[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Acid–Base Equilibria in Glacial Acetic Acid. II. Spectrophotometric Determination of the Ionization and Dissociation Constants of *p,p'*-Dimethylaminoazobenzene and Pyridine. The Abnormal Effect of Water on Indicator Bases[1]

BY S. BRUCKENSTEIN[2] AND I. M. KOLTHOFF

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The following constants were determined spectrophotometrically at 25°: $K_{\mathrm{i}}^{\mathrm{I}}$ (ionization constant of *p,p'*-dimethylaminoazobenzene, (I)) = 0.100; $K_{\mathrm{d}}^{\mathrm{I}}$ (ion-pair dissociation constant of I) = 5.0×10^{-6}, K_{I} (over-all dissociation constant of I) = 4.6×10^{-7}; $K_{\mathrm{H_2O}} = 8.4 \times 10^{-11}$; $K_{\mathrm{i}}^{\mathrm{Py}} = 5.37$ (Py = pyridine); $K_{\mathrm{d}}^{\mathrm{Py}} = 9.4 \times 10^{-7}$; $K_{\mathrm{Py}} = 7.9 \times 10^{-7}$. Upon addition of water to a solution of an indicator base I like *p,p'*-dimethylaminoazobenzene in acetic acid the color changes in favor of that of the acid species, even though water is a base. This abnormal effect of water is attributed to formation of ion quadruplets and triplets: $\mathrm{IH^+Ac^-} + \mathrm{H_3O^+Ac^-} \rightleftarrows \begin{matrix}\mathrm{IH^+Ac^-}\\ \mathrm{Ac^-H_3O^+}\end{matrix}(\mathrm{Q})$, where Q can dissociate into an ion triplet and a simple ion. Other bases instead of I like pyridine and N,N-diethylaniline exhibit a similar behavior with water. The formation constant of Q from $\mathrm{IH^+Ac^-}$ and water was found equal to 2.0 ± 0.1, and its dissociation constant $3.3\ (\pm 1) \times 10^{-5}$. The formation constant of Q from $\mathrm{IH^+Ac^-}$ and pyridine is reported equal to 1.1, and that from N,N-diethylaniline and water to 2.65 ± 0.10.

p,p'-Dimethylaminoazobenzene (DMAAB = I) is a relatively strong base in glacial acetic acid. The spectrum of the basic form of DMAAB and its acid (ionized) forms are easily distinguishable. The ionization and dissociation constants[3] $K_{\mathrm{d}}^{\mathrm{I}} = ([\mathrm{IH^+}][\mathrm{Ac^-}])/[\mathrm{IH^+Ac^-}]$ and $K_{\mathrm{i}}^{\mathrm{I}} = [\mathrm{IH^+Ac^-}]/[\mathrm{I}]$ for reactions 1 and 1a

$$\mathrm{I} + \mathrm{HAc} \rightleftarrows \mathrm{IH^+Ac^-}\ \text{(ionization)} \qquad (1)$$

$$\mathrm{IH^+Ac^-} \rightleftarrows \mathrm{IH^+} + \mathrm{Ac^-}\ \text{(dissociation)} \qquad (1a)$$

were obtained from spectrophotometric measurements of the concentration of acid forms ($\Sigma[\mathrm{IH^+}] = [\mathrm{IH^+}] + [\mathrm{IH^+Ac^-}]$) of the indicator base in solutions of different concentrations of DMAAB in acetic acid. In the calculation of the constants allowance must be made for the effect of trace amounts of water in the solvent. Water is a base in acetic acid and in the calculations it is necessary to consider the acetate ions which arise from the dissociation of water. Equation 2a is obtained from the rule of electroneutrality ($[\mathrm{H_2Ac^+}]$ can be neglected)

$$[\mathrm{H_3O^+}] + [\mathrm{IH^+}] = [\mathrm{Ac^-}] \qquad (2)$$

and the expressions for the over-all dissociation constant of water

$$K_{\mathrm{H_2O}} = \frac{[\mathrm{H_3O^+}][\mathrm{Ac^-}]}{[\mathrm{H_2O}] + [\mathrm{H_3O^+Ac^-}]},\ K_{\mathrm{d}}^{\mathrm{I}} \text{ and } K_{\mathrm{i}}^{\mathrm{I}}.$$

$$\frac{[\mathrm{I}]}{[\mathrm{IH^+}]^2} = \left[\frac{K_{\mathrm{H_2O}}}{(K_{\mathrm{i}}^{\mathrm{I}}K_{\mathrm{d}}^{\mathrm{I}})^2}\right]\left[\frac{C_{\mathrm{H_2O}}}{[\mathrm{I}]}\right] + \frac{1}{K_{\mathrm{i}}^{\mathrm{I}}K_{\mathrm{d}}^{\mathrm{I}}} \qquad (2a)$$

where $C_{\mathrm{H_2O}} = [\mathrm{H_2O}] + [\mathrm{H_3O^+Ac^-}]$. Equation 2a has the form of a straight line, $y = mx + b$, where $y = [\mathrm{I}]/[\mathrm{IH^+}]^2$, $x = \mathrm{C_{H_2O}}/[\mathrm{I}]$, $m = K_{\mathrm{H_2O}}/(K_{\mathrm{i}}^{\mathrm{I}}K_{\mathrm{d}}^{\mathrm{I}})^2$ and $b = 1/(K_{\mathrm{i}}^{\mathrm{I}}K_{\mathrm{d}}^{\mathrm{I}})$.

The water content of the solvent was found by titration with Karl Fischer reagent. [I] is the difference between the analytical concentration of DMAAB and the spectrophotometrically determined quantity $\Sigma[\mathrm{IH^+}]$, while $[\mathrm{IH^+}] = \Sigma[\mathrm{IH^+}] - K_{\mathrm{i}}^{\mathrm{I}}[\mathrm{I}]$. A trial and error method was used to find the value of $K_{\mathrm{i}}^{\mathrm{I}}$ which yielded values of $[\mathrm{IH^+}]$ such that the experimental data resulted in a straight line when plotted according to equation 2a. $K_{\mathrm{d}}^{\mathrm{I}}$ and $K_{\mathrm{H_2O}}$ were calculated from the slope and intercept of this line.

From the effect of pyridine on the dissociation of DMAAB, the over-all dissociation constant of pyridine, K_{Py} $(= ([\mathrm{PyH^+}][\mathrm{Ac^-}])/([\mathrm{Py}] + [\mathrm{PyH^+Ac^-}]))$ was calculated. The addition of pyridine to a solution of DMAAB causes a decrease in the concentration of acid colored indicator species initially, and ultimately an increase. The decrease is caused by repression of the dissociation of $\mathrm{IH^+Ac^-}$ by acetate ions arising from the base, pyridine, while the subsequent increase is caused by formation of higher ionic species which are discussed later in this paper.

In a solution containing only DMAAB and pyridine, the rule of electroneutrality reduces to

$$[\mathrm{IH^+}] + [\mathrm{PyH^+}] = [\mathrm{Ac^-}] \qquad (3)$$

provided the concentration of pyridine is low enough to neglect the formation of ion-triplets. Using K_{Py}, $K_{\mathrm{i}}^{\mathrm{I}}$ and $K_{\mathrm{d}}^{\mathrm{I}}$ equation 3 is easily transformed into equation 3a, where $C_{\mathrm{Py}} = [\mathrm{Py}] + [\mathrm{PyH^+Ac^-}]$. The method of calculating the different quantities in equation 3a involves the trial and error method used in equation 2a.

$$\frac{[\mathrm{I}]}{[\mathrm{IH^+}]^2} = \left[\frac{K_{\mathrm{Py}}}{(K_{\mathrm{i}}^{\mathrm{I}}K_{\mathrm{d}}^{\mathrm{I}})^2}\right]\left[\frac{C_{\mathrm{Py}}}{[\mathrm{I}]}\right] + \frac{\mathrm{I}}{K_{\mathrm{i}}^{\mathrm{I}}K_{\mathrm{d}}^{\mathrm{I}}} \qquad (3a)$$

The value of $K_{\mathrm{i}}^{\mathrm{I}}$ found to fit the data in equation 2a should also fit the data in the plot of equation 3a. The intercept of equation 3a is the same as that of equation 2a, which should further substantiate the reliability of the experimental results and the method of calculations. K_{Py} was calculated from the slope of equation 3a.

The absorption spectrum of the ionized forms of pyridine in acetic acid is different from that of the non-ionized forms. In perchloric acid solutions in acetic acid, pyridine is present entirely in the ionized form thus permitting the determination of the molar absorptivity of this form. By measuring the absorbance of solutions of pyridine in acetic acid the concentration of the ionized form was

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(1) From a thesis submitted by S. Bruckenstein to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1954.

(2) Du Pont Teaching Fellow, 1953–1954.

(3) For notations see I. M. Kolthoff and S. Bruckenstein, THIS JOURNAL, **78**, 1 (1956).

found and from this the equilibrium constant (K_i^{Py}) of the reaction

$$\text{Py} + \text{HAc} \rightleftarrows \text{PyH}^+\text{Ac}^- \qquad (4)$$

was calculated. The dissociation into ions was negligible at the concentrations of pyridine used.

In studying the effect of small amounts of water upon the color equilibrium of various indicators in acetic acid Willman[4] observed that water acted as a base, more perchloric acid being required to produce a given concentration of acid-colored indicator species in the presence of water than in its absence, for crystal violet, malachite green, benzylideneacetophenone and *p*-naphtholbenzein among others. These compounds require the presence of free acid in order to exhibit the color characteristic of their acid forms. However, an "abnormal water effect" was found for indicators which were already partially converted to their acid forms in acetic acid, *e.g.*, metanil yellow, *p,p'*-dimethylaminoazobenzene, tropeolin 00 and thymolbenzein. This "abnormal water effect" was not understood and not reported in the literature. In the present paper evidence is given that the abnormal effect is caused by triple and quadruple ion formation as indicated by equations 5, 5a, and/or 5b. All the ionized forms of the indicator have the same molar absorptivity and absorption spectrum. In the present paper the formation constant of the quadrupole and its overall dissociation constant have been determined spectrophotometrically.

$$\text{IH}^+\text{Ac}^- + \text{H}_3\text{O}^+\text{Ac}^- \rightleftarrows \text{IH}^+\text{Ac}^-\text{H}_3\text{O}^+\text{Ac}^- \qquad (5)$$

$$\text{IH}^+\text{Ac}^-\text{H}_3\text{O}^+\text{Ac}^- \rightleftarrows \begin{cases} \text{IH}^+\text{Ac}^-\text{H}_3\text{O}^+ + \text{Ac}^- & (5a) \\ \text{Ac}^-\text{IH}^+\text{Ac}^- + \text{H}_3\text{O}^+ & (5b) \end{cases}$$

The pronounced tendency of hydronium acetate to form higher ionic aggregates is not limited to *indicator* bases, but also occurs with colorless bases, *e.g.*, pyridine and diethylaniline. The formation of higher ionic aggregates was established by the shift of the ultraviolet spectrum of these two bases in favor of that of the ionic forms upon addition of water. The principal reactions are similar to those given for an indicator base.

Formally the formation of the quadrupole by interaction of I with B can be written in the following three forms

$$\text{IH}^+\text{Ac}^- + \text{BH}^+\text{Ac}^- \rightleftarrows \text{Q}_{\text{I}\cdot\text{B}} \qquad (6)$$

$$\text{IH}^+\text{Ac}^- + \text{B} \rightleftarrows \text{Q}_{\text{I}\cdot\text{B}} \qquad (6a)$$

$$\text{I} + \text{B} \rightleftarrows \text{Q}_{\text{I}\cdot\text{B}} \qquad (6b)$$

where $\text{Q}_{\text{I}\cdot\text{B}} = \text{IH}^+\text{Ac}^-\text{BH}^+\text{Ac}^-$. Defining $K_Q^{\text{I}^+\cdot\text{B}^+} = [\text{Q}_{\text{I}\cdot\text{B}}]/([\text{IH}^+\text{Ac}^-]\ [\text{BH}^+\text{Ac}^-])$, $K_Q^{\text{I}^+\cdot\text{B}} = [\text{Q}_{\text{I}\cdot\text{B}}]/[\text{IH}^+\text{Ac}^-]C_\text{B}$ and $K_Q^{\text{I}\cdot\text{B}} = [Q_{\text{I}\cdot\text{B}}]/C_1C_\text{B}$, where C_I represents the sum of the concentration of the undissociated forms of I, and C_B the same for those of B. $K_Q^{\text{I}^+\cdot\text{B}^+}$ is related to the other constants by equations 6c and 6d.

$$K_Q^{\text{I}^+\cdot\text{B}} = K_Q^{\text{I}^+\cdot\text{B}^+}\left[\frac{K_i^\text{B}}{1 + K_i^\text{B}}\right] \qquad (6c)$$

$$K_Q^{\text{I}\cdot\text{B}} = K_Q^{\text{I}^+\cdot\text{B}^+}\left[\frac{K_i^\text{B}K_i^\text{I}}{(1 + K_i^\text{B})(1 + K_i^\text{I})}\right] \qquad (6d)$$

$K_Q^{\text{I}^+\cdot\text{B}^+}$ can be calculated when K_i^I and K_i^B are known, $K_Q^{\text{I}^+\cdot\text{B}}$ when K_i^I but not K_i^B is known, while $K_Q^{\text{I}\cdot\text{B}}$ can be found when both K_i^I and K_i^B are unknown.

Experimental

Reagents. ***p,p'*-Dimethylaminoazobenzene.**—An Eastman Kodak product was recrystallized from acetic acid and dried over potassium hydroxide *in vacuo* at 50°. Potentiometric titration with perchloric acid in acetic acid indicated a purity of 99.9%.

N,N-Diethylaniline.—An Eastman Kodak product was distilled. Titration in acetic acid with perchloric acid and crystal violet as indicator gave an assay of 100.3%.

Pyridine.—A reagent grade material was analyzed using the same technique as for diethylaniline; the assay corresponded to 99.9% pyridine.

Acetic Acid.—The water content of the acid used was 0.012 *M*. The notation "acetic acid" in the experimental refers to the acid with this water content.

All experiments were carried out at 25 ± 1°.

For further details on all other chemicals and instrumental methods see paper I[3] of this series.

Experimental Results and Discussion

Spectra of DMAAB.—DMAAB, which is red in acid solution, takes on an intermediate shade of orange in pure acetic acid, and approaches a yellow color in the presence of 0.01–0.02 *M* pyridine because of the repression of the dissociation in IH^+Ac^-. It appears that DMAAB is a strong enough base to react with acetic acid to give an appreciable amount of IH^+Ac^- so that even in the presence of excess pyridine detectable concentrations of acid colored species exist. In order to calculate the various constants involved in the ionization of DMAAB it is necessary to know the molar absorptivities of the acid and basic forms at suitable wave lengths. Curve I in Fig. 1 gives the absorption spectrum in acetic acid, curve II the spectrum in the presence of an excess of perchloric acid and curve III the spectrum in the presence of 0.01 *M* pyridine in which the concentration of acid species is a minimum. It is clear that all the acid species of the indicator have the same spectrum with a maximum absorption at 517 mμ and the basic form

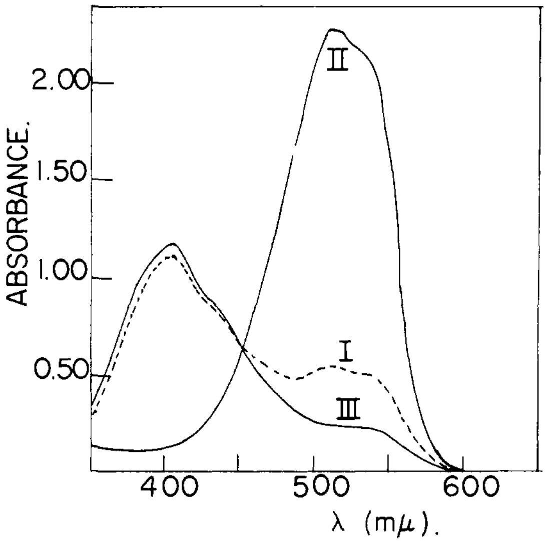

Fig. 1.—Spectrum of DMAAB ($(C_{\text{DMAAB}})_t$ = 1.03 × 10^{-5} *M*, 50 mm. cell used: I, in acetic acid containing 0.012 *M* water; II, in excess HClO_4; III, in 0.01 *M* pyridine.

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[4] A. Willman, Ph.D. Thesis, University of Minnesota, 1933.

at 406 mμ. It will be shown that the shoulder in curve 3 in the 517 mμ region is caused by the presence of IH^+Ac^- in this solution and is not characteristic of the indicator base. This shoulder is not found in pure benzene solutions of DMAAB where ionized species do not exist.

From experiments like those in curve II of Fig. 1 the molar absorptivity of the acid species was found to be 4.20×10^4 liters/mole cm. at 517 mμ and 0.12×10^4 liters/mole cm. at 406 mμ. Similarly, from experiments in the presence of base, the molar absorptivity of the basic form of DMAAB was found to be 2.31×10^4 liters/mole cm. at 406 mμ, assuming the molar absorptivity of the base to be negligible at 517 mμ. The concentration, [I], of the non-ionized form of the indicator base in these solutions was found by calculating the total concentration of acid colored species from the observed absorbance at 517 mμ and the molar absorptivity of acid colored indicator species, and subtracting this concentration from the analytical concentration of DMAAB. Using these values of [I] and the observed absorbances at 407 mμ, the molar absorptivity of I at this wave length was calculated.

Ionization and Dissociation Constants of DMAAB and the Over-all Dissociation Constants of Water and Pyridine.—The absorbance of DMAAB at 517 mμ was studied as a function of total concentration of indicator in acetic acid containing 0.012 *M* water. The experimental results are given in Table I.

Table I

$\Sigma[IH^+]$ at Various Concentrations of DMAAB

Total concn. of DMAAB, $M \times 10^6$	$\Sigma[IH^+]$, $M \times 10^6$	Total concn. of DMAAB, $M \times 10^6$	$\Sigma[1H^+]$, $M \times 10^6$
2.02	0.626	12.09	2.86
4.03	1.20	16.1	3.55
6.04	1.65	20.1	4.21
8.06	2.10		

Figure 2 represents a plot of these data according to equation 2a, adopting a value of K_i^I of 0.100. The slope of 3.38×10^2 and the intercept of 2.00×10^6 correspond to $K_d^I = 5.0 \times 10^{-6}$ and $K_{H_2O} = 8.4 \times 10^{-11}$. The value of the over-all dissociation constant of DMAAB is calculated to be 4.6×10^{-7}.

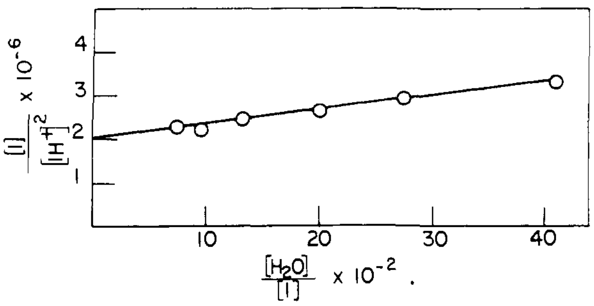

Fig. 2.—Determination of K_{H_2O} and K_d^I; K_i^I taken to be 0.100.

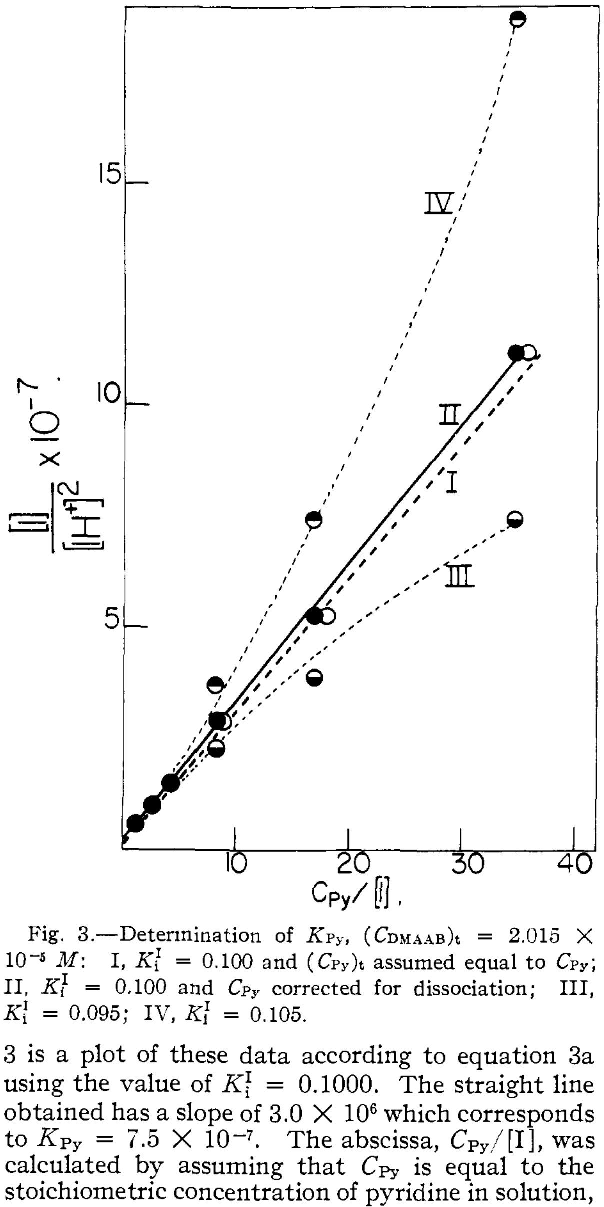

Fig. 3.—Determination of K_{Py}, $(C_{DMAAB})_t = 2.015 \times 10^{-5}$ *M*: I, $K_i^I = 0.100$ and $(C_{Py})_t$ assumed equal to C_{Py}; II, $K_i^I = 0.100$ and C_{Py} corrected for dissociation; III, $K_i^I = 0.095$; IV, $K_i^I = 0.105$.

The variation of $\Sigma[IH^+]$ with pyridine concentration was determined spectrophotometrically in a 2.015×10^{-5} *M* solution of DMAAB and the experimental data are given in Table II. Curve I of Fig. 3 is a plot of these data according to equation 3a using the value of $K_i^I = 0.1000$. The straight line obtained has a slope of 3.0×10^6 which corresponds to $K_{Py} = 7.5 \times 10^{-7}$. The abscissa, $C_{Py}/[I]$, was calculated by assuming that C_{Py} is equal to the stoichiometric concentration of pyridine in solution, an assumption which is not quite correct under our experimental conditions. Although pyridine has a very small over-all dissociation constant the concentrations of pyridine used were so small that dissociation into ions cannot be neglected. Curve II, Fig. 3, represents the straight line which is obtained when correction for this dissociation is made using the values $K_i^I = 0.100$, $K_d^I = 5 \times 10^{-6}$ and as a first approximation the over-all dissociation of pyridine, $K_{Py} = 7.5 \times 10^{-7}$.

$$C_{Py} = (C_{Py})_t \frac{[Ac^-]}{K_{Py} + [Ac^-]}$$

where (C_{Py}) is the stoichiometric concentration of pyridine and

$$[Ac^-] = \sqrt{K_{Py}C_{Py} + K_i^I K_d^I\,[I]}$$

The slope of the line is 3.15×10^6 and the intercept is $\sim 0.2 \times 10^7$. The scale of this figure is such that the intercept cannot be determined precisely, but the observed value agrees with the value predicted by $K_d^I = 5 \times 10^{-6}$. K_{Py} is calculated to be 7.9×10^{-7} from the slope of curve II. Using this value of K_{Py} to calculate C_{Py} further approximations did not alter the above figures.

TABLE II

EFFECT OF PYRIDINE ON DMAAB

$(C_I)_t = 20.15 \times 10^{-6}\ M$

Pyridine– $(C_{Py})_t$, M	A_{517}	$\Sigma[IH^+] \times 10^6$	$\frac{[IH^+]}{[I]}$	$\frac{[\text{Pyridine–IH}^+\text{–aggregates}]}{[IH^+Ac^-]}$
2.5×10^{-5}	0.953	3.44	0.106	
5.1	.674	3.08	.0802	
8.0	.618	2.82	.0629	
16.1	.557	2.54	.0443	
32.1	.518	2.37	.0334	
64.2	.482	2.20	.0223	
1.28×10^{-3}	.454	2.07	.0142	
2.57	.440	2.00	.0099	
5.13	.430	1.96	.0072	
10.25	.423	1.93	.0060	0.060
20.50	.422	1.93	.0060	.060
41.0	.423	1.94		.066
79.7	.437	2.00		.099
1.58×10^{-1}	.466	2.16		.132
3.13	.527	2.47		.395
6.10	.562	2.70		.544

Curves III and IV of Fig. 3 were calculated using K_i^I equal to 0.095 and 0.105 and illustrate that the method used is quite sensitive to small variations in the assumed value of K_i^I, deviations from linearity being observed with slight changes in the value of K_i^I. It is not necessary to correct any of these calculations for acetate ion resulting from the dissociation of water since even at the lowest concentration of pyridine the correction for water content is only about 2%.

Ion-Triplet and Quadruple Formation. DMAAB and Pyridine.—The addition of pyridine to DMAAB in acetic acid results in a decrease in $\Sigma[IH^+]$ initially, but at concentrations of pyridine larger than 0.02 M, $\Sigma[IH^+]$ increases because of the formation of ion-triplets and quadruple ions. The last column in Table II presents the ratio [Pyridine–IH$^+$ Aggregates]/[IH$^+$Ac$^-$] which was calculated from the equation [Pyridine–IH$^+$ Aggregates] = $\Sigma[IH^+] - [IH^+Ac^-]$, where $[IH^+Ac^-] = K_i^I[I]$. Figure 4 is a plot of log [Pyridine–IH$^+$ Aggregates]/[IH$^+$Ac$^-$] against log C_{Py}. If the solution had contained only quadruple ions a slope of one should have been found, while a slope of 0.500 should have been found if only triple ions were present. In these solutions the dissociation of quadruple ions into ion-triplets is suppressed by acetate and pyridinium ions furnished by the dissociation of pyridine. The slope of the line obtained is slightly less than one, 0.96, indicating that the primary species present in solution is $\begin{matrix}\text{PyH}^+\text{Ac}^-\\ \text{Ac}^-\text{IH}^+\end{matrix}$. The value of $K_Q^{I^+\cdot Py}$ (eq. 6a) is 1.1 in 0.1 M pyridine.

In a separate experiment in 0.8 M pyridine it was found that the ratio [Pyridine–IH$^+$ Aggregates]/[IH$^+$Ac$^-$] was independent of the concentration of DMAAB in the concentration range 1–5 $\times 10^{-6}$ molar, indicating that no ionic aggregates exist which contain more than one IH$^+$ unit.

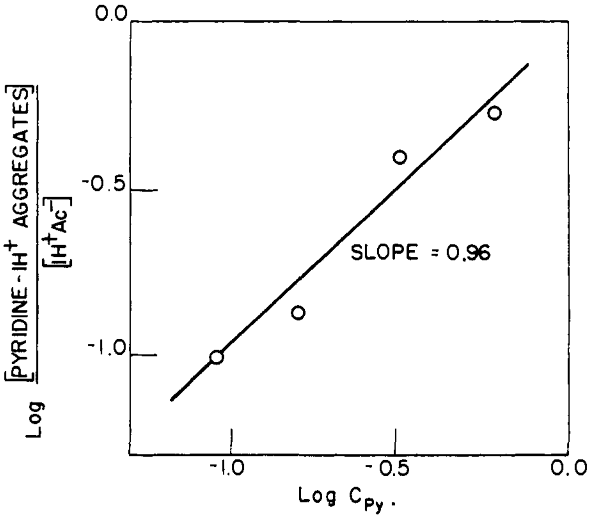

Fig. 4.—Formation of pyridine-IH$^+$ aggregates; $(C_{DMAAB})_t = 2.015 \times 10^{-5}\ M$.

DMAAB and Water.—When water is added to a solution of DMAAB in acetic acid a regular increase in the red acid color occurs accompanied by a corresponding decrease in the yellow base color. The effect of water on a $5.64 \times 10^{-6}\ M$ solution of DMAAB is shown in Table III. An isosbestic point is obtained at 455 mμ which is identical to the isosbestic point obtained when perchloric acid is added to DMAAB in acetic acid, proving that the spectrum of the species produced by the reaction of DMAAB and water is the same as that of IH$^+$ClO$_4^-$. The total concentration of DMAAB, $(C_I)_t$, can be calculated by solving the set of simultaneous equations 7, 7a and 7b for $(C_I)_t$. In these equations

$$(C_I)_t = [I] + \Sigma[IH^+] \tag{7}$$

$$A_{517} = a_{517}^I b[I] + a_{517}^{IH^+} b\Sigma[IH^+] = a_{517}^{IH^+} b\Sigma[IH^+] \tag{7a}$$

$$A_{406} = a_{406}^I b[I] + a_{406}^{IH^+} b\Sigma[IH^+] \tag{7b}$$

subscripts refer to wave lengths in mμ and superscripts to chemical species, while A represents the measured absorbance and b the cell length, 5.00 cm. Table III contains values for [I] and $\Sigma[IH^+]$ calculated from equations 7a and 7b, using the molar absorptivities reported earlier in this section. The calculated average value of $(C_I)_t$, 5.65×10^{-6}, is in excellent agreement with the amount taken,

TABLE III

QUADRUPOLE DISSOCIATION CONSTANT OF IH$^+$Ac$^-$H$_3$O$^+$Ac$^-$

$(C_I)_t = 5.64 \times 10^{-6}\ M$. $K_d^Q = \frac{[T]\,[Ac^-]}{[Q_I\cdot w]}$ where [T] = [IH$^+$Ac$^-$H$_3$O$^+$] and $[Q_I\cdot w]$ = [IH$^+$Ac$^-$H$_3$O$^+$Ac$^-$]

Water, M	A_{406}	A_{517}	$[I] \times 10^6$	Σ-$[IH^+] \times 10^6$	$[Ac^-] \times 10^6$	$[T] \times 10^6$	$Q_I.w. \times 10^6$	$K_d^Q \times 10^5$
0.0120	0.497	0.307	4.23	1.40	1.60	(−0.35)	0.010	..
.0307	.485	.324	4.12	1.48	2.21	0.18	.025	1.6
.0486	.480	.342	4.07	1.56	2.65	.34	.040	2.3
.0847	.475	.370	4.02	1.69	3.34	.61	.068	2.9
.158	.447	.404	3.77	1.84	4.37	.91	.119	3.3
.303	.415	.487	3.47	2.22	5.95	1.37	.210	3.9
.591	.335	.648	2.74	2.96	8.32	2.22	.323	5.7

5.64×10^{-6}. This justifies the earlier assumption that the shoulder on the DMAAB spectrum in the presence of small amounts of a colorless base (curve 3, Fig. 1) is caused by the presence of IH^+Ac^- and is not part of the spectrum of I.

It is possible to determine the quadrupole formation constant, $K_Q^{I^+ \cdot W}$, if sufficient pyridine is added to acetic acid to repress the dissociation of both IH^+Ac^- and $IH^+Ac^-H_3O^+Ac^-$. Table IV contains spectrophotometrically determined values of [I] and $\Sigma[IH^+]$ as a function of the concentration of water in solutions with an initial analytical concentration of 3.63×10^{-6} molar DMAAB and 0.153 *M* pyridine. The concentration of water–IH^+ quadrupoles, $[Q_I \cdot w]$, is given by $[Q_I \cdot w] = \Sigma[IH^+] - ([IH^+Ac^-] + [\text{Pyridine–}IH^+ \text{ Aggregates}])$, where $[IH^+Ac^-] = K_i^I [I]$. The concentration of pyridine–IH^+ aggregates was calculated, assuming that the ratio $[\text{Pyridine–}IH^+ \text{ Aggregates}]/[IH^+Ac^-]$ is constant and equal to 0.28. This value, 0.28, is obtained by assuming that $[Q_I \cdot w]$ is negligibly small in the solution which is 0.01 *M* in water. We thus find that $[Q_I \cdot w] = \Sigma[IH^+] - 0.128 [I]$, since $K_i^I = 0.100$. The average value of $K_Q^{I^+ \cdot W}$, calculated from the data in Table IV, is 2.0 ± 0.1.

TABLE IV

THE QUADRUPOLE FORMATION CONSTANT OF DMAAB AND WATER

$(C_I)_t = 3.63 \times 10^{-6}$ *M*; $(C_{Py})_t = 0.153$ *M*

Water, *M*	A_{406}	A_{517}	[I] × 10^6	$\Sigma[IH^+]$ × 10^6	$[Q_I \cdot w]$ × 10^6	K_Q
0.01	0.380	0.086	3.22	0.41	0.00	
1.43	.302	.211	2.54	1.06	.69	1.9
2.11	.271	.264	2.38	1.26	.95	1.9
2.78	.244	.312	2.05	1.49	1.22	2.1
3.43	.219	.340	1.85	1.62	1.38	2.1

The data in Table III can be interpreted, making use of the known values of the constants K_i^I, K_d^I, K_{H_2O} and $K^{I^+ \cdot W}$ to calculate the concentration of acetate ion and the individual concentrations of all acid colored species present. Starting with the spectrophotometrically determined values of $\Sigma[IH^+]$ and [I], and the expression $\Sigma[IH^+] = [IH^+] + [IH^+Ac^-] + [IH^+Ac^-H_3O^+] + [Q_I \cdot w]$, where $[IH^+Ac^-] = K_i^I[I]$ and $[Q_I \cdot w] = K_Q^{I^+ \cdot W}[IH^+Ac^-]C_{H_2O}$, the sum $([IH^+] + [IH^+Ac^-H_3O^+])$ can be found. Neglecting $[H_2Ac^+]$, the electro-neutrality rule, $[IH^+] + [IH^+Ac^-H_3O^+] = [Ac^-] - [H_3O^+] = [Ac^-] - C_{H_2O} [K_{H_2O}/(K_{H_2O} + [Ac^-])]$, yields the acetate ion concentration. The equilibrium concentration of the indicator ion, $[IH^+] = K_d^I[IH^+Ac^-]/[Ac^-]$ is subtracted from the sum $([IH^+] + [IH^+Ac^-H_3O^+])$ to give the concentration of ion triplets.

Example.—In 0.591 *M* water solution $[I] = 2.74 \times 10^{-6}$ and $\Sigma[IH^+] = 2.96 \times 10^{-6}$ *M*. $[IH^+Ac^-] = 0.100\,(2.74 \times 10^{-6}) = 0.274 \times 10^{-6}$ and $[Q_I \cdot w] = 2.0\,(0.274 \times 10^{-6})\,(0.591) = 0.32 \times 10^{-6}$ so that $[IH^+] + [IH^+Ac^-H_3O^+] = 2.37 \times 10^{-6} = [Ac^-] - 0.591\,[8.4 \times 10^{-11}/([Ac^-] + 8.4 \times 10^{-11})]$, and $[Ac^-] = 8.32 \times 10^{-6}$. $[IH^+] = 5 \times 10^{-6}\,(0.274 \times 10^{-6})/(8.32 \times 10^{-6}) = 0.15 \times 10^{-6}$ and $[IH^+Ac^-H_3O^+] = 2.37 \times 10^{-6} - 0.15 \times 10^{-6} = 2.22 \times 10^{-6}$. The average value of K_d^Q $([IH^+Ac^-H_3O^+][Ac^-]/[Q_I \cdot w])$ is 3.3×10^{-5}. K_d^Q has a distinct trend to increase as C_{H_2O} increases.

This approach neglects the presence of the species $Ac^-IH^+Ac^-$, and is justified, since the product $[IH^+Ac^-]$ $[Ac^-]$ in the above experiment is always smaller than the same product for the experiments which are presented in Table II. In the latter experiment, K_{Py} was obtained and no evidence for the species $Ac^-IH^+Ac^-$ was found.

In order to test the reliability of the constants of the various equilibria involving DMAAB and water, the spectrum of DMAAB was determined at a high concentration of the indicator, 8.52×10^{-4} *M*, in water, using a cell with a path length of approximately 0.07 cm. The ratio A_{517}/A_{406} was found to be 0.243. From the constants found above the equilibrium concentrations of the various species are calculated to be: $[I] = 7.52 \times 10^{-4}$, $[IH^+] = 1.94 \times 10^{-5}$, $[IH^+Ac^-] = 7.52 \times 10^{-5}$, $[IH^+Ac^-H_3O^+] = 0.39 \times 10^{-5}$, and $[Q_I \cdot w] = 0.21 \times 10^{-5}$ or $\Sigma[IH^+] = 1.01 \times 10^{-4}$. Using these values and equations 7a and 7b the calculated ratio A_{517}/A_{406} is 0.242 in excellent agreement with the experimental value of 0.243.

Colorless Bases and Water.—Diethylaniline solutions in acetic acid are colorless. Curve I of Fig. 5 represents the ultraviolet spectrum of the free base in acetic acid and curve II that in the presence of excess perchloric acid. The molar absorptivity of diethylaniline at 306 mμ was found to be 21.1 liters/mole cm., while that of the perchlorate was negligible. The absorbance at this wave length must be due to the non-ionized form of the base.

The addition of water to diethylaniline solutions qualitatively produces the same effect as the addition of perchloric acid at all wave lengths investigated, illustrating that the abnormal effect of water is not restricted to colored bases. The absorbances measured at 306 mμ upon addition of water to a

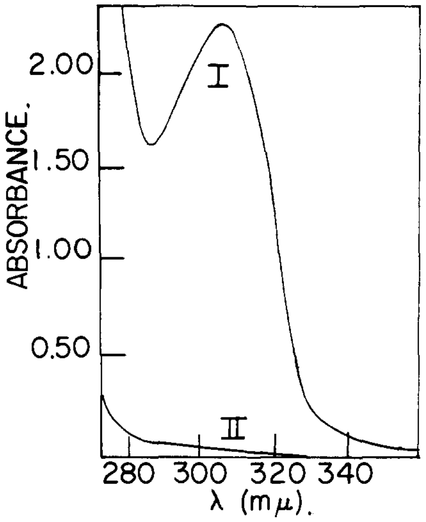

Fig. 5.—Spectrum of N,N-diethylaniline: I, 0.0531 *M* N N-diethylaniline in acetic acid; II, 0.17 *M* diethylaniline perchlorate; 20 mm. cell used.

0.0531 *M* solution of diethylaniline are presented in Table V and the average value of the quadrupole formation constant between diethylaniline and water, $K_Q^{D\cdot W}$ = $[Q_{D\cdot w}]/(C_D C_{H_2O})$, was found to be 2.65 ± 0.10. (D = diethylaniline.)

TABLE V

EFFECT OF WATER UPON DIETHYLANILINE (D)

$(C_D)_t$ = 0.0531 *M* 2.00 cm. quartz cells

Water, *M*	A_{306}	$[Q_{D.w.}]/C_D$	$K_Q^{D.W.}$
0.274	1.39	0.705	2.58
0.551	0.960	1.47	2.67
1.09	0.580	3.09	2.85
2.08	0.380	5.24	2.62
			Av. = 2.65 ± 0.10

Pyridine solutions in acetic acid are also colorless and the spectrum of pyridine in acetic acid (curve I) and in excess perchloric acid (curve 2) are given in Fig. 6. The molar absorptivities in pure acetic acid were found to be 4.62 × 10^3 at 255.5 mμ and 3.12 × 10^3 at 261.0 mμ, while in 0.1 *M* perchloric acid these values at the same wave lengths are 5.48 × 10^3 and 3.74 × 10^3. The ratio of the molar absorptivities of pyridine in acetic acid at 255.5 mμ and 261.0 mμ is 1.49, while this ratio is 1.47 in 0.1 *M* perchloric acid This suggests that the two spectra are identical and are caused by similar species. It is reasonable to assume that the base (Py) does not absorb at either of these wave lengths and the observed absorption is caused by PyH^+Ac^- in acetic acid and by $PyH^+ClO_4^-$ in the presence of excess perchloric acid. Experiments using 1.01 and 2.03 × 10^{-4} *M* pyridine in the presence and absence of excess perchloric acid yielded an average K_i^{Py} of 5.52 ± 0.04 at 255.5 mμ and 5.21 ± 0.09 at 261.0 mμ, assuming that the molar absorptivities of PyH^+Ac^- and $PyH^+ClO_4^-$ are identical at these two wave lengths. These results show that more than 80% of the pyridine is present in the ion-pair form. Adopting the mean value of K_i^{Py} of 5.37 and $K_{Py} = 7.9 \times 10^{-7}$, K_d^{Py} = 9.4 × 10^{-7}.

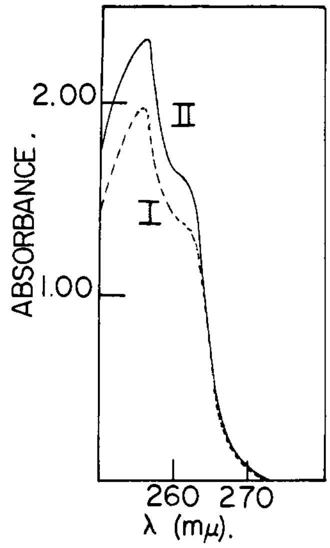

Fig. 6.—Spectrum of pyridine: $(C_{Py})_t$ = 2.03 × 10^{-4} molar: I, in acetic acid; II, in 0.05 *M* $HClO_4$; 20 mm. cell used.

It was noted that when water was added to pyridine the effect on the spectrum was similar to that produced by perchloric acid, but no quantitative measurements were made to determine the species formed. It may be stated that the "abnormal water effect" is a general phenomenon and it is not restricted to indicator bases.

MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORIES OF THE UNIVERSITY OF CHICAGO]

The Outer Sphere Association of Sulfate Ion with Tripositive Cobaltammine Ions

BY FRANZ A. POSEY AND HENRY TAUBE

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The equilibrium quotients, *K*, for the outer sphere association of $Co(NH_3)_6^{+++}$ and $Co(NH_3)_5H_2O^{+++}$ with $SO_4^=$ have been measured at several temperatures and ionic strengths by following the changes in optical density in the ultraviolet region of the absorption spectra of the cations as a function of sulfate ion concentration. Values of ΔF^0, ΔH^0 and ΔS^0 at 25° are −4.53 kcal. mole^{-1}, 0.40 kcal. mole^{-1}, and 16.6 e.u. for the association of $Co(NH_3)_6^{+++}$ with $SO_4^=$. The equilibrium quotients calculated are independent of concentrations, of the wave length of light used, and vary with ionic strength in conformity with a Debye–Hückel equation. The quotient for the equilibrium ratio, $(Co(NH_3)_5H_2O^{+++}\cdot SO_4^=)/(Co(NH_3)_5SO_4^+)$, in 1 *M* $NaClO_4$ at 25° has been measured as 0.90 by following changes in the substitution equilibrium using light of wave length 560 mμ. These experiments have also yielded a value for *K* in agreement with that measured using the instantaneous changes in the ultraviolet extinctions as $SO_4^=$ is added to solutions of $Co(NH_3)_2H_2O^{+++}$.

Linhard[1] has demonstrated that the presence in solution of certain anions can cause marked changes in the absorption spectra of tripositive Co(III) and Cr(III) complex ions in the wave length region of the strong ultraviolet band. In an earlier paper[2] we reported that this effect occurs when $SO_4^=$ is added to a solution containing $Co(NH_3)_5H_2O^{+++}$. The changes in question occur immediately on mixing the reagents, in contrast to changes in the two bands in the wave length region of visible light, which for the ions in question take place quite slowly at room temperature, concomitant with substitution in the inner sphere of coördination of the central metallic ion. Therefore, if the changes of spectrum in the ultraviolet region are caused by the association of the cation with the anions, this interaction must be of such nature that the anion does not become equivalent to the six ligands in the

[1] M. Linhard, *Z. Elektrochem.*, **50**, 224 (1944).

[2] H. Taube and F. A. Posey, THIS JOURNAL, **75**, 1463 (1953).