BROMOXYNIL AND PENTACHLOROPHENOL ACIDITY CONSTANTS IN WATER-METHANOL MEDIA

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ABSTRACT

A pH- metric determination of pK_a values of 3, 5-dibromo-4-hydroxy-benzonitrile (bromoxynil) and pentachlorophenol (PCP) was carried out in water-methanol media with subsequent extrapolation to pure aqueous solutions. pK_a values in water at 25°C were found to be 3.83 ± 0.05 for bromoxynil, and 4.50 ± 0.03 for pentachlorophenol.

Key words: Bromoxynil, Pentachlorophenol, Acidity constants.

INTRODUCTION

Bromoxynil (3, 5-dibromo-4-hydroxy-benzonitrile) is a halogenated aromatic herbicide widely used for post-emergent control of annual broadleaf weeds. Pentachlorophenol (PCP) is used as a pre-harvest defoliant, and a general pre-emergence herbicide. Both are weak organic acids, and the degree of dissociation of weakly acidic organic herbicides determines not only their entry into plants, both via leaf surfaces and roots but also their adsorption, mobility and deactivation in soil and surface water[1]. However, pK_a values reported for bromoxynil and PCP in different literature sources differ drastically. The pK_a values of bromoxynil were given as 3.86[2,3], 4.06[4], 4.1[5], 4.20[1] and even 4.5[6]. Inconsistencies in the reported pK_a values of PCP are even larger, including values of 4.71[1], 4.74[7], 4.8[8], 4.8-5.0[9], 4.75[10] and 5.9[11]. Such inconsistency can be attributed to a possible very low concentration of these pesticides in water. The solubility of bromoxynil is 130 mg/L (only 4.5 x 10^{-4} M)[12]. The solubility of PCP is even smaller. It was reported to lie between 8 mg/L (3 x 10^{-5} M) and 80 mg/L (3 x 10^{-4} M)[12,13]. Accurate measurements at such low concentrations have proved to be difficult. To avoid such difficulties, in this study, We used a water-methanol mixture as the solvent, drastically increasing solubility, with

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subsequent extrapolation of the results to pure water solutions. To determine the acidity constant, We used titration with NaOH and the Henderson-Hasselbalch equation -

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

...(1)

This equation relates pKa and pH values, such that when the acid is 50% dissociated, that is, at half equivalence point, [A⁻] = [HA] and

$$pH = pK_a$$

...(2)

This method does not require knowledge of the exact concentration of acid and base, since only the equivalence point is necessary to calculate pK$_a$. Once the equivalence point is determined, pH at half equivalence is equal to the pK$_a$ as can be seen from eq. (2). Use of other techniques like conductimetry and spectrophotometry requires the preparation of solutions with very accurate concentrations. Even a very small error in concentration can give a large error in acidity constant determination.

EXPERIMENTAL

Orion 920A+ Thermo Electron Corporation advanced ISE/pH/Mv/ ORP (pH meter) and Orion 8102BNJWP Ross Ultra Combination pH Thermo Electron Corporation (glass electrode) were used for all the pH measurements.

All chemicals used were of analytical grade (>99%), except 3, 5-dibromo-4-hydroxybenzonitrile (bromoxynil) and pentachlorophenol (both 98%, Aldrich). All solutions were prepared with bi-distilled water. Stock solutions of bromoxynil (3.63×10^{-2} M), and PCP (3.00×10^{-3} M) in methanol were kept in the dark, and aliquots of these solutions were used to prepare working solutions - 3.63×10^{-3} M in 50% to 25% vol. of methanol for bromoxynil, and 9.30×10^{-4} M in 55% to 35% vol. of methanol for PCP. Concentration of NaOH in 50% to 25% vol. of methanol (55% to 35% for PCP experiments) was approximately the same as the concentration of the acids, so 25 – 27 mL of base was necessary to reach end point for 25.0 mL of acid solution. At the beginning of the titration, the base was added in 3 mL aliquots. Once 21 mL of base had been added, 1 mL aliquots of acid were used. All solvents used were kept in a water bath at 25^0C, and after each addition of base to acid, the temperature equilibrium was established before pH measurements were made. Each experiment was done in duplicate.

RESULTS AND DISCUSSION

A typical titration curve is given in Fig. 1. Exact determination of the equivalence point from the data in Fig. 1 is difficult. However, the first derivative of the curve given in Fig. 1, namely $\Delta pH/\Delta V$ versus $V_{average}$ makes it possible to find the end point with high accuracy (Fig. 2).
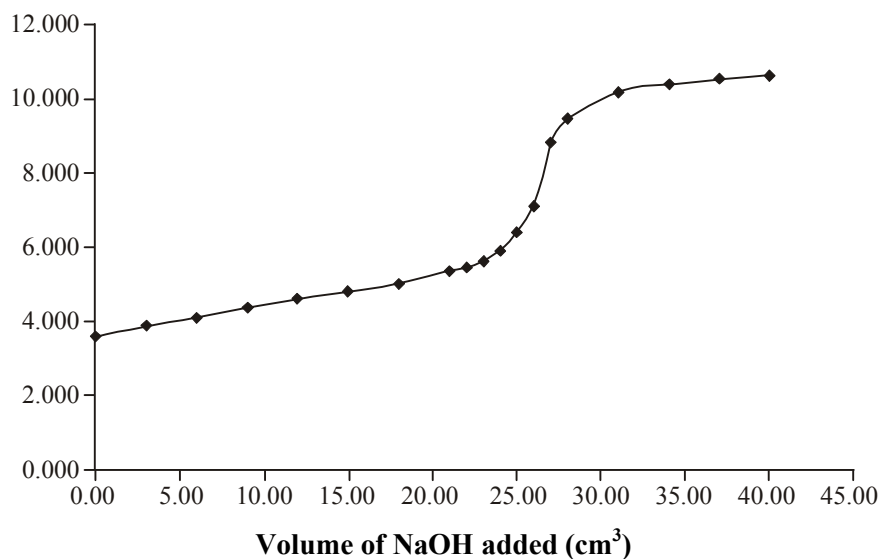
Volume of NaOH added (cm³)
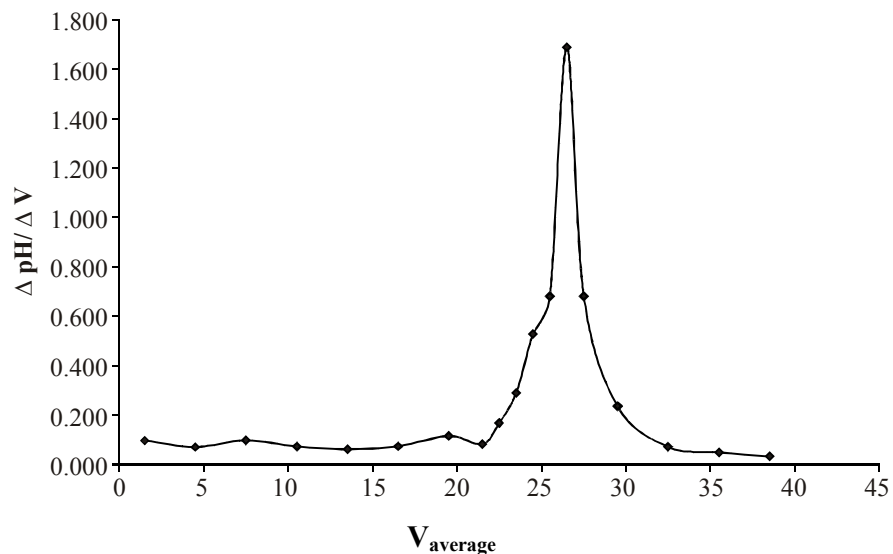
Fig. 1: Titration of bromoxynil in 45% MeOH

Fig. 2: First derivative of the curve presented in Fig. 1 (45% MeOH)

In this particular example, the end point lies at 26.6 mL of NaOH solution added and thus, the half equivalence point is 13.3 mL. Substitution of this value into the equation on the graph, in Fig. 3 allows calculation of the pH measured at the half equivalence point. As can be seen from eq. (1) and eq. (2), the pH at half equivalence point corresponds to the pK_a of bromoxynil in 45% MeOH solution at 25^0C. The calculation is shown below:

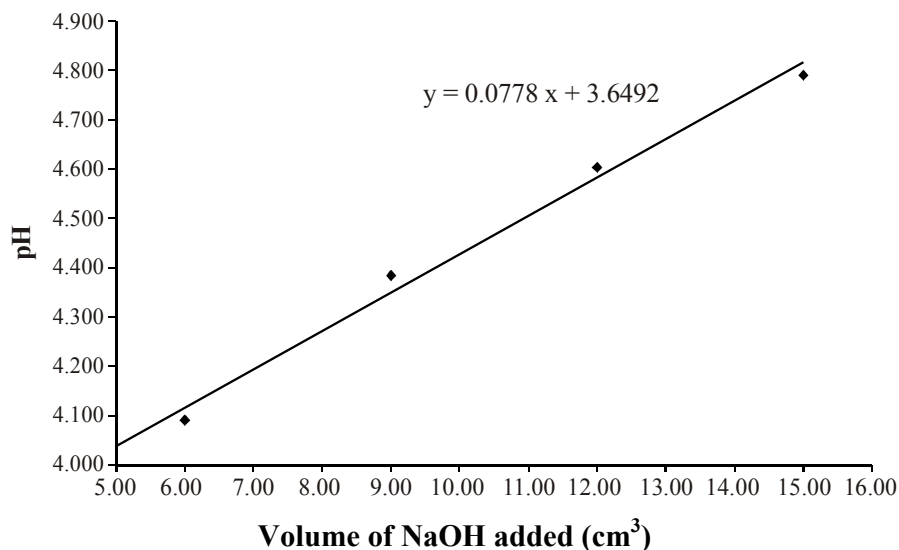$$pK_a = 0.0778 \times 13.3 + 3.6492 = 4.68$$

$$y = 0.0778 x + 3.6492$$

Fig. 3: Titration of bromoxynil in 45% MeOH . Data selected near half equivalence point

The values of bromoxynil pK_a and K_a, calculated in a similar way at different MeOH concentrations are given in Table 1. The smallest possible concentration of MeOH was 25% vol. At concentrations of MeOH smaller than 25% vol., the solubility of bromoxynil decreases drastically and use of the Henderson-Hasselbalch equation is not possible. The pK_a value of bromoxynil in pure water was obtained through extrapolation (Fig. 4, Table 2). This value is 3.83 ± 0.05 at 25^0C, which is in very good agreement with a value of 3.86 reported previously[2,3].

Acidity constants of PCP obtained in a similar manner are given in Table 3. For PCP, the smallest possible concentration of MeOH was found to be 35% vol. Extrapolation of data given in Table 3 to pure water (Fig. 5, Table 4) gives the pK_a of PCP in water at 25^0C as 4.50 ± 0.03, which is significantly smaller than any value reported previously[1,7-11]. The value closest to our result is pK_a of 4.71 determined in spectrophotometrically by Cessna and Grover[1].
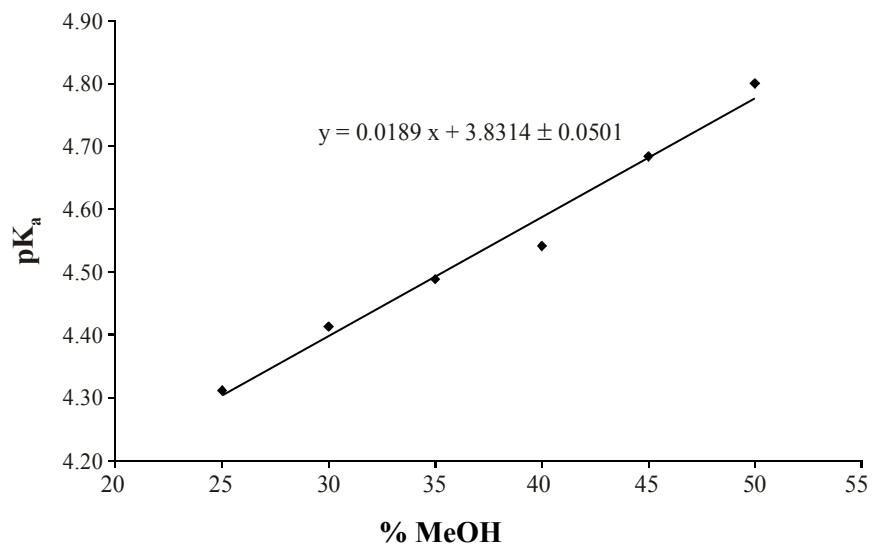
Fig. 4: pK$_a$ values of bromoxynil vs MeOH concentration (%)
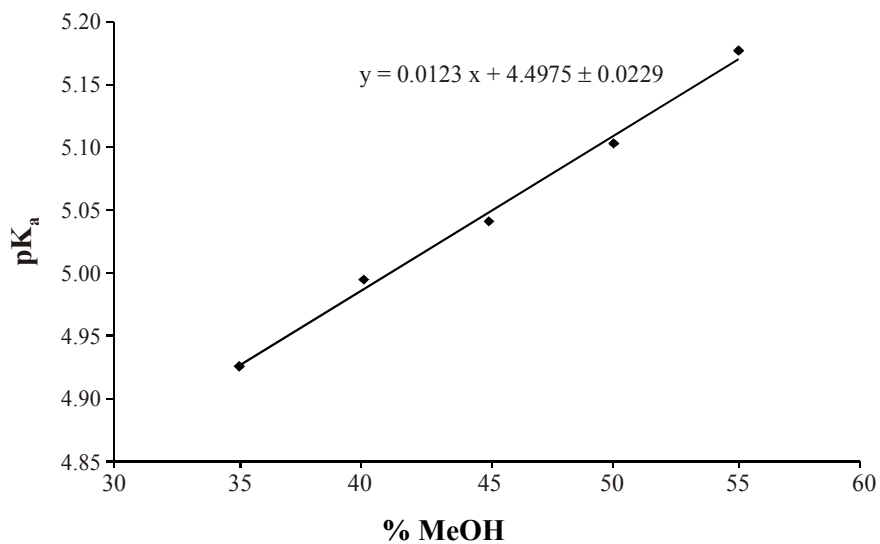

Fig. 5: pK$_a$ values of PCP vs MeOH concentration (%)

Table 1: K$_a$ and pK$_a$ values of bromoxynil in water-methanol media

% MeOH	Half V$_{average}$ of NaOH (cm^3)	pH = pK$_a$	K$_a$
50	12.8	4.80	1.58 x 10^{-5}

% MeOH	Half $V_{average}$ of NaOH (cm^3)	pH = pK$_a$	K$_a$
45	13.3	4.68	2.09 x 10^{-5}
40	13.3	4.54	2.88 x 10^{-5}
35	13.8	4.49	3.24 x 10^{-5}
30	13.8	4.41	3.89 x 10^{-5}
25	13.8	4.31	4.90 x 10^{-5}

Table 2: Results of regression analysis (Based on Fig. 4).

Regression statistics	
Multiple R	0.991
R Square	0.981
Adjusted R square	0.977
Standard error	0.0272
Observations	6

ANOVA

	Df	SS	MS	F	Significance F
Regression	1	0.156	0.156	210.770	0.000131
Residual	4	0.00296	0.000741		
Total	5	0.159			

	Coefficients	Standard error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	3.831	0.0501	76.541	0.000000175	3.692	3.970
X Variable 1	0.0189	0.00130	14.518	0.000131	0.0153	0.0225

Table 3: K_a and pK_a values of pentachlorophenol in water-methanol media

% MeOH	Half $V_{average}$ of NaOH (cm^3)	pH = pK_a	K_a
55	12.3	5.18	6.62×10^{-6}
50	12.3	5.10	7.85×10^{-6}
45	12.3	5.04	9.06×10^{-6}
40	12.3	5.00	1.01×10^{-5}
35	12.3	4.93	1.18×10^{-5}

Table 4: Results of regression analysis (Based on Fig. 5).

Regression statistics	
Multiple R	0.997
R Square	0.995
Adjusted R square	0.993
Standard error	0.00795
Observations	5

ANOVA

	df	SS	MS	F	Significance F
Regression	1	0.0377	0.0377	596.524	0.000150
Residual	3	0.000189	0.0000631		
Total	4	0.0379			

	Coefficients	Standard error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	4.498	0.0229	196.464	2.908E-07	4.425	4.570
X Variable 1	0.0123	0.000503	24.424	0.000150	0.0107	0.0139

REFERENCES

1.   A. J. Cessna and R. Grover, J. Agric. Food Chem., **26(1)**, 289 (1978).

2.   C. Tomlin (Ed.), The Pesticide Manual, 10th Ed., Surrey (1994).

3.   Handling Chemicals Ltd., Bromoxynil. http://www.hdcchem.com/Bromoxynil.html

4.   C. R. Worthing and R. J. Hance (Eds.), The Pesticides Manual. A World Compendium. 9th Ed., The British Crop. Protection Council, Famham, Surrey (1991).

5.   R. J. Flanagan and M. Ruprah, Clin. Chem., **35(7)**, 1342 (1989).

6.   G. Preuss, N. Zullej-Zeibert, B. Grass, F. Heimlich, J. Nolte and Vom Wasser, **84**, 89 (1995).

7.   US EPA. Technical Fact sheet on: Pentachlorophenol. www.**epa**.gov/ OGWDW/ pdfs / **factsheets**/ soc/ tech/ pentachl.pdf

8.   K. Kaiser and I. Valdmanis, Can. J. Chem., **60**, 2104 (1982).

9.   http://wvlc.uwaterloo.ca./biology447/Assignments/Assignment1Submissions/On-Campus/pcp/Pentachlorophenol.html

10. B. I. Esher and R. P. Schwarzenbach, Environ. Sci. Technol., **30**, 260 (1996).

11.   B. Fabre, J. Auele, M. Mazet and P. Lafrance, Rev. Sci. Eau., **3(3)**, 277 (1990).

12.   H. Kidd and D. R. James (Eds.), The Agrochemical Handbook, Third Edition, Royal Soc. Chem. and Information Services, Cambridge, UK (1991).

13. R. A. Petrie, P. R. Grossl and R. C. Sims, Environ. Sci. Technol., **36**, 3744 (2002).