enon, and, in fact, the hydroxide ion must have more than one molecule of solvent to satisfy the observed data. If data were available, it is expected that a maximum in pk would be observed for other weak acids, the anions of which are solvated during the ionization. However, the decrease in pk from the maximum would not be expected to be greater than that for HND. This is because the solvent in excess of the complex is dioxane, which would solvate hydrogen ion but would not likely solvate an anion.

The quantitative analysis of the data for water, HND, and other weak acids will be the subject of a forthcoming report. These data will show that the treatment above suffices to explain the differences in ionization in going from one solvent to another.

The dioxane–water system has been studied rather extensively, and complex formation is supported by data on base strength,[12] infrared,[13-15] heat of solution and azeotrope formation,[16,17] freezing points,[18] and other physical properties.[19] From these data, it is difficult to decide on a particular complex in solution. The azeotrope is a 1:1 mole mixture.

Based on measurements of base strengths of saturated cyclic ethers, Arnett and Wu[12] feel that dioxane is abnormally basic and this is caused by a special cooperative influence of the oxygens of the dioxane in their

(12) E. M. Arnett and C. Y. Wu, *J. Am. Chem. Soc.*, **84**, 1864 (1962).
(13) S. C. Mohr, W. D. Wilk, and G. M. Barrow, *ibid.*, **87**, 3048 (1965).
(14) W. Gordy, *J. Chem. Phys.*, **4**, 769 (1936).
(15) A. Fratiello and J. P. Luongo, *J. Am. Chem. Soc.*, **85**, 3072 (1963).
(16) E. R. Smith and M. Wojciechowski, *J. Res. Natl. Bur. Std.*, **18**, 461 (1937).
(17) R. D. Stallard and E. S. Amis, *J. Am. Chem. Soc.*, **74**, 1781 (1952).
(18) G. Scatchard and M. A. Benedict, *ibid.*, **58**, 837 (1936).
(19) G. Åkerlöf and O. A. Short, *ibid.*, **58**, 1241 (1936).

interaction with water and hydronium ion. They visualize a 1:1 dioxane–water complex by which a water molecule is attached by two hydrogen bonds.

From a recent infrared study centering around the 3-μ region, Mohr, Wilk, and Barrow[13] feel that this latter complex is not possible but that a 1:1 complex is formed utilizing one hydrogen bond. This complex is postulated for low dioxane concentration in water, but a complex involving one water and two dioxane molecules is postulated for higher dioxane concentrations.

The infrared data of Gordy[14] are concerned primarily with the 3-, 4.7-, and 6.18-μ regions for various dioxane–water mixtures covering the total concentration range. The 4.7-μ band is attributed to association between water molecules, and it is not present in mixtures containing 7 vol. % or less water, but appears definitely in a 13 vol. % mixture. This range brackets the concentration which includes the complex postulated here. Gordy attributes the changes in the 3- and 6.18-μ bands to association between water and dioxane. Both of these bands are shifted to shorter wave lengths with increasing dioxane concentration right up to pure dioxane where they are absent. The 3-μ band is shifted 0.2 μ and its intensity is increased, whereas, the 6.18-μ band is shifted 0.1 μ and its intensity is not increased. These shifts are attributed to hydrogen bond linkages.

Similar observations and conclusions were made by Fratiello and Luongo.[15] In addition, they observed displacement to lower frequency of the C–O stretching mode in the dioxane spectrum. This they attribute to hydrogen bond formation at this site.

The interpretation of the data in the present report is considered particularly significant, in that it is suggested that ionization data can be used for determining the structure of solvent complexes.

Equilibria in Solution. II. Evaluation of pK and Solvation Numbers

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Contribution from the U. S. Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland. Received August 2, 1965

The evaluation of the K and n terms in the expression $(H^+)(A^-)/(HA) = K(S)^n = k$ for weak acids has been accomplished. The values of n vary with the acid structure from 1 for 2,2',4,4',6,6'-hexanitrodiphenylamine to 6 for benzoic acid. The values of K and n are shown to be applicable from solvent to solvent if reasonable structures for the solvents are assumed.

In the first article of this series,[1] data were reported for the ionization of 2,2'4,4'6,6'-hexanitrodiphenylamine (HND) in various solvents. These data revealed a maximum in the pk of HND in the system dioxane–water near 91% dioxane. The maximum was at-

tributed to the formation of a stable complex in solution, consisting of dioxane–water–dioxane, which would occur at 90.73% dioxane. In the present article, data are presented for the pk of picric acid in 89.2% dioxane in water and 100% dioxane at 28 ± 1°. The pk values at zero ionic strength in these solvents are 5.05 ± 0.15 and 3.90 ± 0.10, respectively. As the literature value[2] for picric acid in water is 0.38 (25°), these data also show the presence of a maximum in pk in this solvent system.

In the present paper, the data for HND and picric acid as well as literature data for other weak acids are treated quantitatively. Values of pK are derived which

(1) D. J. Glover, *J. Am. Chem. Soc.*, **87**, 5275 (1965).

(2) N. A. Lange, "Handbook of Chemistry," 6th Ed., Handbook Publishers Inc., Sandusky, Ohio, 1946, p. 1380.

are shown to be applicable from solvent to solvent, not being restricted to the system dioxane–water.

Theoretical Considerations. The ionization constant is expressed by eq. 1, where A^- is the anion of the acid

$$nS + HA \overset{K}{\rightleftharpoons} xSH^+ + ySA^- \qquad (1)$$
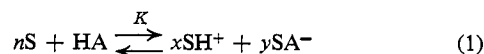
HA, and n is the total of x plus y moles of solvent S bringing about the ionization. The equilibrium expression is given in eq. 2, where the parentheses denote

$$\frac{(xSH^+)(ySA^-)}{(S)^n(HA)} = K \qquad (2)$$

activity. Equation 2 is usually written as (3), where it

$$\frac{(H^+)(A^-)}{(HA)} = K(S)^n = k \qquad (3)$$

is understood that the ions are solvated and k includes the solvent term $(S)^n$.

It was pointed out in the previous paper that the maximum in pk could be explained by assuming that the ionization is promoted by either water or dioxane, but not by the complex, dioxane–water–dioxane. This would mean that water only, in excess of the complex, would cause the ionization until the composition reached 90.73% dioxane; and then dioxane only, in excess of the complex, would cause the ionization. In order to express this quantitatively, the activity of the solvent must be redefined. Instead of defining the activity of the solvent as 1, let the activity coefficient be 1. This is in keeping with substances dissolved in the solvent and gives for a pure solvent an activity equal to its concentration.

It was also pointed out previously that the ionization solvation in the case of HND is probably only that associated with the hydrogen ion. The anion was thought not to be solvated further than the un-ionized acid. In the case of a smaller anion with the charge less diffuse, further solvation will occur upon ionization. For the quantitative expression of eq. 3, these solvated anions are assumed stable with changing dioxane–water concentration. For this primary solvation, this assumption is not unreasonable, and as will be seen below, is probable.

By taking logarithms of eq. 3

$$\log k = \log K + n \log (S) \qquad (4)$$

and

$$pk = pK - n \log (S) \qquad (5)$$

Let it be emphasized that pk defined in eq. 5 is the thermodynamic constant from eq. 3. Thus, pK as defined should be a true constant, regardless of what the solvent is, if the assumptions for S and n are correct.

Calculations. Values for n can be determined by considering eq. 5 for two solvent concentrations

$$pk_1 = pK - n \log (S)_1 \qquad (6)$$

$$pk_2 = pK - n \log (S)_2 \qquad (7)$$

By subtracting

$$pk_2 - pk_1 = -n \log (S)_2 - [-n \log (S)_1] = n[-\log (S)_2 + \log (S)_1] \qquad (8)$$

from which

$$n = (pk_2 - pk_1)/[\log (S)_1 - \log (S)_2] \qquad (9)$$

Values for pK can then be evaluated from eq. 5 in the form

$$pK = pk + n \log (S) \qquad (10)$$

Values of n and pK may also be determined from a plot of pk *vs.* $\log (S)$.

By eq. 5, it can be seen that an experimental verification of pK can be obtained by determining pk when (S) equals 1. At this concentration, the log term will be zero and pk equals pK. This concentration in the dioxane–water system is 89.1% dioxane.

The solvent concentration in the system dioxane–water is calculated on a molality basis by first calculating the molality of water and of dioxane. Then below 90.73% dioxane, the solvent is the water molality minus one-half the dioxane molality. Above 90.73%, the solvent is the dioxane molality minus two times the water molality. For values of k computed on a molality basis, it is necessary to divide k by the density to convert to the molality basis.

Results in Dioxane–Water. As an example of the calculations, the data from Harned and Owen[3] at 30° for acetic acid is used as shown in Table I. For each

Table I. Calculation of pK for Acetic Acid[a]

% dioxane	pk_0	pK	pk_0 (calcd.)
0	4.757	14.48	4.74
20	5.294	14.41	5.34
45	6.313	14.37	6.40
70	8.329	14.47	8.32
82	10.529	14.58	10.41
		Av. = 14.46 ± 0.06	

[a] At 30°, $n = 5.75 \pm 0.24$.

dioxane concentration, the solvent concentration may be obtained by direct calculation, or from a plot of $\log (S)$ *vs.* per cent dioxane. By considering the 0% dioxane pk_0 value, four values of Δpk may be obtained, while for the 20% dioxane value, three Δpk values are obtained, etc. With the corresponding $\Delta \log (S)$ values, ten values of n may be computed. The value for n at 30° is 5.59 ± 0.22, while the average value at 5° intervals from 0 to 50° is 5.57 ± 0.24. The pK values listed in Table I were computed by eq. (10) and the pk_0 (calcd.) values by eq. 5. Similar calculations for formic and propionic acids at 30°[3] give $pk = 12.63 \pm 0.11 - 5.09 \pm 0.44 \log (S)$ and $14.96 \pm 0.02 - 5.78 \pm 0.11 \log (S)$, respectively. For these three acids the pK values from 0 to 50° tend to smooth towards one value. Thus, the known peak in k[4] tends to be flattened. For example, for acetic acid at 25°, $pk = 14.44 \pm 0.06 - 5.54 \pm 0.24 \log (S)$.

The calculations for water can be done with pk_w, but it seems better for comparison to calculate pk_{H_2O}, which is pk_w plus the log of the water activity. The data[3] at 30° are shown in Table II, where the water

(3) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958, p. 756.
(4) Reference 3, p. 663.

Table II. Calculation of pK for Water[a]

% dioxane	pk_w	pk_{H_2O}	pK	$\frac{pk_{H_2O}[b]}{-\log (S)} = pk_w[b]$
0	13.83	15.57	24.25	15.58 − 1.74 = 13.84
20	14.46	16.10	24.23	16.12 − 1.64 = 14.48
45	15.59	17.04	24.22	17.06 − 1.45 = 15.61
70	17.71	18.81	24.29	18.77 − 1.10 = 17.67
			Av. = 24.25 ± 0.02	

[a] 30°, n = 4.97 ± 0.10 [b] Calculated.

activity is (S), for the water combined in the complex is not available for ionization. The value for n at 30° is 4.99 ± 0.11, whereas the average from 0 to 50° is 4.97 ± 0.10.

Similar calculations for the data of Dunsmore and Speakman[5] on benzoic acid at 25° give pk = 15.16 ± 0.01 − 6.29 ± 0.12 log (S). Finally, the data for HND and picric acid give pk = 3.97 ± 0.16 − 0.8 ± 0.4 log (S) and 4.95 ± 0.03 − 2.6 log (S), respectively.

All of the acids considered so far have been of the same charge type, that is, neutral proton acids. Let us now consider an acid of the type R_3NH^+. The ionization is
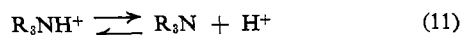
$$R_3NH^+ \rightleftarrows R_3N + H^+ \qquad (11)$$

from which

$$\frac{(R_3N)(H^+)}{R_3NH^+} = k_{R_3NH^+} \qquad (12)$$

In a system where water is the ionizing medium, this constant is obtained from the ratio k_{H_2O}/k_{R_3N}, where

$$\frac{(H^+)(OH^-)}{(HOH)} = k_{H_2O} \qquad (13)$$

and

$$\frac{(R_3NH^+)(OH^-)}{(R_3N)(HOH)} = K_{R_3N}(S)^n = k_{R_3N} \qquad (14)$$

Note the similarity of eq. 14 and 3.

For the purpose of calculation, it is convenient to convert $k_{R_3NH^+}$ to k_{R_3N} as illustrated by the data for ammonium ion in Table III. The data is from Marshall and Grunwald[6] and Table II. Another illustration is afforded by the data[6] for the anilinium ion as shown in Table IV. The results in Table IV were only slightly different using the data of James and Knox.[7]

Table III. Calculation of pK for Ammonia[a]

% dioxane	pk_{H_2O}	$pk_{NH_4^+}$ (exptl.)	pk_{NH_3}	pK_{NH_3}	$pk_{NH_4^+}$ (calcd.)
0	15.74	9.26	6.48	15.34	9.14
20	16.26	...	...	...	9.15
45	17.19	8.97	8.22	15.60	9.11
70	18.96	8.97	9.99	15.59	9.11
82	(20.77)	9.19	11.58	15.30	9.03
				Av. = 15.46 ± 0.14	

[a] At 25°, n = 5.09 ± 0.43.

(5) H. S. Dunsmore and J. C. Speakman, *Trans. Faraday Soc.*, **50**, 236 (1954).
(6) H. P. Marshall and E. Grunwald, *J. Am. Chem. Soc.*, **76**, 2000 (1954).
(7) J. C. James and J. G. Knox, *Trans. Faraday Soc.*, **46**, 254 (1950).

Table IV. Calculation of pK for Aniline[a]

% dioxane	$pk_{PhNH_3}^+$ (exptl.)	pk_{PhNH_2}	pK_{PhNH_2}	$pk_{PhNH_3}^+$ (calcd.)
0	4.63	11.11	22.26	4.59
20	4.44	11.82	22.33	4.47
45	4.00	13.19	22.49	4.19
70	3.51	15.45	22.50	3.71
82	3.51	17.26	21.94	3.15
			Av. = 22.30 ± 0.16	

[a] At 25°, n = 6.41 ± 0.60.

Having obtained pK_{H_2O} and pK_{R_3N}, it is convenient to express the ratio k_{H_2O}/k_{R_3N} as

$$pk_{R_3NH^+} = -\log [K_{H_2O}(S)^a/K_{R_3N}(S)^b] \qquad (15)$$

$$= pK_{H_2O} - pK_{R_3N} + (b - a) \log (S) \qquad (16)$$

The data from Tables III and IV give 8.94 + 0.12 log (S) for ammonium ion and 2.10 + 1.44 log (S) for anilinium ion.

Discussion

The significance of noninteger values of n is not readily apparent. They may result from experimental error in pk. They may reflect the lack of stability of the complex dioxane–water–dioxane. This latter reason is quite probable with acids of the type R_3NH^+, particularly when the water content is low. This is because of the competition between dioxane and R_3N for water.

In regards to NH_3, it is interesting to note that the same number of moles (5) of solvent are involved in its ionization as are involved with water. This means, of course, that only 1 mole of solvent is associated with the ammonium ion. This is true, for the data for HND show that only 1 mole is associated with hydrogen ion, and the data for water show 5; therefore, 1 mole for hydrogen ion and 4 moles for hydroxide ion. It should be emphasized at this point that the moles of solvent considered here are those associated with the ionization, and those are not considered that may be already bound with a given ~cies. For example, Bell[8] summarized the data sho ̣ that H_3O^+ is probably further hydrated with 3 moles of solvent. Likewise, Taft[9] concludes from a study with substituted anilines that the substituted ammonium ions are solvated with 3 or 4 moles of solvent. Additional data for ammonium ions are summarized by Schaleger and Long.[10]

Ionization in Other Solvents. In order for the values of pK and n to be really useful, they must be applicable to other solvents as indicated by eq. 3. Various applications will now be considered, and, where appropriate, the implications as to the solvent structure. Unless otherwise stated, the solvent concentration is obtained by adding the molality of water to the molality of the organic solvent.

Methanol–Water. Data for methanol are given in Table V. The calculated values agree well through 20% methanol but become poorer thereafter. The

(8) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p. 83.
(9) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **82**, 2965 (1960).
(10) L. L. Schaleger and F. A. Long, *Advan. Phys. Org. Chem.*, **1**, 15 (1963).

Table V. Ionization Constants in Methanol–Water

% methanol	Formic acid Calcd.	Found	Acetic acid Calcd.	Found	Propionic acid Calcd.	Found	Benzoic acid Calcd.	Found
10.01[a]	...	...	4.88	4.91	...	...	...	...
16.47[b]	3.90	3.91	4.96	5.00	5.05	5.14	4.40	4.50
20.01[a]	...	...	5.00	5.08	...	...	...	...
34.47[b]	4.09	4.14	5.17	5.31	5.28	5.55	4.64	4.95
40.02[a]	...	...	5.23	5.45	...	...	...	...
54.20[b]	4.33	4.56	5.42	5.78	5.54	6.01	4.92	5.50
60.05[a]	...	...	5.50	5.90	...	...	...	...
75.94[b]	4.63	5.22	5.75	6.45	5.88	6.75	5.30	6.23
80.03[a,c]	...	...	6.84	6.64	...	...	...	...
90.02[a,c]	...	...	7.28	7.31	...	...	...	...
93.74[b,d]	6.91	6.45	8.23	7.77	...	...	8.11	7.38
95.02[a,d]	...	...	8.33	8.00	...	...	...	...
99.99[a,e]	...	...	9.49	9.52	...	...	9.54	9.28

[a] T. Shedlovsky and R. L. Kay, *J. Phys. Chem.*, **60**, 151 (1956). [b] A. L. Bacarella, E. Grunwald, H. P. Marshall, and E. L. Purlee, *J. Org. Chem.*, **20**, 747 (1955). [c] Assumes a dimer of methanol. [d] Assumes a trimer of methanol. [e] Assumes a tetramer of methanol.

Table VI. Ionization Constants[a] in Ethanol–Water

% ethanol	Formic acid Calcd.	Found	Acetic acid Calcd.	Found	Propionic acid Calcd.	Found	Benzoic acid Calcd.	Found
0	3.73	3.75	4.78	4.76	4.86	4.87	4.20	4.20
20.3	4.02	4.01	5.09	5.12	5.19	5.32	4.55	4.76
35.0	4.26	4.22	5.35	5.41	5.46	5.66	4.85	5.22
50.1	4.53	4.56	5.65	5.80	5.77	6.09	5.18	5.72
65.1	4.85	4.95	5.99	6.23	6.09	6.57	5.56	6.13
79.9	5.20	5.57	6.38	6.80	6.53	7.10	6.01	6.72
100.0	5.80	9.05	7.03	10.22	7.21	...	6.74	10.15
100.0[b]	8.87	9.05	10.37	10.22	10.69	...	10.54	10.15

[a] E. Grunwald and B. J. Berkowitz, *J. Am. Chem. Soc.*, **73**, 4939 (1951). [b] Assumes a tetramer of ethanol.

values of k are off by a minimum of a factor of five at 75%. By assuming various polymers, the calculated data once again show good agreement from 80 through 100% methanol. It is probable that the dimer of methanol is predominant even in 75% solution. Support for methanol polymers which depolymerize on addition of other solvents comes from the data of Coplan and Fuoss[11] and Mecke.[12] A ring polymer, $(ROH)_6$, is postulated by Pauling[13] for alcohols in general, and a tetramer has been found in the vapor of methanol.[14]

Ethanol–Water. Ethanol data are given in Table VI. Within a factor of two to three in k, the agreement is good through 65% ethanol and is not too far off in 80% ethanol. There is considerable deviation in 100% ethanol, but by assuming a tetramer, good agreement is again shown.

2-Propanol–Water. Values of pk for propionic acid in 5, 10, and 20% 2-propanol are 4.98, 5.09, and 5.33,[15] respectively. By assuming 1 mole of solvent per mole of alcohol, the corresponding calculated values are 4.94, 5.04, and 5.24.

Glycerol–Water. Harned and Owen,[15] report a value for pk of acetic acid in 50% glycerol as 5.27. By assuming 3 moles of solvent for each mole of glycerol, the calculated value is 5.34.

(11) M. A. Coplan and R. M. Fuoss, *J. Phys. Chem.*, **68**, 1181 (1964).
(12) R. Mecke, *Discussions Faraday Soc.*, **9**, 161 (1950).
(13) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 474.
(14) W. Weltner, Jr., and K. S. Pitzer, *J. Am. Chem. Soc.*, **73**, 2606 (1951).
(15) Reference 3, p. 761.

Formamide. Mandel and Decroly,[16] have determined the pk values for formic acid and acetic acid at various temperatures in formamide. At 25° they find 5.49 and 6.82, respectively. By assuming the solvent concentration is equal to the molality of formamide, the calculated values are 5.47 and 6.67 in good agreement with experiment.

Acetone–Water. Experimental values of pk for acetic, propionic, and benzoic acids,[17] are given in Table VII. Also given are the calculated values based on the solvent concentration being equal to the sum of the molalities. Although this agreement is good, it is

Table VII. Ionization Constants in Acetone–Water

% acetone	Acetic acid Calcd.	Found	Propionic acid Calcd.	Found	Benzoic acid Calcd.	Found
10	4.95	4.89	5.04	4.98	4.38	4.44
25	5.23	5.21	5.33	5.42	4.70	4.98

Table VIII. Ionization Constant of Picric Acid

Solvent	pk	log (S)	pk (calcd.)
Methyl ethyl ketone	3.61	1.14	3.81
Acetone	3.76	1.24	3.71
Acetophenone	4.83	0.92	4.03
Propionitrile	3.27	1.26	3.69
Benzonitrile	3.99	0.99	3.96

(16) M. Mandel and P. Decroly, *Trans. Faraday Soc.*, **56**, 29 (1960).
(17) J. Dippy, S. Hughes, and A. Rozanski, *J. Chem. Soc.*, 1441 (1959).

Table IX. pk Values in Dioxane–Water

% dioxane	Molarity × 10⁵				$\mu^{1/2}$ × 10³	pk
	Picric acid	Picrate ion	Hydrogen ion	HND anion added		
89.2	259.8	5.96	4.92	1.735	8.16	5.95
	6.97	1.28	0.98	1.735	5.22	5.74
	0.775	0.600	0.455	1.735	4.68	5.45
					0	5.05 ± 0.15
100.0	24.69	2.81	2.81	...	5.30	5.49
	11.67	2.08	2.08	...	4.56	5.43
	5.34	1.54	1.54	...	3.93	5.35
	2.21	1.23	1.23	...	3.51	5.25
	0.875	0.844	0.844	...	2.91	5.02
	0.213	0.647	0.647	...	2.55	4.71
					0	3.90 ± 0.10

expected that as the acetone concentration approaches 100%, only the hydrogen ion may be solvated by acetone.

Miscellaneous Solvents. Let us now look at some solvents that might readily solvate the hydrogen ion but not the anion. Moore and Johns[18] measured the pk of picric acid in a number of solvents as shown in Table VIII. The values were corrected to a molality basis by using the density. The calculated values of pk were obtained by subtracting log (S) (where (S) is the molality of the solvent) from 4.95, which is the value of pK reported in the present paper. The only serious discrepancy is in the acetophenone value. This may be due to ion–ion combinations.

Experimental Section

Apparatus. All spectra were determined on a Beckman spectrophotometer, Model DU, using 1-cm. quartz cells. All data were obtained at 28 ± 1°, which was the temperature in the cell compartment.

Dioxane. Dioxane was purified as before.[1]

Reagents. Picric acid was recrystallized from diethyl ether. The potassium salt of picric acid was prepared by dissolving the acid in water, heating the solution to boiling, and adding excess potassium bicarbonate. The salt was filtered, washed with water, dioxane, and ether, and then air dried.

Spectra. The spectrum of the potassium salt of picric acid in dioxane showed two maxima: 418 mμ with a molar absorbancy index of 8380, and 349 mμ with a molar absorbancy index of 14,180. The acid had a maximum at 333 mμ (molar absorbancy index

(18) F. J. Moore and I. B. Johns, *J. Am. Chem. Soc.*, **63**, 3336 (1941).

4200). In 89.2% dioxane the potassium salt had one maximum at 360 mμ (molar absorbancy index 16,070) but also showed a shoulder having a molar absorbancy index of 10,880 at 410 mμ.

pk in Dioxane. A sample of picric acid was dissolved in dioxane and diluted to give a solution approximately 3×10^{-3} M. The spectrum was determined from 500 mμ to shorter wave lengths at 10-mμ intervals until the absorbancy reached 1.0. The solution was diluted by 10 and the procedure repeated. Thereafter, each solution was diluted by two and the procedure repeated. Because of considerable overlap of the spectra of the ionized and un-ionized forms of picric acid, it was not possible to determine the anion concentration directly. Instead, the concentration was determined by solving simultaneous equations using the absorptions at 400 and 335 mμ. The molar absorbancy indexes at these wave lengths are: for the anion, 7400 and 11,910; for the acid, 54.6 and 4180. Having determined the anion concentration, the acid was determined by difference and the hydrogen ion set equal to the anion.

pk in 89.2% Dioxane. The pk was determined by using picric acid in mixtures with the potassium salt of HND. The concentration of the anion of HND was determined above 500 mμ without interference. Using this value for the ionic strength, a value for the pk of HND was obtained from a plot of pk vs. $\mu^{1/2}$, from which a value for the hydrogen ion was obtained. The anion of picric acid was then equal to the hydrogen ion plus un-ionized HND. This anion concentration plus the HND anion allowed a second estimate of the ionic strength, which allowed a second estimate of the pk. This procedure was repeated until there was convergence, usually four substitutions being necessary.

The results for both solvents are given in Table IX.