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A Plot of the pH *vs.* the Logarithm of the Titrant Volume in Potentiometric Titration. The Determination of Phenol in Water

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(Received April 23, 1979)

The determination of phenol in water was successfully carried out by means of a new plot of the potentiometric titration data. The plot of the pH *vs.* the logarithm of the titrant volume gave a titration curve with an inflection between two linear portions, and the center of the inflection obtained by a graphical method was found to correspond to the equivalence point. In the titration of phenol, the data fitted well to the theoretical curve by taking into account the hydrolysis of the phenol ion. The mean of the results obtained from the apparent equivalence point in the concentration range of $1.0—7.7\times10^{-3}$ mol dm^{-3} was 101.2% of the results obtained iodometrically after the bromination of phenol, and the precision of the results was ±2.7% (S.D.).

Nonaqueous solvents have been used for the titration of very weak acids,[1)] but they are somewhat troublesome to use. This paper will discuss the titration data of aqueous phenol. In a plot of the pH *vs.* the titrant volume for the potentiometric titration of a very weak acid in water, the inflection at the equivalence point is not sharp, or even disappears. Gran's plot is well known as a special method for the determination of the equivalence point in potentiometric titration, but it can not apply to a solution containing a weak acid or a weak base. It was found that the plot of the pH *vs.* the logarithm of the titrant volume has an inflection between two linear portions, and that the center of the inflection obtained from a graphical method corresponds to the equivalence point. Measurements were made on the titrating solutions in the range from 1.0×10^{-3} to 7.7×10^{-3} mol dm^{-3} with the titrant of 1.1 mol dm^{-3} NaOH.

Theoretical

Titration Curve. We will first discuss the titration of aqueous phenol with aqueous sodium hydroxide, assuming that the volume change due to the addition of titrant is very small. The equilibrium for the ionization of phenol (AH) may be written as

$$\mathrm{AH} \rightleftarrows \mathrm{A^-} + \mathrm{H^+}, \tag{1}$$

$$K_\mathrm{a} = \frac{[\mathrm{A^-}][\mathrm{H^+}]}{[\mathrm{AH}]}, \tag{2}$$

where K_a is the ionization constant of phenol. The hydrolysis reaction of sodium phenoxide during the titration is expressed as

$$\mathrm{A^-} + \mathrm{H_2O} \rightleftarrows \mathrm{AH} + \mathrm{OH^-}. \tag{3}$$

The equilibrium constant, K_h, in this case is

$$K_\mathrm{h} = \frac{[\mathrm{AH}][\mathrm{OH^-}]}{[\mathrm{A^-}]}. \tag{4}$$

Equation 2 may be written in logarithmic form as

$$\log\,[\mathrm{H^+}] = \log\frac{[\mathrm{AH}]}{[\mathrm{A^-}]} + \log K_\mathrm{a}. \tag{5}$$

The material balance for the dissociation of phenol is

$$[\mathrm{AH}]_0 = [\mathrm{A^-}] + [\mathrm{AH}], \tag{6}$$

where $[\mathrm{AH}]_0$ is the concentration of phenol in the solution before titration. Before the equivalence point, the material balance for hydrolysis is

$$[\mathrm{A^-}] = [\mathrm{NaOH}](1-h), \tag{7}$$

where [NaOH] is the concentration of titrant in the solution titrated and where h is the degree of hydrolysis. From Eqs. 5—7 we obtain

$$\log\,[\mathrm{H^+}] = \log\left\{\frac{[\mathrm{AH}]_0}{[\mathrm{NaOH}](1-h)} - 1\right\} + \log K_\mathrm{a}. \tag{8}$$

On substituting the numerical value,[2)] $\mathrm{p}K_\mathrm{a}=9.998\approx10$, into Eq. 8, pH is expressed as

$$\mathrm{pH} = -\log\left\{\frac{[\mathrm{AH}]_0}{[\mathrm{NaOH}](1-h)} - 1\right\} + 10. \tag{9}$$

Beyond the equivalence point, the material balance for hydrolysis is

$$[\mathrm{A^-}] = [\mathrm{AH}]_0(1-h). \tag{10}$$

From Eqs. 5, 6, and 10, we obtain

$$\log\,[\mathrm{H^+}] = \log\frac{h}{1-h} + \log K_\mathrm{a}. \tag{11}$$

On substituting the same numerical value as Eq. 9, the pH is expressed as

$$\mathrm{pH} = -\log\frac{h}{1-h} + 10. \tag{12}$$

Next, we will deal with the relation between h and [NaOH]. The concentration, $[\mathrm{OH^-}]$, of the hydroxide ion before the equivalence point is expressed as follows:

$$[\mathrm{OH^-}] = h[\mathrm{NaOH}]. \tag{13}$$

The following equation was obtained by eliminating $[\mathrm{OH^-}]$, $[\mathrm{A^-}]$, and [AH] from Eqs. 4, 6, 7, and 13:

$$[\mathrm{NaOH}]h^2 + ([\mathrm{AH}]_0 - [\mathrm{NaOH}] + K_\mathrm{h})h - K_\mathrm{h} = 0. \tag{14}$$

Beyond the equivalence point, $[\mathrm{OH^-}]$ is expressed as follows:

$$[\mathrm{OH^-}] = h[\mathrm{AH}]_0 + [\mathrm{NaOH}] - [\mathrm{AH}]_0. \tag{15}$$

Similarly, the following equation was obtained from Eqs. 4, 6, 10, and 15:

$$[\mathrm{AH}]_0h^2 + ([\mathrm{NaOH}] - [\mathrm{AH}]_0 + K_\mathrm{h})h - K_\mathrm{h} = 0. \tag{16}$$

When the numerical values of $[\mathrm{AH}]_0$, [NaOH], and K_h $(=K_\mathrm{w}/K_\mathrm{a})$ are substituted into Eq. 14 or 16, we can estimate h. Then, the relation between pH and log [NaOH] is determined from Eq. 9 or 12. Assuming that the volume of the titrating solution is 100 cm^3 and that the volume change due to the addition of the titrant is very small, [NaOH] is expressed as follows;

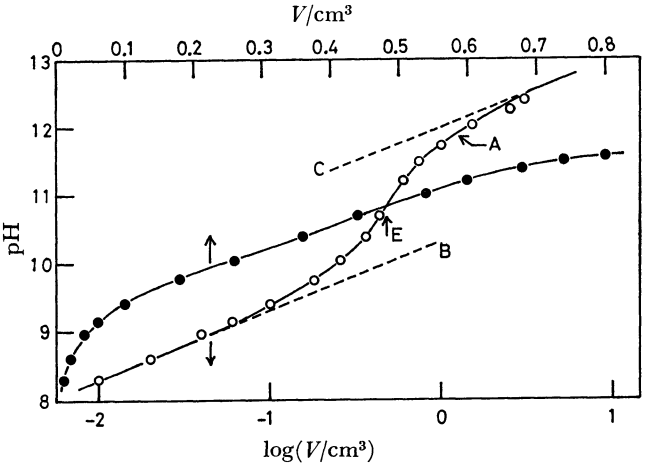

Fig. 1. Theoretical curve and experimental data.
○: Experimental data.
A: Theoretical curve, B and C: asymptotes obtained from Eqs. 18 and 21, respectively. E: Equivalence point, common to Figs. 1—5. Solution titrated: 5.2×10^{-3} mol dm^{-3} phenol, titrant: 1.1 mol dm^{-3} NaOH, temp: 25 °C.

$$[\mathrm{NaOH}] = [\mathrm{NaOH}]_t\frac{V}{100}. \tag{17}$$

Here, $[\mathrm{NaOH}]_t$ is the concentration of the titrant and V is the titrant volume. Therefore, we could obtain the relation of the pH *vs.* the logarithm of the titrant volume as is shown in Fig. 1 (A). The curve, quite consistent with the experimental data, consists of two linear portions.

The asymptotic equation for the linear portion at the beginning of titration is thus obtained for $h \to 0$ in Eq. 9:

$$\mathrm{pH} \simeq \log\,[\mathrm{NaOH}] - \log\,[\mathrm{AH}]_0 + 10. \tag{18}$$

The asymptotic equation for the linear portion far beyond the equivalence point is thus obtained for $h \to 0$ in Eq. 12:

$$\mathrm{pH} \simeq -\log h + 10. \tag{19}$$

Here, h is approximated for $[\mathrm{NaOH}] \gg [\mathrm{AH}]_0$ in Eq. 16 as follows:

$$h \approx \frac{K_h}{[\mathrm{NaOH}]}. \tag{20}$$

Consequently, the following asymptotic equation is obtained from Eqs. 19 and 20:

$$\mathrm{pH} \simeq \log\,[\mathrm{NaOH}] - \log K_h + 10. \tag{21}$$

The slopes of the two linear portions in the theoretical curve were proved identical from Eqs. 18 and 21.

Effect of pK_a *and Concentration of Acid on the Titration Curve.* The method presented above is based on the hydrolysis of the titrating agent, *i.e.*, phenol. Figures 2 and 3 show the relation between h and log V, while Figs. 4 and 5 show the relation between pH and log V. As the equivalence point corresponds to the peak in the curve of h *vs.* log V, the equivalence point is at the maximum of dpH/dlog V. When pK_a is large or the concentration of titrating agent is low, the curve of h *vs.* log V becomes unsymmetrical and the maximum of dpH/dlog V becomes obscure. If the curve of h *vs.* log V is symmetrical, the maximum of dpH/dlog V becomes much clearer and the equivalence point can be obtained by either the mathematical or the graphical method. We can designate the relation between the pK_a and the concentration of the titrating agent by drawing such curves as are shown in Figs. 2—5. Consequently, the concentration of the titrating agent must be higher than about 0.001 mol dm^{-3} for pK_a=10.

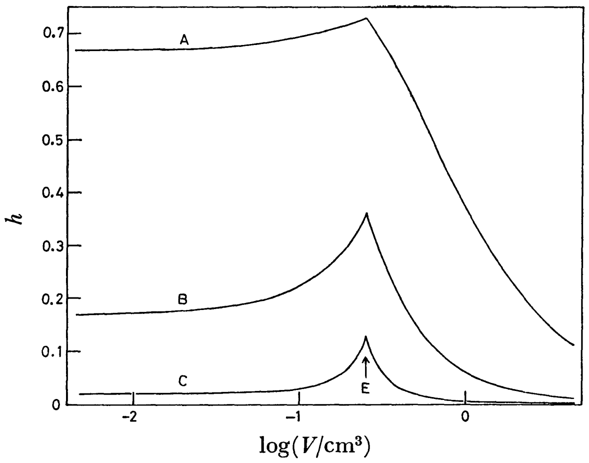

Fig. 2. Theoretical curves; the relation between h and log V.
$[\mathrm{AH}]_0$: 0.005 mol dm^{-3}, concn of titrant: 2 mol dm^{-3}. pK_a; A: 12, B: 11, C: 10.

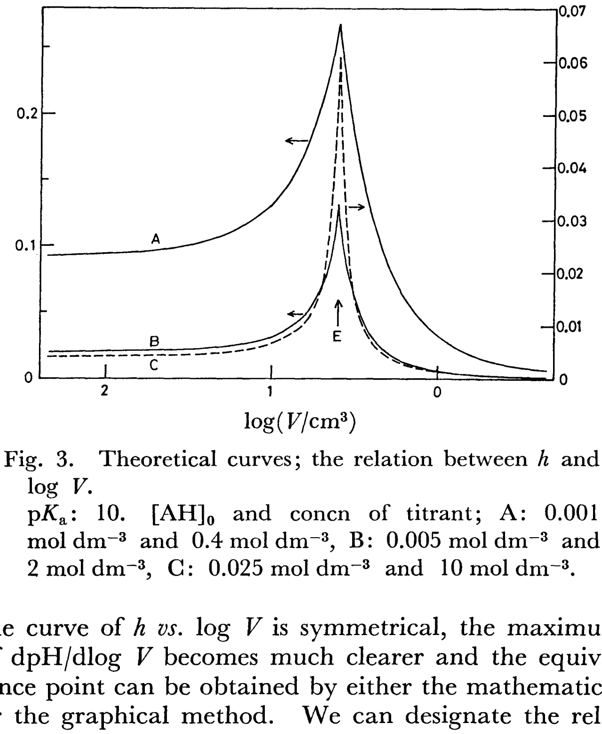

Fig. 3. Theoretical curves; the relation between h and log V.
pK_a: 10. $[\mathrm{AH}]_0$ and concn of titrant; A: 0.001 mol dm^{-3} and 0.4 mol dm^{-3}, B: 0.005 mol dm^{-3} and 2 mol dm^{-3}, C: 0.025 mol dm^{-3} and 10 mol dm^{-3}.

Experimental

Materials. All the chemicals were reagent grade and were used without further purification. The CO_2-free solution of NaOH was prepared from a saturated solution.

Titration Apparatus. A pH meter (Toa Electronics HM-5B) was used to obtain the titration curve. The buret was a pipet with a capacity of 0.2, 1, or 2 cm^3. The titration cell was a 120-cm^3 wide-mouthed bottle, in which the solution was stirred with a magnetic stirrer. All the titrations were carried out in a water bath at 25±0.1 °C. Nitrogen was passed slowly through the solution being titrated in order

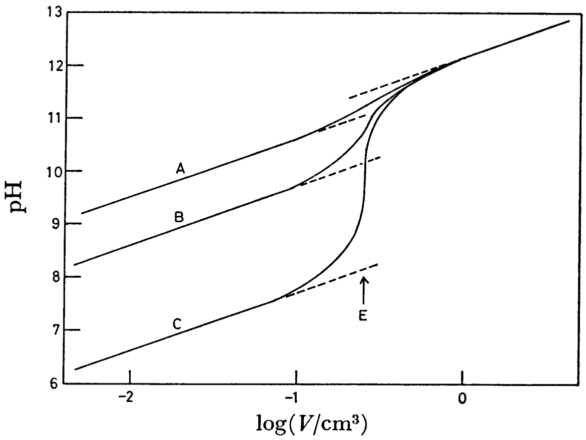

Fig. 4. Theoretical curves; the relation between pH and log V.
$[AH]_0$ and concn of titrant are the same as Fig. 2. pK_a; A: 11, B: 10, C: 8.

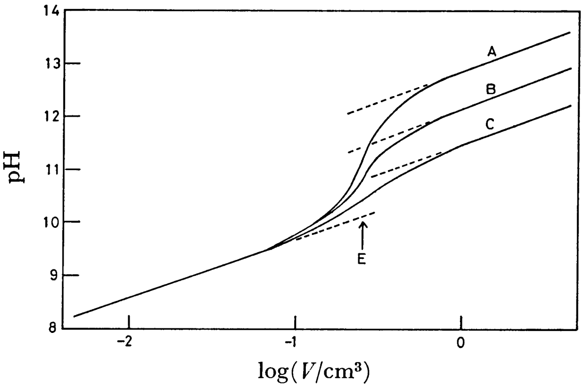

Fig. 5. Theoretical curves; the relation between pH and log V.
pK_a: 10. $[AH]_0$ and concn of titrant; A: 0.025 mol dm^{-3} and 10 mol dm^{-3}, B: 0.005 mol dm^{-3} and 2 mol dm^{-3}, C: 0.001 mol dm^{-3} and 0.4 mol dm^{-3}.

to avoid the absorption of CO_2. The electrodes, buret, and nitrogen inlet were inserted into the titration cell through a rubber stopper.

Titration Procedure. The pH meter was standarized with standard buffers of pH 4.01 and pH 6.86 at 25 °C. Distilled water (100 cm^3) and concentrated phenol (0.2—1.5 cm^3) were placed in the titration cell, and allowed to stand about ten minutes with stirring and while wet nitrogen gas was bubbled in for temperature equilibration at 25 °C. A correction for the volume change due to the addition of titrant has not been made.

Results and Discussion

Graphical Determination of the Equivalence Point. Figure 6 shows a typical potentiometric titration curve of phenol in water. The apparent equivalence point was determined graphically as follows: Line A was drawn at the initial part of the titration curve; Line B was then drawn parallel to A, tangent to the final portion of the titration curve; Line C was then drawn with a maximum slope tangent to the region of the equivalence point; Lines E and F were drawn vertically so as to pass through the intersections of Line C with A and B; Line D was drawn from the intersection of Lines A and F to the intersection of Lines B and E. The intersection of Lines C and D was then taken to be the equivalence point.

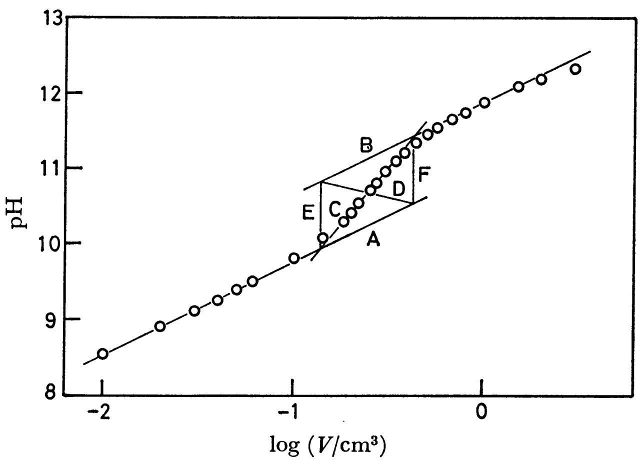

Fig. 6. Typical potentiometric titration curve of phenol in water and graphical determination of equivalence point. The solution titrated is 2.6×10^{-3} mol dm^{-3} phenol and other conditions are the same as those in Fig. 1.

TABLE 1. DETERMINATION OF PHENOL IN WATER

c_1[a] / 10^{-3} mol dm^{-3}	c_2[b] / 10^{-3} mol dm^{-3}	c_2/c_1 / %
1.04	1.08	103.8
1.04	1.10	105.8
2.60	2·68	103.1
2.60	2.62	100.8
5.17	5.12	99.0
5.17	5.00	96.7
7.72	7.76	100.5
7.72	7.69	99.6

a) c_1 is the concn of phenol obtained iodometrically after the bromination of phenol. b) c_2 is the concn determined by this method.

Accuracy of the Method. Table 1 shows the results of the titration of phenol in water. The value of c_2/c_1 is the ratio of the amount of phenol obtained from this method to that obtained iodometrically after the bromination of phenol.[3] The average value of c_2/c_1 was 101.2% in the concentration range (1.0—7.7×10^{-3} mol dm^{-3}) of phenol, and the precision was ±2.7% (standard deviation).

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