6a. Blank on Extraction in Absence of Sodium Cinnamate.—Same as 2, but different standard alkali and 0.1684 g. of cinnamic acid used. Found: 34.92 cc. of 0.03250 *M* sodium propylate.

6b. Blank on Extraction in Presence of Sodium Cinnamate.—Same as 6a, except 1.000 g. of sodium cinnamate added. Found: 34.26 cc.

7. Sodium Acetate in Presence of Sodium Cinnamate.—Same as 5, except 1.000 g. of sodium cinnamate added. Found: 34.14 cc. Calculated from 6b: 34.26.

8. Blank on Extraction in Presence of Sodium Cinnamate.—Same as 6b, except 0.03008 *M* sodium propylate and 0.1559 g. of cinnamic acid used. Found: 33.80 cc.

9. 0.03122 *M* *p*-Hydroxybenzoic Acid in Presence of Sodium Cinnamate.—Same as 3, except 1.000 g. of sodium cinnamate added. Found: 35.57 cc. Calculated from 8: 33.80 cc.

10. 0.01561 *M* *p*-Hydroxybenzoic Acid in Presence of Sodium Cinnamate.—Same as 4, except 1.000 g. of sodium cinnamate added. Found: 10.05 cc. Calculated: 8.87 cc. % deviation = 100 × (10.05 − 8.87)/(33.80 − 8.87) = 5.0%.

We wish to express our thanks to Professor J. J. Beaver for permission to use the conductivity apparatus and to Mr. S. Liotta for performing the conductivity titrations.

Summary

1. A general theory for the quantitative determination of an acid (or base) by extraction with buffers has been developed.

2. The method has been applied to the determination of *p*-hydroxybenzoic acid in dilute solution, an acid which is not amenable to direct titration using phenolphthalein as indicator.

3. The limits of the method have been calculated theoretically for mixtures of various acids and determined experimentally for *p*-hydroxybenzoic acid in the presence of acetic acid.

4. The titration of cinnamic acid in chloroform solution with sodium propylate has yielded highly reproducible and sharp end-points in dilute solution (approximately 0.03 *M* alkali *vs.* 0.005 *M* acid) with phenolphthalein indicator.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Acidimetric Titration of *p*-Hydroxybenzoic Acid Alone and in the Presence of Acetic Acid

BY I. M. KOLTHOFF

p-Hydroxybenzoic acid is a dibasic acid, the first ionization constant[1] at 19° being equal to 3.3×10^{-5} and the second to 4.8×10^{-10}.[1] The ratio of the two constants is about 100,000 and therefore it may be expected[2] that *p*-hydroxybenzoic acid can be determined as a monobasic acid if the titration is carried out until the proper titration exponent is reached. The *p*H at the first equivalence point can be calculated[2] from the first and second ionization constants and is equal to log $\sqrt{K_1K_2}$ or $\frac{1}{2}(pK_1 + pK_2) = 6.90$. The above ionization constants refer to infinitely dilute solutions in which the activities of the various ions and undissociated acid are equal to 1. For the present purpose it is preferable to calculate the titration exponent from the concentration constants. The latter again were calculated from the colorimetrically determined *p*H during the neutralization of 0.035 molar aqueous solution of *p*-hydroxybenzoic acid and were found to be equal to $K_1 = 4.5 \times 10^{-5}$ and $K_2 = 5.6 \times 10^{-10}$, corresponding to a *p*H at the first equivalence point of $\frac{1}{2}(4.35 + 9.25) = 6.8$. The titration of *p*-hydroxybenzoic acid as a monobasic acid should give good results with brom thymol blue or phenol red as indicators, with the use of a buffer with a *p*H of 6.8 containing the same amount of indicator and having the same volume as the solution to be titrated at the end-point, as a comparison solution. Experimentally this was shown to be the case. About 0.3 g. of pure *p*-hydroxybenzoic acid was dissolved in about 50 ml. of warm water; the solution was cooled to room temperature and titrated with

(1) R. Kuhn and A. Wassermann, *Helv. Chim. Acta*, **11**, 1 (1928).

(2) See I. M. Kolthoff, "Volumetric Analysis, I," translated by N. H. Furman, John Wiley and Sons, Inc., New York, 1931, p. 57.

TABLE I

TITRATION OF *p*-HYDROXYBENZOIC ACID TO *p*H = 6.8

p-Hydroxybenzoic acid taken, g.	Water, ml.	0.1 *N* sodium hydroxide used, ml.	*p*-Hydroxybenzoic acid found, g.	Deviation, %
0.3004	50	21.86	0.3016	+0.4
.2996	70	21.79	.3006	+ .3
.3001	70	21.81	.3009	+ .3
.3013	50	21.89	.3020	+ .2
.3014	50	21.91	.3023	+ .3
			Average deviation	+0.3

0.1 N carbonate-free sodium hydroxide using brom thymol blue as indicator. This indicator gives a slightly sharper end-point than phenol red.

With the use of a solution for comparison the end-point can be detected with a reproducibility of 0.2%. This could be expected from the change in pH near the first equivalent point. Colorimetrically the following values of the pH were found in the neighborhood of the first equivalence point: 2% before 6.25, 1% before 6.50, 1% after 7.10, 2% after 7.35.

If the solution of p-hydroxybenzoic acid contains another weak acid, the titration exponent is shifted to higher values, the exact change depending upon the ratio of the concentration of the two acids and upon the ionization constant of the second acid added. La Mer and Greenspan[3] were confronted with the problem of titrating p-hydroxybenzoic acid solutions containing at most an equivalent amount of acetic acid. The ionization constant of the latter is only slightly smaller than the first ionization constant of p-hydroxybenzoic acid. Therefore in a mixture of equivalent amounts of p-hydroxybenzoic acid and acetic acid the titration exponent approximately will be equal to[4] $\frac{1}{2}(pK_1 + pK_2) + \frac{1}{2}\log 2 = 6.95$, at which point the amount of sodium hydroxide added is equivalent to the sum of acetic and p-hydroxybenzoic acid (the latter as a monobasic acid).

Experimentally it was shown that the above conclusions were correct. To a 0.03 N solution of the monosodium salt of p-hydroxybenzoic acid an equivalent amount of sodium acetate was added. The pH of this mixture was determined colorimetrically and found to be equal to 6.95, whereas the solution of the monosodium salt alone had a pH of 6.8. The experiments were repeated and the pH measured with the quinhydrone electrode at 25°. The values found were 6.90 and 7.03, respectively. The difference between the colorimetric and potentiometric results is to be attributed mainly to the salt error of the indicator. Titrations were made with mixtures of equivalent amounts of p-hydroxybenzoic acid and acetic acid with brom thymol blue as indicator using a buffer solution with a pH of 6.95 for comparison. The color change of the indicator was as good and the results as accurate as found in the titration of the p-hydroxybenzoic acid alone.

From the above it is evident that phenolphthalein is not suitable for the titration of p-hydroxybenzoic acid as a monobasic acid. If the first pink is visible at a pH of about 8.2 the titration error would be about 10%, and the color change would be extremely vague. The experimental figures of La Mer and Greenspan[3] show this to be true. Osol and Kilpatrick[5] dissolve the acid in 5 ml. of acid free alcohol, dilute with 25 ml. of water, add 0.5 ml. of 10% phenolphthalein solution and titrate in an atmosphere of nitrogen until a faint pink is visible in broad daylight. There is no reason, however, to work in nitrogen, the same results being obtained if titrated in the ordinary way. The addition of alcohol results in a decrease of all ionization constants including that of the indicator by about the same relative amount; alcohol therefore has no advantage. By using the large amount of indicator that Osol and Kilpatrick recommended the first change to a faint pink should occur at a pH of 7.7 to 7.8. But even then the end-point is passed, the error amounting to about 2 to 3%. Experiments made under conditions as recommended by Osol and Kilpatrick showed this to be true. By comparing with a blank and titrating to the first visible tinge of pink in broad daylight, 2 to 3% too much base was used, the end-point being extremely vague.

Thanks are due to J. J. Lingane for his assistance in the performance of various experiments.

Summary

1. p-Hydroxybenzoic acid can be determined as a monobasic acid if standard sodium hydroxide is added until a titration exponent of 6.8 is reached. Brom thymol blue is a good indicator for the detection of the end-point. The results found were 0.3% high.

2. In the presence of an equivalent amount of acetic acid the titration exponent is equal to 6.95. The sum of acetic and p-hydroxybenzoic acid (monobasic) can be determined by titration to this pH.

3. Phenolphthalein is not suitable as an indicator for the titration of p-hydroxybenzoic acid.

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(3) J. Greenspan, Thesis, Columbia University, 1933; see also V. K. La Mer and J. Greenspan, THIS JOURNAL, **56**, 1492 (1934).

(4) Ref. 2, p. 36.

(5) A. Osol and M. Kilpatrick, private communication.