

## Hydrolytic Equilibria in Sodium Acetate Solutions

I. DANIELSSON and T. SUOMINEN

*Institutet för fysikalisk kemi, Åbo Akademi, Åbo, Finland*

The hydrolytic equilibria in solutions of sodium acetate of constant ionic strength (3 M NaCl) have been investigated at 20°C. The experimental data can be interpreted without assuming the formation of polynuclear complexes. The value of the equilibrium constant of the reaction  $\text{AcO}^- + \text{H}_2\text{O} \rightleftharpoons \text{AcOH} + \text{OH}^-$  (the basicity constant of acetate ion) was found to be  $(3.975 \pm 0.003) \times 10^{-10}$ .

The salts of fatty acids with more than six carbon atoms are typical association colloids, but the lower homologues have until recently been considered to behave like normal unassociated electrolytes. In 1959 Rossotti and Martin published a short communication in which they claimed that polynuclear complexes exist also in solutions of the lowest homologues<sup>1</sup>. In order to study preliminary stages of association and, if possible, to determine at which number of carbon atoms in the paraffin chain the salts begin to behave like association colloids we have examined the hydrolytic equilibria in solutions of salts of the lower fatty acids with a constant ionic strength (3 M NaCl). The following results relate to the hydrolysis of sodium acetate.

We shall employ the usual notation. H and B are the reacting species, in our case hydrogen and acetate ions. We denote by  $h$  the hydrogen-ion concentration, by  $[\text{OH}^-]$  the concentration of hydroxide ion and by  $b$  the concentration of ion B. Further, let  $H$  denote the total analytical concentration of ion H assuming no hydrolysis,  $B$  the total concentration of the acetate ion,  $E$  the electromotive force of the cell  $+\text{Ag}, \text{AgCl}/\text{Cl}^-//\text{L}/\text{H}_2, \text{Pt}-$  or the cell  $+\text{Ag}, \text{AgCl}/\text{Cl}^-//\text{L}$ , glass electrode.  $E^\circ$  is the constant electromotive force in the equation  $E = E^\circ + 58.16 \log [\text{OH}^-] + E_j$ , where  $E_j$  is the liquid junction potential. By  $Z = (H-h)/B$  we denote the average number of protons bound by B. By  $\beta_{pq}$  we will denote the formation constant of the complex  $\text{H}_p\text{B}_q$  formed by the reaction  $p\text{H} + q\text{B} = \text{H}_p\text{B}_q$ . All concentrations are expressed in moles per litre of solution (M). Because of the constant ionic strength activity coefficients can be considered constant in each series of measurements and concentrations can be used instead of activities.

In order to be able to apply the self-medium method of Sillén and his coworkers to the experimental data, the measurements were extended to

solutions containing up to 3 moles of acetate per litre;  $Z [= (H-h)/B]$  thus varied from 0 to 0.1<sup>2</sup>. In addition, solutions 1.5, 0.5 and 0.3 M in acetate were also titrated potentiometrically; in these experiments  $Z$  varied from zero to high values, in the case of 0.3 M acetate solution over the whole range from zero to unity.

With the aid of the self-medium method it should be possible to detect the presence of complexes of the type  $H_pB_q$  where the ratio  $q/p$  has a high value. By this method  $p$ , the number of protons bound per species can be determined directly, but it is not possible to draw reliable conclusions about the size of the complex, *i.e.* the magnitude of  $q$ . If, however, the assumption is made that the activity quotient in the equilibrium constant  $\beta_{pq}$  does not vary in the different series of measurements with various acetate concentrations, the magnitude of  $q$  can be estimated.

The sodium acetate trihydrate employed in the study was a guaranteed reagent from E. Merck AG., Darmstadt. The equivalent weight of the salt was checked by titrating it in glacial acetic acid with standard perchloric acid employing crystal violet as indicator. The values found deviated less than three parts per thousand from the calculated equivalent weight. No carbonate was detected with barium chloride in an alkaline solution of the salt. The solutions were all prepared by weighing and their hydrogen-ion, hydroxide-ion and acetate-ion concentrations were checked titrimetrically.

The potentiometric titrations were carried out on solutions whose ionic strengths were adjusted to a constant level (3 M) by adding sodium chloride. An oil thermostat, a "Wilhelm" bridge and a silver-silver chloride reference electrode were employed<sup>3,4</sup>. The hydroxide-ion activities were measured with both a glass electrode (Radiometer G 202 B) and a hydrogen electrode.

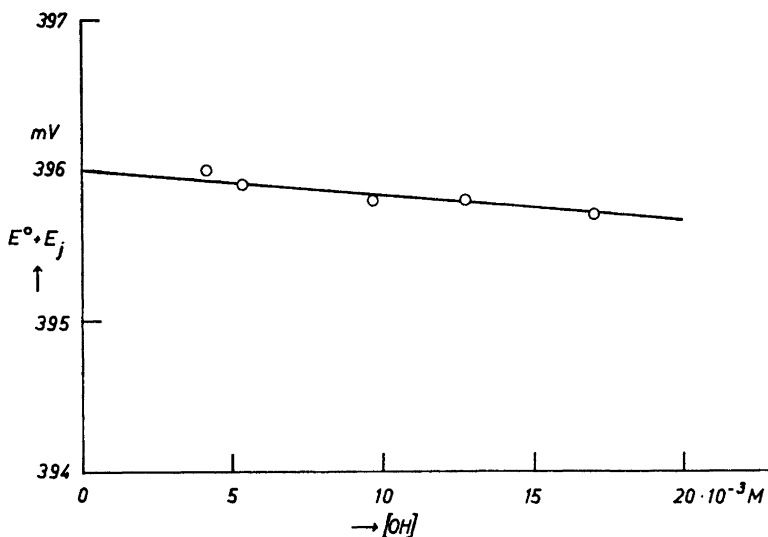


Fig. 1. Evaluation of  $E^\circ$  by extrapolation from the plot of  $E - 58.16 \log [\text{OH}^-]$  against  $[\text{OH}^-]$ .

Table 1. Data for acetate.  $10^4(Z - Z_{\text{calc}})$  is given only for the points used in calculating  $\beta_{11}$ . For calculating  $Z_{\text{calc}}$ , the value  $\beta_{11} = 3.975 \times 10^{-10}$  has been used.

$B = 0.300 \text{ M}$ .

$Z$ ,  $10^4(Z - Z_{\text{calc}})$ ,  $-\log[\text{OH}^-]$ : 0.0007, 7, 4.928; 0.0011, 5.684; 0.0015, 10, 6.122; 0.0019, 6.363; 0.0023, 10, 6.508; 0.0031, 6.721; 0.0047, 10, 6.968; 0.0071, 7.185; 0.0099, 9, 7.360; 0.0138, 7.518; 0.0203, 8, 7.699; 0.0284, 7.854; 0.0423, 7, 8.038; 0.0570, 8.175; 0.0715, 2, 8.285; 0.0891, 8.388; 0.1119, 2, 8.500; 0.1474, 8.639; 0.1756, -16, 8.734; 0.2066, 8.825; 0.2396, -37, 8.908; 0.2627, 8.966; 0.3146, 9.080; 0.3827, 0, 9.193; 0.5087, 9.442; 0.6378, 9.688; 0.7419, 9.905; 0.8169, 10.101; 0.8738, 10.299; 0.9198, 10.526; 0.9453, 10.710; 0.9617, 10.871; 0.9743, 11.047; 0.9843, 11.245; 0.9920, 11.435; 0.0473, 23, 8.074; 0.0772, 8.325; 0.1049, -29, 8.483; 0.1337, 8.609; 0.1877, 8.793; 0.2911, 9.059.

$B = 0.500 \text{ M}$ .

$Z$ ,  $10^4(Z - Z_{\text{calc}})$ ,  $-\log[\text{OH}^-]$ : 0.0034, 3, 6.889; 0.0071, 7.247; 0.0107, -2, 7.441; 0.0160, 7.625; 0.0229, -11, 7.792; 0.0314, 7.934; 0.0411, -28, 8.063; 0.0506, 8.160; 0.0659, -53, 8.285; 0.0802, 8.380; 0.1002, -83, 8.486; 0.1248, 8.598; 0.1523, 8.703; 0.1814, 8.794; 0.2070, 8.868; 0.2295, 8.930; 0.2561, 8.994; 0.2791, 9.047; 0.3039, 9.102; 0.3289, 9.155; 0.3532, 9.205; 0.3790, 9.257; 0.4022, 9.301; 0.4227, 9.339.

0.0018, 3, 6.564; 0.0055, 7.120; 0.0137, 0, 7.544; 0.0274, -4, 7.857; 0.0366, -7, 7.989; 0.0462, -8, 8.094; 0.0586, 8.206; 0.0735, -22, 8.314; 0.0914, -31, 8.419; 0.1130, -43, 8.524; 0.1397, 8.634; 0.1675, 8.730; 0.1947, 8.813, 0.2186, 8.878; 0.2433, 8.944; 0.2681, 9.004; 0.2929, 9.062; 0.3171, 9.112; 0.3418, 9.167; 0.3701, 9.226.

0.1989, 8.828; 0.2167, 8.877; 0.2352, 8.925; 0.2567, 8.976; 0.2792, 9.026; 0.3022, 9.078; 0.3286, 9.133; 0.3572, 9.190; 0.3772, 9.229; 0.4048, 9.277; 0.4287, 9.324; 0.4530, 9.368; 0.4802, 9.415; 0.5072, 9.463; 0.5354, 9.514; 0.5628, 9.563, 0.5823, 9.599; 0.5959, 9.619; 0.6040, 9.635.

$B = 1.500 \text{ M}$

$Z$ ,  $10^4(Z - Z_{\text{calc}})$ ,  $-\log[\text{OH}^-]$ : 0.0001, 5.180, 0.0006, 1, 6.093; 0.0025, 6.745; 0.0060, 4, 7.149; 0.0117, 7.443; 0.0171, 12, 7.610; 0.0269, 7.818; 0.0358, 17, 7.948; 0.0474, 8.077; 0.0606, 21, 8.194; 0.0789, 8.321; 0.0948, -20, 8.431; 0.1258, 8.567; 0.1415, 8.638.

0.0030, 6.810; 0.0060, 8, 7.120; 0.0089, 7.298; 0.0117, 14, 7.419; 0.0171, 7.589; 0.0221, 23, 7.706; 0.0314, 7.869; 0.0437, 36, 8.022; 0.0606, 8.177; 0.0788, 44, 8.306; 0.0963, 8.409; 0.1093, 30, 8.476; 0.1203, 8.528; 0.1326, 11, 8.581, 0.1463, -18, 8.641.

0.0491, 34, 8.081; 0.0698, 42, 8.247; 0.0877, 8.361; 0.1045, 33, 8.452; 0.1249, 8.543; 0.1417, 18, 8.612; 0.1584, 8.672; 0.1735, -14, 8.727; 0.1988, 8.804.

$B = 3.000 \text{ M}$ ;

$Z$ ,  $10^4(Z - Z_{\text{calc}})$ ,  $-\log[\text{OH}^-]$ : 0.0003, 2, 5.311; 0.0009, 6.193; 0.0018, 3, 6.588; 0.0024, 6.748; 0.0035, 2, 6.918; 0.0046, 7.047; 0.0063, 2, 7.190; 0.0082, 1, 7.312; 0.0106, 7.405; 0.0144, 8, 7.541; 0.0186, 8, 7.659; 0.0242, 7, 7.783, 0.0302, 7.910; 0.0397, 12, 8.003; 0.0459, 8.069; 0.0518, 16, 8.124; 0.0572, 19, 8.168; 0.0632, 26, 8.210; 0.0677, 23, 8.246; 0.0360, 11, 0.7959; 0.0413, 14, 8.019; 0.0459, 16, 8.067; 0.0498, 16, 8.105; 0.0523, 12, 8.132; 0.0566, 15, 8.158; 0.0586, 16, 8.182; 0.0620, 20, 8.206; 0.0647, 19, 8.227; 0.0676, 20, 8.247; 0.0709, 20, 8.270; 0.0743, 18, 8.294; 0.0774, 14, 8.316; 0.0807, 10, 8.338; 0.0836, 8, 8.356; 0.0867, 8.375; 0.0901, -1, 8.397; 0.0930, 8.418; 0.0960, -16, 8.435; 0.0980, 8.450.

0.0001, 5.361; 0.0005, 1, 5.974; 0.0010, 6.327; 0.0018, 2, 6.595; 0.0033, 6.870; 0.0065, 7.168; 0.0127, 11, 7.472; 0.0177, 7.620; 0.0263, 15, 7.806; 0.0395, 7.996; 0.0651, 2, 8.242; 0.0003, 1, 5.754; 0.0010, 6.374; 0.0035, 0, 6.946; 0.0090, 7.364; 0.0203, -4, 7.726; 0.0363, -13, 7.993; 0.0545, 8.189.

0.0205, 1, 7.720; 0.0470, -12, 8.105; 0.546, 8.175. 0.0116, 7, 7.441; 0.0293, 15, 7.857; 0.0470, 10, 8.084.

0.0019, 6.638; 0.0070, 5, 7.216.

0.0143, 7.532; 0.0224, 12, 7.737; 0.0407, 14, 8.012; 0.0652, 0, 8.244; 0.0913, 8.407.

The EMF's were measured with a Radiometer model PHM 4 c pH meter with an accuracy of  $\pm 0.2 \text{ mV}$ . A correction for the alkali error of the glass electrode was obtained by carrying out measurements with the hydrogen electrode simultaneously. The potentials became constant within 10 min as a rule, but near the equivalence points it was necessary to wait 15–30 min before the

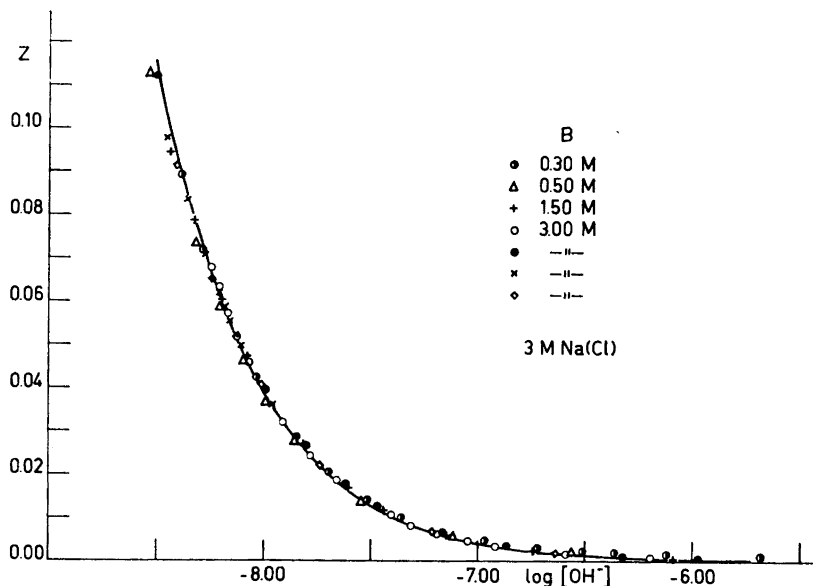


Fig. 2. Plot of  $Z = (H-h)/B$  as a function of  $\log [\text{OH}^-]$  for various concentrations of acetate ion in a medium of ionic strength 3. The curve was calculated from values of  $Z_{\text{exp}}$  smaller than 0.04 assuming that only HB is formed.

potentials became constant. The measurements were made at  $20 \pm 0.1^\circ\text{C}$ . The quantities measured directly in the titrations are  $E$ , the electromotive force of the cell, and  $H$ , the analytical excess of hydrogen ion, or the amount of hydroxide ions necessary to transform all  $\text{H}_p\text{B}_q$  into B. On the alkaline side of the equivalence point there is, of course, a deficit of hydrogen ions. The following fundamental equations are valid:

$$E = E^\circ + 58.16 \log [\text{OH}^-] + E_j \quad (1)$$

$$H-h = ZB = [\text{OH}^-] - \text{OH} \quad (2)$$

Sillén and his coworkers<sup>5,6</sup> have shown that in 3 M sodium perchlorate the liquid junction potential is given by  $E_j = (17h - 8[\text{OH}^-]) \text{ mV/mole}$ , from which it follows that this potential can be neglected in the pH range to which the collected data refer. In order to determine the value of the constant electromotive force  $E^\circ$  in expression (1) the titrations were extended also to the alkaline side of the equivalence point. This point was determined graphically according to Gran, and the excesses of hydroxide ion at the different points on the Gran plots were calculated<sup>7</sup>. The value of  $E^\circ$  was then extrapolated in the usual manner (Fig. 1). The values of  $Z$  were calculated from the experimental values of  $H$  and  $E$  employing eqns. (1) and (2). The calculated values of  $Z$  and  $\log [\text{OH}^-]$  are shown in Table 1.

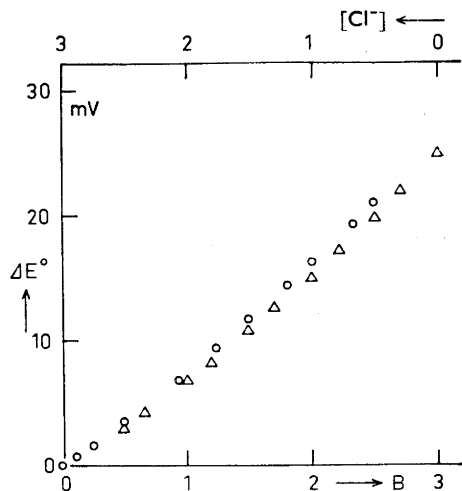


Fig. 3. Variation of the value of the electromotive force  $E^\circ$  of equation (1) when the chloride ion in 3 M sodium chloride solution is replaced by acetate ion.

From Fig. 2 it will be seen that, independent of the level of  $B$ , all the calculated values of  $Z$  are grouped about a single smooth curve. This implies that only one equilibrium prevails in the system. The computed values lie close to a curve that is similar in form to the normalized curve for a system in which only one acid complex  $HB$  exists. It therefore seems justified to consider the experimental data on the assumption that the formation of  $HB$  fully defines the system. With the aid of the expression

$$Z = \frac{\beta_{11}}{[\text{OH}^-] + \beta_{11}} \quad (3)$$

and the method of least squares we have calculated the mean values of the constant  $\beta_{11}$  which is the equilibrium constant of the reaction  $B + \text{H}_2\text{O} \rightleftharpoons \text{HB} + \text{OH}^-$ . The calculations were carried out on a Wegematic 1000 electronic computer at the Computer Centre in Åbo. The full-drawn line in Fig. 2 is the curve calculated by taking the value of the equilibrium constant  $\beta_{11}$  to be  $(3.975 \pm 0.003) \times 10^{-10}$ , the computed mean value. The experimental values are seen to be in excellent agreement with the calculated values.

Our study thus reveals that the hydrolysis in sodium acetate solutions is accurately defined by only one equilibrium constant. In this respect our result is at variance with the conclusions of Rossotti who reported values of stability constants for the complexes  $\text{HB}_2$  and  $\text{H}_2\text{B}_2$ .

It may be pointed out that our observations lead to the conclusion that the value of  $E^\circ$  for the cell varies with the ions and their concentrations in the solution. Fig. 3 shows how the value of  $E^\circ$  varies when the chloride ions are replaced by acetate ions in equimolar solutions. The change from 3 M chloride ion to 3 M acetate ion leads to an increase of about 25 mV in the value of  $E^\circ$ , which corresponds to a change of 0.5 unit in  $\log[\text{OH}^-]$ . What the basic reason

for the shift is we do not know, but similar observations have been made at the Department of Inorganic Chemistry of the Royal Institute of Technology in Stockholm.

We conclude that our data can be explained without assuming the presence of polynuclear complexes, but that the variation of the activity coefficients is not yet fully understood.

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