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Indicator Transition Ranges in Tertiary Butyl Alcohol*

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ABSTRACT

The approximate transition ranges of a number of common indicators in tertiary butyl alcohol are given in terms of potentials measured with a glass-two phase salt bridge-SCE electrode system. Potential control was obtained by the addition of a sulfuric acid-malonic acid mixture and titration with tetrabutylammonium hydroxide. In general, the sulfonphthaleins are recommended for the titration of strong to medium strength acids, and Azo Violet, o-nitroaniline, and p-nitro-p-aminoazobenzene for very weak acids.

The use of tertiary butyl alcohol as a solvent for the potentiometric titration of acids of various functional types has been illustrated by Fritz and Marple (1). For routine analyses, however, an indicator end point is preferred to a potentiometric titration. Previously the inability to reproduce potentials when titrating acids with quaternary ammonium hydroxide titrants in organic solvents has hindered the determination of indicator transition ranges. However, an electrode system recently developed (3) makes it possible to reproduce titration curves in tertiary butyl alcohol very well. It now becomes feasible to titrate an acid (or

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acid mixture) potentiometrically and to choose a suitable indicator for the routine titration of that acid (or mixture). We have determined the visual transition ranges of a number of indicators in tertiary butyl alcohol under conditions approximating an actual titration.

A mixture of sulfuric and malonic acids, when titrated with tetrabutylammonium hydroxide, serves as a suitable buffer over almost all of the potential range available in tertiary butyl alcohol. While it is recognized that the use of two basically different types of buffer systems (neutral and anionic) will lead to some differences in transition ranges of indicators in the weakly acidic range relative to those in the strongly acidic range (2), these differences are minor compared to the effects of other factors such as ionic strength. Moreover, the dissociation of tetrabutylammonium bisulfate, for instance, is so low (at 10^{-2} M concentration) that it is really like a neutral buffer instead of an anionic buffer.

EXPERIMENTAL

The indicators used are all commercially available materials from Eastman Organic Chemicals or Hartman-Leddon Co. Approximately 1 mg of indicator was added to 40 ml. of tertiary butyl alcohol in a titration cell of the type described previously (3). To this, 2 mmoles of a 1:1 sulfuric acid-malonic acid mixture was added, and the solution was titrated with 0.1M tetrabutylammonium hydroxide. The potential was followed with a glass electrode that was used in previous work on the titration of acids (1), so the potentials reported for the transition ranges can be correlated with previously published data. The limits for an indicator transition were

set by the first observable color change, and by the point of no further change. Since the absorption of the basic form of the indicator was generally greater than the acidic form, titration of the basic form of the indicator with acid to establish the basic end of the transition range with greater accuracy was not attempted.

DISCUSSION

The titration curve for the sulfuric acid-malonic acid mixture is shown in Figure 1. Except in the -100 to -200 mv. region, the potential could be changed by as little as 5 mv. by the addition of an increment of base.

Figure 2 shows the transition ranges of the indicators and the colors at each end of the range. In the case of the sulfonphthaleins, a definite green color formed at an intermediate point in the conversion from the yellow acid form to the blue base form. In the case of bromphenol blue, the formation of the green color was sharp enough to use as an endpoint. The change of methyl red from violet to orange takes place in solutions more acidic than sulfuric acid and was determined by perchloric acid titration. The basic edge of the transition range of o-nitroaniline could not be located with certainty since the EMF changes only slightly with an increase in the amount of excess base.

Both o-nitroaniline and p-nitro-p-aminoazobenzene function well as an indicator for very weak acids. The color change of p-nitro-p-aminoazobenzene from orange to green is sharp, although the indicator blank is relatively large. In Table I are shown data for the titration

Figure 1. Titration of sulfuric acid-maleonic acid buffer. First and third potential breaks correspond to the titration of sulfuric acid and tetrabutylammonium bisulfate.

Figure 2. Indicator transition ranges of some common indicators in tertiary butyl alcohol solvent.

of o-phenylphenol with 0.02M tetrabutylammonium hydroxide using p-nitro-p-aminoazobenzene indicator. Correction for the indicator blank gives excellent agreement with the results of a potentiometric titration. The titration of malonic acid using o-nitroaniline was also studied. Here also, the results agreed well with the potentiometric values.

Use of indicators that contain sodium or potassium salts, or indicators that are in the form of a sodium or potassium salt should be avoided unless the transition range is more positive than -0.3 v. At potentials more negative than this, the transference of the alkali ion is so large that the color change interval cannot be established with any certainty. This does not preclude the use of an indicator that contains sodium or potassium, since a trial and error method may still be used to establish its usefulness.

Table I. Titration of o-Phenylphenol using p-Nitro-p-aminoazobenzene Indicator. An Indicator Blank Correction of 0.09 ml. was Applied. The Potentiometric Titration End Point was 13.98 ml.

<u>Trial No.</u>	<u>Ml. Base Req'd.</u>
1	13.98
2	14.03
3	13.99
4	14.01
5	13.99
6	14.00
Ave.	14.00

Titration of Malonic Acid using o-Nitroaniline Indicator. Blank Correction was 0.05 ml.; Potentiometric Titration End Point was 8.41 ml.

<u>Trial No.</u>	<u>Ml. Base Req'd.</u>
1	8.37
2	8.45
3	8.35
4	8.35
Ave.	8.38

LITERATURE CITED

- (1) Fritz, S., Marple, W., Anal. Chem. 34, 921 (1962).
- (2) Kolthoff, I. M., Guss, L. S., J. Am. Chem. Soc. 60, 2518 (1938).
- (3) Marple, L. W., Fritz, J. S., Anal. Chem. 34, 796 (1962).

FIGURE CAPTIONS

Figure 1. Titration of sulfuric acid-malonic acid buffer. First and third potential breaks correspond to the titration of sulfuric acid and tetrabutylammonium bisulfate.

Figure 2. Indicator transition ranges of some common indicators in tertiary butyl alcohol solvent.

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