A New Hydrogen Electrode Applied to the Protolysis of Acetic Acid in Potassium Acetate Solutions

George Biedermann* and Anders Molin

Department of Inorganic Chemistry, The Royal Institute of Technology (KTH), S-100 44 Stockholm 70, Sweden

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A new hydrogen electrode prepared by thermal deposition of platinum black has been applied to emf measurements on the system HAc-KAc-H_2O. The protolysis of acetic acid has been studied at 25 °C, using a coulometric alkalification technique. Measurements at the potassium acetate levels C = 0.125, 0.25, 0.5 and 1 M were performed. The acetic acid concentration used was 8–11 mM. The specific interaction theory (S.I.T) was used in the estimation of the equilibrium constant value log K_a at 0.125, 0.25, 0.5 and 1 M KAc.

The present study originated in a need for complementary data concerning the recovery of penicillin V (phenoxymethylpenicillin) from mother liquors remaining after precipitation of the bulk of penicillin. The penicillin V is precipated by adding a concentrated potassium acetate solution. The idea was to recover the penicillin from the mother liquor by acid extraction. By decreasing the pH to about 4.5, the phenoxymethylpenicillin could be selectively extracted in the presence of phenoxyacetic acid by a solvent such as dichloromethane. One problem is then coextraction of acetic acid due to the high concentration of potassium acetate. As no experimental data concerning the conditional equilibrium constant log K_a for the protolysis of acetic acid were available, it was decided to undertake such a study. The idea was to consider a solution with a constant potassium concentration and a practically constant acetate concentration as a particular solvent. For each concentration level a medium-dependent protolysis constant (log K_a) was determined.

Another goal that was set was to test a method for thermal preparation of hydrogen electrodes on a relatively simple problem. Instead of using a glass electrode, the hydrogen electrode was used directly for potential measurements. In this way the alkaline error always associated with the glass electrode could be avoided. A cell with transference was used.[1] The medium-dependent constants (log K_a) could be determined with a precision of 0.001 log units, except at the lowest ionic strength.

Notation

The equilibrium constant for the reaction HAc $\rightleftharpoons$ H^+ + Ac^- is denoted K_a and K^o_a at the reference states C M KAc and pure water, respectively. The same symbols will be used for constants expressed on the molal scale, specifying the use of molal concentration scale in the text.

$\alpha(H_2O)$ = activity coefficient of water in C M KAc

c_i = molar concentration of the species H^+, HAc and KAc, respectively

$D(I)$ = Debye-Hückel term for solution of ionic strength I when expressed in the molal scale

E_H = electrode potential (mV)

E^o_H = standard electrode potential (mV)

E_j = liquid junction potential (mV)

g = $(RT\ln 10/F) \cdot 10^{-3}$ = 59.159 mV at 25 °C

I = ionic strength (= 1/2 Σ $C_i z_i^2$, where z_i = charge of species i)

K = protolysis constant (thermodynamic) of water in C M KAc

K^o_b = basicity constant of HAc in pure water

K_b = basicity constant of HAc in C M KAc

K^o_w = ion product of pure water

m_I = total molal ion concentration

m_{KAc} = molal concentration of KAc

n_{OH} = total amount of hydroxide ion added (mmoles)

n^o_{HAc} = amount of acetic acid added before the start of the titration (mmoles)

* Dr. Biedermann died in February 1985, before the preparation of this publication.

Correspondence and proofs should be sent to Anders Molin, c/o Neumann, Department of Inorganic Chemistry, The Royal Institute of Technology (KTH), S-100 44 Stockholm 70, Sweden.

v = total volume of solution in titration vessel (ml)

γ_i = molal activity coefficient of i defined so that $\gamma_i \rightarrow 1$ as $I \rightarrow 0$

ε (i,x) = interaction coefficient between the species i and x in the molal scale, in kg solvent (mole solute)$^{-1}$

$\tilde{\varepsilon}$ (i,x) = interaction coefficient between the species i and x in the molar scale, in litre solution (mole solute)$^{-1}$

Φ = osmotic coefficient of potassium acetate solution at 25 °C

Method of investigation

Solutions containing KAc in concentrations of C = 0.125, 0.25, 0.5 and 1.0, respectively, and acetic acid solutions with total concentrations between 8 and 11 M were titrated by generating OH^- ions coulometrically. The equilibrium concentration of the OH^- ions was measured with the help of a H_2(g) electrode in the cell shown in Fig. 1. The cell arrangement is described in the literature.[2] For control of the titrations an automatic computer system was used.[3] The I^-/I_2 couple was used instead of the conventional Ag^+/Ag couple as reference electrode as its equilibrium potential is much more rapidly established, thereby increasing the precision obtained.

Experimental

Chemicals and analysis. Acetic acid and potassium acetate of *pro analysi* grade were supplied by AB Kebo. The stock solutions of 1 M acetic acid were kept under nitrogen atmosphere to prevent bacterial decomposition. Doubly distilled water free from oxygen was used to prepare the solutions. The hydrogen gas used in the experiments was purified by passing it through a series of five wash bottles, the first three containing Cr(II) in contact with amalgamated zinc for complete removal of oxygen by oxidation to Cr(III), the fourth a potassium hydroxide solution to remove carbon dioxide and the fifth a potassium acetate solution of the same concentration as the experimental solution.

Experimental details of the emf measurements. The hydrogen electrode used in the experiments is described as follows. The sensor body was made of an inert metal such as

Pt, H_2(g)	Test sol. C M KAc X M HAc	Bridge sol. C M KAc	Reference sol. I_2(s), I^- C M KAc	Pt

Fig. 1. The composition of the cell used in the experiments.

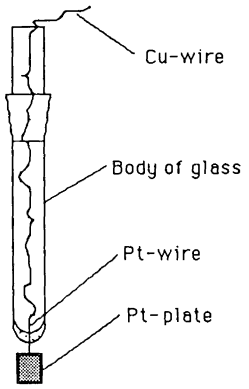

Fig. 2. The hydrogen electrode used in the experiments.

platinum, palladium or iridium. The metal was formed into a thin plate, connected with a platinum wire, attached to a glass holder and washed with aqua regia before the application of hexachloroplatinic acid. The physical appearance of the finished electrode is shown by Fig. 2.

The electrode was placed in aqua regia and boiled for 1–5 min, depending on the condition of the metal. The electrode was then washed immediately with doubly distilled water, dried and stored under conditions where no deposits could be formed on the metal surface.

The sensing surface was prepared as follows. A 1–2 % solution of hexachloroplatinic acid was prepared by dissolving platinum metal in aqua regia. A drop of solution was applied to the sensor body so as to cover its entire surface. The metal plate was heated gently in an ordinary spirit flame. A yellow deposit was formed as the liquid evaporated. The heating was continued until the yellow colour just disappeared, forming a layer of platinum black on the sensor body surface. The procedure was repeated until an even layer covered the surface. Excessive heating was avoided as this results in a layer of greyish appearance and a deactivated electrode. The finally prepared electrode was used immediately to avoid contamination from the air or formation of platinum oxides.

Equilibrium was assumed to be attained in the system when the measured hydrogen electrode potentials agreed to within 10 μV, which was just above the noise level of 3 μV in the measurement system. This state was always obtained in less than 45 min after the last coulometric addition. The hydrogen electrodes were allowed to stabilize in 100 seconds after channel closure before the actual measurement was made.

The measurements were made at 25.00 ± 0.01 °C, using a thermostated silicone oil bath. The generation of OH^- ions was performed at current densities less than $1 \cdot 10^{-3}$ A/cm^2. The potentials were read by a HP 3456 digital voltmeter scaled to 0.1 μV. Two hydrogen electrodes were used in each experiment. The electrodes were checked against each other and against freshly prepared electrodes. Their potentials were required to be stable and reproducible to within 3 μV in the experimental solution before the emf titrations.

Table 1. E°_H values and medium-dependent protolysis constant (log K_b) at trace levels of HAc in different KAc media, determined experimentally and corrected by adding the term SL(H,HAc)$[C_{HAc}]_T$.

C_{KAc}/M	C_{HAc}/mM	E°_H (meas.)	$-\log K_b$ (meas.)	E°_H (corr.)	$-\log K_b$ (corr.)
0.125	8.44	1498.987	9.232±0.002	1500.057	9.235±0.002
0.25	10.96	1468.678	9.222±0.001	1485.664	9.225±0.001
0.50	9.70	1473.907	9.216±0.001	1473.906	9.217±0.001
1.00	10.10	1463.855	9.213±0.001	1463.860	9.214±0.001

Calculations and results

The standard electrode potentials (E°_H) were determined from the part of the titration curve on the alkaline side of the equivalence point ($2 < \text{pOH} < 3$). The pK_b values were calculated from the titration points in the range $6 < \text{pOH} < 8$ with the help of the E°_H values, as described in this section. The calculations were performed according to the following equations:

$$[OH^-] = (n_{OH} - n^{\circ}_{HAc})/v \quad (1)$$

$$\text{pOH} = -\log [OH^-] \quad (2)$$

$$E^{\circ}_H = E_H + 59.159\ \text{pOH} \quad (3)$$

The E°_H values were not corrected for liquid junction potential. They are therefore measured values and are given in Table 1 as the mean of the calculated E°_H values for each potassium acetate concentration.

The equilibrium constants K_b for the reaction

$$HAc + OH^- \rightleftharpoons Ac^- + H_2O \quad (4)$$

for the different potassium acetate concentrations were then calculated as given below:

$$[HAc] = (n^{\circ}_{HAc} - n_{OH})/v \quad (5)$$

$$\text{pOH} = (E^{\circ}_H - E_H)/g \quad (6)$$

$$\text{p}K_b = \log [HAc] + \text{pOH} - \log [Ac^-] \quad (7)$$

where $\text{p}K_b = -\log K_b$. The results are given in Table 1 as measured log K_b values.

The precision of the measured E°_H values can be further improved by statistical weighting.* These values are reported as corrected E°_H values in Table 1.

It was noticed that the potential of the hydrogen electrode was influenced by the presence of the undissociated HAc molecules. This effect of uncharged molecules on the potential of the measuring electrode has also been noted by other authors, e.g. in the presence of boric acid,[4] ascorbic acid[5] and adipic acid.[6] The reason for this is not yet known. The present author believes that this phenomenon can appear due to either adsorption of the uncharged molecules of some acids on the measuring electrode or to change of the activity factor of the acid in question.

A more correct function for E_H can be written in the following way:

$$E_H = E^{\circ}_H - g \log [OH^-] + E_j + \text{SL(H,HAc)}\,[HAc] \quad (8)$$

This is an extended form of eqn. (3) with added terms E_j for the liquid junction potential and SL(H,HAc)[HAc] for the term appearing in presence of HAc. The liquid junction potential E_j was minimized in our experiments by selecting a bridge solution of the same composition as the test solution except for the acetic acid, which was not added.

In the region $2 < \text{pOH} < 3$ where the E°_H values were determined, the E_j dependent upon $[OH^-]$ can be assumed negligible, since $[OH^-] < 0.01$ M. HAc molecules are not formed in this case. The E°_H values are determined by extrapolating the function $E_H + \log [OH^-]$ to $[OH^-] = 10^{-7}$ M ≈ 0.

The "slope function" denoted SL(H,HAc), needed in the acid region of the titration curves, was experimentally determined by an emf titration using the cell free from liquid junction

$$-\ \text{GE}|\text{Test solution}|\text{Ag(s), AgCl(s)}\ +$$

Here, GE denotes a glass electrode. The test solution with the composition 0.01 M KCl, 0.05 M $HClO_4$ was titrated with a solution containing 0.01 M KCl, 0.05 M $HClO_4$ and

* As the precision of the measured potentials E_H is determined by the error in the estimated hydroxide ion concentration, it follows that the more hydroxide ion is added the better is the precision of the E_H values. Therefore, when computing the corrected E°_H values, a quadratic weight function was applied according to

$$E^{\circ}_H = \Sigma\, E_H(i)\, w(i)$$

where the sum is taken over all measured values. The weights $w(i)$ were computed by

$$w(i) = (dn_i/dE_i)^2/\Sigma\, (dn_i/dE_i)^2$$

where the sum is again taken over all measured values. The same weight function was applied when computing the corrected log K_b values.

1.5584 M HAc. $[HAc]_T$ was varied in the range: $0 < [HAc]_T < 0.5$ M.

The following equation can be written for this cell:

$$E_H = E^\circ_H - 59.159 \log 0.050 + SL(H,HAc)\,[HAc] \quad (9)$$

The slope of the plot of E_H versus [HAc] defines the slope function SL(H,HAc), which was −6.7 mV/M HAc. We can then estimate the maximum effect of the undissociated HAc molecules in our experiments:

$$SL(H,HAc)[HAc] <= -6.7^* 0.010 = -0.067 \text{ mV} \quad (10)$$

As can be seen, this effect is rather small, but it was nevertheless taken into account in the acid region where the pK_a values are determined. Hence, considering eqn. (8) we can write:

$$pOH = (E^\circ_H - E_H - SL(H,HAc)\,[HAc])/59.159 \quad (11)$$

The maximum effect caused by the presence of the HAc molecules is approximately 0.003 log units. The results obtained using eqn. (11) are given as corrected log K_b values in Table 1. We obtain the *basicity constant* of acetic acid at *zero ionic strength* and 25 °C from

$$pK^\circ_b = pK^\circ_w - pK^\circ_a \quad (12)$$

The values found in the literature[7] are $pK^\circ_a = 4.756$ and $pK^\circ_w = 13.996$. Using (12), we calculate the value $pK^\circ_b = 9.240$ for $C_{KAc} = 0$.

Plotting pK_b against C_{KAc} gives the plot shown in Fig. 3. We observe that the values change very slightly with C_{KAc}.

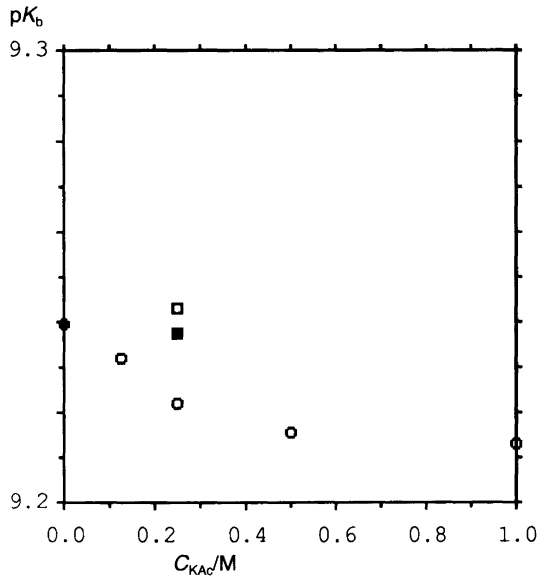

Fig. 3. pK_b vs. C_{KAc} for acetic acid in potassium acetate solutions. Experimental values. ● Literature. ○ Experimental, pK_b (meas.). ■ and □ Experimental, lower precision.

Table 2. Corrected pK_b values in different KAc media.

C_{KAc}(M)	m_{KAc}	$pK^a_{b,corr1}$	$pK^a_{b,corr2}$
0.125	0.1255	9.233	9.236
0.25	0.2485	9.224	9.227
0.50	0.4906	9.221	9.222
1.00	0.9580	9.223	9.224

[a]The average values are 9.225±0.005 and 9.227±0.006 respectively.

In the HAc-KAc-H_2O system, this change can be due to variations in the activity coefficients of the reactants and products of eqn. (4), as no other species are expected to be present. We can define the thermodynamic equilibrium constant as

$$K_{b,corr} = K_b \cdot \gamma_{Ac^-}/(\gamma_{HAc} \cdot \gamma_{OH^-}) \quad (13)$$

According to the S.I.T.:[8]

$$-\log \gamma_{Ac^-} = D(I) - \varepsilon(Ac^-,K^+)m_I \quad (14)$$

$$-\log \gamma_{OH^-} = D(I) - \varepsilon(OH^-,K^+)m_I \quad (15)$$

where the Debye-Hückel term[9] $D(I)$ is given by

$$D(I) = 0.5109\sqrt{I}(1 + 1.5\sqrt{I}) \quad (16)$$

From Ciavatta[10] we obtain the interaction coefficients $\varepsilon(Ac^-, K^+) = 0.09$ and $\varepsilon(OH^-, K^+) = 0.08$ on the molal scale. Assuming $\gamma_{HAc} = 1$, and inserting eqns. (14) and (15) into eqn. (13), we obtain, after taking negative logarithms:

$$pK_{b,corr} = pK_b + 0.01 \cdot m_I \quad (17)$$

The calculated values are shown in Table 2. The value denoted $pK_{b,corr1}$ is obtained using the measured pK_b values from Table 1; $pK_{b,corr2}$ is obtained using the corrected pK_b values. These corrected values and the uncorrected ones are plotted in Fig. 4.

The $pK_{b,corr2}$ values are used in the following computation of the equilibrium constant K_a for the reaction:

$$HAc \rightleftharpoons H^+ + Ac^- \quad (18)$$

The equilibrium constant for eqn. (18) at different KAc concentrations can be calculated as

$$pK_a = pK - pK_b \quad (19)$$

where pK is the thermodynamic equilibrium constant for the protolysis of H_2O, at a given KAc concentration, according to the following definition:

$$H_2O \rightleftharpoons H^+ + OH^- \quad (20)$$

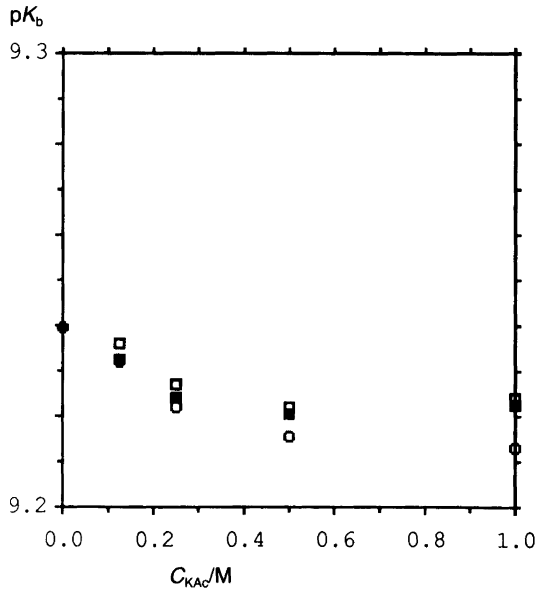

Fig. 4. pK_b vs. C_{KAc} for acetic acid in potassium acetate solutions. Experimental and corrected values. ● Literature. ○ Experimental, pK_b (meas.). ■ Experimental, corrected for activities, $pK_{b,corr1}$. □ Experimental, corrected for activities and adsorption(?), $pK_{b,corr2}$.

and we obtain the pK value from:

$$-\log K = -\log K^{\circ}_{w} - \log \gamma_{OH^-} - \log \gamma_{H^+} + \log \alpha(H_2O) \quad (21)$$

As the log K values for the potassium acetate solutions are not known, we have to estimate them using the S.I.T. Accordingly, $-\log \gamma_{OH^-}$ is given by eqn. (15) and

$$-\log \gamma_{H^+} = D(I) - \varepsilon(H^+, Ac^-)m_I \quad (22)$$

$$+\log \alpha(H_2O) = 2\, m_{KAc}\, \Phi/(\ln 10 \cdot 55.52) \quad (23)$$

where the Debye-Hückel term $D(I)$ is given by eqn. (16).

The pK_a values can now be computed by combining eqn. (19) with eqn. (21):

$$pK_a = -\log K^{\circ}_{w} - \log \gamma_{OH^-} - \log \gamma_{H^+} + \log \alpha(H_2O) - pK_b \quad (24)$$

The value of $\varepsilon(H^+, Ac^-) = 0.13$ (molar scale) was determined in 0.125 M $NaClO_4$ by an emf titration. This is a modified version of a method suggested by Nèher-Neumann,[11] which is to be published soon. The same value can be used on the molal scale as the densities of the potassium acetate solutions are close to unity. The pK_a values obtained by eqn. (24) are shown in Table 3.

For a description of methods used for determination of interaction coefficients, see Nèher-Neumann.[11] For the interested reader, some references from the literature[12-21] concerning pK_a determinations are given in Table 4.

Concerning results of previous investigations, it should be mentioned that formation of the dimeric species H_2Ac_2 and HAc_2^- has been suggested in acetate buffers when the concentration of the buffer components is high.[22] As pointed out elsewhere,[23] under such circumstances the following effects must be taken into account:

(a) the ideal diffusion potential (Henderson term), denoted E_D.

(b) the contribution of the activity factors to E_D, denoted E_{Df}, and to the potential of the measuring electrode ($g \log f_H$). These terms include the potential contribution of the salt component of the buffer to E_H and the effect caused by the exchange of the ions of the ionic medium by the salt.

(c) the effect of the uncharged acid on the measuring electrode

Table 4. pK_a values obtained from the literature.[a]

Method[b]	Temp.	Medium	pK_a	Ref.
gl	20	0.1($NaClO_4$)	4.55	12
gl	25	0.1	4.53	13
H	20	0.2(KCl)	4.64	14
gl	25	0.2(KNO_3)	4.64	15
pH	25	0.5($LiClO_4$)	4.48±0.03	16
H	20	0.55	4.74	17
E	20	1($NaClO_4$)	4.61	18
gl	20	1($NaClO_4$)	4.55	19
qh	20	1($NaClO_4$)	4.59	20
gl	30	1($NaClO_4$)	4.30	21

[a]The table was compiled from Ref. 24. [b]gl = glass electrode; H = hydrogen electrode; qh = quinhydrone electrode;

Table 3. Calculated pK_a values in different KAc media.

m_{KAc}	$D(I)$	$-\log \gamma_{OH^-}$	$-\log \gamma_{H^+}$	$\log \alpha(H_2O)$	$\log K_w$	pK_a
0.1255	0.1180	0.1080	0.1017	0.0018	14.208	4.972
0.2485	0.1457	0.1258	0.1134	0.0037	14.239	5.015
0.4906	0.1745	0.1353	0.1107	0.0076	14.250	5.028
0.9580	0.2086	0.1320	0.0841	0.0159	14.228	5.004

The average value is 5.005±0.024.

As shown by Nèher-Neumann (results to be published), the neglect of these effects resulted in the proposal of dimeric species. In the present study, the HAc concentration is too low for any dimer formation, so this question will not arise.

Conclusion and discussion

The experimental data presented in this study show that precise data can be obtained by the emf method used. These data are used to compute the value of the equilibrium constant K_b for the potassium acetate concentrations 0.125, 0.25, 0.5 and 1.0 M. Extrapolation to zero ionic strength shows that the values obtained are reasonable. Interpolation between the points will give a smooth function which can be used for calculating intermediate values. The values obtained can be used in a model for predicting the distribution of acetic acid when extracting with organic solvents at different pH values.

The results presented are also related to the problem of accurately determining the pH in alkaline aqueous solutions, which is particularly difficult. A characteristic of measurements of the electrochemical potential of hydrogen electrodes prepared in the ordinary way by electrochemical precipitation of platinum on a metal substrate is that no stable potential will be reached in strongly alkaline solutions, e.g. at pH values above 11–12. Consequently, it is of great interest to find a better method for preparing platinized electrodes for analytical purposes. In the present study, a method for thermal preparation of hydrogen electrodes has been developed and applied to the problem of measuring the electrochemical potential. As described in the experimental section, very good precision was obtained in the measurements. Electrodes prepared in the conventional way were also used in the experimental system. However, the conventional electrodes were poor by comparison, a precision of 0.1 mV at best being achieved. A potential drift was also observed, especially in alkaline solutions. Sometimes the electrodes even had to be replaced during the experimental run. The problems might be due to occlusion of hexachloroplatinic acid (or hexachloroplatinate anions) in the platinum layer precipiated during the electrolysis. By the thermal method, all hexachloroplatinic acid will decompose during the preparation.

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