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pK_a Determination of Weak Acids over a Large pH Range

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The results of a potentiometric study of methanoic acid and glucuronic acid using a well-established experimental technique for suspensions of cellulosic fibers are presented. Several experiments for each acid are summarized within the framework of a Student's *t* test distribution. The titrations were performed in the presence of a stronger acid, and the activity coefficients were calculated through the extended Debye–Hückel equation. The method allows rapid determination of pK_a values over a large pH range. A numerical approach for the determination of equivalence points in potentiometric titrations was used.

Introduction and Method

This study may be described as an adaptation to a free acid in solution of the continuous titration technique that has been used in the University of Reading for cellulosic suspensions (*1–6*). The idea of adapting this experimental technique to free acids in solution was pioneered by Petzold (*5, 6*) who presented a plot for glucuronic acid.

The experimental technique applied consists of continuously titrating and following the change of pH, using a combined glass electrode. One aqueous solution to be titrated contained a known amount of hydrochloric acid (to guarantee an initially chosen pH) and the free acid under study. This solution will be referred to as "the run" throughout the rest of this paper. The other solution to be titrated differed only from the former in that the volume of the acid under study was replaced by ultrapurified water. The latter solution will be referred to as "the blank". Figure 1 shows typical raw data.

In order to take into account dilution effects produced either by uneven starting volumes in the two samples (run and blank) or by different volumes of titrant added to attain each pH value, a correction procedure for the pH was carried out for the blank values, following that of Herrington and Midmore (*7*):

$$\mathrm{pH}_{\mathrm{corrected}} = \begin{cases} \mathrm{pH}_{\mathrm{measd}} + \log\left(\dfrac{V_{0\mathrm{R}} + V_{\mathrm{R}}}{V_{0\mathrm{B}} + V_{\mathrm{B}}}\right) & \text{if } \mathrm{pH}_{\mathrm{measd}} < \dfrac{\mathrm{p}K_{\mathrm{W}}}{2} \\ \mathrm{pH}_{\mathrm{measd}} & \text{if } \mathrm{pH}_{\mathrm{measd}} = \dfrac{\mathrm{p}K_{\mathrm{W}}}{2} \\ \mathrm{pH}_{\mathrm{measd}} - \log\left(\dfrac{V_{0\mathrm{R}} + V_{\mathrm{R}}}{V_{0\mathrm{B}} + V_{\mathrm{B}}}\right) & \text{if } \mathrm{pH}_{\mathrm{measd}} > \dfrac{\mathrm{p}K_{\mathrm{W}}}{2} \end{cases} \quad (1)$$

where $V_{0\mathrm{R}}$ and $V_{0\mathrm{B}}$ are the initial volumes of the run sample and blank sample, respectively, and V_{R} and V_{B} are the volumes of titrant for the run and for the blank corresponding to the same value of pH measured.

Interpolation processes were necessary to produce the volumes of titrant in the blank sample corresponding to the pH values obtained in the run sample.

From these data the differences in the dispensed volume of titrant, ΔV = volume of titrant for the run − volume of titrant for the blank, were obtained for each pH value.

Once the pairs of points (ΔV, pH) were obtained, the division of the ΔV values by the one corresponding to the equivalence point of the titration process generated the file of points (α, pH), where α corresponds to the degree of dissociation of the acid under study. A better control of the equivalence point was obtained by minimizing the standard deviation of the distribution of pK_a values generated by this method.

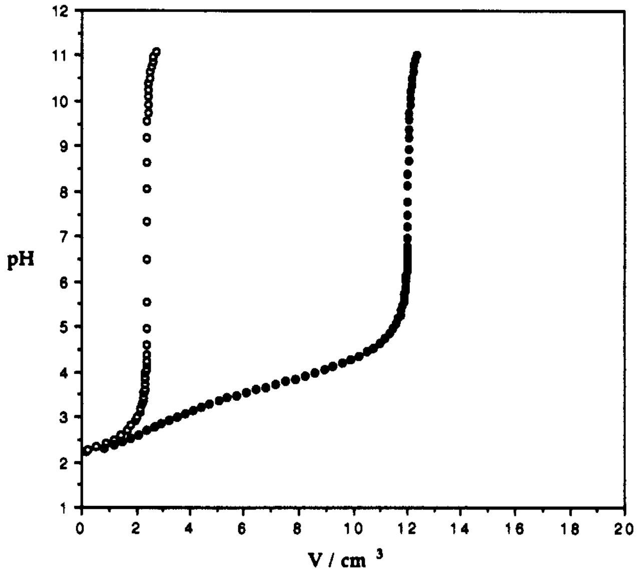

Figure 1. Potentiometric titration of methanoic acid in ultrapurified water at 20.0 ± 0.1 °C: ○, blank; ●, run. *V* is the volume of 0.0960 mol dm^{-3} NaOH solution.

The formalism adopted is the following:

$$\mathrm{p}K_a = \mathrm{pH} + \log\left(\frac{1-\alpha}{\alpha}\right) + \log\frac{f_{\mathrm{HA}}}{f_{\mathrm{A^-}}} \quad (2)$$

This formalism obtains a series of pK_a values over a large pH range. The activity coefficient of the undissociated part of the acid, f_{HA}, was assumed to be unity, following Randall and Failey (*8*) and a IUPAC publication (*9*). The activity coefficient of the dissociated part of the acid, $f_{\mathrm{A^-}}$, was calculated through the extended Debye–Hückel equation (*10, 11*)

$$\log f_{\mathrm{A^-}} = -\frac{A_{\mathrm{D}} z_{\mathrm{C}} z_{\mathrm{A}} I^{1/2}}{1 + B_{\mathrm{D}} a_{\mathrm{D}} I^{1/2}} \quad (3)$$

The values for the constants A_{D} and B_{D} were obtained from Robinson and Stokes (*12*). At 20 °C $A_{\mathrm{D}} = 0.5046$ and $B_{\mathrm{D}} = 0.3276$. Kielland (*13*) tabulates values of a_{D}, the effective diameter of the hydrated ion, for many acids, including methanoic acid ($a_{\mathrm{D}} = 3.5$). For glucuronic acid the estimated value of a_{D} was inferred from other molecules of similar size ($a_{\mathrm{D}} = 6$).

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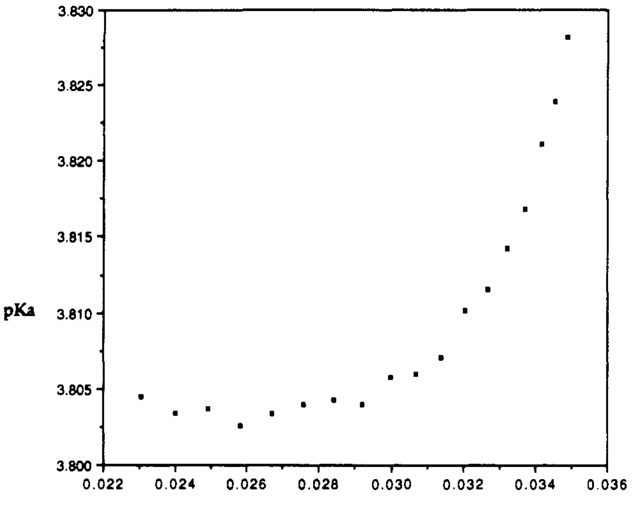

Figure 2. Partial representation of $\mathrm{p}K_a$ values obtained for each ionic strength value attained throughout a titration of methanoic acid in ultrapurified water at 20.0 ± 0.1 °C (experiment 5).

Table I. Titration of Methanoic Acid at 20 °C (Experiment 5)[a]

pH	α	I/(mol dm^{-3})	$\mathrm{p}K_a$
3.634	0.440	0.0240	3.806
3.695	0.476	0.0249	3.805
3.757	0.512	0.0258	3.805
3.818	0.548	0.0267	3.804
3.882	0.585	0.0276	3.804
3.946	0.620	0.0284	3.805
4.012	0.655	0.0292	3.805
4.080	0.690	0.0300	3.805
4.153	0.725	0.0307	3.807
4.226	0.757	0.0314	3.807
4.306	0.789	0.0321	3.808
4.391	0.819	0.0327	3.811
4.479	0.847	0.0332	3.812
4.576	0.873	0.0337	3.815
4.675	0.896	0.0342	3.817
4.784	0.916	0.0346	3.822
4.889	0.933	0.0349	3.824
5.002	0.947	0.0351	3.828

[a] This table shows a list of values of $\mathrm{p}K_a$ and degree of dissociation α corresponding to the pH and ionic strength I of the medium in different stages of the titration.

The results showed that for an initial pH of 1.3 an unacceptable value of 15% was obtained for the standard deviation of the derived $\mathrm{p}K_a$ values. But for a starting pH of 2.0 the standard deviation was less than 1%.

A spreadsheet, *Excel for Macintosh computers*, was used for all of the calculations involved in this method, including the process of minimization of the standard deviation of a series of $\mathrm{p}K_a$ values.

Experimental Section

Materials. The water used in these experiments was submitted to a sequence of two distillations before passing through a reverse osmosis system (Millipore Milli-RO 15) of polyamide membrane, followed by passage through a Milli-Q system (both provided by Millipore Corp.). This is a preassembled wall-mounted unit which consists of a series of four identical head-housing assemblies and a final filter. The first four stages use expendable cartridges, namely, of activated carbon, two ion-exchange units (containing a strong acid/strong base mixed-bed deionizer that removes dissolved inorganic contaminants, each cartridge with an ion-exchange capacity of 6840 ppm as $CaCO_3$), and an Organex filter to remove organic impurities. The resistivity of water inside this system was 18 MΩ cm. This water will be refered to as "ultrapurified water" throughout this paper.

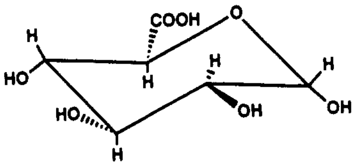

Figure 3. Molecular representation of a conformation of α-D-glucuronic acid.

Table II. Summary of the $\mathrm{p}K_a$ Values Obtained for Methanoic Acid at 20.0 °C[a]

experiment	$\mathrm{p}K_a$	I_{min}/(mol dm^{-3})	I_{max}/(mol dm^{-3})
1	3.79	0.0238	0.0312
2	3.80	0.0239	0.0291
3	3.77	0.0241	0.0292
4	3.79	0.0241	0.0301
5	3.80	0.0240	0.0300

[a] The minimum and the maximum values for the ionic strength I are recorded for each experiment.

Concentrated BDH hydrochloric acid, GPR, was used to prepare an aqueous solution of hydrochloric acid (0.0240 ± 0.0001 mol dm^{-3}). Concentrated BDH "Formic acid 90%" was used to prepare an aqueous solution of methanoic acid (0.100 mol dm^{-3}). An aqueous solution of glucuronic acid (0.100 mol dm^{-3}) was prepared from Aldrich D-glucuronic acid, 98%.

Apparatus. Temperature control was provided by a Stanton Redcroft thermostatic bath maintained at ±0.1 °C. All titrations were performed under a constant flow of CP grade nitrogen, using a Metrohm 670 titroprocessor and a Metrohm 665 Dosimat.

Procedure. Each blank sample consisted of a mixture formed by adding 10.0 cm^3 of 0.0240 mol dm^{-3} HCl to 10.0 cm^3 of ultrapurified water. Each run sample consisted of a mixture formed by adding 10.0 cm^3 of 0.0240 mol dm^{-3} HCl to 10.0 cm^3 of a 0.100 mol dm^{-3} solution of the acid under study.

Results

(1) Methanoic Acid. The results obtained for methanoic acid, HCOOH, are illustrated in Figure 2 and Table I. The summary of the results is presented in Table II. Figure 2 refers to experiment 5, and Table I illustrates in detail the values obtained in this experiment. Table II gives the mean values of $\mathrm{p}K_a$ obtained in each experiment at 20.0 ± 0.1 °C, in the plateau regime of Figure 2. The plateau of $\mathrm{p}K_a$ values may be described in terms of the limits of ionic strength $I \in [I_{\mathrm{min}}, I_{\mathrm{max}}]$.

For the ultrapurified water medium, the average $\mathrm{p}K_a$ value for methanoic acid obtained in this study, with an uncertainty provided by the Student's t test distribution with a 99% level of confidence, is

$$\mathrm{p}K_a = 3.79 \pm 0.03\ (\pm 0.79\%)$$

The standard deviation that expresses the uncertainty shown above is the same order of magnitude as the uncertainty in the pH values guaranteed for the buffer solutions obtained from BDH (0.67%).

The deviation from the tabulated IUPAC value (*9*), obtained by Harned and Embree (*14*) in 1934 for methanoic acid at 20 °C ($\mathrm{p}K_a$ = 3.753), is less than 1.0%.

(2) Glucuronic Acid. Glucuronic acid, $C_6H_{10}O_7$ (Figure 3), occurs in its acidic radical in many natural polymeric

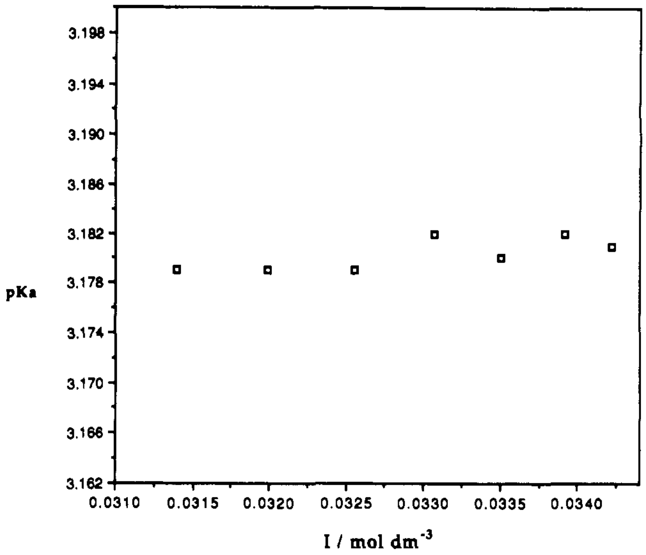

Figure 4. Partial representation of pK_a values obtained for each ionic strength value attained throughout a titration of glucuronic acid in ultrapurified water at 20.0 ± 0.1 °C (experiment 7).

Table III. Titration of Glucuronic Acid at 20 °C (Experiment 7)[a]

pH	α	I/(mol dm^{-3})	pK_a
3.671	0.783	0.0314	3.179
3.752	0.813	0.0320	3.179
3.841	0.843	0.0326	3.179
3.939	0.870	0.0331	3.182
4.033	0.893	0.0335	3.180
4.146	0.915	0.0339	3.182
4.248	0.932	0.0342	3.181

[a] This table shows a list of values of pK_a and degree of dissociation α corresponding to the pH and ionic strength I of the medium in different stages of the titration.

substances, including cellulosic materials (*14*). The paper industry tries to control the electrostatic charge in paper surfaces created by acidic groups. The glucuronic acid group is produced in paper wood pulps through chemical reactions that take place in either the chemical pulping or the bleaching process. Therefore, the study of the glucuronic acid provides some insight in the titration processes of paper wood pulps, and in the charge control of paper surfaces.

Table III illustrates in detail the values obtained for experiment 7. The results obtained for glucuronic acid are summarized in Table IV.

Table IV. Summary of the pK_a Values Obtained for Glucuronic Acid at 20.0 °C[a]

experiment	pK_a	I_{min}/(mol dm^{-3})	I_{max}/(mol dm^{-3})
1	3.18	0.0318	0.0350
2	3.18	0.0319	0.0351
3	3.20	0.0312	0.0350
4	3.20	0.0315	0.0348
5	3.18	0.0316	0.0347
6	3.17	0.0315	0.0347
7	3.18	0.0314	0.0345

[a] The minimum and the maximum values for the ionic strength I are recorded for each experiment.

For the ultrapurified water medium, the average pK_a value for glucuronic acid obtained in this study, with an uncertainty provided by the Student's t test distribution with a 99% level of confidence, is

$$\mathrm{p}K_a = 3.18 \pm 0.02\ (\pm 0.63\%)$$

This result agrees with that obtained by Hirsch (*14*) in 1952 (pK_a = 3.18). However, the authors claim that the result of the present work was obtained in a more reliable fashion, since ultrapurified water was used which was not available in 1952, and account has been taken of activity coefficients, whereas these were ignored in the work of Hirsch.

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