Dissociation Constant of the Primary Amines and Quaternary Ammonium-methylorange Salts.

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Abstract—The data of dissociation constants for aliphatic amines and quaternary ammonium-methylorange salts are based on the electrostatic theory of conductance. Dissociation constants for primary amines and quaternary ammonium-methylorange salts ($1 \times 10^{-5} \sim 1 \times 10^{-3}$ M) in nitrobenzene solution or water solution was evaluated from the relation of the concentration and the electric conductance at 25°C, Plots of ΛC against reciprocal conductance were linear; hence the center-to-center distance of this salt was 1.75 Å in nitrobenzene solution.

If the electrolytic materials, A·MO, are in equilibrium when dissociated, the dissociation of A·MO can be shown as follows;

$$A \cdot MO = A^+ + MO^- \tag{1}$$

The dissociation constant and dissociation degree of salts are expressed by the equations

$$K = C^2 \alpha^2 / (1-\alpha)C = \alpha^2 C / (1-\alpha) \tag{2}$$

$$\alpha = \Lambda / \Lambda_\infty \tag{3}$$

Where K is the dissociation constant, α is the dissociation degree of salt.[1]
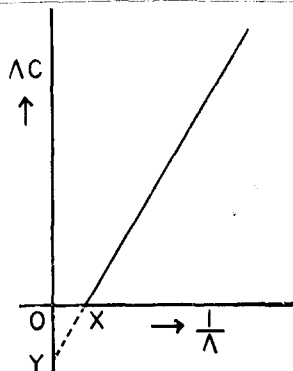Substituting (2) with (3), we find the relations (4) and (5).

$$K = \frac{\Lambda^2 C}{\Lambda_\infty (\Lambda_\infty - \Lambda)} \tag{4}$$

or

$$\Lambda C = K \left(\frac{\Lambda^2_\infty}{\Lambda} - \Lambda_\infty \right) \tag{5}$$

Thus, as shown in Fig. 1, the ΛC vs. $1/\Lambda$ plot was straight line, and the dissociation constant was measured by the equation

$$K = -(OX)(OY) \tag{6}$$

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Fig. 1—Graph of ΛC against $1/\Lambda$.

RESULTS

The values of ΛC and $1/\Lambda$ were calculated by using the conductance, initial concentration and cell constant. And the dissociation constant of salts was calculated from the equation (6). Results were illustrated in Fig. 2, Fig. 3 and Table I.
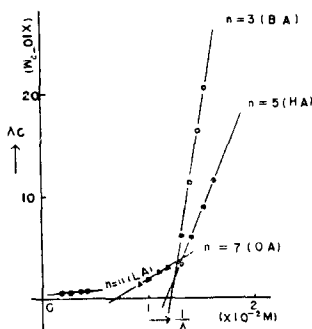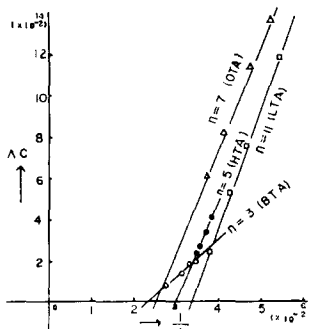

Fig. 2—Relationship of between ΛC and $1/\Lambda$ (CH_3 $(CH_2)_n NH_2$ MO in water).

Fig. 3—Relationship of between ΛC and $1/\Lambda$ ($CH_3(CH_2)_n$ $N^+(CH_3)_3 \cdot MO^-$ in N.B.).

Table I—Differences in dissociation constants of primary amines and quaternary ammonium-methylorange salts in water phase or organic solvent phase.

Compounds	K_{H2O}	$K_{N.B.}$
Butylamine-Methylorange	8.11×10^{-3}	
Hexylamine-Methylorange	3.6×10^{-3}	
Octylamine-Methylorange	0.45×10^{-3}	
Laurylamine-Methylorange	0.06×10^{-3}	
BTA-Methylorange	8.45×10^{-3}	2.16×10^{-3}
HTA-Methylorange	3.0×10^{-3}	3.44×10^{-3}
OTA-Methylorange	1.3×10^{-3}	5.05×10^{-3}
LTA-Methylorange	0.1×10^{-3}	9.1×10^{-3}

BTA: Butyltrimethylammonium.   HTA: Hexyltrimethylammonium.
OTA: Octyltrimethylammonium.   LTA: Lauryltrimethylammonium.

The increase of temperature gives an increment in conductance when the concentration of salts was in constant. But those results from Fig. 4 and Fig. 5 have little difference in their dissociation constant.
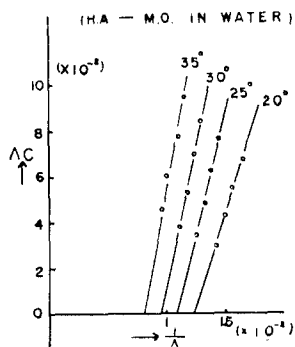

Fig. 4—Plot of against $1/\Lambda$ for $C_8H_{17}N$ $(CH_3)_3$ MO at 20°, 25°, 30° and 35°.
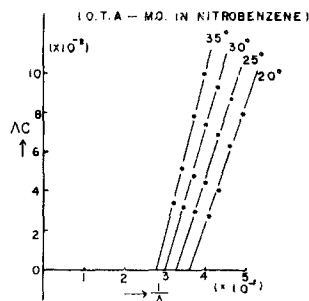
Fig. 5—Plot of ΛC against $1/\Lambda$ for $C_6H_{13}NH_2 \cdot$ MO at 20°, 25°, 30° and 35°.

It has become apparent in recent years that, while Bjerrum's theory[2] of ion-pair dissociation is quite adequate for a given solvent system, the variation of the dissociation constant for an ion-pair from solvent to solvent indicates an inability of the theory to describe experimental results completely. Most of these samples have different dissociation constants in nitrobenzene solvent having dielectric constant of 34.82. The ratios of the dissociation constants were given in Table I.

According to Bjerrum, the reciprocal of the dissociation constant is given by

$$K^{-1} = \frac{4}{1000} \left(\frac{e^2}{DKT} \right)^3 Q(b) \tag{7}$$

Where $b = e^2/a\ DKT$ and values of $Q(b)$ have been tabulated as a function of b^2,[3]. In Fig. 6, $Q(b)$ is plotted against b.
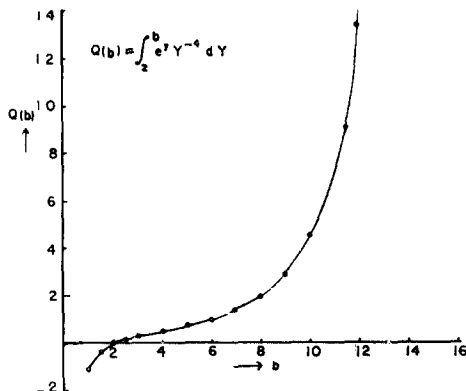

Fig. 6—Plot of $Q(b)$ against b.

If the ions are not separated by solvent molecules in the ion pair[4], the distance of closest approach a of two ions should not vary with the solvent but they are actually in contact.

If this latter assumption[5] is made, Bjerrum's K is only a function of DT alone. So it is thought that there are specific solvent effects other than that due to the dielectric constant.

In a nitrobenzene-carbon tetrachloride mixture, it has been found[6] that the electrostatic model of the sphere-in-a-continuum of Bjerrum fails for tetra-n-butylammoniumbromide.

Fuoss hypothesized about the Bjerrum's model that the approach of two ions continues until they are separated by only one layer of solvent molecules. This fact, the breakdown of the latter allows the intimate contact of ions, is assumed to be a discrete process, describable by a constant K_s. He then obtains an expression for the dissociation constant as $K = K_B/(1+K_s)$.

Fuoss did not indicate any information for calculating the constant K_s. It will be shown that, attacking the problem from a microscopic point of view, an equation for K might be derived which could account for the above relationship. In equation (7), the reciprocal of the dissociation constant is in proportional to $Q(b)$. The value a, the distance of closest approach, was calculated by using the dissociation constants.

Results obtained for $C_4H_9N(CH_3)_3MO$, $C_6H_{13}N(CH_3)_3 \cdot MO$, $C_8H_{17}N(CH_3)_3 \cdot MO$ and $C_{12}H_{25}N(CH_3)_3 \cdot MO$ are presented in Table II.

Table II—Some parameters of quaternary ammonium-methylorange salts in nitrobenzene solution.

Compounds	K	Q(b)	b	a
Butyltrimethylammonium-methylorange	2.00×10^{-3}	15.36	12.08	1.33
Hexyltrimethylammonium-methylorange	3.42×10^{-3}	9.09	11.41	1.41
Octyltrimethylammonium-methylorange	5.75×10^{-3}	5.33	10.33	1.56
Lauryltrimethylammonium-methylorange	9.48×10^{-3}	3.13	9.20	1.75

Now, considering the size of cation and anion used in the experiment, the values of a are too small. However, when the value of conductance[7] is considered, the theoretical value of conductance shall not be so large.

The logarithm of the dissociation constant of a number of different salts is plotted against the methylene number of alkyl groups. The results for aliphatic amine and quaternary ammonium-MO salts were represented linear relationship.

In water solution, the dissociation constant for aliphatic amine and quaternary ammonium salts decreases with increasing the methylene number of alkyl group. But, in organic solution, the dissociation constant for salts increases with increasing the methylene number of alkyl groups.
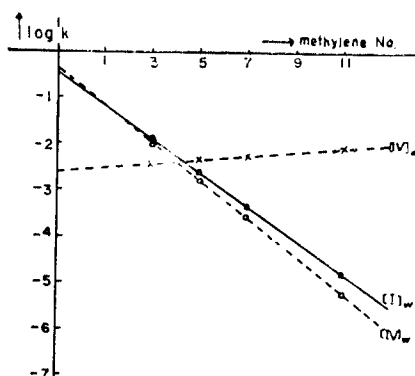
Fig. 7—Plot of log K for primary amine and quaternary ammonium
salts against methylene number of alkyl radicals.
(×) organic solutions of $CH_3 (CH_2)_n \cdot N(CH_3)_3 \cdot MO$
(●) water solution of $CH_3 (CH_2)_n NH_2 \cdot MO$
(○) water solution of $CH_3 (CH_2)_n N(CH_3)_3 \cdot MO$ $(n=3, 5, 7, 11)$
(I) primary amine
(IV) quaternary ammonium salt

EXPERIMENTAL

Reagents and Instruments—Primary amine and quaternary ammonium-methylorange
salts were prepared by using autoclave. Nitrobenzene was purified by distillation; its con-
ductance was approximately 0.2×10^{-7}. The solvent was stored in colored bottle.

Apparatus—The measurement of conductance[8,9] for aliphatic amine and quaternary
ammonium-methylorange salt was performed by using conductometry[10], attached to a
thermostated water bath maintained at $25 \pm 0.5°$. The absorption of the aliphatic amine
or quaternary ammonium-methylorange salt was measured by means of a Shimadzu
spectrophotometer (Model QB 50) in the visible range.

All the salts were studied at approximately 430 nm in organic solution or approximately
466 nm in a water solution.

Measurement of Conductance—$1 \times 10^{-5} \sim 1 \times 10^{-3}$ mol/l of the water solution or organic
solution of aliphatic amine and quaternary ammonium-methylorange salts were used in
measuring the conductance, and the temperature of a thermostated water bath was $25 \pm$
$0.5°$.

Effect of Temperature—The conductances of hexylamine and octyltrimethylammonium-
methylorange salts in water solution or organic solution were measured at temperatures
$20°$, $25°$, $30°$ and $35°$, respectively.

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