

# A Modified Potentiometric Method for the Estimation of Phenol in Aqueous Systems

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A modified potentiometric titration is proposed for the estimation of phenol in aqueous systems. The method is evolved on the basis of a critical dependence of pH on log V rather than simple V, as used in conventional potentiometric titrations. The method incorporates titrants in a concentration range several orders of magnitude greater than that of phenol in the aqueous phase. Derivative potentiometric curves so obtained provide a clear exposition of the equivalence point and the overall error is found to be between  $\pm 1.0$  and  $1.5\%$ . The range of phenol concentration investigated was from  $10^{-2}$  to  $10^{-3}$  M. and that of sodium hydroxide used as the titrant from  $10^{-1}$  to 4.0 M. The maximized titrant concentrations were found to be helpful in controlling the dilution problem during titration. The lowest detection limit achieved was 50 mg phenol/L and the method is well-suited to direct aqueous phase municipal sewage, home effluents and industrial discharges for phenol determination.

## Introduction

During recent years, humans have been plagued with serious environmental pollution problems that have increased tremendously on account of ever-increasing industrial activities. All types of environmental pollution are hazardous, however, water pollution is more dangerous since it acts as a reservoir and transmission medium of human diseases from one place to another. Water pollution by agricultural, municipal and industrial sources has thus become a major concern from the health point of view as it gives rise to various physiological disorders. Among the various water pollutants, i.e., organic, inorganic, suspended solids, sediments and radioactive materials, organic pollutants are of the worst type. These include oxygen demanding wastes, disease causing wastes, synthetic organic compounds, sewage, agricultural run off and oil spills<sup>(1)</sup>.

Phenol is the most detrimental pollutant of the environment. It enters the soil and water through different pathways like cooking, plastic manufacturing, oil purification, and timber and pharmaceutical effluents. Natural sources of phenol include the degradation of natural plant products such as carbonization of coal, carvacrol, thymol and vanilin. Biologically important compounds such as amino acids (tyrosine and estrone) also contain phenol rings<sup>(2)</sup>.

Synthetic production of phenol from coal tar involves the chlorination of benzene with subsequent hydrolysis of chlorobenzene with caustic alkali at high temperature and pressure<sup>(3)</sup>. Once in water reservoirs, phenol may undergo destruction and transformation by the impact of different physiochemical factors and

by the activities of aqueous organisms (fungi, algae, saprophytes, etc.)<sup>(4-7)</sup>.

Investigations have shown that streams contaminated by phenolic organics imparted acidity to waters in the presence of sulphates and nitrates<sup>(8-11)</sup>. The presence of phenol in water consumed by humans results in symptoms such as gastrointestinal illness, nausea, vomiting, diarrhea and abdominal pain<sup>(12,13)</sup>. Phenol, therefore, has been recognized as a contaminant in various waters-drinking, streams waste and liquid plant effluents-and its determination in such waters is thus very important with regard to its harmful effects on humans.

The potentiometric titration method for the estimation of phenol in aqueous solutions is a sensitive and accurater method, if phenol concentrations are high, of the order of few g/L. However, in cases where the phenol is present at milligram levels, the method fails miserably, since both identification of equivalence point of the titration and the subsequent quantification, is adversely affected by the dilution effect. In addition,  $K_a$  for phenol is of the order of  $10^{(10)}$ , which does not warrant sharp inflexional points on the titration curve. An attempt was made during the present study to evolve a modified potentiometric titration process which involves the titration of phenol in aqueous solutions using alkali solutions of very high concentration to overcome the effects arising from dilution and hydrolysis of the reaction product. The investigation revealed that pH critically depends on log V and not simply V, the volume of the added titrant under the analytical conditions outlined above.

## Theoretical Background

The system under investigation comprises of a weak acid (phenol) which obeys the typical dissociation equilibrium:



for which the dissociation constant  $K_a$  is given as:

$$K_a = \frac{[A^-][H^+]}{[AH]} \quad (2)$$

where the equilibrium concentrations pertain to phenoxide anion, hydrogen ion and phenol respectively.

The material balance involved in the above system demands:

$$[AH] + [AH]_0 - [A^-]$$

so that concentration of phenol at equilibrium,  $[AH]$  is lower than its initial concentration,  $[AH]_0$ , by an amount equal to the equilibrium concentration of the phenoxide anion. Transforming equations (2) into a logarithmic format, and incorporating the requirement of material balance we get:

$$\begin{aligned} \text{Log}[H^+] &= \text{log}K_a + \text{log}\left[\frac{[AH]_0 - [A^-]}{[A^-]}\right] \\ \text{or } pH &= pK_a - \text{log}\left[\frac{[AH]_0 - [A^-]}{[A^-]}\right] \end{aligned} \quad (3)$$

For phenol,  $pK_a = 9.989$  at  $20^\circ\text{C}$ .

In the titration medium of the present system, the concentration of the anion depends upon the concentration of sodium hydroxide stemming from two sources, one from the known concentration added

during titration and the other from the fractional contribution of sodium hydroxide (measured as a function of degree of hydrolysis,  $h$ , which is measured as:  $h=K_h/[NaOH]$ ) generated when the anion is backhydrolyzed.

Hence,

$$[A^-] = [N.OH](1 - h) \quad (4)$$

Substituting this in equation (3) we get:

$$pH = pK_a - \log\left[\frac{[AH]_0 - 1}{[NaOH](1 - h)}\right] \quad (5)$$

where the quantitative significance of  $[NaOH]$  at equilibrium is represented by:

$$[NaOH] = [NaOH]_t \frac{V}{100} \quad (6)$$

Here  $[NaOH]_t$  stands for the molar titer concentration of sodium hydroxide and  $V$  is the volume of the titrant system, 100 mL in the present case.

Equation 5) explains the entire sequence of titration events up to equivalence point. Similar deductions, however, may be obtained for all stages beyond the equivalence point, based on a new set of mass balance conditions. For the present case, as  $[NaOH]$  is proportional to the volume of sodium hydroxide added at a given moment, it may be concluded that for such an analytical system where in hydrolysis and neutralization mutually accompany each other, a sigmoid potentiometric titration curve may be obtained from a simple plot of pH vs.  $\log V$ , as evidenced by the incorporation of equation (6) in equation (5).

## Experimental

A digital pH meter, AMA digit (Model AD140) operatable at 3.0 VDC, with an overall precision of  $\pm 0.01$  pH units, was used throughout this study for the precise determination of pH of various aqueous phenol solutions. The working temperature of the aqueous titration systems was adjusted against an adjustable temperature gradient scale on the instrument panel. Calibration with respect to standard buffers, in the range of 4.01 to 9.00 pH, was made using the  $\Delta$ pH grading provided on the instrument.

A magnetic stirrer, Yamato Magnetic Mixer (Model MD 21) was used to achieve thorough, mixing of the interacting solutions at 750 rpm. A digital analytical balance, Sartorius ( $\pm 0.001$ g, Model H 160) was used for weighing the chemicals.

Aqueous solutions of phenol (BDH, guaranteed purit  $>99.8\%$ ) were used as such for carrying out titration against sodium hydroxide (BDH, 99% purity) aqueous solutions of desired concentrations. Double distilled water was employed for the preparation of solutions and for dilutions, as and when required.

Since the titration process required a very small volume of the titrant to be added in steps, a microburette ( $5.00 \text{ mL} \pm 0.01 \text{ mL}$ ) was used. In cases where still smaller volumes were needed, a  $100 \mu\text{L}$  syringe was used for precise control over accuracy.

## Results and Discussion

The selected molar concentrations of aqueous phenol systems were subjected to titration against sodium hydroxide solutions between 0.1 and 4.0 M. The representative potentiometric titration data are given in Table 1.

**Table 1.** Potentiometric differential titration data for 0.01M phenol vs. 0.01M sodium hydroxide

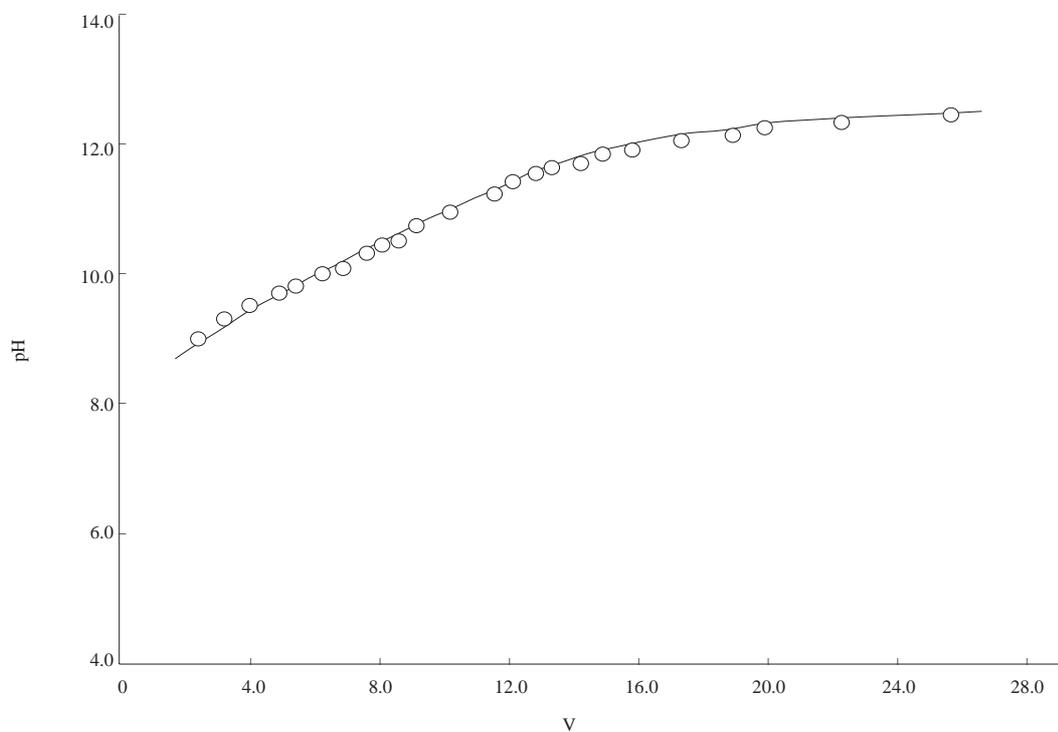
pH	$\Delta$ pH	V(mL)	log V	$\Delta$ log V	$\Delta$ pH/ $\Delta$ log V
5.05	0.00	0.00	0.00	0.00	0.00
8.89	3.84	2.10	0.32	0.32	12.00
9.00	0.11	2.42	0.38	0.06	1.83
9.07	0.07	2.62	0.42	0.04	1.75
9.15	0.08	2.84	0.45	0.03	2.67
9.28	0.13	3.24	0.51	0.06	2.17
9.39	0.11	3.64	0.56	0.05	2.20
9.50	0.11	4.06	0.61	0.05	2.20
9.58	0.08	4.42	0.64	0.03	2.67
9.72	0.14	5.05	0.70	0.06	2.33
9.81	0.09	5.49	0.74	0.04	2.25
9.91	0.10	5.90	0.77	0.03	3.33
10.00	0.09	6.31	0.80	0.03	3.00
10.12	0.12	6.92	0.84	0.04	3.00
10.40	0.28	8.14	0.91	0.07	4.00
10.49	0.09	8.55	0.93	0.02	4.50
10.61	0.12	8.97	0.95	0.02	6.00
10.71	0.10	9.37	0.97	0.02	5.00
10.81	0.10	9.77	0.99	0.02	5.00
10.96	0.15	10.39	1.02	0.03	5.00
11.00	0.28	10.95	1.04	0.02	14.00
11.28	0.19	11.78	1.07	0.03	6.33
11.50	0.22	12.90	1.11	0.04	5.50
11.78	0.28	14.91	1.17	0.06	4.67
12.11	0.33	19.02	1.28	0.11	3.00
12.19	0.08	20.44	1.31	0.03	2.67
12.29	0.10	22.84	1.36	0.05	2.00

The differential pH and differential volume of the titrant solution are also computed and shown in the same table with the view to evaluate  $\Delta$ pH/ $\Delta$ log V function as related to log V. Table 2 summarizes the relevant potentiometric titration data for the 1.0 M sodium hydroxide against the lowest concentration of phenol, i.e., 0.001 M.

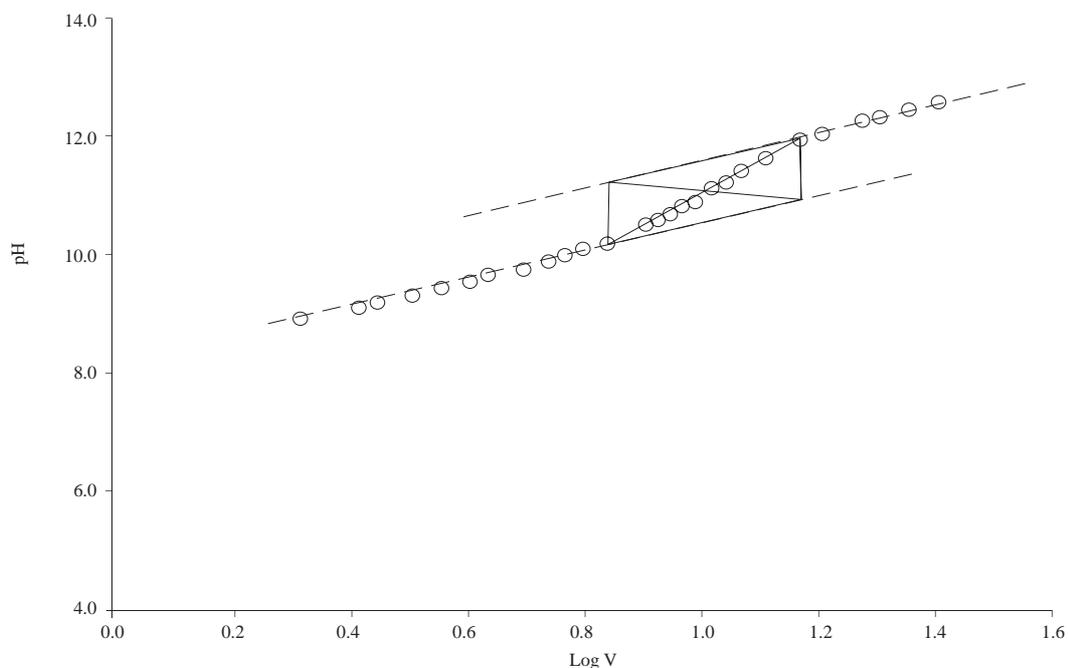
Figure 1 is a typical demonstration of pH vs. V relationship which is non-linear without any obvious equivalence point drawn for the data given in Table 1. In Figure 2, the same system depicted in Figure 1, is plotted as pH vs. Log V, duly supported by the theoretical deduction given earlier.

Conventionally, the titration data are plotted as pH vs. Volume of titrant (Fig. 1) to obtain a sigmoid curve which by way of symmetry helps to locate the equivalence point of a given titration setup at an appropriate pH value. However, as the nature of interacting acids and bases is changed from strong to weak counterparts not only does this obscure the equivalence point but the titration curve does not give an accurate identification of the equivalent point. The present case of phenol titration against sodium hydroxide is a typical case of a very weak acid ( $K_a \simeq 10^{-10}$ ) being titrated against a strong base, which makes the system

unidentifiable at the equivalence point (Fig. 1). It is evident that the titration curve has no inflexional point at all, rather it marks a regularly increasing pH with increasing volume of sodium hydroxide to finally reach a constant pH of about 12.5. Needless to say, this situation is unacceptable quantitatively since no useful information can be extracted from such a plot.



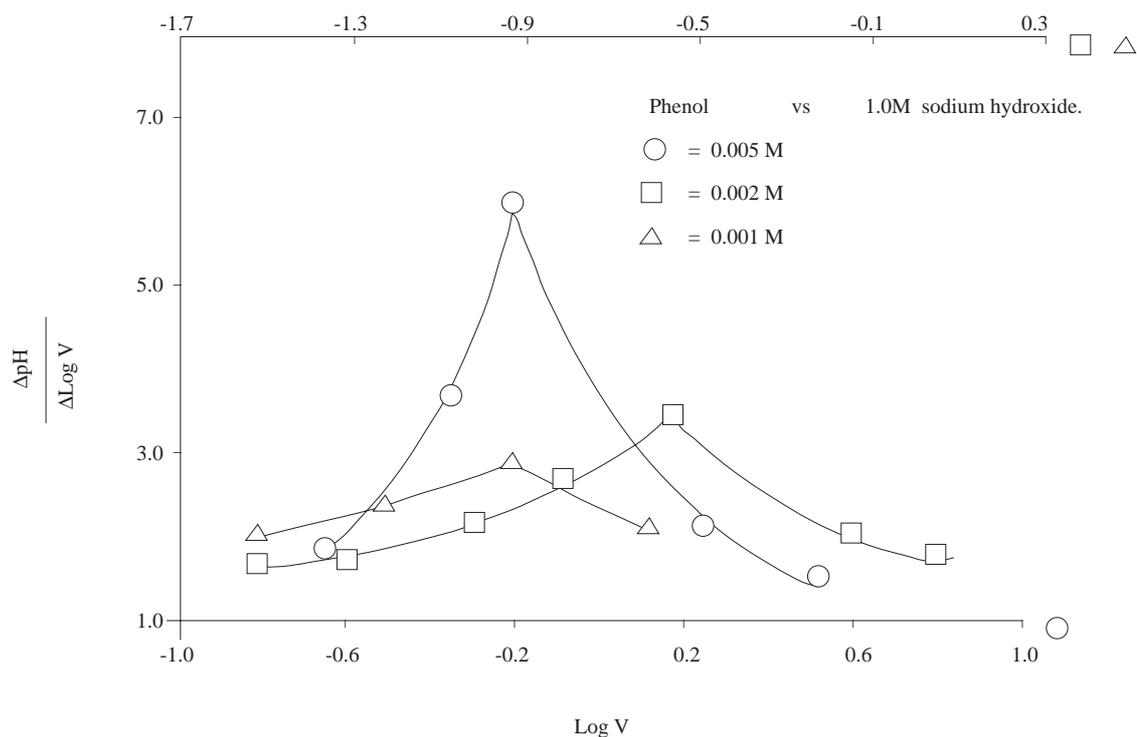
**Figure 1.** Potentiometric titration curve for 0.01M aq. phenol vs 0.1M sodium hydroxide.



**Figure 2.** Potentiometric titration curve for 0.01M aq. phenol vs 0.1M sodium hydroxide.

**Table 2.** Potentiometric differential titration data for 0.001M phenol vs. 1.00M sodium hydroxide

pH	$\Delta$ pH	V(mL)	log V	$\Delta$ log V	$\Delta$ pH/ $\Delta$ log V
5.44	0.00	0.00	0.00	0.00	0.00
7.88	2.44	0.01	-2.00	-2.00	-1.22
8.47	0.59	0.02	-1.70	0.30	1.97
8.83	0.36	0.03	-1.52	0.18	2.00
9.10	0.27	0.04	-1.40	0.12	2.25
9.31	0.21	0.05	-1.30	0.10	2.10
9.50	0.19	0.06	-1.22	0.08	2.37
9.82	0.32	0.08	-1.10	0.12	2.67
10.08	0.26	0.10	-1.00	0.10	2.60
10.32	0.24	0.12	-0.92	0.08	3.00
10.52	0.20	0.14	-0.85	0.07	2.86
10.77	0.25	0.17	-0.77	0.08	3.12
11.05	0.28	0.21	-0.68	0.09	3.11
11.23	0.18	0.25	-0.60	0.08	2.25
11.29	0.06	0.27	-0.57	0.03	2.00



**Figure 3.** Differential pH vs Log V. plots for various phenol systems.

According to theoretical derivations carried out through the course of this study, it turned out that a plot between pH and log V would be more useful. It is clear from Figure 2 that when the data of Table 1 were plotted as pH vs. log V, a distinctly interpretable sigmoid curve was obtained as against the non-inflexional curve of Fig. 1. The varying relation between pH and log V was further realized by using a relatively higher

concentration of sodium hydroxide during titration. Up to 1.0 M sodium hydroxide, the inflexional region became more vivid, thus affording greater reliability of identification of the equivalence point. A subsequent increase in the titrant concentration was found to be of no additional benefit.

The lowest detection limit for phenol was ascertained by employing 0.001 M aqueous phenol vs. 1.0 M sodium hydroxide titration system. The overall error for this system was between  $\pm 1.0$  and 1.5%. However, this situation appeared more creditable when differential plots (instead of the simple pH vs. log V) were drawn as shown in Figure 3. It is also noteworthy that in such differential plots, the equivalence point becomes very sharp and provides a more precise location against which the titrant volume may be identified without doubt. Furthermore, the quantification is not masked by increasing concentrations of sodium hydroxide, thus providing smaller and smaller neutralization volumes for the given phenol solutions. Therefore, the height of the apex becomes immaterial towards quantification.

Another plus point of this study is that by increasing the molar concentration of the titrant, not only does the volume involved become smaller but also the corresponding dilution effect by the addition of sodium hydroxide becomes minimal. Seen in this perspective, the present study promises greater accuracy and precision with higher relative concentrations of sodium hydroxide to be used as the titrant. For example, when 0.01 M phenol was titrated against 4.0 M sodium hydroxide solution, the relative concentration of sodium hydroxide was 400 times greater than that of phenol, unlike conventional titrations where relative acid-base concentrations are preferred to be 1:1. The differential plots pertaining to the evaluation of a lower detection limit represent a more clear exposition of this situation compared with the conventional sigmoid curves. Figure 3 depicts this fact clearly. The titrant concentration here is fixed at 1.0 M against varying concentrations of phenol, dropping from 0.005 M to 0.001 M phenol. The stature of the peaks at the equivalence point, in each case, is shortened progressively as the phenol concentration diminishes. Under the proposed method, therefore, one can go as low as 0.005 M concentration under the normal potentiometric procedure proposed here. However, if a proper modification in the apparatus is used, especially in the volume delivering microburette, a still better detection limit could be achieved. For the present case, the detection limit based on 0.005 M phenol solution (about 45 mg phenol/L) can be achieved in any aqueous phase system. This limit of detection may be enhanced by several multiples simply by selecting larger volumes of sample taken for analysis. For most practical purposes, especially in cases where the phenol content of industrial effluents, for example, is to be determined by the proposed method, a detection limit as low as about 50 mg phenol/L is more than adequate in view of 40-50g phenol/L present in such contaminated waters.

In conclusion, the proposed methodology based on potentiometric estimation of phenol content of aqueous solutions, provides accurately finished results, without any analytical fuss. The method is straightforward, non-time consuming and has the potential of application to varied systems of contaminated waters desired to be analyzed by a simple and precise analytical method. The accuracy limit for the method lies between  $\pm 1.0$  and 1.5% for replicate measurements, as for the synthetic samples. Municipal sewage, home effluents, industrial discharges and processed water systems may all be analyzed by the proposed method which warrants a positive perspective future use also in the field of organic synthesis where simple phenols have to be isolated and quantified in aqueous media from other substituted phenols during a reaction sequence.

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