17. *The Determination of Mobilities and Dissociation Constants by Means of Conductivity Titrations.*

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The possibility of determining mobilities and dissociation constants by means of conductivity titrations is discussed and illustrated. The methods given are not well suited to work of the highest accuracy, but are rapid and may prove valuable where only small quantities of material are available.

It is pointed out that the general effect of a substituent amino-group is to increase, and not decrease, the acidity of a molecule, although at the same time it provides a new centre of basic properties.

The Determination of Anion Mobilities by Titration of Acid with Ammonia.—When the dissociation constant of an acid is determined by the conductivity method, the mobility of the anion of the acid must be known. This is usually determined by measuring the conductivity of the sodium or potassium salt, and extrapolating the results to infinite dilution after applying a combined hydrolysis and solvent correction. The alternative now proposed is to determine the anion's mobility by carrying out conductivity titrations of the pure acid with a standard ammonia solution. This takes a small fraction of the time required by the older method, and avoids the purification, drying, and handling of the solid salt, often troublesome processes. The titration method is less suited to measurements of the highest accuracy, owing to an increased uncertainty in the solvent correction; but it readily gives mobilities accurate to 0·5%, corresponding to Λ_0 values for the parent acids accurate to 0·05%, a degree of accuracy that is seldom exceeded in dissociation-constant measurements.

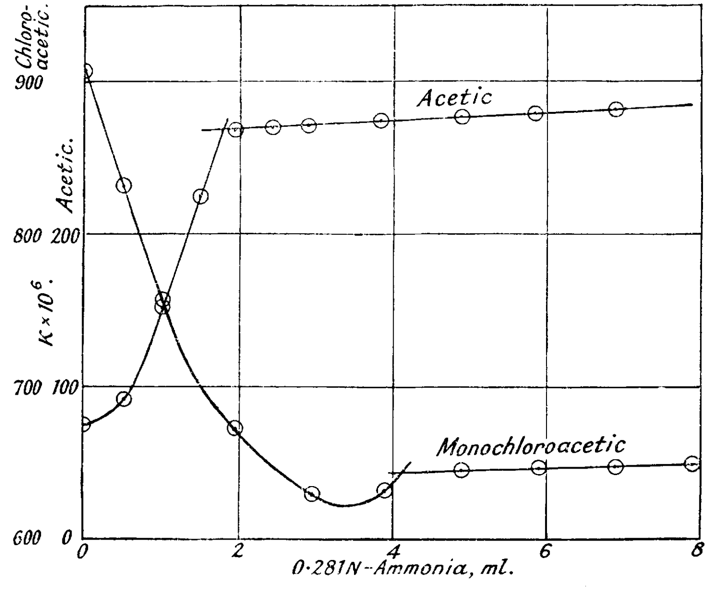
Fig. 1 shows curves for acetic and monochloroacetic acids and illustrates the type of result obtained. After the break the line is almost horizontal, and this enables the specific conductivity at the end-point to be determined with considerable accuracy. As calculations show, the point at which the titration curve becomes almost horizontal corresponds to the complete neutralisation of the organic acid and the conversion of any carbon dioxide present in the water into ammonium hydrogen carbonate. A correction for this on the basis of the measured conductivity of the water can be applied, and the mobility then determined by means of Onsager's equation and the known mobility of the ammonium ion.

The ammonia was prepared by the distillation of a concentrated solution from potassium hydroxide into conductivity water, with precautions against ingress of carbon dioxide. The acetic acid was prepared by fractional crystallisation from " AnalaR " acid, and the monochloroacetic acid was an " AnalaR " sample, used without further purification. The cell (constant = 0·15), containing a known quantity of " equilibrium " conductivity water, was immersed in a thermostat at 25°, and after the solvent's conductivity had been measured a known amount of a stock solution of the acid was added. The ammonia solution was added from a small calibrated burette whilst pure air passed through the cell. At the end of a run the specific conductivity corresponding to the theoretical end-point was read off from a curve, and a correction (2 gemmhos) deducted for the ammonium hydrogen carbonate present. The calculated equivalent conductivity was then converted into the infinite dilution value by means of Onsager's equation, or, for concentrations higher than 0·002N, by the extended equation of Robinson and Davies (J., 1937, 574), and the mobility of the anion was obtained from this by deducting 73·5, the mobility of the ammonium ion at 25° (Longsworth, *J. Amer. Chem. Soc.*, 1935, **57**, 1185). Four titrations were carried out with acetic acid and gave the following results : 0·002417N-acid, l_0OAc = 40·8, 41·2 ; 0·006084N-acid, l_0OAc = 40·5, 40·7 ; mean 40·8, av. devn. 0·2. This is in good agreement with the value 40·87 given by MacInnes and Shedlovsky (*ibid.*, 1932, **54**, 1429) and the value 40·81 by Saxton and Langer (*ibid.*, 1933, **55**, 3638). Three titrations with monochloroacetic acid (0·002—0·006N) gave the results : $l_0CH_2Cl\cdot CO_2' = 39\cdot8, 39\cdot8, 39\cdot7$, in fair agreement with Saxton and Langer's value, 39·92 (*loc. cit.*).

Some titrations were also carried out with difficultly soluble acids. Here the method was less satisfactory, as the acid was often found to dissolve with extreme slowness even in the presence of a small excess of ammonia.

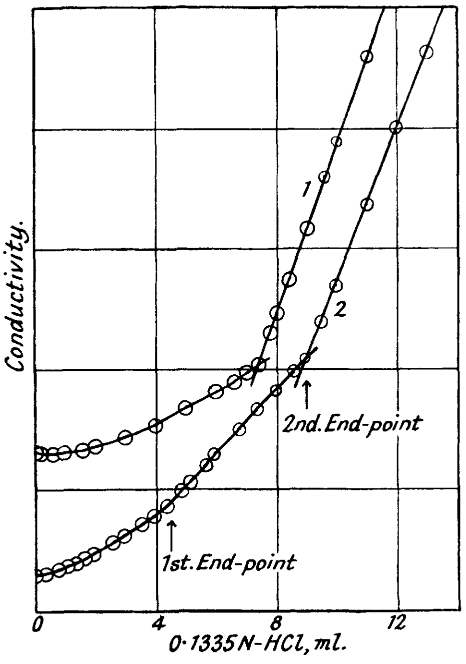
The Ionisation Constants of Some Bases, and their Cationic Mobilities.—Conductivity titrations may be conveniently used, in much the same way, to determine cationic mobilities. Below are reported some measurements made to illustrate the method, and also to see how successfully the ionisation constant of a base could be calculated from a single titration curve.

FIG. 1.



Curve 1 of Fig. 2 shows the titration of an approximately 0·005N-solution of *n*-propylamine with 0·1335N-hydrochloric acid. The equivalence point could be accurately read off as the intersection of the two lines, and thus the initial concentration of the propylamine solution was determined. The solvent's conductivity was now subtracted from the conductivity at the end-point, and the corrected equivalent conductivity of the propylamine hydrochloride was converted into its value at infinite dilution by the extended Onsager equation. The value obtained was $\Lambda_0 = 131\cdot3$, which gives 55·0 for the mobility of the propyl-ammonium ion. The ionisation constant of the base can now be calculated from any point on the first branch of the titration diagram. Such points correspond to mixtures, in known proportions, of propylamine and its hydrochloride, and if we assume that the conductivities of these are approximately additive, and subtract from the total conductivity that calculated for the hydrochloride, we obtain the conductivity due to the propylamine, and, by a short series of approximations, can calculate its degree of ionisation and hence the values of $[\mathrm{PrNH_3^{\cdot}}]$, $[\mathrm{OH'}]$ and $[\mathrm{PrNH_2}]$. These, inserted in the equation $K = f_{\pm}^2 \cdot [\mathrm{PrNH_3^{\cdot}}][\mathrm{OH'}]/[\mathrm{PrNH_2}]$, give the ionisation constant of the base. The values obtained were: for 0, 25, and 50% neutralisation, $K = 4{\cdot}48$, $4{\cdot}77$, and $4{\cdot}56 \times 10^{-4}$; mean $4{\cdot}60 \times 10^{-4}$, av. devn. $0{\cdot}11 \times 10^{-4}$. This agrees well with Bredig's value $4{\cdot}7 \times 10^{-4}$ (*Z. physikal. Chem.*, 1894, **13**, 289), but his mobility value is much smaller than ours. This method of determining approximate ionisation constants is very rapid, and may be valuable where only a few centigrams of material are available.

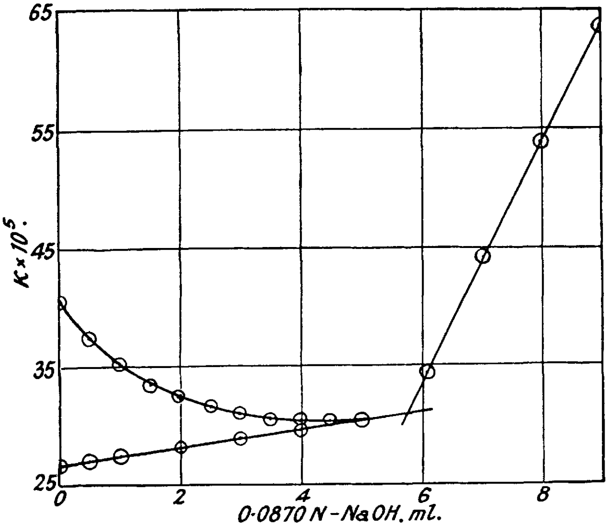
FIG. 2.



Curve 2 of Fig. 2 shows the titration of ethylenediamine with hydrochloric acid. The final end-point can be read off accurately, and gives the concentration of the base, and the mobility of the ion $\mathrm{NH_3^{\cdot}.CH_2{\cdot}CH_2{\cdot}NH_3^{\cdot}}$. The first equivalence point (calculated from the final end-point) gives an approximate value for the mobility of the ion $\mathrm{NH_2{\cdot}CH_2{\cdot}CH_2NH_3^{\cdot}}$, and, as before, the first section of the curve enables the first ionisation constant of the base to be calculated. Two titrations were carried out with the following results: molar concentration, 0·00300, 0·00601; first ionisation constant (for additions of 0, 1, and 2 ml. acid) $1{\cdot}01$, $1{\cdot}14$, $1{\cdot}06$, $1{\cdot}15$, $1{\cdot}25$, $1{\cdot}26 \times 10^{-4}$; mean $1{\cdot}14 \times 10^{-4}$.

Most aromatic bases are too weak for the above methods to be applicable, and it is necessary to prepare the hydrochloride of the base and to titrate this with standard alkali. Fig. 3 shows the titration of a *p*-chloroaniline hydrochloride solution with sodium hydroxide; the upper curve represents the titration of the pure hydrochloride, and the lower line the titration of a hydrochloride solution to which sufficient pure base has been added to suppress hydrolysis completely. The end-point is given with much greater accuracy by the

FIG. 3.



second titration. The mobility of the chloroanilinium ion may be calculated either from the first point of the second titration, as was done by Bredig, or from the slope of the first branch of the second titration curve, which shows by how much the mobility falls short of that of sodium ion. For the approximately 0·0025N-solution investigated the two methods gave values of 35·4 and 33·9. The large difference is probably due mainly to uncertainties in the solvent corrections; the mean is 34·7. The ionisation constant of the base is given by Bredig's method of comparing the first points of the two titrations. For *p*-chloroaniline this gave the value $K_b = 1{\cdot}1 \times 10^{-10}$. During the course of this work the solubility of *p*-chloroaniline in water at 25° was determined. Excess of the base was shaken with water for a week, the mixture kept in the thermostat for a further week, and a sample of the clear aqueous solution analysed by a conductivity titration with hydrochloric acid. It was found to contain 3·00 g. of *p*-chloroaniline per l.

Similar measurements were made with a recrystallised specimen of *m*-chloroaniline hydrochloride, prepared from the redistilled base, and the following results were obtained: mobility of the cation, 34·7, 34·3, mean 34·5; ionisation constant of base, $3{\cdot}6 \times 10^{-11}$; the saturated aqueous solution at 25° contained 6·11 g. of *m*-chloroaniline per l. The dissociation constants agree reasonably well with the following values determined potentiometrically by Brönsted and Duus (*Z. physikal. Chem.*, 1925, **117**, 299): *p*-chloroaniline, $1{\cdot}0 \times 10^{-10}$; *m*-chloroaniline, $3{\cdot}3 \times 10^{-11}$.

An interesting point illustrated by our results concerns the effect of the amino-group on the properties of a molecule in which it is a substituent. It is stated in many textbooks that this effect is to increase the basic and to decrease the acidic nature of the molecule, an idea which probably originated from early investigations on the amino-acids, carried out before their " zwitter-ion " structure had been recognised. This appears to be incorrect. The amino-group provides a new centre of basic properties on account of the readiness of the nitrogen to increase its covalency, but its influence on the remainder of the organic molecule, as modern theory would seem to demand, is to increase, and not to decrease, the acidity. Thus the ionisation constant of propylamine is four times as great as the first basic constant of ethylenediamine. Further comparisons are given by the following ionisation constants, which are taken from the literature: ammonia $1{\cdot}8 \times 10^{-5}$, hydrazine 3×10^{-6}; ethylamine $5{\cdot}6 \times 10^{-4}$, ethylenediamine $1{\cdot}1 \times 10^{-4}$; *n*-propylamine $4{\cdot}6 \times 10^{-4}$, propylenediamine $3{\cdot}5 \times 10^{-4}$; aniline $4{\cdot}6 \times 10^{-10}$, *o*-phenylenediamine $3{\cdot}3 \times 10^{-10}$.

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