

The Stability Constants of the Proton Acetate Complexes in 5 volume per cent Water/Methanol

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The complex formation between the proton and the acetate ion has been studied using the solvent 5 volume per cent water in methanol. The work was performed at 25.00°C and an ionic strength, $I = 0.500 \text{ M Na}^+(\text{ClO}_4^-)$, using a glass electrode which was found to respond well in methanolic acetate solutions. A family of \bar{n}_h vs. $-\log[\text{H}^+]$ curves has been interpreted by assuming only the complexes, HA, HA_2^- , and H_2A_2 exist.

In connection with an investigation of the complex-formation in mixed solvents between the conjugate bases of weak acids and various lanthanoids, we were interested in an accurate determination of the stability constants of the various complexes formed between the proton and the acetate ion in a water/methanol solvent. Most investigations of this type in water solutions are performed by measuring the hydrogen-ion concentrations in suitable galvanic cells. In order to facilitate the interpretation of the results, the activity coefficients of the various species participating in the reaction, and the various diffusion potentials, are maintained constant by employing a suitable ionic medium.¹ This same method ought to be applicable to a mixed solvent. To avoid unnecessarily large diffusion potentials, the mixed solvent must be used throughout the cell.

Several investigations of the dissociation constants of acetic acid in different water/methanol solvents have been reported.²⁻⁴ All these constants are "thermodynamic" constants, *i.e.* they refer to a medium of ionic strength $I = 0$. All the experimental data were described by assuming that the only species present in solution were H^+ , A^- , and HA. Dimeric forms of carboxylic acids have been found^{5,6} at high total concentrations of acid. In order to establish whether or not such species are present, the measurements must be made over a fairly large concentration range of acetate. The investigation reported in this paper describes a potentiometric determination of the stability constants of the various species formed between acetate ions and protons in

a water/methanol solvent having ionic strength $I = 0.500$ M. The results refer to a temperature of 25.00°C , and the concentration of acetic acid and of acetate were varied over a sufficient range to establish the presence of dimers.

EXPERIMENTAL

Chemicals used. Perchloric acid (Baker analysed) was standardised against recrystallised borax and sodium hydroxide. Sodium perchlorate was prepared by neutralising perchloric acid with anhydrous sodium carbonate (Merck *p.a.*). The solution was maintained at pH 9 for three days and was then filtered through "Millipore" filters of pore size $5\ \mu$ and $0.45\ \mu$. The solution was then rendered acid, boiled to remove carbon dioxide, cooled under a carbon dioxide free atmosphere and then the pH was adjusted to 7. Finally, the anhydrous sodium perchlorate was prepared by heating the solution to 140°C and collecting the crystals above 100°C . The purity of this perchlorate was checked by potentiometric titrations. Protolytic impurities were less than 2×10^{-6} moles per mole of sodium perchlorate. Solutions of acetic acid (Riedel-de Haën, "für Analyse und für Chromatographie") were standardised against sodium hydroxide. Sodium acetate trihydrate (Merck *p.a.*) was analysed by a cation exchange procedure. The water content of the sample was determined ($\text{H}_2\text{O}/\text{Na}^+ = 3.000$). All water used was distilled and deionised. Analytical grade methanol (Merck *p.a.*) was used. The possibility of acid impurities in the solvent was investigated in two ways: The solvent was titrated with sodium hydroxide. No acid was found. One sample of the solvent was then refluxed with calcium oxide, redistilled and stored under nitrogen. Solutions of 0.500 M sodium perchlorate in the solvent, *S*, were then prepared using both this purified and the suppliers methanol. The two samples were titrated with sodium hydroxide and perchloric acid in solvent *S*. The hydrogen ion concentration was measured using a glass electrode and a potentiometer (*vide infra* p. 343). The hydrogen ion concentration measured was the same as that calculated from the amount of titrant added (see Table 1). Thus, the two methanol samples were apparently identical and neither the solvent nor the other chemicals contained protolytic impurities.

Table 1. A portion of the glass electrode calibration showing a constant $E_0 \pm 0.2$ mV which increases at $-\log[\text{H}^+] = 2.7$ because of diffusion potentials.

E (mV)	198.1	233.6	261.6	283.0	297.8	326.1
$RT/F \ln [\text{H}^+]$ (mV)	259.8	224.3	196.2	174.6	160.5	132.5
E_0 (mV)	457.9	457.9	457.8	457.6	458.3	458.6

Medium and preparation of solutions. The solvent, *S*, used was 5.000 volume per cent water in methanol. An ionic background of 0.500 M Na^+ (ClO_4^-) was maintained throughout. A 0.5000 M stock solution of sodium acetate in *S* was prepared from sodium acetate trihydrate, water and methanol. Stock solutions of acetic acid in water were prepared from the concentrated acid. A 1 M sodium perchlorate solution in *S* was also prepared. The solutions needed for each titration were prepared from these stock solutions, methanol, and water. The solutions used in the titrations had the composition:

$$T_1 \begin{cases} C_A \text{ M HA} \\ 0.500 \text{ M NaClO}_4 \end{cases} \text{ and } T_2 \begin{cases} C_A \text{ M NaA} \\ (0.500 - C_A) \text{ M NaClO}_4 \end{cases}$$

and were of density 0.850 g/ml. C_A for the various series varied from 1.000 mM to 200 mM. The reference solution had the composition:

$$C_{\text{NaCl}} = 0.01000 \text{ M}, \quad C_{\text{NaClO}_4} = 0.490 \text{ M}.$$

This sodium chloride (Merck *p.a.*) was dried before use.

Procedure. In order to establish whether it was possible to measure hydrogen ion concentrations in the solvent used, we measured the emf, E , of galvanic cells of the following type:

Ag, AgCl	ref.soln.	0.500 M NaClO ₄	[H ⁺] M HClO ₄ (0.500 - [H ⁺]) M NaClO ₄	glass electrode
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A few results are shown in Table 1 where E_0 has been calculated from

$$E = E_0 + RT/F \ln [\text{H}^+]$$

the $[\text{H}^+]$ being known from the amount of titrant added. E_0 was found to be constant throughout the range investigated except for the deviations occurring at high hydrogen ion concentrations which are presumably caused by diffusion potentials similar to those found in water,¹ but of smaller magnitude. The stability constants of the proton acetate complexes were determined by a standard potentiometric technique, *viz.* the determination of the hydrogen ion concentrations occurring in cells of the following type:

Ag, AgCl	ref.soln.	0.500 M NaClO ₄	C_{HA} M HAc C_{NaA} M NaAc (0.500 - C_{NaA}) M NaClO ₄	glass electrode
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C_{HA} and C_{NaA} are the total concentrations of acetic acid and sodium acetate, respectively, their sum is kept constant throughout a titration. The concentrations of C_{HA} and C_{NaA} in the right half cell were changed systematically by a titration procedure in which known volumes of a sodium acetate solution were added to 30.00 ml of an acetic acid solution of the same concentration, and *vice versa*. After each addition, the emf of the cell was measured over a period of time. Stable and reproducible potentials were obtained within 5 min. The titrant was added from a 10 ml piston burette (Metrohm, E274), the volume delivered having been checked by weighing. Titrations were performed at six different values (1.00, 10.00, 20.00, 50.00, 100.0, and 200.0 mM) of the total concentrations of acetic acid and acetate. All titrations were repeated at least twice. The reproducibility of the emf was usually to within ± 0.1 mV. For every value of C_A , the titrations were started from high \bar{n}_h values by using sodium acetate as a titrant, and from low \bar{n}_h values using acetic acid as titrant. E_0 was checked before and after each titration by measuring the emf of a solution having a known hydrogen ion concentration. The E_0 drift over four weeks was within ± 0.2 mV. The electrodes used were a Beckman general purpose electrode (type 40498) and silver-silver chloride electrodes prepared according to Brown.⁷ It was not found necessary to take special precautions during the preparation of the latter.² The emf was read on a potentiometer of the type Radiometer PHM4d. The glass electrode readings were occasionally checked by measuring the hydrogen ion concentration of acetate solutions using a hydrogen electrode. Throughout the $-\log[\text{H}^+]$ range 3 to 9 the electrodes agreed to within 0.3 mV. An Ingold Universal Titration Vessel of type 605 was used. The temperature was maintained at 25.00°C by pumping thermostated water through the mantle of the vessel. Magnetic stirring was employed.

Factors particular to using a water/methanol solvent. Methanol evaporates more readily than water so all flasks were sealed with plastic stoppers. The coefficient of expansion of methanol is larger than that of water and it was necessary to have the burette covered with a thermostated water jacket. All solutions were equilibrated in a thermostat bath at 25.0°C before topping up the level to the graduation mark. Pipettes were recalibrated for the new medium. All acetic acid solutions used were freshly prepared in order to avoid the formation of methyl acetate. In this way it was possible to avoid the formation of ester sufficient to affect the measurements. The glass electrode was stored in distilled water when not in use. The silver-silver chloride electrodes were permanently in the reference solution.

RESULTS AND CALCULATIONS

Titration of acetic acid and of sodium acetate. The titration results are given in Table 2. The data are listed as ml titrant (T_1 or T_2) added, \bar{n}_h and $-\log[H^+]$ for the varying values of C_A . \bar{n}_h is the average number of H^+ per acetate ion. The $-\log[H^+]$ values have been calculated from the measured emf's, E and E_0 , using:

$$-\log[H^+] = (E_0 - E)/59.16$$

From Table 2 it is clear that \bar{n}_h vs. $-\log[H^+]$ curves are dependent upon the total concentration C_A , i.e. species of the type H_pA_q , where p and $q > 1$, must be present in the solutions. The curves are of the same shape as shown in Ref. 8, p. 374. A cross over point occurs in the region of $\bar{n}_h = 0.571$. The spread of the curves is rather small, a fact that indicates the dominating complex in the solution to be HA. Since, however, the spread and the cross over point do exist, at least three complexes must be present in the solution (see Ref. 8, p. 372). These complexes are presumably HA, HA_2^- , and H_2A_2 . The feasibility of three such complexes was confirmed, and their stability constants determined by Sillén's method of normalised curves.^{8,9} The normalised curves were computed from the relationships:

Table 2. $\bar{n}_h - \log[H^+]$ data for the proton complexes of the acetate ion at various total acetate concentration.

Volume titrant added in ml		C_A (mM)	1 ^a	10	20	50	100	200
T_1	T_2	\bar{n}_h	$-\log[H^+]$					
2.00		0.0625	8.035	8.064	8.105	8.141	8.168	8.199
3.00		0.0909	7.889	7.916	7.944	7.977	8.001	8.024
5.00		0.1428	7.698	7.715	7.737	7.762	7.781	7.800
7.00		0.1892	7.572	7.588	7.595	7.620	7.639	7.652
10.00		0.2500	7.431	7.440	7.445	7.463	7.480	7.494
14.00		0.3182	7.290	7.299	7.304	7.314	7.330	7.337
	50.00	0.3750	7.177	7.184	7.189	7.197	7.210	7.219
20.00		0.4000	7.141	7.143	7.150	7.155	7.159	7.165
	40.00	0.4285	7.087	7.090	7.095	7.099	7.107	7.112
30.00		0.5000	6.970	6.972	6.973	6.979	6.983	6.985
	30.00	0.5000	6.969	6.974	6.973	6.978	6.983	6.985
40.00		0.5714	6.851	6.850	6.849	6.851	6.851	6.851
	20.00	0.6000	6.800	6.798	6.795	6.794	6.792	6.790
50.00		0.6250	6.758	6.751	6.748	6.749	6.748	6.747
	14.00	0.6818	6.650	6.645	6.640	6.637	6.633	6.628
	10.00	0.7500	6.503	6.499	6.493	6.484	6.480	6.478
	7.00	0.8108	6.353	6.345	6.337	6.329	6.320	6.308
	5.00	0.8571	6.219	6.199	6.187	6.178	6.166	6.150
	3.00	0.9091	6.088	5.985	5.972	5.955	5.939	5.906

^a For low total acetate concentrations, the ionisation of the medium was allowed for in the \bar{n}_h actually plotted.

$$C = \frac{[H + (1 + H)\bar{n}_h] [H(1 - 2R) - 1]}{H[2\bar{n}_h(1 + RH) - (1 + 2RH)]^2} \text{ and}$$

$$R = \frac{(2\bar{n}_h^* - 1)}{2\bar{n}_h^*}$$

where C and H are normalised variables corresponding to C_A and $[H^+]$ and \bar{n}_h^* is the value of \bar{n}_h at the cross over point.

A set of normalised curves were computed for each experimental value of \bar{n}_h . From the axial displacements between the experimental \bar{n}_h vs. $-\log[H^+]$ curves and the normalised curves under the conditions of best fit, $\log \beta_{11}$ and $(\log \beta_{12} - \log \beta_{11})$ were measured. $\log \beta_{22}$ was then calculated from:

$$\log \beta_{22} = \log R + \log \beta_{11} + \log \beta_{12}$$

The value of R used was 0.200, and the positions of best fit is shown in Fig. 1. The following results were obtained:

$$\log \beta_{11} = 6.97 \pm 0.01$$

$$\log \beta_{12} - \log \beta_{11} = 0.08 \pm 0.02$$

$$\log \beta_{22} = 13.34$$

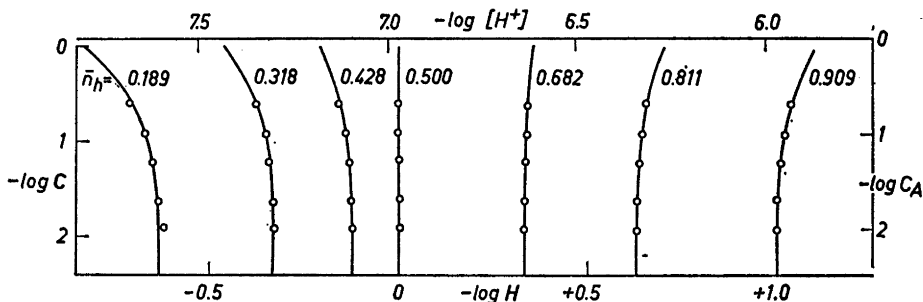


Fig. 1. Normalised curves treatment of experimental $-\log[H^+]$ vs. $-\log C_A$ data. The figure shows the "best" fit chosen.

No large change was caused by varying R throughout the range of possibilities for \bar{n}_h^* ($0.125 < R < 0.275$).

Table 3. The stability constants with their corresponding standard deviations for the various proton acetate complexes in 5 % water/methanol.

Stability constants	by normalised curves	by "Letagrop Vrid"
$\beta_{11} = \frac{[HA]}{[H^+][A^-]}$	$9.32 \pm 0.06 \times 10^6 \text{ M}^{-1}$	$9.234 \pm 0.027 \times 10^6 \text{ M}^{-1}$
$\beta_{12} = \frac{[HA_2^-]}{[H^+][A^-]^2}$	$1.12 \pm 0.05 \times 10^7 \text{ M}^{-2}$	$1.111 \pm 0.069 \times 10^7 \text{ M}^{-2}$
$\beta_{22} = \frac{[H_2A_2]}{[H^+]^2[A^-]^2}$	$2.2 \pm 0.6 \times 10^{13} \text{ M}^{-3}$	$2.49 \pm 0.29 \times 10^{13} \text{ M}^{-3}$

Refinement of the stability constants. The experimental data were finally analysed by the least squares approach "Letagrop Vrid" ¹⁰ using a high speed digital computer (SAAB D21). We minimised the sum $\sum_{i=1}^n \bar{n}_{h,i} - \bar{n}_{h,i,c}$, where $\bar{n}_{h,i,c}$ is the value of $\bar{n}_{h,i}$ calculated from the "best" constants. The experimental data were best explained by assuming that three complexes HA, HA₂⁻, H₂A₂ were present. The results of the least square analysis are given in Table 3. Experimental errors are most evident for the C_A = 1.000 mM titrations, so less weight was placed upon this series both in the graphical and in the least square calculations.

CONCLUSIONS

It is possible to perform accurate measurements of stability constants in the water/methanol solvent we have used. The accuracy of the measurements is as good as in water.

The complexes HA₂⁻ and H₂A₂ reported in water ⁶ are also found in this mixed solvent. The higher polymers, reported in 50 % dioxan/water, ¹² could not be detected by these measurements, possibly due to too low total acetate concentrations.

It is noticeable that as the water content of the solvent decreases, the stabilities of the complexes increase (log β₁₁ in water 4.52, ¹¹ in 50 % dioxan/water = 5.618, ¹² and in 5 vol. % water/methanol = 6.97). This variation cannot be attributed wholly to a change in the dielectric constant of the medium since the dioxan/water and water/methanol systems have almost the same dielectric constant but vastly different stabilities. Here it is of interest to note that, compared to water, the increased stability of the first complex in water/methanol arises from a tenfold increase in the enthalpy of formation (-220 ¹³ cf. -2120 ¹⁴ cal.mole⁻¹) and from an increase in TΔS from 5960 cal.mole⁻¹ in water to 7360 cal.mole⁻¹ in water/methanol.

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