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A comparison of two methods to determine the second ionization constant of weak polyprotic acids using their monobasic acidic salts

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Abstract

The second ionization constants of various weak polyprotic acids as their monobasic acidic salts were determined using two methods. In the first method (FM), an aqueous solution of the salt of the weak acid was subdivided into two equal volumes. One part was neutralized by titration with sodium hydroxide solution to equivalence point using Phenolphthalein as indicator. This neutralized weak acid – in the form of its conjugate base - was then added to the part that had not been subjected to titration. The pK_{a2} for the weak acid was determined from the pH of the resultant mixture which contained equal moles of the weak acid and its conjugate base. The ionization constant, K_{a2} was then calculated. In the second method (IM), half the volume of NaOH solution with a molarity equal to that of the aqueous solution of the salt of the weak acid and a solution of the salt of the weak acid were mixed together and the pKa_2 for the weak acid was determined from the pH of this solution. The K_{a2} was then calculated as before. There was no significant difference in the pK_{a2} values for method FM and method IM, $p<0.28$ except for the pK_{a2} values for $KHC_4H_4O_6$, $p<0.03$. The FM method employed the inherently error-prone indicator utilized neutralization titration with a subjective visual evaluation of the colorless-to-pink endpoint. The IM method required significantly lesser time, materials, and apparatus, was simpler to perform, and did not involve any error arising out of subjective visual evaluation of color. However, while the concept of the half-neutralization point being equal to the ionization constant was explicitly evident from the FM method, it was not as easily discernible using the IM method.

Introduction

The net ionic equation for the dissociation of two salts is shown in equations 1 and 2

$HSO_4^- + HOH === SO_4^{2-} + H_3O^+$ equation 1

$K_{a2} = [SO_4^{2-}][H_3O^+] / [HSO_4^-]$

When $[SO_4^{-2}] = [HSO_4^-]$, the acid is half ionized and $K_{a2} = [H_3O^+]$ or $pK_{a2} = pH$.

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$H_2PO_4^-$ + HOH === HPO_4^{2-} + H_3O^+ equation 2

$K_{a2} = [HPO_4^{2-}][H_3O^+] / [H_2PO_4^-]$

The pH of a solution of a monobasic salt of a polyprotic acid is acidic because of the hydrolysis of water by the conjugate base of the monobasic salt as shown in equations 1 and 2 above. Equations 3 and 4 apply when the salt is being titrated with a strong base.

HSO_4^- + OH^- → SO_4^{2-} + H_2O equation 3

Hence, when $[OH^-] = ½ [HSO_4^-]$, the acid is half ionized and $K_{a2} = [H_3O^+]$ or pK_{a2} = pH.

$H_2PO_4^-$ + OH^- → HPO_4^{2-} + H_2O equation 4

Materials and methods

Potassium dihydrogen phosphate reagent grade, lot 204271, Potassium hydrogen sulfate reagent grade, lot 205350, Potassium hydrogen phthalate reagent grade, lot 204871, Potassium hydrogen tartrate laboratory grade, lot 204273 and Sodium hydroxide (NaOH) as a 0.1 M solution were from Flinn Scientific, Batavia, IL, and were used as received. The indicators Phenolphthalein, as a 0.5% alcohol solution, lots 207127, 189656, 190068, methyl red 0.02% aqueous indicator solution, lot 179493, methyl orange 0.1% aqueous solution, lot 178963, bromothymol blue 0.04% aqueous solution, lot 189842 were also from Flinn Scientific. A 60 mL monoject syringe to which was attached a stopcock, "Poor man's burette" (d=0.5 mL), catalog no. AP8753 was from Flinn Scientific, a Vernier pH probe connected to a Vernier labquest, SN 74928 was obtained from Vernier Software and Technology, Beaverton, OR. The pH probe was standardized immediately prior to performing the experiment using standard solutions of pH 4.0, lot 224612 and pH 7.0, lot 193944 from Flinn Scientific, with buffer accuracy of ± 0.02 at 25ºC. All measurements were performed at room temperature, 22ºC. All solids were weighed to a precision of 0.001 g on an Ohaus Pioneer balance model no. PA153 (Ohaus Corporation, Parsippany, NJ). When using the FM method, solutions were subdivided using appropriately sized measuring cylinders. When using the IM method, solutions of appropriate molarity were prepared using appropriately sized volumetric flasks. City water was used for all the experiments. Its pH was not determined before use since the final solutions were buffered.

0.01 M solutions of the monobasic acid salts were prepared and used for all the experiments. 0.01 M solution of NaOH was prepared by diluting 100 mL of the 0.1 M solution in a volumetric flask to 1000 mL in a volumetric flask. Briefly, for method FM, a 200 mL of solution was prepared. 50 mL of this solution measured in a graduated cylinder was titrated against an equimolar solution of NaOH using phenolphthalein as an indicator until a faint pink endpoint. The volume of NaOH required to reach the endpoint was recorded. To this solution was added 50 mL

the un-titrated solution and the pH determined after mixing. For method IM, to 50 mL of the un-titrated solution was added 25 mL of equimolar NaOH solution and the pH determined after mixing. The procedures to determine the pK_{a2} values using both the FM and IM methods were performed in triplicate.

The pH of buffer solutions 4.0 and 7.0 was measured repeatedly by a procedure where the probe was held under flowing water between measurements. This procedure served to assure that the intra or inter-method difference in pH measurements using the two methods (FM and IM) was real and not due to an artifact of the measurement procedure, or due to the variability of the pH probe itself.

A two-tailed, unpaired t-test was performed using the individual pK_{a2} values for each acidic salt using the calculator provided at the website https://www.graphpad.com/quickcalcs/ttest2/

Results and discussion

The variability in the pH probe itself was determined based on three measurements in pH 4.0 and pH 7.0 buffers where the probe was placed under running water between the measurements. The measurements were accurate (±0.01 pH units difference from standard buffer value) and precise (±0.01 pH units of one another). Hence, it can be concluded that any experimental difference in pH values was not due to the variability of the pH probe itself.

Table 1 lists the acidic salts used in the study with their corresponding second ionization constants (1). The salts of diprotic acids were in the form of their monohydrogen salts while the one of a triprotic acid (phosphoric acid) was the dihydrogen salt. In each case, the second ionization constant corresponding to the acid, K_{a2} , was determined.

Table 1: Characteristics of acid salts used in the study

Acid salt	Formula	Second ionization constant, K_{a2}	pK_{a2}
Potassium dihydrogen phosphate	KH_2PO_4	6.2×10^{-8}	7.21
Potassium hydrogen sulfate	$KHSO_4$	1.0×10^{-2}	2.00
Potassium hydrogen phthalate	$KHC_8H_4O_4$	3.9×10^{-6}	5.41
Potassium hydrogen tartrate	$KHC_4H_4O_6$	4.6×10^{-5}	4.34

Table 2: Reproducibility of the neutralization titration using method FM (n=3)

Acid salt	mL of NaOH used for neutralization	Mean (mL NaOH) ± %relative standard deviation (RSD)	Theoretical pK_{a2} calculated from the Henderson-Hasselbach equation (see below)
KH_2PO_4	53.0, 55.0, 54.0	54.0 ± 1.85%	6.93
$KHSO_4$	47.0, 57.0, 53.0	52.3 ± 9.62%	2.89*
$KHC_8H_4O_4$	50.0, 55.0, 56.0	53.7 ± 5.99%	5.38
$KHC_4H_4O_6$	45.0, 49.0, 48.0	47.3 ± 4.40%	4.33

*the actual pK_{a2} value for this salt was found to be significantly different than the one stated in reference 1 (see Table 1). It is speculated that inadvertent contamination could be responsible for the discrepancy.

The variability in the volume of NaOH required to neutralize the acidic salt resulted was due to the precision limits of the measuring cylinder (±1%, d=0.5 mL in 50 mL), the 'poor-man's buret' (±2%, d=1.0 mL in 50 mL) and the subjective visual error arising from estimating the identical shade of pink color in the three experiments. It therefore follows, that assuming an additive error of 3% from the first two sources, a minimum of 6.62 %RSD (for the experiment with the largest %RSD) can be attributed to the visual variability in registering the pink color of the endpoint. The FM method therefore had a propensity to overestimate the pK_{a2} due to the excess OH^- ions. The ratio of [conjugate base]/[acid] was >1 in the FM method. From Table 2, for the salt KH_2PO_4, it is evident that 4 mL greater than a stoichiometric amount of base was required to observe the endpoint for the titration. This translated into 0.04 mMol excess of OH^- ions as can be seen in the initial-change-equilibrium, (ICE) chart below:

$H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O$

I	0.5 mMol	0.54 mMol	0.00 mMol
C	-0.5	-0.5	+0.5
E	0.00 mMol	0.04 mMol	0.5 mMol

When 50 mL of the non-titrated acid is added to the neutralized solution, the following ICE results:

$H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O$

I	0.5 mMol	0.04 mMol	0 mMol
C	-0.04 mMol	-0.04 mMol	+0.04 mMol
E	0.46 mMol	0.00 mMol	0.54 mMol

When the result from the preceding ICE Table was substituted into the Henderson-Hasselbach equation:

$pH = pK_{a2} + \log\{[HPO_4^{2-}] / [H_2PO_4^-]\}$ equation 5

$pH = 6.863 + \log (0.54/0.46)$

$pH = 6.93$

It should be noted that the pK_{a2} values reported in Table 1 are nominal and can (and have been reported to be) affected by composition, purity, grade and time of sampling during the storage life of the material. Since the pK_{a2} value obtained using the IM method was stoichiometrically accurate and did not involve the visual determination endpoint error, it was taken to be the comparator value in the Henderson-Hasselbach equation (equation 5). The increase in pH as measured by the FM method was due to the stoichiometric excess of OH^- ions required to observe the neutralization point. Similar theoretical pK_{a2} values calculated using the stoichiometric excess or deficit of OH^- ions are shown in Table 2 for the various salts.

Table 3: Ionization constants (±%RSD) determined using the two methods, n=3

salt of weak acid	pK_{a2} using FM method	pK_{a2} using IM method
KH_2PO_4	6.89, 6.94, 6.79	6.88, 6.92, 6.79
$KHSO_4$	2.84, 2.89, 2.90	2.85, 2.83, 2.87
$KHC_8H_4O_4$	5.24, 5.37, 5.44, 5.47	5.23, 5.32, 5.31, 5.42
$KHC_4H_4O_6$	4.42, 4.47, 4.5	4.36, 4.38, 4.38

Table 4: Statistical analysis of the two methods

salt of weak acid	Mean pK_{a2} ±%RSD using FM method	pK_{a2} ±%RSD using IM method	Two-tailed unpaired t-test comparing pK_{a2} for the two methods
KH_2PO_4	6.873 ± 1.11%	6.863 ± 0.97%	P=0.8726
$KHSO_4$	2.877 ± 1.12%	2.850 ± 0.70%	P=0.2895
$KHC_8H_4O_4$	5.380 ± 1.90%	5.32 ± 1.46%	P=0.3867
$KHC_4H_4O_6$	4.460 ± 0.91%	4.373 ± 0.27%	P=0.0207

The pH at the end point of the titration is determined by the hydrolysis of the conjugate base of the weak acid. For KH_2PO_4, the conjugate base HPO_4^{-2} hydrolyzes water according to the following equation:

$$HPO_4^{2-} + H_2O \;==\; H_2PO_4^- + OH^-$$

The pH at the end point is hence basic, consistent with the titration of a weak acid and a strong base. The pH at equivalence point is calculated using the equation:

$$pK_b = [H_2PO_4^-][OH^-] / [HPO_4^{2-}] \qquad \text{equation 6}$$

where $[HPO_4^{2-}] = 0.005$ M and $pk_b = pk_w/pk_{a2}$

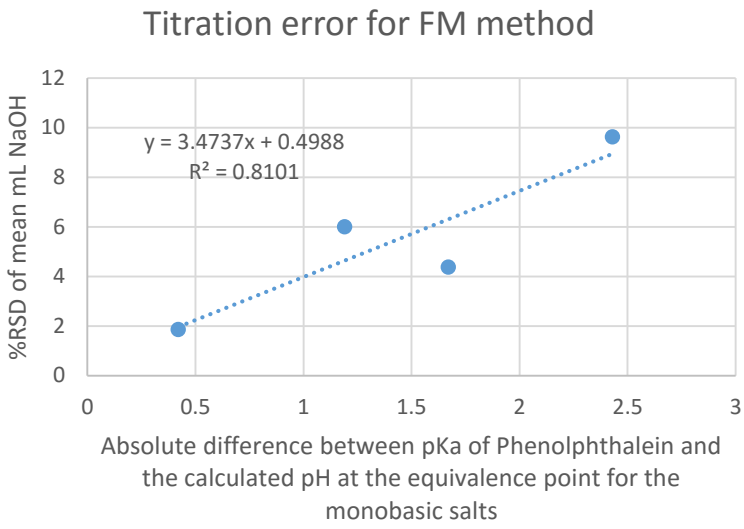
Table 5 shows the pH at the equivalence point for all the acid salts used in the study using the pk_{a2} values from the third column of Table 4 for the respective salt.

Table 5: root cause analysis of error in method FM

salt of weak acid	pK_{a2} ±%RSD using IM method	Calculated pH at the equivalence point using equation 6	Absolute difference between Pk_a of Phenolphthalein(2) and calculated pH at equivalence point	%RSD of mean (mL NaOH) from Table 2
KH_2PO_4	6.863 ± 0.97%	9.28	0.42	1.85
$KHSO_4$	2.850 ± 0.70%	7.27	2.43	9.62
$KHC_8H_4O_4$	5.32 ± 1.46%	8.51	1.19	5.99
$KHC_4H_4O_6$	4.373 ± 0.27%	8.03	1.67	4.37

As can be seen from Table 5, the stronger the acid, the lesser the pK_{a2} and the less basic (closer to pH 7.0) the calculated pH at the equivalence point. Since, phenolphthalein has a pK_a of 9.3, 1% of it exists as its colored conjugate base at a pH of 7.3 and 10% exists as its colored conjugate base at a pH of 8.3. Therefore, the greater the difference between the calculated pH at the equivalence point and the pK_a of the indicator, the greater variability in determining the volume of NaOH for a colorless-to-pink change would be expected. This correlation is shown in Figure 1 and explains the variability in the NaOH volume when using the FM method. Although the experiments were performed by different individuals, and parts of each experiment were performed on different days, the correlation coefficient of 0.81 nevertheless, indicates that the independent and dependent variables do exhibit correlation; and that the closer the equivalence pH is to the pK_a of the indicator, the less the variation in titrant volume and the greater the precision in the determination of pK_a of the titrate.

Figure 1: Indicator pK_a as determinant of variability in titrant volumes



Based on the correlation above, more precise results would be expected for the FM method if the indicator used were to have a pK_a within ± 1.0 pH units of the calculated pH at the equivalence point of the titration.

Representative indicators are presented in Table 6 that could reduce the variability of the FM method. Future studies will be performed to evaluate this hypothesis.

Table 6: Choice of indicator to decrease variability in titrant volume using the FM method

salt of weak acid	pK_{a2} ±%RSD using IM method	Calculated pH at the equivalence point using equation 6	Recommended indicator (pK_a)
KH_2PO_4	6.863 ± 0.97%	9.28	Phenolphthalein (9.7)
$KHSO_4$	2.850 ± 0.70%	7.27	Phenol red (7.9)
$KHC_8H_4O_4$	5.32 ± 1.46%	8.51	Thymol blue (8.9)
$KHC_4H_4O_6$	4.373 ± 0.27%	8.03	Phenol red (7.9)

Conclusions

The second ionization constant, pK_{a2} of monobasic salts of polyprotic weak acids could be precisely measured by adding a stoichiometric amount of half the quantity of strong base (method IM). This method was found to yield significantly similar results for pK_{a2} values measured using the FM method, $p<0.28$ except for the pK_{a2} values for $KHC_4H_4O_6$, $p<0.03$; was considerably simpler and faster than completely neutralizing half the solution of the monobasic salt followed by addition of an equivalent volume of the non-neutralized solution of the monobasic salt (method FM). Although not statistically

significant, the %RSD for the IM method was lesser than that for the FM method for all the salts used in the study. This was because the FM method involved a considerable subjective error arising due to the variation in visual observation of the colorless-to-pink end point of the titration. This variation was partly attributable to the absolute difference between the pK_a of the indicator and the calculated pH at the equivalence point for each salt. The analysis underscores the importance of choosing an indicator whose pK_a lies in the range of the equivalence pH. The IM method eliminated the titration step entirely, and consequently, eliminated this error.

References

1. The values are at 25^{o}C obtained from the Flinn Scientific AP-Chemistry Catalog no. AP6358, publication no. 6358B, 'Determination of K_a of weak acids, Instructor's guide', 2017
2. https://pubchem.ncbi.nlm.nih.gov/compound/phenolphthalein