then a $\pi\sigma^2$ quenching cross section of 47 Å^2 is obtained, in reasonable agreement with the value obtained by the chemical product analysis. The singlet energy-transfer cross section from benzene to cyclohexanone is nearly equal to those obtained earlier for the benzene–cyclobutanone[3] and benzene–cyclopentanone[4] systems, provided that they are evaluated on the basis of the newly obtained value of the $^1B_{2u}$ lifetime.[19,29] It is apparent that, on the average, the singlet energy transfer takes place in every other collision.

The triplet energy transfer from benzene to cyclohexanone has a cross section of ~1.3 Å^2, if a triplet lifetime value of 70 μsec[30] for the $^3B_{1u}$ benzene and a $P_{1/2}$ value of 0.09 Torr of cyclohexanone are used. Again, the triplet-quenching cross sections obtained for cyclohexanone, cyclobutanone,[3] and cyclopentanone[4] are alike within the accuracy of the measurement. The smallness of these triplet-quenching cross sections is understandable in terms of the rate–energetics correlation,[31] since the triplet energies of these ketones are likely to be 75–80 kcal/mol as compared to 84 kcal/mol for benzene.

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(30) (a) C. S. Parmenter and B. L. Ring, *J. Chem. Phys.*, **46**, 1998 (1967); (b) see footnote 23 of ref 3.

(31) (a) R. E. Rebbert and P. Ausloos, *J. Amer. Chem. Soc.*, **87**, 5569 (1965); (b) M. W. Schmidt and E. K. C. Lee, *ibid.*, **90**, 5919 (1968).

Reevaluation of the Formation Constants of the Hydrated Proton in Acetonitrile[1]

M. K. Chantooni, Jr., and I. M. Kolthoff

Contribution from the School of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. *Received October 13, 1969*

Abstract: Values of the hydration constants $K^f_{H^+_{nw}}$ of the proton in acetonitrile (AN), calculated previously[2] from spectrophotometric measurements of the activity of the solvated proton, $a_{H_s^+}$ in dilute perchloric acid solutions in the presence of water, using *o*-nitro-, *m*-nitro-, *o*-nitro-*p*-chloroaniline, and dibromothymolbenzein as indicators, are somewhat in error because the calculations were based on the incorrect assumption that the monoprotonated acid forms, BH^+, of these bases are not being hydrated under the experimental conditions. In the present paper it is found that BH^+ forms a mono- and a dihydrate. The following values for the formation constants $K^f_{BH_w^+}$ and $K^f_{BH_{2w}^+}$ were found: *m*-nitroanilinium, 1.0, 5.2; 2-nitro-4,5-dimethylanilinium, 0, 1.2 × 10; anilinium, 0.8, 1.8; and *p*-naphtholbenzeinium, 2.1 and 4.3, respectively. $pK^d_{BH^+}$ of 2-nitro-4,5-dimethylaniline was found to be 5.66. From infrared and, in some instances, from potentiometric p*a*H measurements it is found that the above bases B in the uncharged form are not hydrated in AN up to a water concentration of 1.5 *M*. Using the above hydration constants, values of $K^f_{H^+_{nw}}$ have been recalculated. The hydration constants of the proton were also obtained from conductivity data and from spectrophotometrically determined paH_s values in poorly buffered picric acid solutions containing water, using *p*-naphtholbenzein as indicator. Hydration of the protonated indicator base was taken into account. In general, agreement between the *y* values (eq 5) and hence between the hydration constants of the proton from the perchloric and picric acid data is satisfactory. Values of the overall proton hydration constants are $K^f_{H_w^+} = 1.6 \times 10^2$, $K^f_{H_{2w}^+} = 8 \times 10^3$, $K^f_{H_{3w}^+} = 6 \times 10^4$, and $K^f_{H_{4w}^+} = 2 \times 10^5$. When the water concentration is 1 *M*, about 80% of the protons are in the form of tetrahydrate.

In a previous paper[2] data were presented on the hydration of the solvated proton, H_s^+, in acetonitrile (AN) and values of the formation constants $K^f_{H_{nw}^+}$ were calculated. Hammett indicators were used to determine $[H^+]_s$ in dilute perchloric acid solutions in AN in the presence of water. Evidence was presented that the indicators used, *o*-nitro- and *o*-nitro-*p*-chloroaniline, are not hydrated in AN when the water concentration is <1 *M*. This is verified in the present study from the spectrum of the first overtone of the –OH stretch of free water at 1410 mμ in AN in the presence of the bases *o*- and *m*-nitroaniline, and also of aniline. It is assumed, as it was by Coetzee,[3] that the hydrogen-bonded H···NH band does not overlap with that of the free –OH band. Inconclusive evidence was presented in a previous study that the monoprotonated forms IH^+ of the indicators (I) used are not hydrated. From the spectrophotometric determination in AN of the overall dissociation constant of picric acid in the presence of water[4] strong indication was obtained that in perchloric acid–water mixtures the reported values of y^2 in the equation $[H^+]_s = C_{HClO_4}/y$ are too small. The most plausible explanation for the deviation is that the protonated forms of the uncharged indicator bases used are being hydrated. In the present paper the hydration of IH^+ was calculated from the effect of water on the potentiometric determined values of paH_s with the glass electrode in buffered mixtures of perchloric acid containing an excess of 2-nitro-4,5-dimethyl- or *m*-nitroaniline. Results are also presented with aniline. These bases are sufficiently strong such that when $C_{H_2O} \leqq 0.5$, $\Sigma[H^+] = [H^+]_s + \sum_{n=1}^{n=4}[H^+]_{nw}$

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(1) This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-1223-67.

(2) I. M. Kolthoff and M. K. Chantooni, Jr., *J. Amer. Chem. Soc.*, **90**, 3320 (1968).

(3) W. S. Muney and J. F. Coetzee, *J. Phys. Chem.*, **66**, 89 (1962).

(4) I. M. Kolthoff and M. K. Chantooni, Jr., *J. Amer. Chem. Soc.*, **91**, 6907 (1969).

in the above buffers is considerably smaller than $[IH^+]_s + [IH^+]_w + [IH^+]_{2w} = \Sigma[IH^+]$, the subscript s denoting unhydrated species. Under the conditions described, and stipulating that I is not hydrated

$$\sum[IH^+]/[I] = K^f{}_{IH_s} + va_{H_s^+}/f \qquad (1)$$

where

$$v = 1 + \sum_{m=1}^{m=m} K^f{}_{IH^+{}_{mw}}[H_2O]^m \qquad (2)$$

and f is the activity coefficient calculated from the limiting Debye–Hückel expression. Thus, from the measured $a_{H_s^+}$ the various hydration constants of IH^+ could be calculated[2] without considering the hydration of the proton. Using the values of the hydration constants of IH^+ thus determined, values of y reported previously[2] in dilute perchloric acid solutions containing very small concentrations of Hammett indicators were recalculated from the experimentally determined indicator ratios, $\Sigma[IH^+]/[I]$, the values of v (eq 2), and the relation[2]

$$vy[H^+]_s{}^2K^f{}_{IH_s^+} + \{v(C_I - C_{HClO_4})K^f{}_{IH_s^+} + y\} \times [H^+]_s - C_{HClO_4} = 0 \qquad (3)$$

In eq 1 and 3 $K^f{}_{IH_s^+} = [IH^+]_s/[H^+]_s[I]$ $(f_{IH^+} = f_{H^+})$, where C refers to analytical concentration. In applying eq 3 it is assumed that $K^f{}_{IH_s^+}$ is not affected by water when its concentration is <1 M and that perchloric acid and the salts IH_sClO_4 and $IH_{mw}ClO_4$ are completely dissociated. From the various values of y the formation constants of the hydrated proton were calculated from

$$y = 1 + K^f{}_{H_w^+}[H_2O] + \ldots K^f{}_{H_{nw}^+}[H_2O]^n \qquad (4)$$

In the previous paper[2] we also determined the paH_s spectrophotometrically in buffered perchloric acid–*o*-nitro- or *o*-nitro-*p*-chloroaniline solutions in the presence of water using dibromothymolbenzein or *p*-naphtholbenzein as indicators. It was assumed that the monoprotonated acid form of these indicators is not hydrated under the experimental conditions. Actually it is shown in the present paper that the *p*-naphtholbenzeinium ion IH^+, which structurally is closely related to the dibromothymolbenzeinium ion, forms a mono- and a dihydrate (Table II).

Independent evidence of the reliability of the new values of the hydration constants of the proton was derived from the effects of water on the spectrophotometrically determined paH_s in picric acid solutions containing various amounts of water. These data are presented in ref 4. As additional checks on the hydration constants of the proton we have determined in the present paper the specific conductivity of water-containing picric acid solutions and the paH_s spectrophotometrically using *p*-naphtholbenzein as indicator. Knowing the hydration constants of the *p*-naphtholbenzeinium ion, paH_s was calculated using eq 1 and 2, assuming the spectra of the unhydrated and hydrated protonated forms of the indicator to be the same. The total picrate concentration, $[Pi^-]_t$, in picric acid solutions containing water and a small concentration of basic impurity, C_{BH^+} present in the solvent is[4]

$$[Pi^-]_t = [Pi^-]_s(V + K^f{}_{HPi_2^-}[HPi]) = C_{BH^+} + \sum[H^+] = C_{BH^+} + y[H^+]_s \qquad (5)$$

In eq 5 $V = 1 + K^f{}_{Pi_w^-}[H_2O]$, where $K^f{}_{Pi_w^-} = [Pi^-]_w/[Pi^-]_s[H_2O]$. Substituting the dissociation constant $K^d{}_{HPi} = a_{H_s^+}[Pi^-]_sf/[HPi]$ in eq 5 gives

$$ya^2{}_{H_s^+} + fa_{H_s^+}C_{BH^+} - K^d{}_{HPi}[HPi](V + K^f{}_{HPi_2^-}[HPi]) = 0 \qquad (6)$$

Solving eq 6 for $a_{H_s^+}$ and substituting into eq 5 gives

$$f^2[Pi^-]_t{}^2 - f^2[Pi^-]_tC_{BH^+} - yK^d{}_{HPi}[HPi](V + K^f{}_{HPi_2^-}[HPi]) = 0 \qquad (7)$$

It has been assumed in eq 6 and 7 that $pK^d{}_{HPi}$, $K^f{}_{HPi_2^-}$, and $K^f{}_{Pi_w^-}$ are unaffected by water to a concentration of at least 1 M. The estimation of C_{BH^+} from spectrophotometric determination of picrate in water-free picric acid solution was described previously.[4]

Values of potentiometrically[4] and spectrophotometrically determined paH_s were introduced into eq 6 to calculate y.

Experimental Section

Chemicals and Instrumentation. Solvent. Purified acetonitrile was the same batch as used previously,[2,4] having a water content of 1–2 × 10^{-3} M and a concentration of basic impurities of 0.4–1.1 × 10^{-5} M as estimated from the absorption of the picrate ion in water-free solutions of picric acid.[2] *o*-Nitro-,[5] *m*-nitro-,[2] *o*-nitro-4-chloroaniline,[5] aniline,[6] anilinium perchlorate,[7] *p*-naphtholbenzein,[8] picric acid,[5] perchloric acid "monohydrate"[2] (actually $HClO_4 \cdot 1.57\ H_2O$), benzoic acid,[9] and tetraethylammonium benzoate[9] were used previously. *m*-Nitroanilinium perchlorate was prepared in this laboratory by H. Smagowski following the procedure of Jasinski and Smagowski.[10] Assay from spectrophotometric titrations in acetonitrile at 440 mμ with triethylamine was 99.5%. For all other mixtures of the nitroanilines and their perchlorates, perchloric acid monohydrate was added to a solution of the nitroaniline in AN, the water introduced with the perchloric acid taken into account. 2-Nitro-4,5-dimethylaniline was a Chemical Procurement Laboratories product, recrystallized from ethanol, mp 141°. Spectrophotometric, conductometric, potentiometric glass-electrode paH, and near-ir techniques have been described elsewhere.[2,4]

Results and Discussion

Hydration of Uncharged Bases. Values of paH_s in 3.00 × 10^{-3} M benzoic acid–3.20 × 10^{-2} M tetraethylammonium benzoate in the presence of 0–1.14 M *m*-nitroaniline and 0–1.24 M water are presented in Table I. As does *o*-nitroaniline,[2] *m*-nitroaniline forms a mono- and a diheteroconjugate with benzoate, $K^f{}_{Bz1^-}$ and $K^f{}_{Bz21^-}$ being 2.4 and 2.7, respectively. From the data in Table I there is no evidence of hydration of *m*-nitroaniline since the experimental and calculated paH values agree.

From the near-infrared spectrophotometric data of the –OH stretch band of water at 1410 mμ in the presence of 0.19–0.37 M of the uncharged bases, *o*- and *m*-nitroaniline and aniline, it appears that these bases are not hydrated, even in presence of 1.5 M water. The absorbance index of water at 1410 mμ was found to decrease with increasing concentration of water,[4] in agreement with the values reported by Coetzee.[3] The

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(5) I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, Jr., *J. Amer. Chem. Soc.*, **83**, 3927 (1961).

(6) I. M. Kolthoff and M. K. Chantooni, Jr., *ibid.*, **87**, 1004 (1965).

(7) I. M. Kolthoff, M. K. Chantooni, Jr., and S. Bhowmik, *Anal. Chem.*, **39**, 1627 (1967).

(8) I. M. Kolthoff, M. K. Chantooni, Jr., and S. Bhowmik, *ibid.*, **39**, 315 (1967).

(9) I. M. Kolthoff and M. K. Chantooni, Jr., *J. Phys. Chem.*, **70**, 856 (1966).

(10) T. Jasinski and H. Smagowski, *Chem. Anal.* (Warsaw), **11**, 1203 (1966).

Table I. Effect of *m*-Nitroaniline (I) and Water on the p*a*H$_s$ of 3.00 × 10^{-3} *M* Benzoic Acid–3.20 × 10^{-2} *M* Tetraethylammonium Benzoate Mixture

C_I, *M*	C_{H_2O}, *M*	p*a*H$_s$ Obsd	p*a*H$_s$ Calcd
0	0	23.56	23.56
0.12	0	23.27	23.32
0.305	0	22.97	22.96
0.565	0	22.54	22.55
0.82	0	22.20	22.27
1.14	0	21.83	21.86
1.14	0.277	21.41	21.65
1.14	0.486	21.12	21.38
1.14	0.693	20.87	21.06
1.14	0.970	20.59	20.62
1.14	1.24	20.34	20.26

$K^f_{Bz_I^-} = 2.4$, $K^f_{Bz_{2I}^-} = 2.7$, $K^f_{Bz_w^-} = 2.3$,[a] $K^f_{Bz_{2w}^-} = 15.2$,[a] $K^f_{Bz_{3w}^-} = 10.2$,[a] $pK^d_{HBz} = 20.7$,[b] $K^f_{H(Bz)_2^-} = 4.0 \times 10^3$.[b]

[a] I. M. Kolthoff and M. K. Chantooni, Jr., *Anal. Chem.*, **39**, 1080 (1967). [b] Reference 9.

absorbance of the free bases at 1410 mμ could be neglected in every case, their absorbance indices being <0.02.

Hydration of Monoprotonated Bases. Glass-electrode p*a*H measurements were made in buffered solutions 1.35 × 10^{-2} *M* in 2-nitro-4,5-dimethylaniline, to which 0.489 *M* perchloric acid in acetic acid was added. In these measurements a glass electrode different from the one previously[2] used was employed. It gave driftless and reproducible potentials. The values of $[BH^+]_s$ were found from the difference $c_B - c_{HClO_4}$, c_{HClO_4} varying from 4.9 × 10^{-4} to 1.12 × 10^{-2} *M*. A value of 5.65 ± 0.02 for $pK^d_{BH^+}$ was obtained. Glass-electrode p*a*H$_s$ data were obtained in mixtures of 1.15 × 10^{-2} *M* *m*-nitro-, 8.05 × 10^{-2} *M* 2-nitro-4,5-dimethylaniline, or 1.72 × 10^{-2}*M* aniline and the corresponding perchlorates, 3.80 × 10^{-3}, 2.48 × 10^{-3}, and 2.06 × 10^{-2}*M*, respectively, in the presence of 0–1.2 *M* water. The hydration constants are those values which yield the best agreement between the experimental and calculated p*a*H$_s$ values, which amounted to ±0.03 p*a*H unit, using eq 1 and 2. The uncharged bases were regarded as being unhydrated and $\Sigma[H^+]_{nw}$ or $y[H^+]_s \ll C_{BHClO_4}$ (see first section of the paper). In Table II the potentiometric p*a*H$_s$ values of a solution 6.0 × 10^{-4} *M* in *m*-nitroaniline and 1.08 × 10^{-2} *M* in its perchlorate in presence of water are compared with the spectrophotometric values found in the same solution using *p*-naphtholbenzein as indicator. Assuming that the hydrated benzeinium ions have the same absorption spectrum as that of the unhydrated red IH$_s^+$ ion, $\Delta paH_s = paH_{s_{potent}} - paH_{s_{spectro}} = v$ (see eq 1). The hydration constants of the benzeinium ion are readily calculated[2] from the values of v at various concentrations of water (eq 2), and from these hydration constants values of ΔpaH_s were back-calculated in Table II. Potentiometric and spectrophotometric p*a*H$_s$ data for the *o*-nitroaniline system were taken from a previous paper.[2] Values of $pK^d_{BH^+}$ of *o*- and *m*-nitroanilinium, anilinium, and *p*-naphtholbenzeinium equal to 4.85,[6] 7.60,[2] 10.60,[11] and 6.80[9] have previously been reported.

Table II. Hydration of *p*-Naphtholbenzeinium Ion (IH$^+$) from Difference in Spectrophotometric and Potentiometric p*a*H$_s$ Values in Buffered Mixtures of *o*- or *m*-Nitroaniline (B) and Its Perchlorate

C_{H_2O}, *M*	p*a*H$_{s_{obsd}}$ Potent	p*a*H$_{s_{obsd}}$ Spectro	Δp*a*H$_s$[a] Found	Δp*a*H$_s$[a] Calcd
$K^f_{IH_w^+} = 2.1$, $K^f_{IH_{2w}^+} = 4.3$, B = *m*-nitroaniline, 6.0 × 10^{-4} *M* B, 1.08 × 10^{-2} *M* BHClO$_4$, 2.40 × 10^{-5} *M* I (*p*-HBz)				
0	6.53	6.55	−0.02	0
0.10	6.76	6.67	+0.09	+0.10
0.20	6.99	6.77	+0.22	+0.20
0.30	7.20	6.89	+0.31	+0.31
0.50	7.57	7.09	+0.48	+0.48
0.70	7.91	7.30	+0.61	+0.66
0.90	8.08	7.48	+0.70	+0.81
1.20	8.50	7.71	+0.79	+0.99
B = *o*-nitroaniline, 3.02 × 10^{-2} *M* B, 4.2 × 10^{-3} *M* BHClO$_4$, 2.21 × 10^{-5} *M* I				
0.10	6.20	5.86	+0.34	+0.10
0.20	6.40	6.00	+0.40	+0.20
0.50	7.11	6.45	+0.66	+0.48
0.90	8.00	7.20	+0.80	+0.81

[a] $\Delta paH = paH_{s_{potent}} - paH_{s_{spectro}}$.

Values of $K^f_{IH_w^+}$ and $K^f_{IH_{2w}^+}$ were found in the present study for the following ions: *m*-nitroanilinium, 1.0, 5.2; 2-nitro-4,5-dimethylanilinium, ~0, 1.2 × 10; *p*-naphtholbenzeinium ion, 2.1, 4.3; and anilinium, 0.8, 1.8. The hydration constants of *o*-nitro- and *o*-nitro-4-chloroanilinium ions are taken to be the same as that of 2-nitro-4,5-dimethylanilinium, while those of dibromothymol and *p*-naphtholbenzeinium ions are assumed to be equal.

Hydration of the Proton

Uncharged Indicator Bases in Perchloric Acid Solutions Containing Water. Spectrophotometrically determined values of the indicator ratio $\Sigma[IH^+]_s/[I]$ in dilute perchloric acid solutions in the presence of water using *o*-nitro-, *o*-nitro-4-chloro-, and *m*-nitroaniline and dibromothymolbenzein as indicators are taken from a previous paper.[2] Perchloric acid was in large excess over the indicator base. Using the hydration constants of IH$_s^+$ in this paper, values of v are calculated (eq 2) and, in turn, $[H^+]_s$ (eq 1). Knowing $[H^+]_s$ and v, values of y are then found using eq 3. Equilibrium concentrations of water were calculated as described previously.[2]

Table III. Conductometric Picrate Measurements in Picric Acid Solutions in AN Containing Water

C_{H_2O}, *M*	L[a], ohm^{-1} cm^{-1} × 10^5	$[Pi^-]_t$, *M* × 10^4	L[a], ohm^{-1} cm^{-1} × 10^5	$[Pi^-]_t$, *M* × 10^4
	2.81 × 10^{-2} *M* HPi		1.21 × 10^{-1} *M* HPi	
0.210			1.15	0.70
0.234			1.45	0.88
0.334	0.98	0.59	1.72	1.03
0.444	1.38	0.83	2.69	1.61
0.556	2.05	1.24	3.89	2.33
0.667	2.50	1.51	4.63	2.77
0.778			6.80	4.08
0.889	4.22	2.5	8.92	5.36
1.11	6.28	3.8	13.7	8.23
1.54	11.6	7.0	25.1	15.1

[a] L is specific conductance.

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(11) J. F. Coetzee and G. Padmanabhan, *J. Amer. Chem. Soc.*, **87**, 5005 (1965).

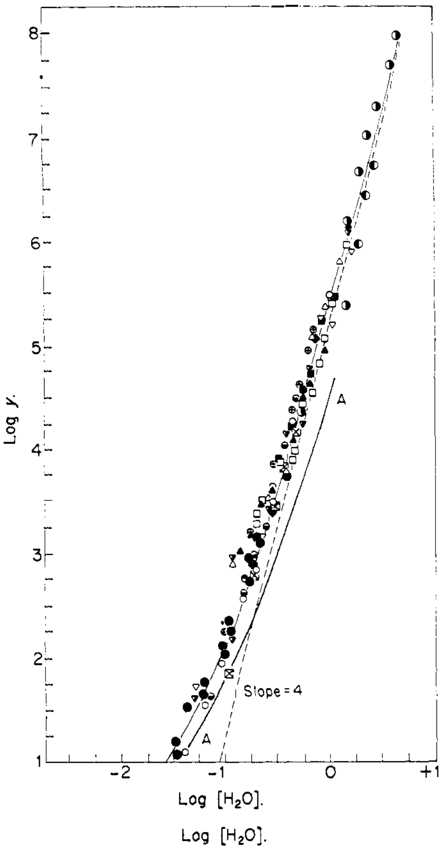

Figure 1. Plot of log y *vs.* log [H_2O]. Perchloric acid spectrophotometric data are represented by circles: ◑, 6.10 × 10^{-3} *M* $HClO_4$, 2.85 × 10^{-4} *M* *m*-NA; ◐, 1.38 × 10^{-2} *M* $HClO_4$, 2.75 × 10^{-4} *M* *m*-NA; ⊕, 6.82 × 10^{-3} *M* $HClO_4$, 1.75 × 10^{-5} *M* BrTBz; ◓, 6.10 × 10^{-3} *M* $HClO_4$, 1.33 × 10^{-4} *M* *o*-NA; ◒, 1.38 × 10^{-2} *M* $HClO_4$, 1.00 × 10^{-4} *M* *o*-NA; ●, 6.10 × 10^{-3} *M* $HClO_4$, 8.5 × 10^{-5} *M* *o*-N-*p*-ClA; ○, 1.38 × 10^{-2} *M* $HClO_4$, 6.95 × 10^{-5} *M* *o*-N-*p*-ClA. Picric acid data: spectrophotometric picrate, ▲, 2.70 × 10^{-2} *M* HPi; △, 1.76 × 10^{-1} *M* HPi; conductometric, ■, 2.8 × 10^{-2} *M* HPi; □, 1.21 × 10^{-1} *M* HPi (spectrophotometric p*a*H: ◆, 2.41 × 10^{-2} *M* HPi, ⊠, 1.08 × 10^{-1} *M* HPi, 4.9 × 10^{-5} *M* *p*-naphtholbenzein, 625 mμ); potentiometric p*a*H, ▼, 2.70 × 10^{-2} *M* HPi, and, ▽, 1.76 × 10^{-1} *M* HPi. Curve A, plot of log y *vs.* log [H_2O] in previous publication.[2]

Dissociation of Picric Acid in Presence of Water. Potentiometric p*a*H_s data and spectrophotometric data of $[Pi^-]_t$ in picric acid solutions containing water have been taken from a previous publication.[4] Conductometric data of $[Pi^-]_t$ in similar solutions are presented in Table III, taking $\Lambda_{0_{HPi}} = 160^5$ and $\Lambda_{0_{HHPi_2}} = 137.$[12] The ionic strength of these solutions was so small that ionic atmosphere corrections could be neglected.

In the spectrophotometric determination of p*a*H_s in picric acid solutions in the presence of water with *p*-naphtholbenzein as indicator, measurements of $\Sigma[IH^+]$ were carried out at 625 mμ, the wavelength of maximum absorption of IH_s^+ ($\epsilon_{IH_s^+} = 3.0 \times 10^4$).[8] At this wavelength the absorption of I, picric acid, and picrate are negligible. The results are given in Table IV. Values of y are calculated from conductometric $[Pi^-]_t$ data using eq 7 and from the spectrophotometric p*a*H_s data using eq 6 (upon replacing C_{BH^+} by the sum $C_{BH^+} + \Sigma[IH^+]$ in eq 6) and taking $pK^d_{HPi} = 11.0$,[13] $K^f_{HPi_2} = 2^{13}$, and $K_{Pi_w^-} = 0.5.$[14] Since the overall degree of dissociation of 10^{-2}–10^{-1} *M* picric acid is of the order of 1% in the presence of 1 *M* water and the undissociated acid is not hydrated,[4] the equilibrium and analytical picric acid and water concentrations were taken equal.

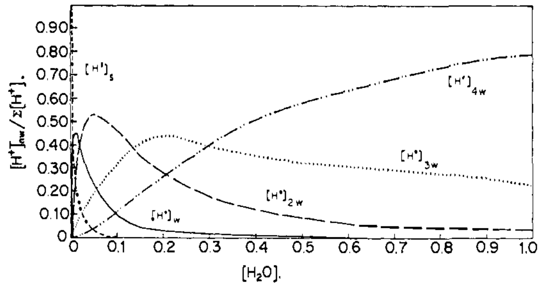

Figure 2. Plot of calculated values of $[H^+]_{nw}/\Sigma[H^+]$ *vs.* [H_2O].

Table IV. Spectrophotometric p*a*H_s Measurements in Picric Acid Solutions in AN in the Presence of Water

C_{H_2O}, *M*	A_{625}[a]	p*a*H_s[b]	A_{625}[a]	p*a*H_s[b]
—2.43 × 10^{-2} *M* HPi—			1.08 × 10^{-1} *M* HPi	
0.185	0.163	7.70	0.332	7.32
0.278	0.135	7.79	0.277	7.43
0.370	0.115	7.86	0.238	7.51
0.463	0.099	7.94	0.209	7.58
0.556	0.091	7.97	0.187	7.63
0.74	0.074	8.09	0.156	7.72

[a] Concentration of *p*-naphtholbenzein, 4.85 × 10^{-5} *M*, 1-cm cell. [b] $C_{BH^+} = 5 \times 10^{-6}$ *M*, $K^f_{1H_w^+} = 2.1$, $K^f_{1H_{2w}^+} = 4.3$.

A plot of log y *vs.* log [H_2O] constructed from all the perchloric and picric acid data is presented in Figure 1. The multitude of data obtained by the various methods yields satisfactory agreement in the values of y. At water concentrations greater than about 0.6 *M* the experimental curve approaches a straight line with a slope of 4, indicating that the greatest fraction of the proton is present as H_{4w}^+ (see Figure 2). From Figure 1 the following approximate values of the hydration constants of the proton are obtained: $K_{H_w^+} = 1.6 \times 10^2$, $K^f_{H_{2w}^+} = 8 \times 10^3$, $K^f_{H_{3w}^+} = 6 \times 10^4$, and $K^f_{H_{4w}^+} = 2 \times 10^5$, as compared with the previously reported values of 1.4 × 10^2, 2.7 × 10^3, 3.3 × 10^4, and 1.2 × 10^4, respectively.[2]

In conclusion it should be stated that the protonated forms of the indicators in the presence of alcohols used in the previous[2] paper undoubtedly will be alcoholated, and that the previously reported values of alcoholation constants of the proton need some correction.

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