strong base, and 4.1% (4.6% by plot) for the weak base.

Just as the titer deviation in titration by a weak base exceeds that by a strong base, although κ_A is the same, so the titer error (of locating the end-point) is also in slight excess for the same value of κ_A and in proportion to the magnitude of $1/f_A$.

It is found by plot that for titration by a weak base the inflection point still appears if $\kappa_A = 10^{-1.5}$. The titer deviation is from the plot 20%. With κ_A decreased however to $10^{-1.4}$, the inflection point does not seem to appear. Thus the condition of the appearance of an inflection point for titration by a weak base is equal to or nearly so to that for titration by a strong base for which the condition is $\kappa_A < 10^{-1.42}$.[3]

Since the titer error and titer deviation are greater than when titrating with a strong base, theory requires that titration by a weak base be at all times avoided; likewise weak acid salts should be excluded from the titrating solution.

In connection with the general formulation for the titer error (equation (1) of reference 3) it may be remarked that for Δ small, sinh Δ may be taken equal to Δ. For all practical purposes, since the *p*H or m. v. error of titration is ordinarily small, equation (1) may therefore be simplified to

$$E = \pm 200 \sqrt{\kappa}\, \Delta \qquad \text{(1a)}$$

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The Limiting Effect of the Debye Equation on Polarization Concentration Curves

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The polarization P_2 of most liquids possessing a permanent moment varies with the concentration c_2 when measured in a liquid with zero moment. The explanation given for this variation of P_2 with c_2 has been molecular association [Debye, "Handbuch der Radiologie," (Marx) Leipzig, 1925, p. 636; Höjendahl, Thesis, Copenhagen, 1928; Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., N. Y., 1931, p. 188; Sidgwick, "The Covalent Link in Chemistry," Cornell University Press, Ithaca, N. Y., 1933, p. 170].

There is another factor affecting this variation. The mathematical nature of the Debye equation puts a limiting value on P_2 which without any recourse to association at all will account for most of the decrease in the value of P_2 at high concentrations. This limiting effect of the Debye equation has been observed in other connections by Wyman and by v. Arkel and Snoek [Wyman, THIS JOURNAL, **56**, 536 (1934); v. Arkel and Snoek, *Trans. Faraday Soc.*, **160**, 707 (1934)].

For nitrobenzene the value of P_2 goes from 330 cc. at infinite dilution to 90 cc. at pure nitrobenzene. Even if the dielectric constant of nitrobenzene were infinite the largest value the polarization could have for the pure substance as calculated by the equation is

$$P_2 = \frac{\epsilon - 1}{\epsilon + 2}\,\frac{M}{d} = 1 \times \frac{123}{1.2} = 102 \text{ cc.}$$

Thus the value of P_2 would have to decrease to less than 102 due to the limitation of the equation without any effect due to association. Even with a substance with as small a moment as ethyl alcohol 1.7 the limitation of the equation is affecting the polarization in the region of high concentration. The limiting value for the pure liquid is less than 58 cc.

$$P_2 = \frac{\epsilon - 1}{\epsilon + 1}\,\frac{M}{d} = 1 \times \frac{46}{0.79} = 58 \text{ cc.}$$

and the value of the polarization at mole fraction 0.5 is about 90 cc. Hence the downward slope of this curve at high concentrations is necessitated by the limitations of the equation.

With diethyl ether (moment 1.12) the value of $M/d(104)$ is sufficiently high in comparison with the value of $P_2(54)$ so that no such effect is introduced by the equation when the polarization is calculated for the pure substance. Its P_2, c_2 curve, as is well known, is a straight horizontal line.

Molecular association probably has some effect on polarization but it is apparent that no conclusions can be drawn from polarization concentration curves in regard to association unless the limiting factor due to the nature of the Debye equation itself is first excluded.

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