

room temperature, the amount of the gas in J at any time was easily determined. The difference between the initial amount of the gas in J and the amount at any given time represents the amount of the gas present in G.

After recording pressures on E and F and the room temperature, the tube G was maintained at Dry Ice temperature, while the gas in J was condensed with a liquid nitrogen bath. The mercury in valve H was lowered sufficiently so that a small amount of hydrogen halide in G would bubble slowly into J. The coarse sintered glass disk in the right-hand side of valve H prevented mercury from being carried over into J. The valve H was then closed and the constant temperature bath once again raised around tube G. The gas in J was allowed to warm to room temperature, and, after equilibrium had been established in tube G, pressures and room temperature were again recorded. Additional quantities of hydrogen halide were removed from the solubility tube in the manner just described until a sufficient number of points (usually about four) had been taken so that a plot of pressure of hydrogen halide in G vs. mole fraction of the hydrogen halide in solution could be made. Data for a typical determina-

Table VI. Solubility of Hydrogen Chloride in 0.5 M *n*-Heptane Solution of Benzene at -78.5°

P_{HCl} , mm.	HCl in soln., mmoles	N_{HCl} \times 10^{3a}	Henry's law const., mm.
94.00	1.151	29.59	3180
85.65	1.046	26.97	3180
71.40	0.869	22.51	3170
53.45	0.641	16.70	3200
34.60	0.410	10.75	3220
			Av. 3190

^a Benzene = 2.413 mmoles; *n*-heptane = 35.31 mmoles.

tion of the solubility of hydrogen chloride in 0.5 M *n*-heptane solution of benzene at -78.5° are summarized in Table VI.

The following materials were used for the constant temperature baths: Dry Ice at sublimation pressure of 760 mm., -78.5° ; chloroform solid-liquid slush, -63.5° ; and chlorobenzene solid-liquid slush, -45.2° . The apparatus used to maintain Dry Ice at sublimation pressure of 760 mm. was adequately described previously.¹⁰

Equilibria in Solution. I. Ion Solvation and Mixed Solvent Interaction

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

A maximum in the pK values of 2,2',4,4',6,6'-hexanitrodiphenylamine (HND) is observed in the system dioxane-water. The maximum is attributed to the solvation of hydrogen ion by water or dioxane in excess of a dioxane-water complex. The complex consists of two molecules of dioxane and one of water. The fact that there is a decrease in k_w of water of about 7×10^3 in going from water to 70% dioxane, while the k of HND decreases by only two- to threefold, is explained by solvation effects. The anion of HND is not considered to be further solvated than un-ionized HND, while the hydroxide ion is thought to be solvated with more than one molecule of solvent.

Although the law of mass action is used to express equilibria in solution, no general attempt to incorporate the solvent into the expression has been made. There have been correlations of acid ionization data in various solvents, the most notable being the work of Grunwald and co-workers.¹

Much has been written about the effect of changes in dielectric constant on ionization constants. Usually a plot of pK vs. the reciprocal of the dielectric constant is presented, which is based on the Born equation.

(1) (a) H. P. Marshall and E. Grunwald, *J. Am. Chem. Soc.*, **76**, 2000 (1954); (b) E. Grunwald and B. J. Berkowitz, *ibid.*, **73**, 4939 (1951); (c) B. Gutbezahl and E. Grunwald, *ibid.*, **75**, 559 (1953).

Invariably, these plots are linear *only* over a very small range of dielectric constant change. As Harned and Owen^{2a} observed, when the plots are extended over a great range such as represented by going from water to 82% dioxane-water, the linearity fails. Such a plot is improved by considering the addition of a water concentration term.³ Even here the extension of the linear plot is not great.

It would seem that a consideration of the direct participation of the solvent in the ionization would lead to a better understanding of the solvent composition and the composition of ion solvates. For example, such a participation might be implied by the finding of Harned and Owen^{2b} that a plot of pK vs. mole fraction of dioxane gives a nearly linear plot.

The marked changes in ionization in the system dioxane-water make this system particularly intriguing. Generally, a neutral proton acid decreases in strength from its value in water as the dioxane concentration is increased to 82%, a decrease of 10^5 or 10^6 being usual. It is not unusual for the same decrease to be observed

(2) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958: (a) p. 682; (b) p. 662; (c) p. 756.

(3) M. Yasuda, *Bull. Chem. Soc. Japan*, **32**, 429 (1959), introduces (HOH) into the ionization expression for a weak acid in order to get a better plot of pK vs. the reciprocal of the dielectric constant. Curvature still occurs at high concentrations of organic solvent.

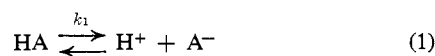
Table I. Molar Absorbancy Indexes ($\times 10^{-3}$) of the Potassium Salt of HND

Solvent	Wave length, $m\mu$																		
	340	360	370	380	390	400	410	420	430	440	460	480	500	510	520	530	540	550	560
Water	10.8	14.6	17.2	19.6	21.5	23.0	25.1	25.8	26.0	25.4	22.0	16.7	10.7	...	5.7	...	2.4	...	1.0
Wt. % dioxane in water																			
40.2	10.9	14.6	17.3	20.1	22.7	25.2	27.2	28.1	28.1	27.0	23.4	17.5	11.0	8.0	5.3	3.4	2.2	1.4	0.7
79.4	10.1	14.0	17.0	20.1	23.1	25.8	28.0	29.1	28.9	27.5	23.3	17.0	10.0	6.9	4.3	2.6	1.5	0.8	0.4
87.4	...	14.9	17.9	21.0	24.1	27.0	29.1	30.0	29.8	28.4	23.9	17.4	10.4	7.2	4.5	2.8	1.6	1.0	0.5
89.2	9.9	13.9	16.8	19.9	22.9	25.6	27.6	28.3	28.0	27.0	22.9	16.7	9.9	6.9	4.2	2.6	1.4	0.8	0.4
90.7	9.9	13.7	16.5	19.3	22.1	24.7	26.7	27.4	27.1	25.9	21.9	16.0	9.7	6.8	4.5	2.8	1.7	1.0	0.6
91.1	10.4	14.2	16.9	19.7	22.2	24.5	26.1	26.9	26.3	25.1	21.0	15.5	9.6	6.9	4.6	2.9	1.8	1.2	0.5
100.0	9.9	13.4	15.6	17.3	18.4	19.0	19.3	18.8	18.2	17.4	15.3	12.5	8.8	6.8	4.9	3.5	2.4	1.6	0.9
Wt. % methanol in water																			
31.0	11.0	15.2	17.9	20.4	23.0	25.0	26.5	27.2	26.9	25.5	21.7	16.1	10.2	7.6	5.1	3.7
86.6	11.8	16.7	19.7	22.7	25.4	28.0	29.6	29.6	28.8	26.9	21.8	15.2	8.4	...	3.6	...	1.4	...	0.5
99.8	11.2	16.5	19.6	22.5	25.4	27.7	29.4	29.5	28.1	26.3	21.0	13.8	7.68	...	3.3	...	1.3	...	0.4
Wt. % acetone in water																			
42.0	10.8	15.1	17.9	20.7	23.4	25.9	27.7	28.3	27.8	26.5	21.9	15.6	9.2	...	4.0	...	1.4
76.5	12.5	16.3	19.4	22.2	25.3	27.8	29.8	30.1	29.4	27.7	22.4	15.6	9.0	...	4.0	...	1.5
100.0	11.6	16.5	19.5	22.7	25.3	28.0	29.7	29.7	28.8	26.8	21.5	14.7	8.1	5.5	3.2	2.0	1.1	...	0.3

over the total concentration range in ethanol or methanol. There are much data in the literature for ionizations in solutions having concentrations up to 82% by weight dioxane. The search for a suitable neutral proton acid showed a scarcity of ionization data for the total composition range in the system dioxane-water.

Kertes and Goldschmidt⁴ report that the pK of 2,2',4,4',6,6'-hexanitrodiphenylamine (HND) in dioxane is 0.35, while Schill and Danielsson⁵ report a value of 2.81 in water. Apparently, the value of 0.35 is in fact the pH meter reading in dioxane-ethanol at half-neutralization. However, these values indicated that this acid might allow the total dioxane-water composition to be studied. There are other values of the pK of HND reported for water,^{6,7} but they appear to be in error.

In this laboratory, the pK of HND was determined in water, in water-organic solvent mixtures, and in pure organic solvents spectrophotometrically at $28 \pm 1^\circ$. The ionization is expressed by eq. 1 and 2, where HA is the un-ionized acid, A^- is the anion, and the parentheses denotes concentration.



$$\frac{(H^+)(A^-)}{(HA)} = k_1 \quad (2)$$

Experimental Section

Apparatus. All spectra were determined on a Beckman spectrophotometer, Model DU, using 1-cm. quartz cells unless stated otherwise. All data were obtained at $28 \pm 1^\circ$, which was the temperature in the cell compartment.

(4) S. Kertes and J. M. E. Goldschmidt, *J. Chem. Soc.*, 401 (1956).

(5) G. Schill and B. Danielsson, *Anal. Chim. Acta*, 21, 248 (1959).

(6) W. D. Treadwell and H. Hepenstrick, *Helv. Chim. Acta*, 32, 1903 (1949).

(7) K. Pan and S. Lin, *J. Chinese Chem. Soc. (Taiwan)*, 2, 1 (1955) *Chem. Abstr.*, 49, 14534 (1955).

HND and Its Potassium Salt. Eastman HND gave an assay of 100.0% by potentiometric titration with standard sodium hydroxide in acetone-water as solvent. The potassium salt of HND was prepared by F. Taylor, Jr., of this laboratory and assayed 99.7% by potentiometric titration with standard hydrochloric acid. These analytical procedures will be the subject of a later report.

Solvents. Methanol was Baker Analyzed Reagent (0.05% water) and acetone was Fisher Certified Reagent. Dioxane was purified according to the procedures of Fieser.⁸

Spectra. The spectrum of the potassium salt of HND in water showed a maximum at 428 $m\mu$, with a molar absorbancy index of 2.60×10^4 and a minimum at 295 $m\mu$, with a molar absorbancy index of 0.66×10^4 . In solvents other than water, the maximum for un-ionized HND is generally at 370-380 $m\mu$ with a molar absorbancy index near one-half that of the anion ($2-3 \times 10^4$) at its maximum (415-430 $m\mu$). Furthermore, although the anion still absorbs strongly at 500 $m\mu$, the un-ionized acid does not. Its molar absorbancy index at 410 $m\mu$ is 6.7×10^3 and at 420 $m\mu$, 2.6×10^3 . Consequently, the anion concentration in a solution containing both can usually be determined at the longer wave lengths without interference by HND. A summary of the molar absorbancy indexes for the anion is given in Table I.

pK in Water. A solution of the potassium salt of HND was prepared by dissolving 24.831 mg. in boiled distilled water in a 100-ml. volumetric flask and diluting the solution to volume with water. This solution was diluted by one-tenth to give a solution $5.20 \times 10^{-5} M$. For the pK determination, four solutions were prepared from the latter solution as follows.

To 2 ml. of the $5.20 \times 10^{-5} M$ solution pipetted into a 100-ml. volumetric flask, was added water to about 85 ml. To three such solutions, 10.00, 1.00, and 0.1000

(8) L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., New York, N. Y. 1941, pp. 368, 369.

Table II. Ionization of HND in Hydrochloric Acid Solutions

Wave length, $m\mu$	HND, % ionized		
	HCl, M		
	9.31	9.31	9.31
	$\times 10^{-5}$	$\times 10^{-4}$	$\times 10^{-3}$
520	22.0
510	95.2	71.4	21.4
500	96.4	71.6	22.0
490	95.7	69.0	20.9
480	94.1	69.2	19.5
470	96.0	69.9	19.1
460	95.2	68.2	19.9
450	95.2	68.1	19.8
440	94.7	68.0	20.6
430	96.6	70.5	...
Average	95.5	69.5	20.6
Av. dev.	± 0.6	± 1.0	± 0.9

This procedure was continued until the ionization was more than 85% complete. Usually, at least six determinations of the anion concentration were made over a 60- $m\mu$ range to give a value constant within 1%. This value was set equal to the H^+ concentration and was subtracted from the added acid to give the unionized acid concentration. A summary of the data is given in Tables IV and V where A^- (anion) means no strong acid was added.

Results and Discussion

The results given in Tables III, IV, and V also contain the values of pK at zero ionic strength. These values were obtained by extrapolating from a plot of pK vs. $\mu^{1/2}$, where the ionic strength is less than 9×10^{-4} . These extrapolations are probably quite good. How-

Table III. pK of HND in Water at $28 \pm 1^\circ$ by Spectrophotometric Measurements^a

pH ^b	HCl ^c		Molarity Anion		HND	pK HND	$\mu^{1/2}$
1.95	93.1	$\times 10^{-4}$	2.14	$\times 10^{-7}$	8.26×10^{-7}	2.62	0.0965
2.93	9.31	$\times 10^{-4}$	7.23	$\times 10^{-7}$	3.17×10^{-7}	2.67	0.0305
4.02	0.931	$\times 10^{-4}$	9.94	$\times 10^{-7}$	0.46×10^{-7}	2.70	0.00965

^a Added anion concentration = $1.040 \times 10^{-6} M$. ^b Measured. ^c Used for hydrogen ion concentration.

ml. of 0.0931 N hydrochloric acid were added, while to a fourth solution was added 0.1 ml. of 0.1026 N sodium hydroxide. These solutions were diluted to volume with water and mixed. The solution containing the sodium hydroxide did not show a difference from one without NaOH.

The absorbancies of each of the solutions were determined in a 10-cm. spectrophotometer cell from 520 through 290 $m\mu$ at 10- $m\mu$ intervals. Assuming no absorbancy due to HND, the per cent of HND ionized was calculated for each reading based on the absorbancies of the solution containing sodium hydroxide. The values so calculated were constant above 430 $m\mu$ (Table II) and increased below this wave length, indicating that HND did not interfere above 430 $m\mu$. The hydrochloric acid solutions, which were 9.31×10^{-3} , 9.31×10^{-4} , and $9.31 \times 10^{-5} M$, were found to be in order 20.6, 69.5, and 95.5% ionized with respect to HND. The pK values are given in Table III.

The Ionization in Organic Solvents and Their Mixtures with Water. In the mixtures where the water concentration was large, it was generally necessary to obtain some data by adding a strong acid (perchloric) as described above for water only. When the water concentration was small, k was calculated by determining the anion concentration (= H^+ concentration) in solutions where the initial HND concentration was known. An example of the latter procedure follows.

A 4.725-mg. sample of HND was weighed into 8.00 ml. of dioxane in a 10-ml. volumetric flask, 1.300 ml. of water added, and the solution was diluted to volume with dioxane (required 0.780 ml.). The total dioxane was 8.78 ml. or 9.00 g. to give a solution 87.4 wt. % in dioxane. The spectrum of this solution was determined from 600 $m\mu$ until the optical density exceeded 1 (530 $m\mu$). Five milliliters of this solution was then diluted to 10 ml. with 87.4% dioxane, and the spectrum of the latter solution was determined as before.

Table IV. pK ($-\log k$) Values of HND in Dioxane-Water

Solvent, wt. % dioxane	Molarity $\times 10^5$		pK	pK_0^b
	HND	HND anion, A^-^a		
40.2	9.82	36.9	2.86	
	3.26	20.1	2.91	
	1.04	10.64	2.96	
	0.30	5.54	2.99	
	0.07	2.85	2.94	
79.4	35.0	196.0	1.96	3.03 ± 0.01
	12.7	102.6	2.08	
	16.2	86.0	2.34	
	6.1	45.0	2.48	
	1.05	24.5	2.24	
87.4	0.42	9.8	2.64	3.23 ± 0.02
	65.0	42.6	3.55	
	26.3	27.5	3.54	
	9.70	17.2	3.52	
	3.05	10.4	3.45	
89.2	0.995	5.73	3.48	3.44 ± 0.05
	16.18	7.18	4.50	
	6.68	5.00	4.43	
	2.54	3.30	4.37	
	0.82	2.10	4.27	
90.7	14.77	6.56	4.54	4.05 ± 0.05
	4.31	6.36	4.53	
	2.93	2.40	4.45	
	1.92	0.75	4.31	
	33.24	9.42	4.57	
91.1	15.12	6.21	4.59	4.22 ± 0.05
	6.41	4.26	4.55	
	2.26	3.07	4.38	
	212.3	1.02	7.32	
	105.7	0.98	7.03	
100.0	52.42	0.914	6.80	4.34 ± 0.15
	25.89	0.773	6.64	
	0.578	0.489	5.38	
	1.703	0.43	5.96	
			2.88 \pm 0.20	

^a Also solvated H^+ concentration and ionic strength. ^b $\mu = 0$.

ever, above this ionic strength, the extrapolated values are only approximate and are not included in the tables.

Table V. pK ($-\log k$) Values of HND in Methanol-Water and Acetone-Water

Solvent	Molarity			pK	pK_0^b
	HND	HND anion, A ⁻	Solvated H ⁺ ^a		
Wt. % methanol	$\times 10^6$	$\times 10^6$	$\times 10^3$		
31.0	6.984	0.666	105.4	2.00	
	6.04	1.61	31.5	2.08	
	5.06	2.59	13.66	2.16	
	3.58	4.07	6.84	2.11	
	2.04	5.61	3.15	2.06	
86.6	$\times 10^6$	$\times 10^6$	$\times 10^3$		
	1.46	1.09	10.51	2.11	
	1.09	1.46	5.255	2.15	
	0.49	2.06	1.051	2.35	
	0.56	8.98	A ⁻	2.84	2.73 ± 0.10
99.8	$\times 10^6$	$\times 10^6$			
	11.04	8.03	A ⁻	4.23	
	5.97	6.78	A ⁻	4.11	
	4.18	5.36	A ⁻	4.16	
	1.308	3.46	A ⁻	4.04	
	0.647	3.31	A ⁻	3.77	
	0.197	1.71	A ⁻	3.83	3.50 ± 0.15
Wt. % acetone	$\times 10^4$	$\times 10^4$			
42.0	4.66	15.8	A ⁻	2.27	
	1.78	8.45	A ⁻	2.40	
	0.485	4.57	A ⁻	2.37	2.50 ± 0.10
76.5	$\times 10^4$	$\times 10^4$			
	6.96	13.5	A ⁻	2.58	
	0.902	3.19	A ⁻	2.99	
	0.0374	0.781	A ⁻	2.79	2.90 ± 0.10
100.0	$\times 10^4$	$\times 10^4$			
	9.72	0.393	A ⁻	5.80	
	7.84	0.398	A ⁻	5.69	
	4.72	0.343	A ⁻	5.60	
	2.25	0.281	A ⁻	5.45	
	1.04	0.220	A ⁻	5.33	
	0.614	0.211	A ⁻	5.14	
	0.349	0.133	A ⁻	5.29	
	0.449	0.183	A ⁻	5.13	
	0.214	0.172	A ⁻	4.86	
	0.115	0.126	A ⁻	4.86	
	0.150	0.166	A ⁻	4.74	
	0.0469	0.146	A ⁻	4.34	3.3 ± 0.3

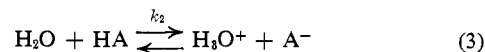
^a Also the value of the ionic strength. ^b $\mu = 0$.

The extrapolated value for water is 2.71 and is included here because it is used in the following discussion.

The results for the various solvents were surprising in that the pK ($\mu = 0$) values do not vary very much from the value in pure water. Normally a proton acid of this charge type (neutral) becomes much weaker as the organic solvent concentration is increased. This is particularly true for dioxane-water mixtures. For example, the pK_w values (25°) from Harned and Owen^{2c} for water are 14.00, 14.62, 15.74, and 17.86 for 0, 20, 45, and 70 wt. % dioxane in water. Note that there is a decrease in k of about 7×10^8 in going from water to 70% dioxane, while for HND the decrease is at most threefold. Furthermore, although the pK of HND continues to increase (1.6 pK units from water) with further increase of dioxane concentration, it reaches a maximum, then again decreases.

The comparison with water quite likely reflects solvation effects rather than dielectric properties. During the ionization, the anion of HND is undoubtedly less further solvated than the anion of water, and, in fact, it may well be not further solvated at all, compared to the un-ionized acid. In any event, we are

concerned with only that solvation which causes the ionization, the difference in solvation between the un-ionized HND and the ionized HND. If only the solvation of the hydrogen ion to give H_3O^+ is involved in the case of HND, its ionization might be explained as follows. The ionization constant of eq. 2 may be rewritten to include the water concentration.

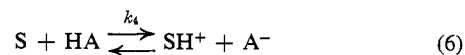


$$\frac{(H_3O^+)(A^-)}{(H_2O)(HA)} = k_2 \quad (4)$$

$$\frac{(H_3O^+)(A^-)}{(HA)} = k_2(H_2O) = k_3 \quad (5)$$

Qualitatively, then, as the water concentration is decreased in going from pure water to pure dioxane, the measured ionization constant, k_3 , will decrease continuously. This is also true even if dioxane plus water replaces water in the equilibrium expression above (eq. 3-5). The maximum decrease is represented by the concentration of pure water (55.5 M or 1.74 pK units). This does not explain the maximum in pK near 91% dioxane.

The maximum can be explained by the formation of a stable complex between water and dioxane. Equation 3 may be rewritten as eq. 6 with S instead of water,



$$\frac{(SH^+)(A^-)}{(S)(HA)} = k_4 \quad (7)$$

$$\frac{(SH^+)(A^-)}{(HA)} = k_4(S) = k_5 \quad (8)$$

where S represents water, dioxane, or any solvent promoting the ionization. If the stable complex does not promote the ionization, then as S decreases, the pK will increase, reach a maximum at the composition represented by the complex, and then decrease as the solution becomes enriched with "free" dioxane (more than necessary for the complex).

It is instructive to consider the types of complexes one might expect in a dioxane-water mixture. There are three logical ones: (a) water-dioxane-water; (b) water-dioxane, and (c) dioxane-water-dioxane. The three dioxane compositions corresponding to these three complexes are 70.97, 83.03, and 90.73%, respectively. Of the three, the dioxane-water-dioxane complex would explain the HND data most satisfactorily.

To return to the comparison with water, the anion of water is likely solvated with more than one molecule of solvent.⁹⁻¹¹ It is generally accepted that the solvation of the hydrogen ion with one solvent molecule is a stable configuration. It is not unreasonable that the solvated hydroxide ion is also a stable configuration. Even one molecule of solvent would introduce S^2 into the equilibrium expression (eq. 8). This would mean that the ionization of water would decrease faster than for HND. This is, of course, the observed phenom-

(9) B. R. Agarwal and R. M. Diamond, *J. Phys. Chem.*, **67**, 2785 (1963), report three molecules.

(10) T. Ackerman, *Discussions Faraday Soc.*, **24**, 133 (1957), reports three molecules.

(11) J. Padova, *J. Chem. Phys.*, **39**, 1552 (1963), reports four molecules.

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 Wu¹² feel that dioxane is abnormally basic and this is caused by a special cooperative influence of the oxygens of the dioxane in their

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 Barrow¹³ 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 Gordy¹⁴ 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.

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

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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 $28 \pm 1^\circ$. The pK values at zero ionic strength in these solvents are 5.05 ± 0.15 and 3.90 ± 0.10 , respectively. As the literature value² 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

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