LXXXVI. THE BASIC DISSOCIATION CONSTANT OF VALINE.

By LESLIE JULIUS HARRIS.

From the Biochemical Laboratory, Cambridge.

(Received August 3rd, 1923.)

A KNOWLEDGE of the basic dissociation constant of valine was desired by the writer in connection with the methods which he has recently devised [1923] for estimating amino-acids by titrating under conditions governed by K_a and K_b values.

The present determination has been derived from the p_H -neutralisation curve. Known volumes of valine dissolved in water at a given concentration were treated with varying amounts of 0.1N HCl, and the resulting p_H values determined by means of the quinhydrone electrode. p_H was calculated from the observed E.M.F. reading by the formula

$$p_H = \frac{c - (\text{E.M.F. obs.})}{.059},$$

the value of the calomel half cell, c , being determined by reading against solutions of accurately known p_H : 0.1 HCl and buffer solutions of amino-acids plus HCl. All determinations were carried out in a box at 25°.

To obtain the "ideal titration curve," each reading was corrected for the amount of acid necessary to bring the solvent alone (without valine) to the same p_H and the same total volume, in the manner previously described by the writer [1923], and in accordance with the formula

$$i = d - \frac{ge}{100}$$

where i = corrected amount of acid used in titrating to a given p_H ;

d = uncorrected amount of acid used in titrating to a given p_H ;

g = blank for 100 cc. (no. of cc. of $N/10$ acid necessary to bring solvent alone to the given p_H and to a final volume of 100 cc.);

e = final volume of titrated fluid, after addition of d cc. of HCl.

The value of g corresponding to each p_H reading is based on the formula

$$p_H = -\log \left(\alpha \cdot \frac{g}{0.001} \right)$$

and in practice is read from a curve constructed by the writer [1923].

In the table below are shown the results obtained in a typical titration of valine with HCl, and also the manner of introducing the blank correction to obtain the ideal curve.

Titration of 10 cc. of M/20 valine.

(d)	(e)	(f)	(g)	(h)	(i)
N/10 HCl added cc.	Total vol. of liquid after titration ($e = d + 10$) cc.	Corresponding p_H values	Blank for 100 cc. total vol. (read from curve) cc.	Blank for given total vol., e ($h = \frac{ge}{100}$) cc.	Corrected vol. of N/10 HCl added ($i = d - h$) cc.
0.1	10.1	3.98	—	—	0.1
0.4	10.4	3.38	0.5	0.05	0.35
1.0	11.0	2.93	1	0.1	0.9
1.3	11.3	2.79	2	0.2	1.1
1.6	11.6	2.69	2	0.2	1.4
2.0	12.0	2.58	3	0.4	1.6
2.3	12.3	2.51	4	0.5	1.8
3.0	13.0	2.34	5	0.7	2.3
3.2	13.2	2.29	5	0.7	2.5
3.4	13.4	2.24	6	0.8	2.6
4.0	14.0	2.12	8	1.1	2.9
5.0	15.0	1.96	12	1.8	3.2
6.0	16.0	1.85	15	2.4	3.6
7.0	17.0	1.78	19	3.2	3.8
8.0	18.0	1.69	23	4.1	3.9
9.0	19.0	1.64	25	4.8	4.2
10.0	20.0	1.58	29	5.8	4.2
12.0	22.0	1.51	35	7.7	4.3
15.0	25.0	1.46	40	10	5

Values in columns (g) are given to the nearest integer, in columns (h) and (i) to the first place.

In successive titrations agreement between duplicates could be obtained to within about p_H 0.2.

In the diagram, circled points represent uncorrected readings, crosses the ideal corrected values deduced therefrom. The latter are in very close agreement with the titration curve¹ of a base with $K_b = 2 \times 10^{-12}$, which is represented by the unbroken line calculated from the formula

$$\log \frac{1}{[H^+]} = \log \frac{K_b}{K_w} + \log \frac{(1-a)}{a}.$$

The quinhydrone electrode has not previously been utilised for the determination of a dissociation constant, but it should prove of general applicability when used in conjunction with the above method. The writer has also found that provided it be properly standardised it may be conveniently employed for the accurate determination of amino-groups in amino-acids and generally of both basic and acidic groups.

¹ At the acid end of the titration the ideal corrected values tend to lie around the theoretical curve rather than to be strictly coincident with it, due to the very large magnitude of the blank corrections; a very slight percentage error in reading the correction, g , leading to a comparatively large error in the ideal corrected value.

SUMMARY.

Known amounts of HCl were added to valine and the resulting p_H values were determined by means of the quinhydrone electrode. Correcting for the effect of the solvent by the writer's method the ideal titration curve was deduced and showed a value of $14 - p_{K_b} = 2.3$, or $K_b = 2 \times 10^{-12}$ at a dilution of $\frac{M}{20}$, and $t = 25^\circ$.

REFERENCE.

L. J. Harris (1923). *Proc. Roy. Soc. Lond. B.* 95, 440.