

The Complex Formation in the Zinc Acetate and the Proton Acetate Systems

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The complex formation in the zinc acetate and the proton acetate systems in aqueous solution has been studied by potentiometric measurements at 25.0°C in 3.0 M NaClO₄.

The zinc acetate system. For the zinc acetate system, three mononuclear complexes were established, and the following overall stability constants were obtained: $\beta_1 = 8.15 \pm 0.02 \text{ M}^{-1}$; $\beta_2 = 23.0 \pm 0.2 \text{ M}^{-2}$; $\beta_3 = 36.9 \pm 0.3 \text{ M}^{-3}$. (The stated errors are three times the standard deviations.)

The proton acetate system. For the proton acetate system, measurements have been performed both with a diffusion free cell and with a cell with liquid junction. In both cases, the measurements can be described by supposing species HAc, HAc₂⁻ and H₂Ac₂ to be formed.

The stability constant for HAc was found to be $(1.035 \pm 0.002) 10^5 \text{ M}^{-1}$ by both methods, but the stability constants for the dimeric species obtained from the two methods did not agree.

Results from separate measurements with cadmium amalgam electrodes indicate that measurable concentrations of dimeric species do not exist.

It can be concluded, that the pH-measurements in acetic acid-acetate solutions are influenced more by changes in activity factors and liquid junction potentials than by hypothetical dimeric acetate species.

The complexity of the zinc acetate system has been subject to several investigations.¹⁻⁶ In general, only the stability constants for the first mononuclear complex have been determined, although up to five mononuclear complexes have been proposed.⁵

To determine the number of mononuclear complexes that may be formed at reasonable acetate concentrations and their strength, potentiometric measurements with zinc amalgam electrodes were performed.

Formation of dimeric species H₂Ac₂ and HAc₂⁻ in acetate buffers has been reported by several authors.^{1,7-11} A proper analysis of the rather weak complex formation in the zinc acetate system presupposes a knowledge of the extent to which such dimeric proton acetate species are formed and also a determina-

tion of the diffusion potential arising when sodium perchlorate in solution is exchanged for sodium acetate and acetic acid. Potentiometric investigations with a glass electrode, a hydrogen gas electrode, and in the preliminary studies also a quinhydrone electrode, were therefore performed to study the proton acetate system thoroughly and to determine the diffusion potential mentioned above. Cells with and without liquid junction were used. The measurements from both types of cells could be described by assuming dimeric species to be formed in the solutions, but the corresponding two sets of equilibrium constants did not agree, although the emf's from the cell with liquid junction were corrected for the diffusion potential. Hence no quantitative proof of the existence of dimeric proton acetate species was attained by these measurements.

Another possibility to check the existence of HAc_2^- in the acetate solutions is offered by measurements with a metal amalgam electrode, keeping the total concentrations of metal ions and acetate ions constant and varying the acetic acid concentration. Such measurements were performed with cadmium amalgam electrodes, for which the experimental difficulties are less than for zinc amalgam electrodes.

THE PROTON ACETATE SYSTEM

Calculation of stability constants

The stability constants have been evaluated, using the graphical method described below and then refined, using the data program "Letagrop vrid."¹²

Symbols used (see also Measurements):

C_A = total concentration of sodium acetate.

C_H = total concentration of perchloric acid.

h = concentration of free hydrogen ions.

a = concentration of free acetate ions.

E_H = emf for the galvanic cell described under Measurements.

The complexes formed in the solutions are presumably HA , HA_2^- and H_2A_2 . The corresponding cumulative stability constants are:

$$\beta_{11} = \frac{[\text{HA}]}{h a}; \quad \beta_{12} = \frac{[\text{HA}_2^-]}{h a^2}; \quad \beta_{22} = \frac{[\text{H}_2\text{A}_2]}{h^2 a^2} \quad (1), (2), (3)$$

The ligand number, z , defined as

$$z = (C_H - h)/C_A \quad (4)$$

may also be written

$$z = \frac{\beta_{11}h + \beta_{12}ha + 2\beta_{22}h^2a}{1 + \beta_{11}h + 2\beta_{12}ha + 2\beta_{22}h^2a} \quad (5)$$

For low values of C_A , the species HA_2^- and H_2A_2 may be neglected. Eqn. (5) is then reduced to

$$\beta_{11} = z/h(1 - z) \quad (6)$$

z is calculated from eqn. (4), where h has been obtained from the relation

$$E_H = E_H^\circ + \frac{RT}{F} \ln h \quad (7)$$

E_H° is determined from glass electrode measurements in a solution with a known hydrogen ion concentration. z and h being known, β_{11} may be calculated from eqn. (6). In order to determine β_{12} , we rearrange eqn. (5)

$$\psi(h) = z h^{-1} - (1-z)\beta_{11} = (1-2z)\beta_{12}a + 2(1-z)\beta_{22}ah \quad (8)$$

$$\lim_{h \rightarrow 0} \psi(h) = \beta_{12} C_A$$

A plot of $\psi(h)$ for every titration series, extrapolating to $h=0$, gives as intercept $\beta_{12}C_A$ and so β_{12} .

β_{22} may be determined in the following way. From the expressions of C_A and C_H may be derived

$$\beta_{22} = (2C_H - C_A + a - 2h - \beta_{11}ha) / 2h^2a^2 \quad (9)$$

Now β_{11} and β_{12} are known. The value of the free acetate ion concentration, a , can be obtained by solving the eqn.

$$\beta_{12}ha^2 + a = C_A - C_H + h \quad (10)$$

for a , and then eqn. (9) may be used to calculate β_{22} .

The stability constants obtained in this way have been refined by using the data program "Letagrop vrid".¹²

Experimental

Chemicals

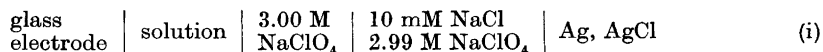
Acetic acid (Merck's *p.a.*) was standardized against a sodium hydroxide solution.

Sodium acetate solutions were prepared from Merck's sodium acetate trihydrate.

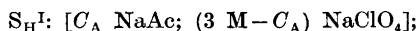
Sodium perchlorate solutions were prepared from Fluka's *p.a.* sample, as described in a previous paper.¹³ The solutions of sodium acetate and sodium perchlorate were both analysed by a cation exchange procedure. Perchloric acid was Baker's *p.a.* sample.

Measurements

A. Galvanic cell with salt bridge. The emf, E_H , of galvanic cells of the following composition was measured.



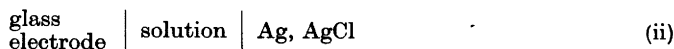
The solution in the left-hand half cell was prepared by adding a volume v of a solution T_{H^I} to a volume V_0 of a solution S_{H^I} .



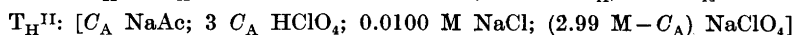
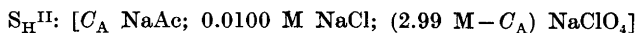
Titration series were performed with $C_A = 1000, 500, 250, 100, 50, 25,$ and 10 mM , and $V_0 = 25.00 \text{ ml}$. The glass electrode was a Beckman general purpose electrode (type

40498). An Ingold Universal Titration Vessel of type 605 was used. The solution T_{H^I} was added with a 20 ml glass syringe (Fortuna Optima Interchangeable) fitted with a specially made micrometer screw. With this outfit, an accuracy of about 0.1 % was obtained, even at low titrant volumes. Magnetic stirring was employed. The emf, E_H , was measured with a potentiometer of the type Radiometer pHM 4C. The reproducibility of the emf was usually within 0.2 mV. E_H^0 was determined before and after every titration series from measurements with the solution (10.00 mM $HClO_4$; 2.99 M $NaClO_4$) in the left-hand half cell. To check the readings obtained with the glass electrode, identical titration series were performed for $C_A = 500$ mM and $C_A = 50$ mM, and with a hydrogen electrode instead of a glass electrode. In order to investigate the curious behaviour of a quinhydrone electrode in acetate solutions, measurements were also carried out with such an electrode in the left-hand half cell for the concentrations $C_A = 500$ mM and $C_A = 50$ mM. (An early attempt to determine the dissociation constant for acetic acid, using quinhydrone electrodes, gave an almost invariable value of this constant over a very broad range of acetate concentration.)

B. Diffusion free cell. In order to eliminate the influence of liquid junction potential on the results, measurements were performed in diffusion free cells for $C_A = 1000, 500, 250, 100,$ and 20 mM. The galvanic cell used had the following composition



The solution was prepared by titrating a volume V_0 of a solution $S_{H^{II}}$ with a volume v of a solution $T_{H^{II}}$.



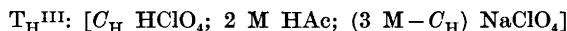
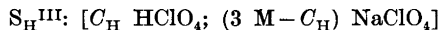
A Jena glass electrode of type U 9201/21 was used in these measurements.

C. Correction of E_H^0 in cells with liquid junction. The interpretation of the measurements in a cell with liquid junction is hampered by the diffusion potential. Using a diffusion free cell is one way of avoiding this difficulty.

Another possible method is that used by Danielsson and Suominen,¹⁴ and later by Farrer and Rossotti,¹⁰ who corrected E_H^0 for varying acetate concentrations. Such corrections have to be determined in a pH region, where a possible formation of dimeric proton acetate complexes does not influence the results.

Since the results obtained in the present work from measurements with a diffusion free cell diverge from those obtained by Farrer and Rossotti,¹⁰ we decided to correct our data from the measurements with a cell with salt bridge, adopting the hypothesis of a variable E_H^0 in the same way as Farrer and Rossotti. To obtain a correction for the variation of E_H^0 with the concentrations of acetic acid and acetate ions, titration series were performed using a galvanic cell of type (i) with a hydrogen gas electrode instead of a glass electrode.

Variation of E_H^0 with the concentration of acetic acid. The titration solutions were composed as follows:



Taking into account the liquid junction potential, E_j , and the change of the activity factor for hydrogen ions, γ_H , eqn. (7) may be written:

$$E_H = E_H^{00} + E_j + \frac{RT}{F} \ln \gamma_H + \frac{RT}{F} \ln h \quad (11)$$

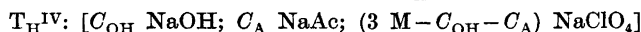
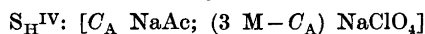
where $\lim_{h \rightarrow 0} \gamma_H = 1$ in 3.0 M $NaClO_4$.

Two series were performed with $C_H = 30.00$ mM and 60.00 mM. A plot of $E_H - (RT/F) \ln C_H = E_H^0$ against $[HAc]$ was linear, and gave $E_H^0 = E_H^{00} + 3.40 [HAc]$.

It should be pointed out that the factor 3.40 is valid in 3.0 M $NaClO_4$. Subsequent measurements showed, however, that this factor depends on the concentration of sodium

perchlorate (a change of about 1 mV/M sodium perchlorate was observed), which is in fact considerably changed during the course of the measurements. However, this variation of the correction term is a second order effect, which does not affect significantly the results, and the factor 3.40 has been used throughout.

Variation of E_{H}° with the concentration of acetate ions. The titration solutions were



Five titration series were performed for $C_{\text{A}} = 0, 100, 250, 500,$ and 1000 mM. For each series, $E_{\text{H}} + (RT/F) \ln C_{\text{OH}} = E_{\text{OH}}^{\circ}$ was extrapolated to $C_{\text{OH}} = 0$, giving corresponding values ($C_{\text{A}}, E_{\text{OH}}^{\circ}$). A plot of E_{OH}° against C_{A} gave approximately the straight line $E_{\text{OH}}^{\circ} = E_{\text{OH}}^{\circ\circ} - 6.32 [\text{Ac}^-]$ in the range $0 < [\text{Ac}^-] < 1$ M. Eqn. (11) may now be written

$$E_{\text{H}} = E_{\text{H}}^{\circ\circ} + 3.40 [\text{HAc}] - 6.32 [\text{Ac}^-] + (RT/F) \ln h \quad (12)$$

From the values of $E_{\text{H}}^{\circ\circ}$ and $E_{\text{OH}}^{\circ\circ}$, a value of $\text{p}K_{\text{w}} = 14.184 \pm 0.002$ may be calculated. Ågren¹⁵ has earlier obtained $\text{p}K_{\text{w}} = 14.15 \pm 0.01$, and Ingri *et al.*¹⁶ $\text{p}K_{\text{w}} = 14.22 \pm 0.02$, both values obtained in 3 M NaClO₄.

Results

A. In Tables 1 and 2, some corresponding values of v , E_{H} , $\log h$, and z , obtained from measurements with a glass electrode in a cell with liquid junction, are collected for series with $C_{\text{A}} = 25, 250, 500,$ and 1000 mM. From

Table 1. Corresponding values of v , E_{H} , $\log h$, and z for the proton acetate system from measurements performed with a cell with liquid junction. (v in ml, E_{H} in mV, and h in M.)

$C_{\text{A}} = 25.00$ mM $E_{\text{H}}^{\circ} = 383.0$ mV				$C_{\text{A}} = 250.0$ mM $E_{\text{H}}^{\circ} = 382.5$ mV			
v	E_{H}	$-\log h$	z	v	E_{H}	$-\log h$	z
0.0820	-24.2	6.883	0.00981	0.0820	-32.9	7.020	0.00981
0.3281	5.6	6.379	0.0389	0.3281	1.7	6.435	0.0389
0.656	23.1	6.084	0.0767	0.656	20.0	6.126	0.0767
1.640	48.2	5.659	0.1846	1.312	39.3	5.798	0.1496
2.296	58.5	5.485	0.2523	1.968	51.5	5.593	0.2190
2.953	66.6	5.348	0.3168	2.296	56.4	5.510	0.2524
3.609	73.1	5.238	0.3782	2.953	64.9	5.368	0.3169
4.27	79.9	5.123	0.437	3.609	71.8	5.250	0.3784
4.92	85.5	5.029	0.493	4.27	78.5	5.137	0.437
5.58	91.0	4.936	0.547	4.92	84.4	5.037	0.493
6.23	96.4	4.844	0.598	5.58	90.1	4.941	0.547
6.89	101.9	4.751	0.647	6.23	95.7	4.846	0.598
7.55	107.3	4.660	0.695	6.89	101.2	4.752	0.648
8.20	113.1	4.562	0.740	7.55	107.1	4.653	0.696
8.86	119.5	4.454	0.784	8.20	113.0	4.552	0.741
9.51	126.3	4.339	0.825	8.86	119.7	4.441	0.785
10.17	134.1	4.207	0.865	9.51	126.9	4.319	0.827
10.83	143.8	4.043	0.903	9.84	130.9	4.251	0.847
11.48	156.9	3.822	0.938	10.50	140.2	4.094	0.887
12.14	175.7	3.504	0.968	11.15	152.6	3.884	0.925
12.47	187.0	3.313	0.979	11.81	172.7	3.545	0.961
12.79	198.2	3.123	0.986	12.30	206.9	2.967	0.985

Tables 1 and 2, it is obvious that the (z , $\log h$) curves are dependent upon the value of C_A which might be caused by the existence of other proton acetate species than HAc in the solution.

Table 2. Corresponding values of v , E_H , $\log h$, and z for the proton acetate system from measurements with a cell with liquid junction. (v in ml, E_H in mV, and h in M.)

$C_A = 500 \text{ mM}$ $E_H^o = 382.2 \text{ mV}$				$C_A = 1000 \text{ mM}$ $E_H^o = 383.3 \text{ mV}$			
v	E_H	$-\log h$	z	v	E_H	$-\log h$	z
0.0820	-33.7	7.030	0.00981	0.0820	-36.6	7.106	0.00981
0.3281	-0.5	6.467	0.0389	0.3281	-2.8	6.535	0.0389
0.656	17.7	6.161	0.0767	0.656	15.6	6.224	0.0767
1.312	37.1	5.833	0.1496	1.312	35.2	5.893	0.1496
1.968	49.4	5.625	0.2190	1.968	47.9	5.679	0.2190
2.625	58.8	5.467	0.2850	2.625	57.3	5.519	0.2850
3.281	66.7	5.333	0.3480	3.281	65.5	5.381	0.3480
3.937	73.2	5.223	0.408	3.937	72.5	5.262	0.408
4.59	79.8	5.110	0.466	4.59	79.4	5.145	0.466
5.25	85.8	5.010	0.520	5.25	85.7	5.038	0.521
5.91	91.5	4.914	0.573	5.91	91.6	4.939	0.573
6.56	97.2	4.817	0.624	6.56	97.5	4.839	0.624
7.22	103.0	4.719	0.672	7.22	103.8	4.733	0.672
7.87	108.9	4.618	0.719	7.87	110.0	4.629	0.719
8.20	112.1	4.566	0.741	8.53	116.5	4.518	0.763
8.86	118.7	4.454	0.785	9.19	123.7	4.397	0.806
9.51	126.0	4.331	0.827	9.84	131.6	4.262	0.847
10.17	134.5	4.187	0.867	10.50	141.2	4.101	0.887
10.83	145.2	4.007	0.906	11.15	154.0	3.884	0.926
11.48	160.4	3.749	0.944	11.81	174.2	3.542	0.962
12.14	191.1	3.230	0.979	12.30	211.1	2.920	0.988
12.47	232.9	2.524	0.992	12.63	266.9	1.975	0.996

Table 3. A comparison between values of $\log h$ determined in acetate solutions with a glass electrode, a hydrogen electrode, and a quinhydrone electrode, respectively.

$C_A = 50.0 \text{ mM}$				$C_A = 500 \text{ mM}$			
z	$-\log h$			z	$-\log h$		
	glass electrode	hydrogen electrode	quinhydrone electrode		glass electrode	hydrogen electrode	quinhydrone electrode
0.1136	5.909	5.906	5.902	0.1136	5.973	5.974	5.927
0.1847	5.661	5.663	5.663	0.2523	5.543	5.542	5.501
0.2523	5.489	5.492	5.488	0.3479	5.334	5.336	5.300
0.3783	5.237	5.230	5.232	0.437	5.161	5.162	5.136
0.493	5.028	5.027	5.030	0.520	5.010	5.010	4.989
0.648	4.748	4.743	4.752	0.598	4.867	4.865	4.844
0.741	4.555	4.552	4.556	0.672	4.719	4.718	4.703
0.826	4.329	4.327	4.331	0.741	4.566	4.565	4.553
0.905	4.020	4.016	4.019	0.846	4.261	4.261	4.257
0.958	3.614	3.616	3.606	0.923	3.891	3.894	3.903

In Table 3, a comparison is made between some values of $(z, \log h)$ obtained using a glass electrode, a hydrogen electrode, and a quinhydrone electrode, respectively, at $C_A = 50$ mM and 500 mM. All electrodes show good agreement at low concentrations of acetate ions, but at high concentrations, the quinhydrone electrode presents a striking divergence.

The measurements with glass electrodes were then used for calculations. β_{11} was computed from eqn. (6), using the series with $C_A = 10, 25,$ and 50 mM, where possible diacetate species should have little influence. Values of β_{11} were calculated from each series, and indeed no systematic variation with C_A was observed. A mean value $\beta_{11} = (1.035 \pm 0.002) \times 10^5 \text{ M}^{-1}$ was obtained. From plots of $\psi(h)$, using the series with $C_A = 250, 500,$ and 1000 mM, a value of $\beta_{12} = (3.6 \pm 0.2) \times 10^4 \text{ M}^{-2}$ was calculated, and $\beta_{22} = (1.5 \pm 0.5) \times 10^9 \text{ M}^{-3}$ was obtained from eqn. (9). Later measurements show, however, that an appreciable liquid junction potential influences these measurements.

Table 4. Corresponding values of $v, E_H, \log h,$ and z for the proton acetate system from measurements performed with a diffusion free cell. (v in ml, E_H in mV, and h in M.)

v	$C_A = 20.00 \text{ mM}$ $E_{H^0} = 513.5 \text{ mV}$			$C_A = 250.0 \text{ mM}$ $E_{H^0} = 513.4 \text{ mV}$		
	E_H	$-\log h$	z	E_H	$-\log h$	z
0.1667	117.4	6.696	0.0199	114.7	6.739	0.0199
0.500	145.2	6.226	0.0588	143.7	6.249	0.0588
1.000	164.2	5.904	0.1153	162.9	5.925	0.1154
1.667	178.9	5.657	0.1874	177.7	5.674	0.1875
2.333	189.2	5.482	0.2560	188.3	5.495	0.2561
3.000	197.5	5.342	0.3213	196.7	5.353	0.3215
3.666	204.5	5.223	0.3835	203.9	5.231	0.3838
4.33	210.8	5.117	0.443	210.5	5.120	0.443
5.00	216.7	5.017	0.500	216.5	5.018	0.500
5.67	222.3	4.922	0.554	222.4	4.919	0.554
6.33	227.8	4.829	0.606	228.0	4.823	0.606
7.00	233.3	4.736	0.655	233.7	4.727	0.656
7.67	239.0	4.641	0.703	239.6	4.627	0.704
8.33	244.9	4.541	0.749	245.7	4.525	0.750
9.00	251.3	4.433	0.792	252.4	4.412	0.794
9.67	258.3	4.313	0.834	259.7	4.288	0.837
10.33	266.6	4.173	0.874	268.6	4.138	0.877
11.00	276.8	4.001	0.912	279.7	3.950	0.916
11.67	290.3	3.772	0.946	296.3	3.670	0.954
12.33	309.3	3.453	0.974	332.8	3.053	0.988

B. In Tables 4 and 5, some corresponding values of $v, E_H, \log h,$ and $z,$ obtained from measurements with a glass electrode in a diffusion free cell, are collected for the series with $C_A = 20, 250, 500,$ and 1000 mM. The spread of the $(z, \log h)$ curves is now less than in the measurements with a cell with salt bridge, which indicates that an appreciable liquid junction potential has been eliminated. The stability constants were evaluated graphically and then

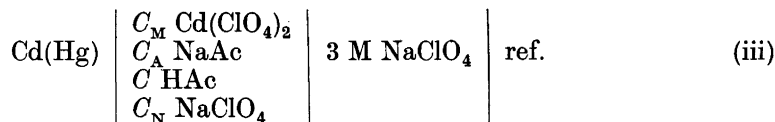
Table 5. Corresponding values of v , E_H , $\log h$, and z for the proton acetate system from measurements performed with a diffusion free cell. (v in ml, E_H in mV, and h in M.)

v	$C_A = 500 \text{ mM}$ $E_H^\circ = 513.3 \text{ mV}$			$C_A = 1000 \text{ mM}$ $E_H^\circ = 513.3 \text{ mV}$		
	E_H	$-\log h$	z	E_H	$-\log h$	z
0.1667	112.3	6.778	0.0199	110.4	6.810	0.0199
0.500	141.9	6.278	0.0588	139.7	6.316	0.0588
1.000	161.2	5.951	0.1154	159.0	5.989	0.1154
1.667	176.4	5.694	0.1875	174.7	5.724	0.1875
2.333	187.2	5.512	0.2561	185.7	5.538	0.2561
3.000	195.8	5.366	0.3215	194.7	5.386	0.3215
3.666	203.3	5.240	0.3838	202.5	5.254	0.3838
4.33	210.0	5.126	0.443	209.5	5.135	0.443
5.00	216.3	5.021	0.500	216.1	5.024	0.500
5.67	222.3	4.919	0.554	222.4	4.918	0.554
6.33	228.1	4.803	0.606	228.7	4.812	0.607
7.00	234.0	4.723	0.656	234.7	4.709	0.656
7.67	240.0	4.620	0.704	241.2	4.599	0.704
8.33	246.2	4.514	0.750	247.9	4.487	0.750
9.00	253.0	4.400	0.794	255.0	4.367	0.794
9.67	260.6	4.272	0.837	263.0	4.232	0.837
10.33	269.4	4.122	0.877	272.1	4.077	0.877
11.00	280.4	3.938	0.917	283.8	3.879	0.917
11.67	297.1	3.655	0.954	301.1	3.588	0.954
12.33	334.3	3.026	0.989	342.3	2.891	0.990

refined, using the data program "Letagrop vrid".¹² In the numerical calculations, the value of β_{11} , which had been determined separately, using series with small values of C_A , was kept constant, while β_{12} and β_{22} were varied. The following results were obtained: $\beta_{11} = (1.035 \pm 0.002) \times 10^5 \text{ M}^{-1}$; $\beta_{12} = (3.37 \pm 0.1) \times 10^4 \text{ M}^{-2}$; $\beta_{22} = (2.22 \pm 0.3) \times 10^8 \text{ M}^{-3}$. (The stated errors are three times the standard deviations.) The values of β_{12} , and especially β_{22} , were very sensitive to changes in β_{11} , and the error limits obtained above are therefore probably much too narrow.

C. The values of E_H , given in Tables 1 and 2, were corrected, supposing a variable E_H° according to eqn. (12). As before, a set of stability constants was determined graphically and then refined using the data program "Letagrop vrid". The following results were obtained: $\beta_{11} = (1.035 \pm 0.002) \times 10^5 \text{ M}^{-1}$; $\beta_{12} = (1.45 \pm 0.2) \times 10^4 \text{ M}^{-2}$; $\beta_{22} = (1.1 \pm 0.1) \times 10^9 \text{ M}^{-3}$. These constants agree well with those obtained by Farrer and Rossotti.¹⁰

Check of possible acetate dimers with use of amalgam electrodes. To check to what extent a possible formation of dimeric proton acetate species influenced the amalgam measurements, the emf, E , of the following galvanic cell was measured.



Cadmium amalgam electrodes were chosen, because a zinc electrode does not function so well in solutions with $\text{pH} > 5$. Cadmium is less sensitive in this respect, and so a low starting value of the acetic acid concentration, C , could be chosen. In each series, C_M , C_A , and C_N were kept constant, while C was varied.

For the cell (iii), an equation analogous to eqn. (12) should be valid:

$$E = E_{\text{Cd}}^{\circ} + k_1[\text{HAc}] + k_2[\text{Ac}^-] + \frac{RT}{2F} \ln [M] \quad (13)$$

Let us now consider the changes in the emf, ΔE_i , $i = 1, 2, 3$, that can be expected to be caused by the three last terms in eqn. (13), when the concentration of acetic acid, C , is increased from zero to 1 M at constant values of $C_A = 1$ M and $C_N = 2$ M.

We assume further that the values of $k_1 = +3.4$ mV M^{-1} and $k_2 = -6.3$ mV M^{-1} , as determined for cell (i), are still valid. Three alternatives can be distinguished.

Alt. 1. Dimeric proton acetate species are formed (H_2Ac_2 is neglected), and HAc_2^- forms much weaker complexes than Ac^- with cadmium ions. This latter assumption seems very probable. In a thorough study of dicarboxylate complexes with lanthanoid ions, Grenthe and Dellien¹⁷ have found that the strength of mixed proton-metal-complexes decreases with decreasing distance between proton and metal ion in the mixed complex. The complex between a lanthanoid ion and hydrogen malonate is considerably weaker than the corresponding malonate complex, and in the oxalate-lanthanoid systems no acid complexes could be detected at all, apparently because of the small distance between proton and metal ion which should be formed in such a complex. For a complex between HAc_2^- and a metal ion, this distance should also be very short. Hence it is very improbable, that HAc_2^- could compete successfully with Ac^- for the cadmium ions.

Term 1. $\Delta E_1 = +3.4 \Delta[\text{HAc}]$ mV = +3.4 mV.

Term 2. $[\text{Ac}^-]$ is decreased by the reaction $\text{HAc} + \text{Ac}^- \rightleftharpoons \text{HAc}_2^-$ (with $K_{12} = 0.33$ M^{-1} according to the measurements with a diffusion free cell).

$$\Delta E_2 = 6.3 \Delta[\text{Ac}^-] \text{mV} \approx -6.3 \times 0.21 \text{ mV} \approx -1.3 \text{ mV}.$$

Term 3. It may be easily derived that

$$\Delta E_3 \approx -\frac{RT}{2F} \frac{\bar{n}}{[\text{Ac}^-]} \Delta[\text{Ac}^-]$$

At $[\text{Ac}^-] \approx 0.9$ M, $\bar{n} = 2.7$.²⁵ With $\Delta[\text{Ac}^-] = -0.21$ M, we obtain $\Delta E_3 \approx +12.8 \times (2.7/0.9) \times 0.21$ mV ≈ 8.1 mV. Then $\Delta E = (3.4 - 1.3 + 8.1)$ mV = +10.2 mV. (If the value $K_{12} = 0.14$ M^{-1} , obtained from the corrected measurements with cell with liquid junction, is used instead, we get $\Delta E \approx (3.4 - 0.7 + 4.0)$ mV = +6.7 mV.)

Alt. 2. Dimeric proton acetate species are formed, and cadmium ions form complexes of about equal strength with HAc_2^- and Ac^- , which is not very probable, as discussed under *Alt. 1.* H_2Ac_2 is neglected. In the same way as outlined above we obtain:

$$\Delta E_1 = 3.4 \text{ mV}; \Delta E_2 = -1.3 \text{ mV}; \Delta E_3 = 0 \text{ mV}$$

$$\Delta E = +2.1 \text{ mV (with } K_{12} = 0.14 \text{ M}^{-1} \text{ we get } \Delta E = +2.7 \text{ mV)}.$$

Alt. 3. No dimeric proton acetate species are formed.

$$\Delta E_1 = +3.4 \text{ mV}; \Delta E_2 = 0 \text{ mV}; \Delta E_3 = 0 \text{ mV}$$

$$\Delta E = +3.4 \text{ mV}$$

In four measurements with different compositions of the solutions, the following results were obtained (all concentrations in M, and ΔE in mV). [ΔE_{calc} has been obtained presuming $k_1 = 3.4 \text{ mV M}^{-1}$, $k_2 = -6.3 \text{ mV M}^{-1}$, and $K_{12} = 0.33 \text{ M}^{-1}$ (values in brackets with $K_{12} = 0.14 \text{ M}^{-1}$)].

C_M	C_A	C_N	$(\Delta E)_{\text{exp}}$ for $\Delta C = 1 \text{ M}$	ΔE_{calc}		
				Alt 1	Alt 2	Alt 3
0.005	3.00	0	+0.6	—	—	—
0.010	1.00	2.00	+2.8	+10.2 (+ 6.7)	+2.1 (+2.7)	+3.4 (+3.4)
0.010	1.00	3.00	+3.8	+10.2 (+ 6.7)	+2.1 (+2.7)	+3.4 (+3.4)
0.010	—	3.00	+4.3	+ 3.4	+3.4	+3.4

From the results tabulated above, we may draw the following conclusions:

1) The assumption that no dimeric species are formed, provides a good fit with experimental data (3.4 mV expected, compared with 2.8 mV measured), but the possibility that dimeric species are formed and complexes $\text{Cd}^{2+} - \text{HAc}_2^-$ are about as strong as complexes $\text{Cd}^{2+} - \text{Ac}^-$ cannot be ruled out. However, this assumption is improbable from other reasons already given.

2) The influence of acetic acid on the emf is rather dependent on the concentration of sodium perchlorate. The value of $k_1 = 3.4 \text{ mV M}^{-1}$, valid in 3 M NaClO_4 , should in (1 M NaAc , 2 M NaClO_4) be reduced to about 2.6 mV M^{-1} and thus provide a still better fit with experimental data.

The present investigation thus indicates that formation of proton acetate dimers in water solution is very questionable, and if such species exist at all they are formed to a negligible extent. Therefore, no corrections of the measurements on the zinc acetate system with respect to such dimers have been made.

THE ZINC ACETATE SYSTEM

The measurements were designed in the following way: I. Potentiometric measurements with zinc amalgam electrodes were performed; II. The amalgam measurements were corrected for the liquid junction potential caused by the exchange of sodium perchlorate for acetic acid and acetate ions.

Calculations of stability constants

The stability constants were determined both graphically with the method outlined by Fronæus (Ref. 18, p. 18) and numerically using a data program elaborated by Sandell.¹⁹ The symbols used are those proposed by Fronæus.¹⁸

Suppose that only mononuclear complexes are formed. The cumulative stability constant, β_n , is defined from the equation

$$\beta_n = \frac{[MA_n]}{[M][A]^n} \quad n = 0, 1, 2, \dots N \quad (14)$$

$$E_M = E - E_0 = \frac{RT}{\nu F} \ln \sum_{i=0}^N i \beta_i [A]^i \quad (15)$$

The ligand number \bar{n} may be expressed as

$$\bar{n} = \frac{\sum_{i=1}^N i \beta_i [A]^i}{\sum_{i=0}^N \beta_i [A]^i} \quad (16)$$

and also in the form

$$\bar{n} = \frac{\nu F}{RT} \cdot \frac{dE_M}{d \ln[A]} \quad (17)$$

Experimental

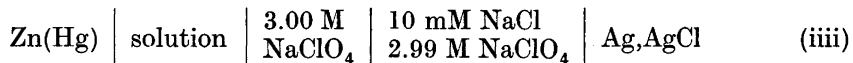
Chemicals

Acetic acid, sodium acetate, and perchloric acid as described for the proton acetate system.

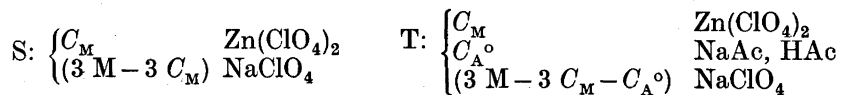
Zinc amalgam (1 % by weight) and zinc perchlorate were prepared as described previously.¹³

Measurements and results

I. *Measurements with zinc amalgam electrodes.* The emf, E , of a galvanic cell of the following composition was measured.



The solution in the left-hand half cell was prepared by adding a volume v of a solution T to a volume V_0 of a solution S.



The temperature was $(25.00 \pm 0.05)^\circ\text{C}$. The measurements were performed exactly as described for the zinc thiosulfate system.¹³ The reproducibility was better than 0.2 mV. Each series was repeated at least once. First the validity of the eqn. $E = E^\circ - (RT/2F) \ln[\text{Zn}^{2+}]$ for the galvanic cell used was checked by titrations without acetate. It was found to be satisfied within 0.2 mV for $7 \text{ mM} < [\text{Zn}^{2+}] < 70 \text{ mM}$.

Table 6. Corresponding values of C_A and E_M for the zinc acetate system. (C_A in mM, and E_M in mV.)

C_A	E_M for $C_M =$			C_A	E_M for $C_M =$		
	10.20 mM	30.60 mM	51.0 mM		10.20 mM	30.60 mM	51.0 mM
24.39	2.45	2.07	1.86	310.3	25.70	23.69	22.05
47.6	4.68	4.02	3.51	333.3	27.27	25.22	23.56
69.8	6.75	5.85	5.31	365.1	29.32	27.26	25.51
90.9	8.64	7.56	6.87	393.9	31.12	29.05	27.28
111.1	10.44	9.19	8.36	429	33.25	31.13	29.36
137.9	12.74	11.29	10.31	460	35.05	32.93	31.13
166.7	15.12	13.49	12.36	500	37.35	35.25	33.43
193.5	17.25	15.49	14.25	535	39.28	37.15	35.33
218.7	19.20	17.33	16.00	565	40.86	38.75	36.93
242.4	20.90	19.01	17.59	600	42.65	40.58	38.74
264.7	22.54	20.59	19.12	636	44.43	42.40	40.54
285.7	24.02	22.04	20.48	667	45.92	43.88	41.99

Titration series were then performed with $C_M = 10.20, 30.60,$ and 51.0 mM. The value of E_0 for each series was determined by graphical extrapolations of $E = f(C_A)$ to $C_A = 0$. Corresponding values of C_A and E_M are collected in Table 6. The data were treated numerically, using Sandell's¹⁹ program, and the following stability constants were obtained for the mononuclear complexes:

$$\beta_1 = (8.70 \pm 0.04) \text{ M}^{-1}; \beta_2 = (23.5 \pm 1.2) \text{ M}^{-2}; \beta_3 = (68.1 \pm 2.5) \text{ M}^{-3}$$

(The stated errors are three times the standard deviations.) A graphical determination gave constants that agree very closely with those from the numerical calculations.

II. *Correction for liquid junction potential.* In the amalgam measurements, the continued exchange of sodium perchlorate for acetic acid and sodium acetate produces a liquid junction potential. This junction potential has been determined as the difference between the emf's of two cells. In both cells a glass electrode was used at varying acetate buffer concentration. One cell contained a salt bridge, while the other was diffusion free (see The Proton Acetate System). The liquid junction potential, E_j , at varying concentration of 1:1 acetic acid/sodium acetate buffer in the actual galvanic cell is represented in Fig. 1.

The values of (C_A, E_M), corrected for the diffusion potential, have been collected in Table 7. A second set of stability constants was calculated, using these corrected data.

$$\beta_1 = (8.15 \pm 0.02) \text{ M}^{-1}; \beta_2 = (23.0 \pm 0.2) \text{ M}^{-2}; \beta_3 = (36.9 \pm 0.3) \text{ M}^{-3}$$

(The stated errors are three times the standard deviations.) The differences between the experimental E_M' and the E_M'' values, computed from the "best" β_i -values, are given in Table 7. (E_M'' was calculated as outlined previously.¹³) These differences are fairly small and are probably due to medium changes caused by the metal ions. \bar{n} , calculated from eqn. (16), is represented as a function of $\log [\text{Ac}^-]$ in Fig. 2.

Table 7. Corresponding values of C_A and E_M for the zinc acetate system (E_M' are the values of E_M given in Table 4, corrected for the liquid junction potential). E_M'' has been calculated from the stability constants. (C_A in mM, and the emf's in mV.)

C_A	$C_M = 10.20$ mM		$C_M = 30.60$ mM		$C_M = 51.0$ mM	
	E_M'	$E_M' - E_M''$	E_M'	$E_M' - E_M''$	E_M'	$E_M' - E_M''$
24.39	2.29	-0.01	1.91	-0.10	1.70	-0.09
47.6	4.38	-0.03	3.72	-0.16	3.21	-0.25
69.8	6.30	-0.04	5.40	-0.22	4.86	-0.17
90.9	8.06	-0.06	6.98	-0.25	6.29	-0.21
111.1	9.73	-0.04	8.48	-0.26	7.65	-0.23
137.9	11.86	-0.02	10.41	-0.28	9.43	-0.25
166.7	14.05	-0.02	12.42	-0.30	11.29	-0.29
193.5	16.01	-0.01	14.25	-0.32	13.01	-0.29
218.7	17.80	0.00	15.93	-0.32	14.60	-0.30
242.4	19.35	-0.06	17.46	-0.34	16.04	-0.33
264.7	20.85	-0.04	18.90	-0.32	17.43	-0.29
285.7	22.19	-0.05	20.21	-0.32	18.65	-0.32
310.3	23.71	-0.06	21.70	-0.32	20.06	-0.35
333.3	25.14	-0.03	23.09	-0.30	21.43	-0.30
365.1	26.98	-0.06	24.92	-0.29	23.17	-0.35
393.9	28.60	-0.06	26.53	-0.29	24.76	-0.33
429	30.51	-0.06	28.39	-0.33	26.62	-0.34
460	32.11	-0.09	29.99	-0.35	28.19	-0.38
500	34.15	-0.06	32.05	-0.31	30.23	-0.34
535	35.86	-0.06	33.73	-0.32	31.91	-0.35
565	37.24	-0.06	35.13	-0.34	33.31	-0.37
600	38.80	-0.07	36.74	-0.32	34.90	-0.38
636	40.33	-0.10	38.30	-0.34	36.47	-0.41
667	41.62	-0.12	39.58	-0.39	37.69	-0.53

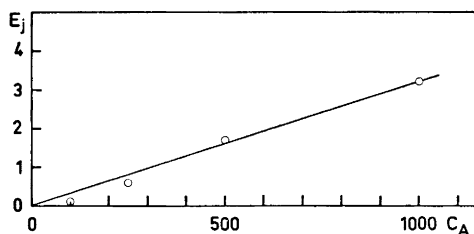


Fig. 1. The liquid junction potential, E_j , at varying total concentration, C_A , of acetate in a 1:1 buffer solution. (C_A in mM, E_j in mV.)

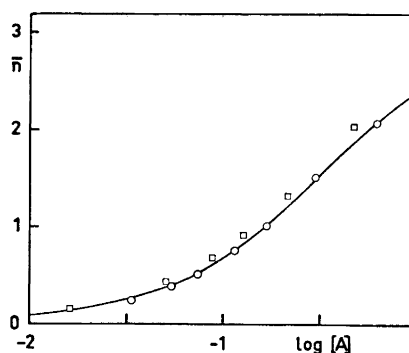


Fig. 2. The complex formation curve for the zinc acetate system. The full-drawn curve represents \bar{n} calculated from eqn. (16). \bar{n} calculated from eqn. (17) is denoted by (O), and k_0 from the slope of the C_A , C_M curves by (□).

DISCUSSION

The investigations performed on the proton acetate system with a diffusion free cell as well as the corrected measurements with a cell with salt bridge can be described within the experimental errors by supposing that the species HAc , HAc_2^- , and H_2Ac_2 are formed.

The sets of constants obtained from the two types of cells are, however, fairly different. This is rather strange, because both methods imply essentially an elimination of the liquid junction potential. There are, however, a few circumstances that might possibly offer an explanation.

In the measurements with the diffusion free cell, the chloride ion activity for the reference electrode may vary with varying concentrations of acetic acid and acetate ions, although this change should be quite small as only neutral and negative species are exchanged.

On the other hand, with the "method of variable E_{H}° ", a change in the activity factor for the hydrogen ions is eliminated in each series as well as the liquid junction potential.

Furthermore, as mentioned above, the correction applied for the influence of acetic acid on E_{H}° ($+3.4 \text{ mV M}^{-1}$) is only valid in 3 M NaClO_4 . Taking the variation of the concentration of sodium perchlorate into consideration would imply a decrease of β_{22} .

The hypothesis of formation of acetate dimers in water, adopted by Farrer and Rossotti,¹⁰ is supported by the results of investigations in different solvents *e.g.* the potentiometric measurements by Grenthe and Williams²⁰ in a water/methanol solvent, and also by investigations performed with different methods.⁷⁻¹¹ It should be pointed out, however, that formation of dimeric acetate species is more likely to take place in methanol than in water.

Calorimetric measurements by different authors do not give unequivocal results. Schlyter and Martin,²¹ and Gerding²² interpreted their results by supposing that dimeric proton acetate species are formed, but Wadsö²³ could not find any effect caused by dimeric species.

The differences between the results obtained with various methods may give reason to doubt the dimer formation and to interpret the effect under investigation entirely as activity changes. The results from the separate investigation with cadmium amalgam electrodes (*vide ultra*) also support this conclusion.

The effect that may be interpreted by assuming that dimeric proton acetate species are formed is in any case so small that it is impossible to state the existence of such species with any certainty.

The potentiometric measurements on the zinc acetate system can be accounted for if it is assumed that three mononuclear complexes are formed. While the stability constants of the first two complexes seem to have been firmly established, the value of β_3 is more uncertain. When a correction for the liquid junction potential was applied, β_3 decreased to about half of its original value.

A preliminary set of uncorrected stability constants has been applied by Gerding²⁴ to calorimetric measurements and found to give a good description. The corrected constant values also describe the measured enthalpies with about the same precision.

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