The Dissociation Constant of Methylamine at 25° C.[1]

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An electromotive force method for the determination of the ionization constants of weak acids and weak bases has been developed by Harned and his associates (1). Application of the method to solutions of ammonia and organic bases presents the difficulty of finding an electrode, reversible to the anion, which is sufficiently insoluble in those solutions. In preliminary measurements made in ammonia solutions, Owen (2) studied the silver-silver iodide electrode and found that this electrode gave promise of being suitable to a limited extent in solutions of bases.

In the present investigation, the dissociation constant of methylamine has been determined at 25° C., employing the silver-silver iodide electrode in a cell of the following type,

$$(\mathrm{Pt})\ H_2/CH_3NH_2\ (m_1),\ CH_3NH_3I\ (m_2),\ KI\ (m_3)\ /\ AgI,\ Ag$$

Applying the method of Harned and his co-workers in the manner used by Nims and Smith (3) for the second acid constant of *dl*-alanine, the electromotive force of the cell may be expressed by,

$$\frac{(E-E_0)F}{2.3026\,RT} + \log \frac{m_I\,(m_{OH}+m_I-m_K)}{m_1-m_{OH}} = F_1$$

$$= \log K_b - \log \frac{\gamma_{CH_3NH_2}\,\gamma_I}{\gamma_{CH_3NH_2}}, \qquad (1)$$

in which m_I, m_{OH} and m_K refer to the total molalities of the indicated ions, m, to the molality of methylamine, and K_b to the dissociation constant of methylamine, which is given by the equation,

$$K_b = \frac{a_{CH_3NH_3}}{a_{CH_3NH_2}\,a_H}. \qquad (2)$$

The molality of the hydroxyl ion is evaluated from the ionization constant of water as was done by Nims and Smith (3). At zero ionic strength ($\mu = 0$), log ($\gamma CH_3NH_3\ \gamma I/\gamma CH_3NH_2$) becomes equal to zero, so that F_1 equals log K_b. Thus, an extrapolation to zero ionic strength of a plot of the values of F_1 obtained for a series of cells in which the constituents are at varying concentrations against the ionic strength enables evaluation of K_b.

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[1] This paper is constructed from a dissertation presented by Ambrose F. Schmelzle to the Faculty of the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

Experimental

Materials. Monomethylamine hydrochloride purchased from the Eastman Kodak Co. was dried at 110° C and extracted with purified chloroform (4). The extracted salt was again dried and stored over calcium chloride. Methylamine solutions were prepared by dissolving in redistilled water methylamine gas generated by dropping a concentrated solution of sodium hydroxide on the purified hydrochloride (mixed with a small quantity of yellow mercuric oxide). The solutions were standardized with constant boiling hydrochloric acid.

Methylamine hydroiodide was prepared by dissolving methylamine gas generated as described above in ether and then passing hydrogen iodide vapors over the solution. The hydrogen iodide was prepared by dropping a 57% solution of hydroiodic acid on phosphorus pentoxide. The hydroiodide was recrystallized twice by dissolving in a minimum of ethyl alcohol and then adding a large excess of ether. The recrystallized salt was dried first by centrifugation and then in an oven at 50° C. for about 24 hours. It was stored over activated alumina. Baker's special C. P. grade of potassium iodide was recrystallized twice from redistilled water at 45° C., (5) and dried in a vacuum.

The cell solutions were prepared by weighing out a definite quantity of the methylamine solution, and adding weighed quantities of water, methylamine hydroiodide, and potassium iodide to give a solution of desired ionic strength. Weights were corrected for the buoyancy effect of air when necessary.

Apparatus. The cell vessel employed was similar to that used by Nims and Smith (6) with the modification that it was constructed from two elements of a Pyrex ground glass joint. The vessel was joined by means of a ground glass joint to two Bichowsky and Storch (7) saturators containing solutions of approximately the same concentration as the cell solution. The silver-silver iodide electrodes were of the thermal type prepared as described by Owen (8). The hydrogen electrodes were prepared according to the directions of Popoff, Kunz and Snow (9) with the exception that no lead acetate was added to the chloroplatinic acid plating solution. Commercial tank hydrogen was purified by passing over copper gauze heated to 450° C. and then through a series of wash bottles containing successively water, dilute potassium hydroxide solution, dilute potassium permanganate solution, and water.

The cell vessel and the saturators were immersed in a constant temperature bath kept at 25° ± 0.07° C. At least one-half hour was allowed for the apparatus to reach thermal equilibrium. The hydrogen purification train was flushed out for five minutes before hydrogen gas was passed through the cell. Potential readings were made at one minute intervals by means of a Leeds and Northrup type K potentiometer and a type R reflecting galvanometer. The potentiometer circuit was balanced against an Eppley standard cell which was certified by the manufacturer and checked against another certified cell.

Data and Results

The values obtained for the electromotive force of cells containing the methylamine-methylamine hydroiodide buffer solutions and potassium iodide at 20° C. are listed in Table I. The ionic strength was calculated on the basis of complete dissociation of potassium iodide and of methylamine hydroiodide, and of 15% dissociation of methylamine. The electromotive force values listed represent the maximum values observed for each experiment corrected to one atmosphere pressure. This maximum value was generally reached within a half-hour. The potential remained constant to within 0.05 millivolt for about ten minutes and then drifted off indefinitely at the rate of about 0.1 millivolt every five minutes. This drift was thought not to be due to the loss of methylamine in the hydrogen stream in view of the low vapor pressure at the concentration employed (10). Owen (11) reported a similar drift in measurements with the silver iodide electrode in ammonia solutions. The possibility of the potential drift being due to the solvent action of the solutions on the glass vessels was ruled out by coating the inner walls of all vessels with paraffin.

In Figure 1 the values of F_1 (equation 1) are plotted against the ionic strength. The values of E_0 used in the computation of the extra-

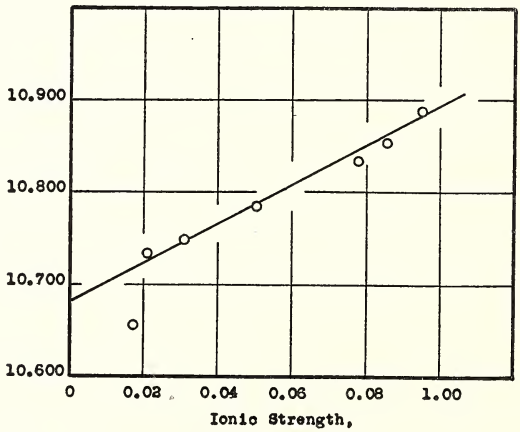

Fig. 1. Plot of F_1 against the ionic strength in the determination of the dissociation constant of methylamine at 25°C.

polation function, F_1 were taken from the work of Owen (8). These are opposite in sign to the measured electromotive force values since, as is pointed out by Pearce and Fortsch (12) a change in the sign of the potential of the silver-silver iodide electrode occurs between a hydrogen iodide concentration of 0.079 *m* and 0.050 *m*. The extrapolated value of F_1 is log K_b, which, when subtracted from the value of K_w reported by Harned and Greary (13), gives the classical dissociation constant of methylamine.

TABLE I.—Electromotive Force Data for the Cell, (Pt) H_2/CH_3NH_2 (m_1), CH_3NH_3I (m_2), KI (m_3)/AgI, Ag, at 25° C.

m CH_3NH_2	m CH_3NH_3I	m KI	Ionic Strength (μ)	E	F_1
0.02945	0.03012	0.04311	0.0776	0.5536	10.8251
0.01186	0.01210	0.01731	0.0212	0.5707	10.7353
0.02705	0.02741	0.01970	0.0512	0.5628	10.7863
0.01664	0.01687	0.01212	0.0315	0.5726	10.7498
0.02969	0.03009	0.06018	0.0947	0.5525	10.8979
0.02983	0.02987	0.05082	0.0852	0.5530	10.8504
0.00850	0.00837	0.00869	0.0172	0.5804	10.6551

The value of K_b for methylamine computed from the data is 4.71×10^{-4} at 25° C. compared to 4.38×10^{-4} obtained by Harned and Owen (14) from potentiometric data employing cells with negligible liquid junctions. From conductivity data, Bredig (15) obtained a value of 5.0×10^{-4}. Although better agreement might be desirable the value of 4.71×10^{-4} obtained from the electromotive force measurements reported in this paper is as accurate as could be expected considering the experimental difficulties encountered. As a general conclusion, the method as outlined seems to lack the precision and reproducibility in the determination of the dissociation constants of bases which it enjoys in the study of acid solutions.

Summary

The dissociation constant of methylamine has been determined from measurements of the electromotive force of cells of the type,

(Pt) H_2/CH_3NH_2, CH_3NH_3I, KI/AgI, Ag.

The classical dissociation constant of this organic base was found to be 4.71×10^{-4} at 25° C.

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