The titration of mixtures of ferrous and vanadyl solutions yields correct results for both iron and vanadium. This process finds practical application in the direct determination of vanadium and the indirect determination of chromium in ferro alloys.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE STRENGTH OF ACETAMIDE AS AN ACID

BY G. E. K. BRANCH AND J. O. CLAYTON

RECEIVED APRIL 10, 1928 PUBLISHED JUNE 5, 1928

Introduction

The determination of the strength of a very weak acid, such as acetamide, through measurements of the electrical conductivity of a solution containing both the weak acid and a strong base, necessitates a knowledge of the equivalent conductivity of the resulting salt. This cannot be obtained directly. Consequently measurements must be made under conditions in which the degrees of neutralization of the base differ, and the resulting equations solved for both the equivalent conductivity of the salt and its hydrolysis constant. Such a solution assumes that neither the mobilities of the ions nor the hydrolysis constant of the salt change when the conditions are varied. It is therefore necessary to correct for or avoid changes in these quantities.

Variation in the concentration of total electrolyte will produce marked changes in the mobilities of the ions and in the hydrolysis constant. Consequently our measurements were made at a constant and low value of the concentration of total electrolyte. Since the salt and the base are strong electrolytes of the same valence type, and are both dilute, variation of the ratio between salt and base will lead to negligible errors.

It did not seem possible to correct in any way for the effect of the change of the concentration of acetamide on the hydrolysis constant. This can be avoided by the use of very dilute solutions of the weak acid, but this cannot be done in the case of acetamide, as appreciable reaction between it and a base can only be obtained with concentrated solutions.

The influence of acetamide on the mobilities of the ions cannot be neglected. This difficulty was overcome by the use of an approximate correction formula. The nature and derivation of this formula are discussed later.

Acetamide is so weak an acid that in aqueous solution containing only small concentrations of base its concentration is always very large in comparison with that of its salt. Consequently the presence of very small traces of impurities which either react with a base or are themselves electrolytes will cause an appreciable error in a conductivity measurement. To avoid this difficulty the rates of change of conductivity with change of total base added at constant acetamide concentrations were measured instead of the actual conductivities.

The Method

The method consists of making up a series of solutions containing small but varying quantities of barium hydroxide (0.02 N to 0.08 N) and a constant concentration of acetamide. The conductivities of these solutions were measured at 25° and the results plotted against the concentration of total base added. The slope of this curve at 0.05 N total base is the rate of change of conductivity with variation of total base concentration at the concentration of acetamide which was used. Such a value we have called the L of the solution. Since only small fractions of acetamide, less than 0.01, react with the base, the concentration of free acetamide and the ratio of barium hydroxide to barium acetamide remain constant in any one series of measurements. L is therefore the partial differential of the conductivity with respect to the concentration of total base at a fixed composition of the electrolyte.

Several such values of L at 0.05 N total base were measured at concentrations of acetamide varying between 0 N and 10 N. These values were plotted against the concentration of acetamide (see curve 1 of the figure). From this curve more accurate values of L were obtained at several concentrations of acetamide.

The variation of L with the concentration of acetamide is not only due to differences in the ratios of acetamide ion to hydroxide ion but also to the influence of acetamide on the mobilities of these ions. This latter factor must be corrected for before the ratio base to salt can be obtained.

The equivalent conductivity of an electrolyte at infinite dilution, λ_∞, changes with the nature of the solvent, and this variation may be expressed by the equation $\lambda_\infty \eta$ = a constant, in which η is a property of the solvent only. For solutions of acetamide this may be put in the form $\lambda_\infty/\lambda_{\infty 0} = \eta_0/\eta$, in which the subscript zero indicates that the quantity refers to aqueous solution without any acetamide. This convention will be followed throughout the rest of this article. Now $L = [1-f(N)]\lambda_\infty$, in which $f(N)$[1] is a function of the normality, but is not independent of the nature of the electrolyte. Similarly $L_0 = [1-f_0(N)]\lambda_{\infty 0}$, so that $L/L_0 = (\eta_0/\eta) \times \{[1-f(N)]/[1-f_0(N)]\}$. Now $1-f_0(N)$ must be very nearly equal to $1-f(N)$ when dilute solutions of the same electrolyte at equal concentrations are compared, so that $L/L_0 = \eta_0/\eta = D$, in which D is independent of the nature of the electrolyte. The values of D for various concentrations of acetamide were found by measurements of L

---

[1] $f(N)$ is approximately proportional to $N^{1/2}$.

for 0.05 N solution of sodium chloride.[2] It was found that L of sodium chloride is a linear function of the acetamide normality (see curve 2 in the figure). Consequently $L = L_0(1-E[\mathrm{A}])$ in which [A] is the normality of acetamide and E is a property of acetamide related to D by the equation $D = 1-E[\mathrm{A}]$. The corrected values of L were therefore obtained from the equation $L_0 = L/(1-E[\mathrm{A}])$. The value of E was obtained by dividing the slope of L_{NaCl} against [A] by the measured value of $L_{0\mathrm{NaCl}}$.

The L_0 obtained when barium hydroxide is mixed with an acetamide solution is that of a definite mixture of barium hydroxide and barium acetamide. As the base and the salt are both strong electrolytes of the same valence type in dilute solutions, the law of mixtures will be approximately applicable to this property, or $L_0 = \alpha L_{0\mathrm{B}} + (1-\alpha)L_{0\mathrm{S}}$, in which $L_{0\mathrm{B}}$ and $L_{0\mathrm{S}}$ are the values for the pure base and pure salt, respectively, while α is the fraction of the total electrolyte which is the free base. This equation may be more conveniently expressed as $(L_0-L_{0\mathrm{S}})/(L_{0\mathrm{B}}-L_0) = [\mathrm{B}]/[\mathrm{S}]$ in which [B] and [S] are the normalities of the base and salt, respectively. The ratio $[\mathrm{B}]/[\mathrm{S}] = K/[\mathrm{A}]$, in which K is the hydrolysis constant of acetamide ion, so that $(L_0-L_{0\mathrm{S}})/(L_{0\mathrm{B}}-L_0) = K/[\mathrm{A}]$. $L_{0\mathrm{B}}$ was obtained by direct measurement in the absence of acetamide and K and $L_{0\mathrm{S}}$ were obtained by graphical solution from several values of L_0 obtained from the curve. [A] is, of course, always equal to the initial values of acetamide, as never more than 1% of the acetamide was neutralized.

The above method is not applicable to all weak acids and bases. Dissociation constants greater than 10^{-12}, or markedly less than 10^{-15}, cannot be measured in this way. It is also necessary that the acid or base shall be sufficiently soluble; the lower the constant, the greater the solubility necessary.

Results

The experimental results are given below in tabular and graphic form. They were all obtained at 25°.

In Table I the observed values of the specific conductivities in reciprocal ohms per centimeter cube are shown for the various concentrations of acetamide at total barium hydroxide concentrations equal to 0.02 N, 0.04 N, 0.06 N and 0.08 N. The last column shows L, the rate of change of conductivity with change of normality of total base at 0.05 N total base.

The values of L are plotted against the normality of acetamide in curve 1.

---

[2] It would have been slightly more accurate to have used $BaCl_2$ instead of NaCl. However the fractional decrease of λ in going from 0 N to 0.1 N is roughly the same for $Ba(OH)_2$ as for NaCl, 0.19 and 0.16, respectively. $f(N)$ is 3/2 of this fraction, so that the slight variation of $\{1-f(N)\}/\{1-f_0(N)\}$ from unity is approximately the same for $Ba(OH)_2$ as for NaCl.

TABLE I

CONDUCTIVITIES OF MIXTURES OF $Ba(OH)_2$ AND CH_3CONH_2 IN AQUEOUS SOLUTION AT 25°

Concn. of CH_3CONH_2, N	Total base = 0.02 N	Total base = 0.04 N	Total base = 0.06 N	Total base = 0.08 N	L at 0.05 N[a]
0	0.00449	0.00863	0.01234	0.01618	0.193
.2	.00428	.00820	.01210	.01561	.189
.4	.00433	.00825	.01220	.01558	.187
.6	.00412	.00777	.01152	.01516	.1835
1.0	.00431	.00766	.01113	.01459	.172[b]
2.0	.00351	.00688	.01001	.01345	.1635
3.0	.00312	.00609	.00898	.01215	.150
6.0	.00227	.00462	.00690	.00921	.116
10.0	.001034	.00270	.00432	....[c]	.0825

[a] The curvature of the plot of conductivity against total base concentration is too slight to be obtained from any series of four measurements; it was assumed that its small variation from a straight line was the same in all cases and equal to that of the plot of the conductivity of barium hydroxide against normality, which can be obtained from the values given in the literature. The best curve of this type was drawn through the four values in each case, and the slope of the line across the curve from 0.02 N to 0.08 N was taken as the value of L at 0.05 N. The uncertainty in choosing the slope was about 0.5%. The values so obtained differ but little from the slopes of the best straight lines drawn through each series of measurements.

[b] This value is not concordant with the other values of L and has been neglected in the determination of the curve of L against the normality of acetamide.

[c] A value of 0.00503 reciprocal ohm was obtained at 0.0682 N total base.

Table II shows the corresponding measurements, using sodium chloride instead of barium hydroxide.

TABLE II

CONDUCTIVITIES OF MIXTURES OF NACL AND CH_3CONH_2 IN AQUEOUS SOLUTION AT 25°

Normality of acetamide	NaCl = 0.02 N	NaCl = 0.04 N	NaCl = 0.06 N	NaCl = 0.08 N	L at 0.05 N
0	0.00195	0.00372	0.00545	0.00729	0.0879
3	.00202	.00343	.00502	.00654	.0756
6	.00201	.00318	.00453	.00581	.0640
10	.00189	.00283	.00354	....[a]	.0486

[a] A value of 0.00437 reciprocal ohm was obtained at 0.071 N NaCl.

Curve 2 shows the values of L for sodium chloride plotted against the normality of acetamide. It can be seen that the points fall on a straight line within experimental errors. The slope of this straight line is -0.003955, so that E in the equation $L = (1-E[\text{A}])L_0$ is equal to 0.045.

Table III shows in the first two columns values of the normalities of acetamide and the corresponding values of L for 0.05 N barium hydroxide taken from curve 1. The third column shows the corrected values of L, as given by the equation $L_0 = L/(1-0.045[\text{A}])$. The values of the hydrolysis constants are given in the fourth column. These values are calculated from each value of L_0 assuming that the value of L_0 for barium acetamide is 0.0964, which is the value obtained from a solution of the simultaneous equations $(L_0 - L_{0S})/(L_{0B} - L_0) = K/[A]$; the corresponding solution for K is 12.0.

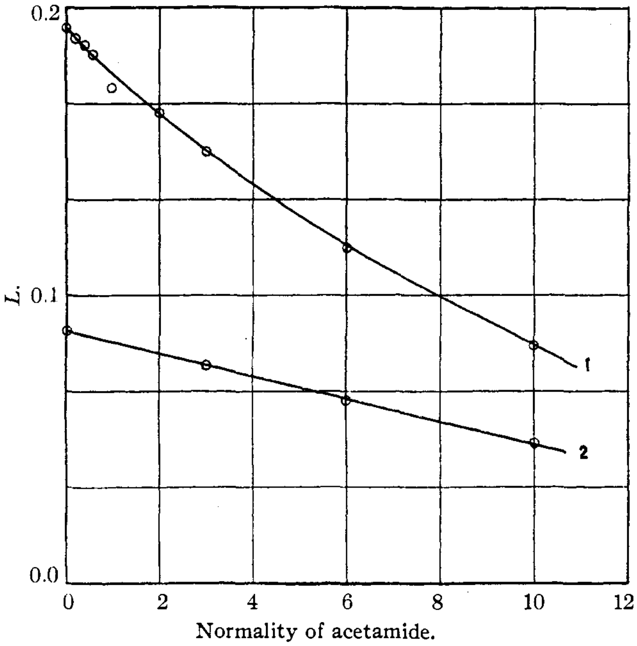

Fig. 1.—Rate of change of conductivity with change of total electrolyte plotted against concentration of acetamide: (1) $Ba(OH)_2$; (2) NaCl.

TABLE III

CORRECTED VALUES OF L AND THE HYDROLYSIS CONSTANT OF ACETAMIDE ION

Normality of acetamide	L	L_0	K (hydrolysis constant of acetamide ion)
0	0.1928	0.1928	..
0.5	.1847	.1891	12.0
1.0	.1771	.1855	12.2
2.0	.1631	.1792	12.2
3.0	.1502	.1736	12.1
4.0	.1382	.1686	11.9
5.0	.1272	.1641	11.8
7.0	.1075	.1569	11.8
10.0	.822	.1495	12.3

The close agreement of K does not indicate a corresponding accuracy in the determination, for if there is any trend in the values of K with the normality of acetamide, there would be a corresponding error in the value of L_0 for barium acetamide, such as to make the values of K agree with themselves; so that the hydrolysis constant of acetamide must be taken as equal to 12 ± about 2.

Since the order of L_0 for various electrolytes corresponds roughly to the order of their λ_∞'s, the value obtained for the L_0 of barium acetamide (0.0964) gives us an approximate measure of the mobility of the acetamide ion. This mobility appears to be between that of chloride ion and acetate ion. A mobility very close to that of acetate ion might be expected, so that the value of $K = 12$ is more likely to be too low than too high.

The dissociation constant of acetamide as an acid may be taken as equal to 10^{-14} divided by 12 or 8.3×10^{-16}. The effect of 0.05 N barium salts on the hydrolysis constant has been neglected in obtaining this value, but the error introduced is probably no greater than other uncertainties in the determination. Acetamide is therefore very nearly as strong an acid as it is a base. The basic constant has been measured as 3×10^{-15} at 25° by Walker.[3]

Experimental Details

The usual conductivity apparatus was used. The cell was balanced against a variable box type resistance by means of a Leeds and Northrup Kohlrausch bridge. The two sides were also balanced for capacity by means of a variable condenser. All the measurements at any fixed concentration of acetamide were made at practically the same time, a battery of conductivity cells, previously calibrated against each other, being used. In the time necessary for a comparison of the cells there was no sign of a change of conductivity.

The acetamide was purified by repeated crystallization from ethyl acetate and from chloroform. The characters of the curves obtained by plotting conductivity against concentration of total barium hydroxide added at various acetamide concentrations show that the acetamide was sufficiently pure. Such curves should point toward the ordinate, as the values of L are less than those of λ_∞ at the concentrations used, but if any acidic impurity is present they should point to lower positions on the ordinate, or even appear as if they would cut the abscissa in the more concentrated solutions of acetamide. If the acidic impurity is not all neutralized by the first addition of base, then the curves will tend to flatten out at the lower values of base. The former of these phenomena was observed but the latter was absent. This shows that there was enough acidic impurity (probably ammonium acetate) present to have caused significant errors in conductivity measurements, but not enough to change the values of the rate of change of conductivity with respect to total base added.

Benzamide

An attempt was made to measure the acidic strength of benzamide by the same method. However, only slight changes in the values of L from that of pure barium hydroxide could be obtained with solutions saturated with respect to benzamide. At 0.02 N and 0.04 N benzamide the values of L were about 1 and 2% less than that of pure barium hydroxide. These changes are only about five times as great as those in corresponding solutions of acetamide, so that the rough estimate may be

---

[3] Walker, *Z. physik. Chem.*, **4**, 319 (1889).

made that benzamide is about five times as strong as acetamide. Oliveri-Mandala[4] found a value of 1.2×10^{-7} for the acid dissociation constant of benzamide at 20°. If benzamide were so strong an acid, 0.02 N benzamide would have completely neutralized the very dilute solutions of barium hydroxide used, and the values of L should be those of barium benzamide. That this salt has the same L as barium hydroxide is extremely unlikely, so that it may be concluded that the value of 1.2×10^{-7} for the acid dissociation constant of benzamide is erroneous.

Summary

The partial differential of the electrical conductivity of solutions of barium hydroxide with respect to the concentration of total base at constant acetamide concentration was measured at 25°.

The values of this quantity were obtained at several concentrations of acetamide and in pure water. All the measurements were made over the same range of total electrolyte concentration and the differential quantity was estimated in all cases at the same electrolyte concentration.

It has been shown that the influence of acetamide on the mobilities of the ions can be eliminated from these measurements. This correction has been made, and from the variation of the corrected values with the concentration of acetamide, the hydrolysis constant of acetamide ion was calculated. It was found to be 12. This value corresponds to an acid dissociation constant for acetamide equal to 8×10^{-16}.

Similar measurements on benzamide showed that it is an acid whose dissociation constant is between 1×10^{-14} and 1×10^{-15}. A more accurate determination was not possible owing to the low solubility of benzamide in water.

The value obtained for the dissociation constant of benzamide is in marked disagreement with that at present in the literature, which is 1.2×10^{-7} at 20°.

BERKELEY, CALIFORNIA

---

[4] Oliveri-Mandala, *Gazz. chim. ital.*, **46**, I, 298 (1916).