tyric acid are configurationally identical and, by the previous correlation[5] of this latter compound into the natural amino acid series, the methionine derived from proteins is *l*(−)-methionine.

Experimental

Hydrogenolysis of *d*(+)-Methionine.—A solution of 150 mg. of *d*(+)-methionine[1] in 15 ml. of water was heated with about 1.5 g. of Raney nickel catalyst[3] at 90–95° for one-half hour. The nickel was removed by filtration and was washed on the filter with 350 ml. of hot water, the washings being added to the filtrate. The aqueous solution was concentrated *in vacuo* to a 1-ml. volume. Addition of absolute alcohol precipitated the amino acid, which was recovered by filtration. Recrystallization from dilute alcohol gave 16.9 mg. of *d*(−)-α-aminobutyric acid, m. p. 275° (dec.) (macro-block); $[\alpha]^{23}\text{D}$ −17.1° (*c*, 1.1 in *N* hydrochloric acid). The recorded[4] melting point for this compound is 303° (cor.). The recorded[4] rotation for the hydrochloride is $[\alpha]^{20}\text{D}$ −14.34°; if the above be recalculated on the basis of the hydrochloride, the value becomes $[\alpha]^{23}\text{D}$ −13.1°.

***d*(−)-α-Benzoylaminobutyric Acid.**—The α-aminobutyric acid used to determine the rotation was recovered by neutralization of the solution, followed by concentration and precipitation with alcohol. It was combined with the aminobutyric acid recovered from the recrystallization filtrates and used to prepare the benzoyl derivative.

The *d*(−)-α-aminobutyric acid was dissolved in 10 ml. of *N* sodium hydroxide. To the cooled solution was added 0.5 ml. of benzoyl chloride. The mixture was stirred for four hours at 0°. At the end of this time some insoluble material was removed by filtration. The filtrate was slightly acidified by addition of *N* hydrochloric acid, and was extracted continuously with chloroform for fifteen hours to remove the greater part of the benzoic acid. This extract was evaporated to dryness and the residue was extracted with hot petroleum ether (b. p. 90–100°); the residue was entirely soluble and was discarded.

The aqueous solution in the extractor was made acid to congo red by addition of concentrated hydrochloric acid, and was again extracted continuously with chloroform for sixteen hours. Evaporation of the chloroform extract gave a crystalline material which, after being extracted twice with boiling petroleum ether (b. p. 90–100°), weighed 55.9 mg.; m. p. 108–110°. This was recrystallized from ethyl acetate–petroleum ether to constant melting point, 110–111°; $[\alpha]^{24}\text{D}$ −31.4° (*c*, 1.2 in 0.07 *N* sodium hydroxide). The literature values are m. p. 120–121° (cor.),[4] 110–111°,[6] 111–112°[7] and 113–114°[7]; $[\alpha]^{20}\text{D}$ −31.8° (in sodium hydroxide solution).

Anal. Calcd. for $C_{11}H_{13}O_3N$: C, 63.76; H, 6.32; N, 6.76. Found: C, 63.46; H, 6.60; N, 6.51.

Hydrogenolysis of *l*(−)-Cystine.—To a solution of 9.6 g. of *l*(−)-cystine in 300 ml. of water was added about 60 g. of Raney nickel catalyst. The mixture was shaken vigorously for a few minutes, and then was heated at about 45° for one-half hour. At the end of this time the nickel was removed and was washed on the filter with 600 ml. of water, these washings being added to the filtrate. Concentration *in vacuo* of this aqueous solution to a sirup, followed by the addition of absolute alcohol, gave white crystals of *l*(+)-alanine. This product was recrystallized from dilute alcohol; $[\alpha]^{21}\text{D}$ +13.5° (*c*, 6.29 in 1.07 *N* hydrochloric acid). Recalculation of the specific rotation based upon the concentration of alanine hydrochloride in the solution gives $[\alpha]^{21}\text{D}$ +9.6°; the recorded value[8] is $[\alpha]^{20}\text{D}$ +10.4° for *l*(+)-alanine hydrochloride in water.

RESEARCH LABORATORIES
MERCK AND CO., INC.
RAHWAY, N. J.

RECEIVED JANUARY 11, 1947

The Basic Dissociation Constants of Some Aliphatic Hydroxyamines[1]

BY SAMUEL GLASSTONE AND ALFRED F. SCHRAM

The aliphatic hydroxyamines form a group of compounds of considerable interest. A comprehensive study of their electrochemical properties had been planned, but the work was interrupted by the war emergency; as its continuation is uncertain, the results so far obtained, on the basic dissociation constants in aqueous solution of four mono- two di-, and one tri-hydroxyamines, are reported here.

With the exception of 2-amino-1-propanol, which was obtained from the Eastman Kodak Company, the hydroxyamines were supplied by the Commerical Solvents Corporation. The liquids were in general purified by fractional distillation under reduced pressure, and the solids by crystallization from absolute alcohol. Since 2-amino-1,3-propanediol is very viscous, it could not be distilled satisfactorily. It was therefore purified by dissolving in chloroform and adding ether until about half of the original material had separated. This procedure was repeated until a clear, colorless liquid was obtained.

The dissociation constants were calculated from *p*H measurements, made with a glass electrode, of aqueous solutions of the hydroxyamines to which had been added various known amounts of hydrochloric acid. It can be readily shown[2] that in such solutions

$$a_{\text{OH}^-} = K_b \frac{b - B}{B} \cdot \frac{\gamma_{\text{B}}}{\gamma_{\text{BH}^+}} \qquad (1)$$

where a_{OH^-} is the activity of the hydroxyl ions, K_b is the true (or thermodynamic) dissociation constant of the base, γ_{B} and γ_{BH^+} are the activity coefficients of the undissociated base (RNH_2) and of the corresponding ammonium ion (RNH_3^+), respectively, b is the initial concentration of the base in moles per liter, and B is defined by

$$B = a + c_{\text{OH}^-} - c_{\text{H}^+}$$

where a is the concentration of the added acid in the solution, and c_{OH^-} and c_{H^+} represent the concentrations of the hydroxyl and hydrogen ions, respectively. In virtually all the cases studied c_{H^+} was negligible, and c_{OH^-} was taken as K_w/a_{H^+}, with a_{H^+} derived from the measured *p*H value. Upon taking logarithms of eq. (1) and utilizing the fact that $p\text{H} + p\text{OH} = pK_w$, it is seen that

$$pK_w - p\text{H} = pK_b + \log \frac{B}{b - B} + \log \frac{\gamma_{\text{BH}^+}}{\gamma_{\text{B}}} \qquad (2)$$

According to the Debye–Hückel–Brønsted equation, $\log \gamma_{\text{BH}^+}/\gamma_{\text{B}}$ may be replaced by $-A\sqrt{\mu} + C\mu$, where μ is the ionic strength of the solution, and the Debye–Hückel constant A is 0.509 at 25°.

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(6) Smorodinzew, *Z. physiol. Chem.*, **124**, 123 (1923).

(7) Abderhalden and Bahn, *ibid.*, **245**, 246 (1937).

(8) Fischer, *Ber.*, **39**, 453 (1906).

(1) From the Master's Thesis of Alfred Francis Schram, University of Oklahoma, 1943.

(2) *Cf.* S. Glasstone, "An Introduction to Electrochemistry," D. Van Nostrand Co. Inc., New York, N. Y., 1942, p. 394.

The value of C is immaterial for the present purpose. Upon inserting this result in eq. (2) and rearranging, it follows that

$$pH + \log\frac{B}{b - B} - A\sqrt{\mu} = pK_w - pK_b - C\mu$$

The plot of the left-hand side of this expression, for various values of a and b, against μ should thus be a straight line, the intercept for zero ionic strength giving $pK_w - pK_b$. Since pK_w is known to be 14.00 at 25°, pK_b for the base can be evaluated.

The glass electrode was calibrated by means of solutions which give a good approximation to "thermodynamic" results.[3] The pK_b values obtained may thus be regarded as giving true dissociation constants. The reliability of the method was confirmed by its use to determine pK_1 for glycine; the result was 2.35 at 25°, in agreement with that obtained from cells without liquid junction.[4]

The dissociation constants found in the present work are recorded in Table I; the pK_b for ethylamine, for comparison purposes, is 3.25.

TABLE I

BASIC DISSOCIATION CONSTANTS IN AQUEOUS SOLUTION AT 25°

	Base	pK_b
Monohydroxyamines		
I.	2-Amino-1-ethanol	4.55
II.	2-Amino-1-propanol	4.57
III.	2-Amino-1-butanol	4.48
IV.	2-Methyl-2-amino-1-propanol	4.28
Dihydroxyamines		
V.	2-Methyl-2-amino-1,3-propanediol	5.24
VI.	2-Ethyl-2-amino-1,3-propanediol	5.20
Trihydroxyamine		
VII.	Tris-(hydroxymethyl)-aminomethane	5.97

The results show that the introduction of an hydroxyl group into an aliphatic amine decreases the basic strength, as is to be expected from the electron attracting ($-I$) effect of this group. The first OH group increases pK_b by 1.3, the second by 1.0, and the third by about 0.75. From the pK_b values of the compounds I, II and III it is seen that the influence of the methyl group is small, although the anticipated $+I$ effect, resulting in an increase in strength of the base, is evident in IV, where both hydrogen atoms on the carbon attached to the nitrogen have been replaced by methyl groups.

Acknowledgment.—The authors wish to thank the Commercial Solvents Corporation for the gift of generous samples of six hydroxyamines.

BERKELEY, CALIFORNIA RECEIVED FEBRUARY 3, 1947

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[3] Hitchcock and Taylor, THIS JOURNAL, **59**, 1812 (1937); **60**, 2710 (1938); MacInnes, Belcher and Shedlovsky, *ibid.*, **60**, 1094 (1938).

[4] Owen, *ibid.*, **56**, 24 (1934).

The Interaction of Hydrous Alumina with Salt Solutions

BY R. P. GRAHAM AND A. E. HORNING[1]

This note is concerned with the changes in pH of certain potassium salt solutions caused by the addition of powdered hydrous alumina. The samples of alumina used (with the exception of one of powdered bauxite) were the same as those studied in a recently-published investigation of the reactivity of hydrous alumina toward acids,[2] and the present work was carried out immediately after the study involving acids.

Experimental

The potassium salt solutions were prepared from analyzed grade reagents and distilled water freed of carbon dioxide by boiling. By reference to a Leeds and Northrup pH meter (no. 7662) standardized by the use of recrystallized analyzed grade potassium acid phthalate, the solutions were brought to a pH of 7.00 ± 0.01 using a 0.1 N solution of potassium hydroxide or of the appropriate acid. The solution under study was pipetted into a 400-ml. beaker clamped in a bath maintained at 25.0 ± 0.1°, the sample of hydrous alumina added while the solution was being agitated mechanically, and the changes in the pH of the solution followed by means of the pH meter (the stirrer was stopped momentarily when a reading was being taken). The meter was standardized immediately before each run, and the standardization checked at the conclusion of it. The pH values given in the table below are the maximum values attained (rounded to the nearest tenth of a pH unit); maximal values were reached in most cases in less than thirty minutes.

TABLE I

INCREASE IN pH OF POTASSIUM SALT SOLUTIONS UPON ADDITION OF POWDERED HYDROUS ALUMINA[a]

I. Variation in Nature of Salt Soln.			II. Variation in Concn. of Salt Soln.	
Salt (M)		pH attained[b]	M of pot. oxalate	pH attained[b]
Fluoride	0.1	9.6	0.0005	8.0
Oxalate	.05	8.6	.0050	8.3
Sulfate	.05	8.0	.0125	8.4
Nitrate	.1	7.3	.0250	8.5
Chloride	.1	7.3	.0500	8.6
Perchlorate	.1	7.1	.250	8.7
Phosphate	.1	7.0	1.000	8.7

III. Variation in Mass of Alumina		IV. Variation in Nature of Alumina	
G. of alumina "60"	pH attained[c]	Alumina (0.5000 g.)	pH attained[c]
0.1000	7.7	"26"	8.0
.2000	8.5	"60"	8.6
.5000	8.6	"95"	8.6
1.000	8.7	Bauxite	8.1

[a] Sample of hydrous alumina added in each case to 100.0 ml. of salt solution, the pH of which had previously been adjusted to 7.00 ± 0.01. [b] Using 0.5000 g. of alumina "60." [c] Using 0.05 M potassium oxalate solution.

Discussion

The increase in the pH of neutral potassium salt solutions upon the addition of hydrous alumina

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[1] Present address: Calco Chemical Division, American Cyanamid Co., Bound Brook, N. J.

[2] Graham and Thomas, THIS JOURNAL, **69**, 816 (1947).