## 855. *The Dissociation Constant of Phenol in Alcoholic Solvents.*

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The solvolysis constants of sodium phenoxide in methanol and ethanol have been determined by a spectrophotometric method, and dissociation constants are calculated from these values and the known autoprotolysis constants. The results are compared with those obtained by other methods; a large discrepancy between the present results and the dissociation constant of phenol in 95% ethanol found by workers who used an E.M.F. method is attributed to a faulty value of the autoprotolysis constant of 95% ethanol determined by the latter.

IT is difficult to measure the extinction coefficient of sodium phenoxide in alcoholic solvents by straightforward methods because, even in solutions containing a large excess of alkoxide, phenol is not fully converted into phenoxide. We have therefore measured the extent of solvolysis of sodium phenoxide, $PhO^- + ROH \rightleftharpoons PhOH + RO^-$, at 25° and 45° in absolute methanol and in absolute ethanol by Stearns and Wheland's method,[1] which is particularly suitable for strong bases. The method involves an extrapolation to find the extinction coefficient ($k$) of the phenoxide ion, and the solvolysis constant, $K'_s = [RO^-][PhOH]/[PhO^-]$, is also found from the results. Stearns and Wheland point out that, if the activity coefficient of phenol is unity, and if the activity coefficients of sodium alkoxide and phenoxide are considered equal, in accordance with the Debye–Hückel limiting law, then $K'_s = K_s$, the thermodynamic solvolysis constant.

The results were plotted according to the equation $1/k' = 1/k + K_s/(k[OR^-])$, where $k'$ (the " apparent " extinction coefficient) = optical density/([PhOH] + PhO^-]), the optical density being measured in a 1 cm. cell at a fixed wavelength ($\lambda_{max.}$ for phenoxide ion), and [RO^-] is the equilibrium alkoxide concentration, *i.e.*, the concentration added in making up the solutions provided this is always much larger than the phenol concentration. A graph of $1/k'$ against $1/[RO^-]$ should be linear and, from the intercept and slope of the line, $k$ and $K_s$ are calculated. The results in Table 1, when plotted in this

### TABLE 1.

| Temp. | [PhOH] (10⁻⁵M) | [NaOR] (10⁻⁵M) | Optical density | Wavelength (mμ) | Temp. | [PhOH] (10⁻⁵M) | [NaOR] (10⁻⁵M) | Optical density | Wavelength (mμ) |
|---|---|---|---|---|---|---|---|---|---|
| | | In methanol | | | | | In ethanol | | |
| 25° | 8·05 | 849 | 0·698 | 238 | 25° | 5·45 | 589 | 0·555 | 239 |
| ,, | ,, | 566 | 0·639 | ,, | ,, | ,, | 354 | 0·533 | ,, |
| ,, | ,, | 283 | 0·487 | ,, | ,, | ,, | 236 | 0·518 | ,, |
| 45 | 7·86 | 829 | 0·660 | ,, | ,, | ,, | 118 | 0·427 | ,, |
| ,, | ,, | 552 | 0·599 | ,, | ,, | ,, | 94·3 | 0·400 | ,, |
| ,, | ,, | 276 | 0·442 | ,, | 45 | 5·33 | 576 | 0·549 | 240 |
| | | | | | ,, | ,, | 346 | 0·495 | ,, |
| | | | | | ,, | ,, | 231 | 0·452 | ,, |
| | | | | | ,, | ,, | 115 | 0·335 | ,, |
| | | | | | ,, | ,, | 92·2 | 0·317 | ,, |

manner, gave good straight lines. The values of $k$ and $K_s$ calculated by the method of least squares are given in the first part of Table 2 together with p$K_a$ values for phenol calculated from the equation, p$K_a$ = p$K_{auto}$ − p$K_s$. Corresponding values for aqueous solutions are included for comparison.

The p$K_s$ value for sodium phenoxide increases in the order MeOH < EtOH < H₂O. A similar order is observed for carboxylate ions in these solvents.[2]

The p$K_a$ value for phenol in methanol agrees closely with that (p$K_a$ = 14·0 at 25°) determined by Kolthoff and Guss[3] who used a colorimetric method with Thymol Blue

[1] Stearns and Wheland, *J. Amer. Chem. Soc.*, 1947, **69**, 2025.
[2] Bell, " The Proton in Chemistry," Cornell Univ. Press, Ithaca, N.Y., 1959, p. 44.
[3] Kolthoff and Guss, *J. Amer. Chem. Soc.*, 1938, **60**, 2516.

TABLE 2.

| Solvent | Temp. | $h$ for NaOPh | $10^4 K_s$ | $pK_s$ | $pK_{auto}$ | $pK_a$ |
|---|---|---|---|---|---|---|
| Methanol ............ | 25° | 11,000 | 24 | 2·6 | 16·7 *† | 14·1 |
| ,, ............ | 45 | 11,400 | 28 | 2·5 | 16·27 † | 13·8 |
| Ethanol ............... | 25 | 11,200 | 5·0 | 3·3 | 19·1 *‡ | 15·8 |
| ,, ............... | 45 | 11,900 | 9·7 | 3·0 | — | — |
| Water .................. | 25 | — | 0·934 | 4·03 | 14·00 § | 9·97 ¶ |
| ,, .................. | 50 | — | 2·51 | 3·60 | 13·26 § | 9·66 ¶ |

* Bell, " The Proton in Chemistry," Cornell Univ. Press, Ithaca, N.Y., 1959, p. 37.   † Koskikallio, *Suomen Kem.*, 1957, **30**, B, 155.   ‡ Danner, *J. Amer. Chem. Soc.*, 1922, **44**, 2832.   § Robinson and Stokes, " Electrolyte Solutions," Butterworths, London, 1955, p. 506.   ¶ Binns, *Trans. Faraday Soc.*, 1959, **55**, 1900.

as indicator.   A value of 12·0 has been estimated by Leahy and Miller[4] by adding 2·0 to the $pK_a$ value in water.

There is a serious discrepancy between the $pK_a$ value for phenol in ethanol above and the value 12·82 determined by Schwarzenbach and Rudin[5] in 95% ethanol.   Their results were obtained by measuring the E.M.F. of the cell, Pt,$H_2$|A|sat. aq. KCl|$Hg_2Cl_2$,Hg, the compartment A containing either (a) a buffer prepared by mixing solutions of phenol and base (sodium ethoxide and sodium hydroxide) in 95% ethanol, or (b) base alone in the same solvent.   Although this is not stated by these authors, it is apparent that the latter E.M.F. measurement is used to calculate the autoprotolysis constant of the solvent, and this quantity is determined, for a series of measurements of dissociation constants of phenols and thiophenols, by a single measurement of the E.M.F. of the cell with A containing base of known concentration.   The activity of the base is determined from its concentration and the activity coefficient, determined by the application of the Debye–Hückel limiting law.   Their measurements lead to a value of $pK_{auto} = 16·5$ for ethanol, which is probably at least 2 units too low, and it appears, therefore, that a large part of the discrepancy between Schwarzenbach and Rudin's measurements and ours is due to their faulty value of $pK_{auto}$.   It appears that there is a similar large error in all the dissociation constants of phenols and thiophenols determined by these authors in 95% ethanol.

The $K_s$ values above show that there is a considerable proportion of sodium alkoxide present in solutions of sodium phenoxide in alcohols, especially in methanol.   As the alkoxides have a much greater nucleophilic reactivity than phenoxide, a large proportion of substitution by alkoxide occurs when alkyl or activated aryl halides react with sodium phenoxide in alcoholic solutions that do not contain a sufficient excess of phenol.   This has not always been realised in kinetic studies with sodium phenoxide, with the result that the rate constants that are quoted in the older literature are too high.

An approximate solvolysis constant can be determined from a study of the variation of the measured rate constant as phenol is added to reaction mixtures in which phenoxides and alkoxide are both reacting bimolecularly with the same alkyl halide.   In replacement reactions, product analyses can also be combined with kinetic data to give approximate values of the solvolysis constant.   Values of $K_s$ which have been obtained for sodium phenoxide by these methods are, in methanol, $3·3 \times 10^{-3}$ (70·2°)[6] and $2·7 \times 10^{-3}$ (25°),[7] and, in ethanol, $4·5 \times 10^{-4}$ (60·2°)[8] and $1 \times 10^{-3}$ (70·2°).[7]

*Experimental.*—Solutions were made up for spectrophotometric measurements by mixing solutions of phenol with solutions of sodium alkoxide, made by adding clean sodium to the alcohols.   " AnalaR " phenol was used without further purification; the purity was checked by volumetric measurement of the amount of bromine destroyed by a known mass of phenol.

[4] Leahy and Miller, *Chem. and Ind.*, 1953, 40.
[5] Schwarzenbach and Rudin, *Helv. Chim. Acta*, 1939, **22**, 360; cf. Schwarzenbach and Egli, *ibid.*, 1934, **17**, 1176.
[6] England, *Chem. and Ind.*, 1954, 1145.
[7] England and Fraser, unpublished results.
[8] Baker and Neale, *J.*, 1954, 3225.

" AnalaR " methanol was used; ethanol was dried by Vogel's method.[9] Spectrophotometric measurements were made with a Unicam S.P. 500 spectrophotometer in silica cells kept at constant temperature by a water-circulating device. As a check on the method described, the optical densities of methanol solutions at 25° containing various concentrations of phenol and a fixed concentration of sodium methoxide were plotted against the added phenol concentration and gave a straight line passing through the origin within the error of measurement. Solutions of phenol in either alcohol have a minimum absorption at about 240 m$\mu$ (extinction coefficient 80 l. mole$^{-1}$ cm.$^{-1}$) and a maximum at 273 m$\mu$ (extinction coefficient 1800).

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[9] Vogel, " A Text Book of Practical Organic Chemistry," Longmans, Green and Co., London, 1954, p. 167.