methyl ether. This acid was also prepared from methyl 3-hydroxy-5-*bisnor*-cholenate.

2. Several rearrangement and conversion products of methyl 6-methoxy-*i*-*bisnor*-cholenate have been described.

EVANSTON, ILLINOIS RECEIVED DECEMBER 28, 1942

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

Studies on High Molecular Weight Aliphatic Amines and their Salts. X. Ionization Constants of Primary and Symmetrical Secondary Amines in Aqueous Solution

BY C. W. HOERR, M. R. MCCORKLE AND A. W. RALSTON

The ionization constants of the lower amines in aqueous solution have been accurately determined by several methods.[1-7] However, no constants have yet been reported for the amines containing 6 or more carbon atoms. Studies upon other high molecular weight organic derivatives of ammonia[4] and upon the higher fatty acids[8] have demonstrated methods by which the relative strengths of compounds which have limited solubility in water can be evaluated indirectly.

The method adopted for this investigation was the measurement of the conductance of the amines in various dilutions of alcohol. It has been shown that when the apparent strength in alcohol is plotted in logarithmic units against the alcohol content, the form of the curve obtained is always such as to permit satisfactory extrapolation to the strength in pure water.[9] Hence, for the amines whose limited solubility in water precluded direct measurement, the conductivity was determined in various dilutions of ethanol, the log of their equivalent conductance was plotted against the volume percentage of ethanol, and the ionization constants were calculated from the extrapolated values obtained.

The amines used in this investigation, with the exception of the butyl- and amylamines, were prepared by hydrogenation of the corresponding nitriles.[10] The primary amines were separated from the secondary amines by vacuum distillation. The secondary amines were purified by crystallization from ethanol with the exception of dihexyl- and dioctylamines which were distilled. Normal and isobutylamine and normal and isoamylamine were commercial products purified by distillation. All of the amines were protected from the atmosphere to minimize absorption of carbon dioxide.

The conductivity apparatus employed and the preparation of the conductivity water have been described elsewhere.[11] The specific conductance

TABLE I

IONIZATION CONSTANTS OF THE ALIPHATIC AMINES IN WATER AT 25°

Amine	Λ_0	Concn. range investigated, moles/liter	$K_B \times 10^{-4}$
Butyl[a]	235	0.0004–0.073	4.1
Isobutyl[b]	235	.0008– .057	2.7
Amyl[c]	232	.0008– .049	4.3
Isoamyl[d]	232	.0008– .040	4.0
Hexyl	229	.0008– .046	4.4
Dihexyl	214	.0008– .030	10.2
Heptyl	226	.0008– .022	4.6
Octyl	223	.0008– .016	4.5
Dioctyl	208	.0008– .014	10.2
Nonyl	220	.0008– .015	4.4
Decyl	217	.0008– .012	4.4
Undecyl	214	.0008– .011	4.3
Dodecyl	211	.0008– .011	4.3
Didodecyl	197	.0008– .011	9.9
Tridecyl	208	.0008– .011	4.3
Ditridecyl	193	.0008– .008	9.9
Tetradecyl	205	.0008– .008	4.2
Pentadecyl	202	.0008– .008	4.1
Dipentadecyl	187	.0008– .008	10.0
Hexadecyl	199	.0008– .008	4.1
Heptadecyl	196	.0008– .008	4.0
Octadecyl	193	.0008– .008	4.0
Dioctadecyl	180	.0008– .008	9.9
Docosyl	180	.0008– .008	4.0

[a] Hall, *et al.*,[4] $K_B = 4.1 \times 10^{-4}$. [b] Bredig,[1] $\Lambda_0 = 235$, $K_B = 2.6 \times 10^{-4}$; Hall, *et al.*,[4] $K_B = 2.6 \times 10^{-4}$; Marcinkow, *et al.*,[7] $K_B = 3.1 \times 10^{-4}$. [c] Hall, *et al.*,[4] $K_B = 4.4 \times 10^{-4}$. [d] Bredig,[1] $\Lambda_0 = 232$, $K_B = 4.0 \times 10^{-4}$; Hall, *et al.*,[4] $K_B = 4.4 \times 10^{-4}$; Marcinkow, *et al.*,[7] $K_B = 5.10 \times 10^{-4}$.

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(4) Hall and Sprinkle, *ibid.*, **54**, 3469 (1932).

(5) Britton and Williams, *J. Chem. Soc.*, 796 (1935).

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(8) Halford, THIS JOURNAL, **53**, 2944 (1931).

(9) Michaelis and Mizutani, *Z. physik. Chem.*, **116**, 135 (1925); **118**, 318, 327 (1925).

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(11) Ralston, Hoerr and Hoffman, THIS JOURNAL, **64**, 97 (1942).

of the amine solutions was corrected for the conductivity of dissolved carbon dioxide by the usual method.[2]

Results

The limiting equivalent conductances (Λ_0) of the amines were calculated from their measured conductances by means of Ostwald's dilution law, which has been applied satisfactorily to other weak organic bases.[1] The ionization constants were calculated by the usual equation. The values obtained are shown in Table I.

The limiting equivalent conductances are probably accurate to ±2 mhos, and the ionization constants are probably accurate within $\pm 0.2 \times 10^{-4}$ over the concentration ranges tabulated.

Nonyl- and decylamines were each studied in both pure water and in various dilutions of ethanol. Extrapolation of the equivalent conductances in the ethanol solutions yielded values which agreed with those measured in pure water. Figure 1 shows the curves for three decylamine solutions in various dilutions of ethanol. Ionization constants were obtained in this manner for the homologs above decylamine and for the secondary amines.

Bredig[1] and Hall[4] have reported a difference of about 0.39 pK unit between the lower amines and their corresponding secondary homologs. The values in Table I show an average difference of 0.37 ± 0.03 pK unit.

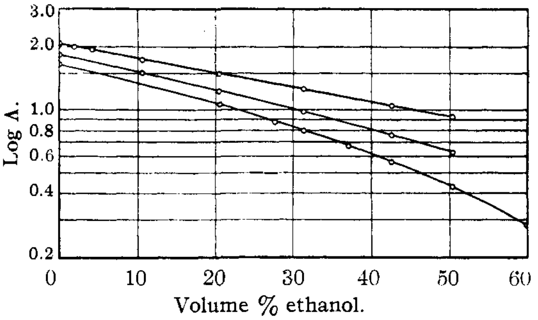

Fig. 1.—Equivalent conductance of decylamine in ethanol: from top to bottom, 0.00080, 0.00322 and 0.00800 *M*, respectively.

Halford[8] states that lengthening of the hydrocarbon chain of aliphatic acids produces a definite weakening effect in the relative strength of the acids. This effect has not been noted in the amines which we have investigated.

Summary

Ionization constants have been calculated from conductivity measurements for the normal primary aliphatic amines containing 4 to 18 carbon atoms, inclusive, isobutyl- and isoamylamines, docosylamine, and the symmetrical normal secondary aliphatic amines containing 6, 8, 12, 13, 15 and 18 carbon atoms in each hydrocarbon chain.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Stereochemistry of Coördination Number Eight[1]

BY LOUIS E. MARCHI,[2] W. CONARD FERNELIUS[3] AND JAMES P. MCREYNOLDS

The stereochemistry of compounds of elements exhibiting coördination numbers four and six has been definitely established. However, very little is known concerning the stereochemistry of compounds of elements exhibiting coördination number eight even though many such compounds are known (Table I) and the possibilities for the preparation of many more are great. J. D. Main Smith[4] presents tables showing (for both mono- and bidentate groups) the types, classes, and isomeric forms theoretically expected for compounds exhibiting coördination numbers four (planar and tetrahedral) and six (octahedral). He intimates that the same has been done for compounds showing coördination number eight, assuming a cubic arrangement. The consideration of possible configurations and the numbers and types of isomers arising from these configurations is a necessary preliminary to any chemical approach to the

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(4) J. D. Main Smith, "Chemistry and Atomic Structure," Ernest Benn, Ltd., London, 1924, p. 97.