_{\text{OH}}^0 = 357.2 \text{ mV}$

Amount of $\text{OH}^-$ added mmol	$E$ mV	$p\text{OH}$	$Z_{\text{exp}}$	$1000(Z_{\text{calc}} - Z_{\text{exp}})$
0	-120.3	7.685	0.0950	6.9
0.1865	-118.1	7.650	0.0898	4.8
0.3731	-116.0	7.616	0.0847	3.2
0.5596	-113.9	7.582	0.0795	2.1
0.7462	-111.7	7.547	0.0743	1.1
0.9327	-109.4	7.510	0.0691	0.2
1.119	-107.0	7.471	0.0639	-0.5
1.305	-104.3	7.428	0.0587	-1.4
1.492	-101.6	7.384	0.0536	-1.8
1.678	-98.6	7.336	0.0484	-2.2
1.865	-95.3	7.283	0.0432	-2.5
2.052	-91.6	7.223	0.0380	-2.6
2.238	-87.5	7.157	0.0328	-2.5
2.425	-82.6	7. 78	0.0277	-2.5
2.611	-76.8	6.985	0.0225	-2.1
2.798	-69.5	6.868	0.0173	-1.5
2.984	-59.6	6.708	0.0122	-0.7
3.171	-44.1	6.459	0.0069	0.3
3.357	-6.2	5.849	0.0017	1.7

Table 4. Titration of 1.5 M sodium butyrate at 40°C.

$$C_B = 1.500 \text{ M}$$

$$C_{H^{\circ}} = 0.1439 \text{ M}$$

$$V = 30.00 \text{ ml}$$

$$\delta Z = -0.006 \pm 0.002$$

$$E_{OH^{\circ}} = 361.8 \text{ mV}$$

Amount of OH <sup>-</sup> added mmol	<i>E</i> mV	<i>p</i> OH	<i>Z</i> <sub>exp</sub>	1000( <i>Z</i> <sub>calc</sub> - <i>Z</i> <sub>exp</sub> )
0	-115.3	7.680	0.0959	15.7
0.1865	-113.1	7.645	0.0917	11.9
0.3731	-111.4	7.618	0.0876	10.1
0.5596	-109.7	7.590	0.0834	8.5
0.7462	-108.0	7.563	0.0793	7.1
0.9327	-106.2	7.534	0.0752	5.5
1.119	-104.5	7.506	0.0710	4.5
1.305	-102.7	7.478	0.0669	3.4
1.492	-100.8	7.447	0.0627	2.3
1.678	-98.8	7.415	0.0586	1.2
1.865	-96.6	7.379	0.0544	-0.1
2.052	-94.3	7.342	0.0503	-1.3
2.238	-91.1	7.291	0.0461	-3.8
2.425	-89.2	7.260	0.0420	-3.4
2.611	-86.3	7.214	0.0378	-4.3
2.798	-83.0	7.161	0.0337	-5.4
2.984	-79.4	7.103	0.0296	-6.3
3.171	-75.2	7.035	0.0254	-7.0
3.357	-70.4	6.958	0.0213	-7.5
3.544	-64.6	6.864	0.0171	-7.6
3.731	-56.2	6.729	0.0130	-8.2
3.917	-44.8	6.546	0.0088	-8.0
4.104	-26.7	6.254	0.0047	-7.4

Table 5. Titration of 2.0 M sodium butyrate at 40°C.

$$C_B = 2.000 \text{ M}$$

$$C_{H^{\circ}} = 0.2681 \text{ M}$$

$$V = 30.00 \text{ ml}$$

$$\delta Z = 0.0068 \pm 0.0004$$

$$E_{OH^{\circ}} = 368.5 \text{ mV}$$

Amount of OH <sup>-</sup> added mmol	<i>E</i> mV	<i>p</i> OH	<i>Z</i> <sub>exp</sub>	1000( <i>Z</i> <sub>calc</sub> - <i>Z</i> <sub>calc</sub> )
0	-102.8	7.585	0.1340	0.5
0.3731	-100.7	7.552	0.1278	-0.8
0.7462	-98.8	7.521	0.1216	-1.2
1.119	-96.9	7.491	0.1154	-1.4
1.492	-95.1	7.462	0.1091	-1.0
1.865	-93.2	7.431	0.1029	-0.9
2.238	-91.2	7.399	0.0957	-0.9
2.611	-89.2	7.367	0.0905	-0.7
2.984	-87.1	7.333	0.0843	-0.6
3.357	-84.9	7.297	0.0780	-0.4



Table 5. Continued.

3.731	-82.5	7.259	0.0718	-0.5
4.104	-79.9	7.217	0.0656	-0.6
4.477	-77.1	7.172	0.0594	-0.8
4.850	-74.0	7.122	0.0532	-1.1
5.223	-70.6	7.067	0.0470	-1.2
5.596	-66.8	7.006	0.0407	-1.1
5.969	-62.4	6.935	0.0345	-1.0
6.342	-57.3	6.853	0.0283	-0.6
6.715	-51.0	6.752	0.0221	0.1
7.088	-43.0	6.623	0.0159	1.4
7.462	-31.7	6.441	0.0096	3.4
7.648	-20.8	6.266	0.0065	4.2
7.835	-2.5	5.971	0.0034	5.2

Table 6. Titration of 2.5 M sodium butyrate at 40°C.

$C_B = 2.500 \text{ M}$   
 $C_H^\circ = 0.4047 \text{ M}$   
 $V = 30.00 \text{ ml}$

$\delta Z = 0.019 \pm 0.002$   
 $E_{OH^\circ} = 367.7 \text{ mV}$

Amount of $OH^-$ added mmol	$E$ mV	pOH	$Z_{exp}$	$1000(Z_{calc} - Z_{exp})$
0	-92.2	7.402	0.1619	-26.9
0.3731	-91.0	7.383	0.1569	-25.8
0.7462	-90.5	7.375	0.1519	-22.5
1.119	-89.6	7.360	0.1469	-20.4
1.492	-88.8	7.347	0.1420	-18.0
1.865	-88.0	7.334	0.1370	-15.6
2.238	-87.3	7.323	0.1320	-12.8
2.611	-86.5	7.310	0.1270	-10.3
2.984	-85.6	7.296	0.1221	-8.2
3.357	-84.7	7.281	0.1171	-5.9
3.731	-83.7	7.265	0.1121	-3.9
4.104	-82.8	7.251	0.1071	-1.6
4.477	-81.8	7.235	0.1022	0.4
4.850	-80.7	7.217	0.0972	2.2
5.223	-79.5	7.198	0.0922	3.8
5.596	-78.1	7.175	0.0872	5.0
5.969	-76.7	7.153	0.0823	6.1
6.342	-75.0	7.125	0.0773	6.7
6.715	-73.3	7.098	0.0723	7.4
7.088	-71.3	7.066	0.0674	7.6
7.462	-69.3	7.033	0.0624	8.0
7.835	-67.0	6.996	0.0574	8.1
8.208	-64.7	6.959	0.0524	8.5
8.581	-62.2	6.919	0.0475	8.8
8.954	-59.4	6.874	0.0425	9.1
9.327	-56.2	6.823	0.0375	9.3
9.700	-52.7	6.766	0.0325	9.8
9.887	-50.1	6.724	0.0300	9.3
10.07	-47.2	6.678	0.0276	8.8
10.26	-44.1	6.628	0.0251	8.7
10.44	-40.6	6.571	0.0226	8.6
10.82	-34.1	6.467	0.0176	10.0
11.19	-25.8	6.333	0.0126	11.8
11.56	-13.8	6.140	0.0077	14.1

Table 7. Titration of 3.0 M sodium butyrate at 40 °C.

$$C_B = 3.000 \text{ M}$$

$$C_H^{\circ} = 0.4877 \text{ M}$$

$$V = 30.00 \text{ ml}$$

$$\delta Z = -0.0060 \pm 0.0009$$

$$E_{\text{OH}^{\circ}} = 386.4 \text{ mV}$$

Amount of OH <sup>-</sup> added mmol	<i>E</i> mV	pOH	<i>Z</i> <sub>exp</sub>	1000( <i>Z</i> <sub>calc</sub> - <i>Z</i> <sub>exp</sub> )
0	-81.4	7.529	0.1626	-1.2
0.3731	-79.8	7.503	0.1584	-2.5
0.7462	-78.5	7.482	0.1543	-2.7
1.119	-77.3	7.463	0.1501	-2.6
1.492	-76.3	7.447	0.1460	-1.8
1.865	-75.2	7.429	0.1418	-1.3
2.238	-74.2	7.413	0.1377	-0.5
2.611	-73.2	7.397	0.1335	0.4
2.984	-72.3	7.383	0.1294	1.5
3.357	-71.3	7.367	0.1252	2.4
3.731	-70.2	7.349	0.1211	2.9
4.104	-69.3	7.334	0.1170	4.1
4.477	-68.2	7.317	0.1128	4.7
4.850	-66.9	7.296	0.1087	4.6
5.223	-65.8	7.278	0.1045	5.3
5.596	-64.6	7.259	0.1004	5.6
5.969	-63.5	7.241	0.0962	6.4
6.342	-62.3	7.222	0.0921	6.7
6.715	-60.9	7.199	0.0879	6.6
7.088	-59.5	7.177	0.0838	6.5
7.462	-58.1	7.154	0.0796	6.5
7.835	-56.8	7.133	0.0755	6.8
8.208	-55.2	7.107	0.0714	6.3
8.581	-53.6	7.082	0.0672	6.0
8.954	-51.9	7.054	0.0631	5.4
9.327	-50.0	7.024	0.0589	4.6
9.700	-48.1	6.993	0.0548	3.8
10.07	-46.0	6.959	0.0506	2.8
10.44	-43.9	6.926	0.0465	2.0
10.82	-41.5	6.887	0.0423	0.9
11.19	-38.9	6.845	0.0382	-0.4
11.37	-37.1	6.816	0.0361	-1.8
11.56	-35.1	6.784	0.0340	-3.3
11.75	-33.1	6.752	0.0320	-4.7
11.93	-30.8	6.715	0.0299	-6.2
12.12	-28.4	6.676	0.0278	-7.5
12.31	-25.7	6.633	0.0257	-8.8
12.49	-22.9	6.588	0.0237	-10.0
12.68	-19.8	6.538	0.0216	-10.9
12.87	-16.2	6.480	0.0195	-11.8
13.05	-12.1	6.414	0.0175	-12.6
13.43	-4.7	6.295	0.0133	-12.1

Table 8. Calculations with LETAGROPVRID on the hydrolysis of sodium butyrate at 40°C.

<i>p,q</i>	Stability constants ( $-\log \beta_{pq}$ ) of tried complexes ( <i>p,q</i> )						
	I	II	III	IV	V <sup>a</sup>	VI <sup>b</sup>	VII <sup>b</sup>
1,1	8.84 ± 0.07	8.84 ± 0.07	8.725 ± 0.002	8.725 ± 0.002	8.725 ± 0.002	8.749 ± 0.058	8.630 ± 0.021
1,2	rej. <sup>c</sup>				rej.	rej.	rej.
1,3		rej.	rej.				
2,3			rej.	rej.			
3,3				rej.			
1,4	9.68 ± 0.25	9.68 ± 0.25	rej. rej.		rej.	rej.	
2,4	16.95 ± 0.06	16.95 ± 0.06			rej.	17.020 ± 0.082	
3,4	rej.				rej.	rej.	
1,5		rej.	rej.	rej.	rej.		rej.
2,5			17.257 ± 0.036	17.257 ± 0.036	17.257 ± 0.036		17.170 ± 0.029
3,5				rej.	rej.		rej.
4,5				rej.			
1,6		rej.	rej.				
2,6					rej.		
1,7			rej.				
2,7			rej.				
<i>U</i>	0.023444	0.023444	0.010936	0.010936	0.010936	0.009113	0.007763
$\sigma(y)$	0.0114	0.0114	0.00777	0.00777	0.00777	0.00726	0.00670

<sup>a</sup> A systematic error  $Z=0.021 \pm 0.002$  was introduced for the *Z*-values in titration 6. <sup>b</sup> Systematic errors for all titrations were introduced; values for run VII are given in Tables 1–7. <sup>c</sup> rej.=rejected. The complex was tried together with the complexes for which stability constants are given in the same column, but the standard deviation came out more than twice as large as the stability constant.

or  $H_3B_5$ . Indeed, introduction of  $H_1B_5$  together with HB and  $H_2B_5$  gives a slightly lower value of *U*, but the uncertainty in the stability constant for  $H_1B_5$  is too large to merit a value for this constant to be given in Table 2. Introduction of  $H_3B_5$  also yields a slightly lower value of *U* but values for the stability constants have not been given for the same reason as above.

The standard deviation is of the same order of magnitude as the estimated experimental error in  $Z_{\text{exp}}$ . The difference  $Z_{\text{calc}} - Z_{\text{exp}}$  is given for each point in Tables 1–7. It is seen that most of the large differences fall in *pOH* ranges where  $Z_{\text{exp}}$  is very low, i.e., close to the equivalence point. Hence, the value of  $\sigma(y)=0.0067$  should be considered quite satisfactory. The systematic errors in *Z* for each titration are of the same magnitude as the estimated experimental uncertainties with the exception of titration 6 at  $C_B=2.5$  M, where  $\delta Z=0.019$ . It is seen from Fig. 2 that this curve seems to be slightly higher than all the others.

*The variation in  $E_{\text{OH}}^\circ$  with  $C_B$ .* In the previous investigations of carboxylates it was found that the constant  $E_{\text{OH}}^\circ$  varies linearly with  $C_B$ . This is so also in the present case, as is seen from Fig. 3. The reasons for this variation

have been discussed in Refs. 21 and 22. It is only noted here that the uncertainties in the calculations due to the shift in the energy of  $\text{OH}^-$  ions in the standard state which seems to be reflected in the variation in  $E_{\text{OH}^\circ}$  apply to these calculations in the same way as those reported before.

## DISCUSSION

The final result is compared to results at 25°C in Table 9. The following differences are noted

(i) no improvement in the fit of theoretical data to the experiments can be obtained by introducing dimers at 40°C;

(ii) The complex found at 40°C is larger than any of those found at 25°C.

Both results indicate an increased association at 40°C. There does not seem to be any specific chemical bonds (or hydrogen bonds) holding the aggregates together, since the aggregation numbers are not very definitive and probably should be considered as mean aggregation numbers. This conclusion is supported by the following attempt to estimate the enthalpy of aggregate formation.

It was assumed that only HB and  $\text{H}_2\text{B}_4$  or HB and  $\text{H}_2\text{B}_5$  are formed at 25°C and the resulting stability constants were calculated with LETAGROP-VRID. These results are compared to the results from similar calculations for the data at 40°C in Table 9 (rows B and C). It is seen, that these assumptions decrease the agreement between the values predicted by the assumed association equilibria and the experiments at 25°C. However, the standard deviation  $\sigma(y)$  is still smaller than at 40°C and close to the experimental error.

For this reason, it seems feasible to estimate the enthalpy of formation of HB and  $\text{H}_2\text{B}_5$  using van't Hoff's equation

$$\ln(\beta'/\beta'') = (\Delta H^\ominus/R)(1/T'' - 1/T') \quad (12)$$

and the values of  $\beta_{1,1}$  and  $\beta_{2,5}$  found at 25°C and 40°C, respectively. The standard Gibbs' energy of formation is calculated from

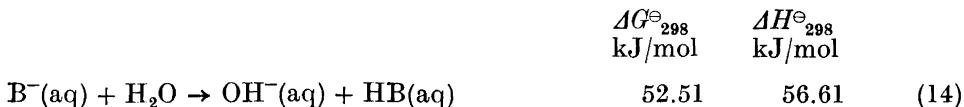
Table 9. A comparison of the complex formation of sodium butyrate at 25°C and 40°C.

Temp. °C	$-\log \beta_{1,1}$	$-\log \beta_{1,2}$	$-\log \beta_{1,4}$	$-\log \beta_{2,4}$	$-\log \beta_{1,5}$	$-\log \beta_{2,5}$	$U$	$\sigma(y)$
40	$8.630 \pm 0.021$					$17.170 \pm 0.029$	0.0078	0.0067
25 A	$9.216 \pm 0.005$	$9.89 \pm 0.06$	$11.03 \text{ max}^a$ 10.76	$19.17 \pm 0.25$	$27.89 \pm 0.17$		0.0013	0.0025
25 B	$9.200 \pm 0.005$			$18.619$ 0.035			0.0031	0.0038
25 C	$9.187 \pm 0.005$					$-18.843 \pm 0.048$	0.0046	0.0047

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

$$\Delta G^\ominus = -RT \ln \beta \quad (13)$$

and the following results then are obtained:



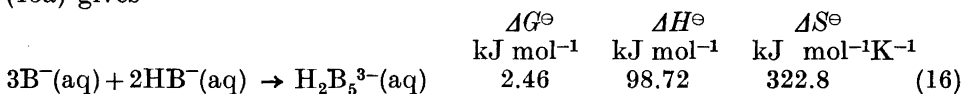
The standard Gibbs' energy and enthalpy of formation with hydrogen ions was obtained by adding the energies for the association<sup>23</sup>



once to (14) and twice to (15). This gives



It is seen that the process of aggregation is endothermic and that the aggregation of the anions probably causes the large change in enthalpy, since the enthalpy for (14a) is very small. Subtracting (14a) twice from (15a) gives



The standard Gibbs energy of formation now becomes positive, *i.e.* the strong tendency of the carboxylate groups to bind hydrogen ions in the cause of the negative  $\Delta G^\ominus$  in eqn. 15a. This is a strong case for assuming that hydrogen bonding cannot be an important part of the forces that hold the aggregates together. They are formed only at very high concentrations even in acid solutions. Moreover, there is evidence that they do exist also in weakly alkaline solutions (pH > 9).<sup>2,24</sup>

A very rough estimate of the different contributions to  $\Delta G^\ominus$  may be made in the following way:

$\Delta G^\ominus$  is divided into three parts:

$$\Delta G^\ominus = \Delta G_{\text{el.stat}}^\ominus + \Delta G_{\text{aggr.entr.}}^\ominus + \Delta G_{\text{sol}}^\ominus$$

(a)  $\Delta G_{\text{el.stat}}^\ominus$  is the contribution to  $\Delta G^\ominus$  from the energy required to bring the three charges close together in  $\text{H}_2\text{B}_5^{3-}$ . Assuming that the aggregate is spherical with a diameter  $r$  equal to the length of the butyrate chain + 0.2 nm and that this sphere bears the charge  $q = 3 e^-$  (that is, ion pair formation is neglected), the work of charging the sphere may be calculated from

$$W_{\text{charging}} = \int_0^{3e^-} \frac{q}{\epsilon_r r} dq; \Delta G_{\text{el.stat.}}^{\ominus} = N_A W_{\text{charging}} \quad (17)$$

where  $\epsilon_r$  is the dielectric constant of water at 25° (= 78.30).<sup>25</sup> This gives

$$\Delta G_{\text{el.stat.}}^{\ominus} = 35.73 \text{ kJ mol}^{-1} \quad (18)$$

(b)  $\Delta G_{\text{aggr.ent.}}^{\ominus}$  is the contribution to  $\Delta G^{\ominus}$  from the decrease in entropy due to the aggregation of five molecules into one. This may be calculated from

$$\begin{aligned} \Delta G_{\text{aggr.ent.}}^{\ominus} &= -T \Delta S_{\text{aggr.ent.}} = -RT \ln \frac{x_{2.5}}{x_m} = \\ &= -RT \ln 0.2 = 2.89 \text{ kJ mol}^{-1} \end{aligned}$$

since the mol fraction of aggregates,  $x_{2.5}$  is 1/5 of the mol fraction of the monomers forming the aggregate.

(c) If it is assumed that no other forces bind the hydrophilic parts of the molecule together, the residual change in Gibbs' energy is due to attraction forces between the hydrocarbon chains and/or rearrangements in the solute-solvent interaction and is given by

$$\begin{aligned} \Delta G_{\text{sol}}^{\ominus} &= \Delta G^{\ominus} - \Delta G_{\text{el.stat.}}^{\ominus} - \Delta G_{\text{aggr.ent.}}^{\ominus} \\ &= -36.57 \text{ kJ/mol} \end{aligned}$$

This negative contribution thus according to the admittedly very crude calculation given above is the cause of the formation of aggregates. The enthalpy change is too large to be explained by the energy required to force the charges together only. It seems that one may at least draw the conclusion, that there is a large increase in entropy due to an increased mobility of the hydrocarbon chains and/or rearrangements in the water structure on association which is the ultimate cause of aggregation. This is in agreement with other investigations,<sup>3-8</sup> of which particular importance should be given to the non-thermodynamic confirmation given by recent NMR investigations.<sup>24</sup> However, it is not possible to assert whether the entropy change is due to a rearrangement of solvent molecules around the changed end-groups or due to hydrophobic hydration. There is some evidence that the first few CH<sub>2</sub> groups close to the polar group in a surfactant are strongly affected by the solvation water of surrounding the polar end group.<sup>26,27</sup> Very recently, Birch and Hall<sup>28</sup> have pointed out that it is not possible to assert with certainty whether the enthalpies of dilution of surfactants below the c.m.c. can be explained by the Debye-Hückel theory for monomeric 1-1 electrolytes or by the formation of dimers. The main difficulty according to these authors is insufficient knowledge of activity coefficients. It seems that the investigation reported here shows that it is possible to circumvent these difficulties by working at high constant ionic strengths.

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