Thermodynamic Ionization Constants of *N*-Arylhydroxamic Acids

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Thermodynamic ionization constants (pK_a) of substituted hydroxamic acids have been determined in 10–70% v/v dioxane–water media at 25 and 35 ± 0.1 °C. An empirical pH correction for mixed aqueous media has been applied. The pK_a's in aqueous media (at 0% dioxane) have been obtained using the method of extrapolation and least squares. The pK_a values do not vary linearly with the reciprocal of the dielectric constant of the medium, but a plot of pK_a vs. the mole fraction of dioxane is linear at a given temperature. Values of $\Delta G°$, $\Delta H°$, and $\Delta S°$ are tabulated.

The hydroxamic acids are versatile reagents in the field of analytical chemistry. For their rational applications the knowledge of an ionization constant is desirable. *N*-*m*-Tolyl-*m*-nitrobenzohydroxamic acid has been used as a analytical reagent for gravimetric analysis and solvent extraction of rare earths (*2, 27, 28*). Data on the ionization constants of its substituted acids should be of importance in various analytical process and useful in elucidation of the resulting metal complexes. With this view, in the present communication the thermodynamic ionization constants (pK_a) of several *m*-nitro-substituted hydroxamic acids in 10–70% aqueous dioxane water media at 25 and 35 °C have been determined.

The pK_a's are determined by the pH titration method using a glass and saturated calomel electrode in cells with liquid junction potential. The Van Uitert and Haas relation (*3, 43*) was used to obtain the hydrogen ion concentration from the values read on the pH meter (*B*):

$$-\log\,[\mathrm{H}^+] = B + \log U^{\circ}_{\mathrm{H}} - \log \frac{1}{y_{\pm}} \qquad (1)$$

The values of log U°_{H} were determined experimentally (*4*) and the mean activity coefficients were obtained from the data of Harned and Owen (*23*). The ionization of hydroxamic acid (HA) in aqueous solution gives hydrogen ion [H$^+$] and hydroxamate ion [A$^-$] and the equilibrium constant is given by eq 2 in aqueous medium

$$Ka(\mathrm{aq}) = ([\mathrm{H}^+][\mathrm{A}^-]/[\mathrm{HA}])(y_{\mathrm{H}^+}y_{\mathrm{A}^-}/y_{\mathrm{HA}}) \qquad (2)$$

or

$$\mathrm{p}K_a(\mathrm{aq}) = -\log\,[\mathrm{H}^+] + \log\,([\mathrm{HA}]/[\mathrm{A}^-]) + 2\log \frac{1}{y_{+}} \qquad (3)$$

Assuming y_{HA}, the activity coefficient of un-ionized acid is unity, the final form of the equation for calculating the ionization constant in the dioxane water mixture is obtained by equation (*1, 3*)

$$\mathrm{p}K_a = B + \log U^{\circ}_{\mathrm{H}} + \log\,([\mathrm{HA}]/[\mathrm{A}^-]) + \log \frac{1}{y_{\pm}} \qquad (4)$$

Hydrolysis of the salt in aqueous medium was taken into consideration via equation (*5, 6*)

$$\mathrm{p}K_a(\mathrm{aq}) = -\log\,[\mathrm{H}^+] + \log \frac{[\mathrm{HA}] + [\mathrm{OH}^-]}{[\mathrm{A}^-] - [\mathrm{OH}^-]} + 2\log \frac{1}{y_{\pm}} \qquad (5)$$

and for mixed aqueous media by

$$\mathrm{p}K_a = B + \log U^{\circ}_{\mathrm{H}} + \log \frac{[\mathrm{HA}] + [\mathrm{OH}^-]}{[\mathrm{A}^-] - [\mathrm{OH}^-]} + \log \frac{1}{y} \qquad (6)$$

Experimental Section

Chemicals. All the chemicals used were of G.R. and AnalaR grades of E. Merck and B.D.H., respectively, unless otherwise stated.

Materials. Water. The glass distilled water used was tested for carbonate by the Kolthoff method (*30*).

Dioxane. *p*-Dioxane was purified by the method as described by Vogel (*44*). Its purity was established by freezing point, which varied from 11.65 to 12.0 °C (*16, 44*).

Tetrabutyl Ammonium Hydroxide. Tetrabutylammonium hydroxide was prepared by the method of Cundiff and Markunas (*17*). It was diluted to 0.1 M with the dioxane of desired composition.

Hydroxamic Acids. The hydroxamic acids used in the present investigation (Table I) were synthesized by the methods described earlier (*5, 36*). These were recrystallized, before use, from the mixture of benzene and petroleum ether and dried in vacuo over P_2O_5. Their purity was established by TLC, elemental analysis, and IR and UV spectra.

Benzohydroxamic acid was prepared by the modified method of Shukla et al. (*41*).

pH Meter. The Beckman pH meter Models G and 76 equipped with Beckman glass and calomel electrodes was used for pH measurements.

Procedure for the Determination of Ionization Constants. The titration procedure for determining the ionization constants has been essentially the same as recommended by Albert and Serjeant (*8*). Generally a 0.01 M solution of hydroxamic acids was titrated without the addition of inert salt.

In the thermostated (25 or 35 ± 0.1 °C) titration vessel, carrying a glass electrode, a calomel electrode, and microburette, 0.5 mM of hydroxamic acid and 47.5 mL of solvent (of desired composition) were taken. It was titrated with 0.5-mL increments of 0.1 M tetrabutylammonium hydroxide after being

Table I. *N*-Arylhydroxamic Acids Used for the Present Investigation

Compd no.	Hydroxamic acid	Trival name	Mp, °C Found	Reported
I	Benzo-	BHA	128	128 (24)
II	*N*-Phenylbenzo-	PBHA	122	121–122 (40)
III	*N*-*o*-Tolyl-*m*-nitrobenzo-	*o*-T-NBHA	116	None
IV	*N*-*m*-Tolyl-*m*-nitrobenzo-	*m*-T-NBHA	118	118 (5)
V	*N*-*p*-Tolyl-*m*-nitrobenzo-	*p*-T-NBHA	106	106 (18)
VI	*N*-*p*-Chloro-*m*-nitrobenzo-	*p*-c-NBHA	125	124 (2)

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Table II. Thermodynamic Ionization Constants of Hydroxamic Acids at 25 °C[a]

Compd no.	Hydroxamic acid	Vol % dioxane 10	20	30	40	45	50	60	70
I	BHA[b]	9.71	9.45	9.79	10.14	10.41	10.69	11.34	12.25
II	PBHA[b]	9.84	9.23	9.76	10.30	10.63	11.04	12.04	13.39
III	*o*-T-NBHA	8.43	8.73	9.02	9.48	9.78	10.06	10.83	11.83
IV	*m*-T-NBHA	8.56	8.90	9.24	9.75	10.00	10.33	11.06	12.10
V	*p*-T-NBHA	8.64	8.95	9.34	9.82	10.08	10.40	11.17	12.21
VI	*p*-c-NBHA	ins.	ins.	ins.	ins.	9.00	9.27	9.90	10.70
Dielectric constant		68.5	60.5	51.8	42.5	37.5	33.0		

[a] ins., the hydroxamic acid is insoluble in the solvent. The average pK_a generally falls within a spread of ±0.02 unit but not beyond ±0.03, in any case.
[b] Values of Y. K. Agrawal (*6*) reported up to 50% dioxane–water media, all are repeated and extended up to 70% dioxane–water media.

Table III. Thermodynamic Ionization Constants of Hydroxamic Acid at 35 °C[a]

Compd no.	Hydroxamic acid	Vol % dioxane 10	20	30	40	45	50	60	70
I	BHA[b]	9.02	9.29	9.64	10.03	10.26	10.57	11.21	12.12
II	PBHA[b]	8.58	9.07	9.45	10.12	10.40	10.82	11.95	13.28
III	*o*-T-NBHA	8.28	8.60	8.96	9.36	9.63	9.93	10.70	11.74
IV	*m*-T-NBHA	8.37	8.70	9.05	9.50	9.80	10.08	10.87	11.92
V	*p*-T-NBHA	8.50	8.83	9.20	9.67	9.96	10.26	11.03	12.07
VI	*p*-c-NBHA	ins.	ins.	ins.	ins.	8.81	9.12	9.73	10.55

[a] ins., the hydroxamic acid is insoluble in the solvent. The average pK_a generally falls within a spread of ±0.02 unit but not beyond ±0.03 in any case.
[b] *Values of Y. K. Agrawal (6) reported up to 50% dioxane water media. Values are repeated and extended up to 70% dioxane–water media.*

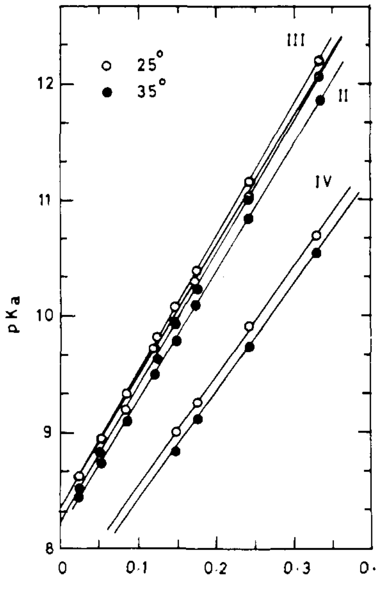

Figure 1. Variation of pK_a with mole fraction of dioxane.

deaerated by passing nitrogen (presaturated with solvent) for 15 min, the highest steady *B* value being noted after each increment.

Ionic Product of Water. The pK_w has been obtained from the Harned and Owen data (*4*) in different dioxane water mixtures. The numerical equations expressed for the linear relationship are as under (*6*)

$$\text{At } 25\ ^\circ\text{C } pK_w = 11.93n_2 + 14.00 \quad (7)$$

$$\text{At } 35\ ^\circ\text{C } pK_w = 12.01n_2 + 13.68 \quad (8)$$

The experimental values indicate a maximum deviation from linearity of the order of 0.04 or about 0.3% in pK_w.

Table IV. Empirical Relation between pK_a and n_2 of Dioxane

Hydroxamic acid	25 °C pK_a = $mn_2 + C$ m	c	r	35 °C pK_a = $mn_2 + C$ m	c	r
BHA	10.10	8.92	0.999	10.10	8.79	0.999
PBHA	14.15	8.46	0.999	14.95	8.36	0.999
o-T-NBHA	11.14	8.14	1.241	11.20	8.01	1.248
m-T-NBHA	11.50	8.31	1.011	15.54	8.07	1.001
p-T-NBHA	11.69	8.36	1.183	11.61	8.24	1.110
p-C-NBHA	9.27	7.65	1.100	9.48	7.45	1.100

Results and Discussion

The values of pK_a of *N*-arylhydroxamic acids in various dioxane water media at 25 and 35 °C are given in Tables II and III, respectively. The average pK_a generally falls within a spread of ±0.02 but not beyond ±0.03, in any case. The pK_a's are plotted against mole fraction of dioxane (n_2) Figure 1 and the empirical relations derived therefrom are given in Table IV. The values of thermodynamic functions, ΔG°, ΔH°, and ΔS° are summarized in Table V.

The hydroxamic acids are very weak acids (*3, 15, 42*) and their acidity may be attributed essentially to the -OH group. The suppression of acidic character may be attributed to the intramolecular hydrogen bonding as shown by infrared spectroscopic studies (*7, 20, 35*).

Temperature Effects. The data given in Tables II and III show that the pK_a of all hydroxamic acids in all solvent media are lower at 35 than 25 °C. There temperature of maxima K_a, T_{max}, can be known if the pK_a are determined at several temperatures.

Effect of Medium. A solvent of low dielectric constant increases the electrostatic forces between the ions and facilitates formation of molecular species and should increase the pK_a, as borne out for hydroxamic acid by Tables II and III.

It has been pointed out by Gurney (*19*) and others (*10, 38*) that the standard free energy change accompanying the proton

Table V. Free Energy, Enthalpy, and Entropy Changes for Ionization of Hydroxamic Acids[a]

	Dioxane, % v/v							
	10	20	30	40	45	50	60	70
				Hydroxamic acid				
I	II	III	IV	V	VI	VII	VIII	IX
BHA $\Delta G°$	(12.61)	(12.89)	(13.36)	(13.83)	14.20	(14.58)	14.48	16.72
	(12.72)	(13.10)	(13.59)	(14.14)	14.46	14.90	15.82	17.17
($\Delta H°$ 5.5), $-\Delta S°$	23.6	24.9	26.5	28.0	29.3	30.6	30.1	37.6
	23.5	24.8	26.3	28.1	29.2	30.6	33.5	37.6
PBHA $\Delta G°$	(12.08)	(12.60)	(13.32)	(14.00)	14.52	15.06	16.43	18.28
	(12.32)	(12.87)	(13.58)	(14.38)	14.68	(15.67)	16.86	18.74
($\Delta H°$ 4.2), $-\Delta S°$	26.4	28.1	30.6	32.8	34.6	36.4		41.0
47.2								
	26.3	28.1	30.4	33.0	34.0	36.5	34.7	47.2
o-T-NBHA $\Delta G°$	11.51	11.92	12.31	12.94	13.35	13.73	14.78	16.15
	11.68	12.13	12.64	13.20	13.58	14.01	15.10	16.57
($\Delta H°$ 5.5), $-\Delta S°$	20.3	21.6	22.9	25.0	26.4	27.7	31.2	35.8
	20.1	21.6	23.3	25.1	26.3	27.7	31.	36.1
m-T-NNBHA $\Delta G°$	11.68	12.15	12.61	13.34	13.65	14.13	15.10	16.52
	11.81	12.27	12.76	13.41	13.82	14.22	15.34	16.82
($\Delta H°$ 10.1), $-\Delta S°$	5.3	6.9	8.4	10.9	11.9	13.5	16.8	21.6
	5.6	7.0	8.6	10.7	12.1	13.4	17.0	21.2
p-T-NBHA $\Delta G°$	11.80	12.23	12.74	13.41	13.74	14.19	15.24	16.66
	11.99	12.46	12.98	13.64	14.06	14.47	15.50	17.03
($\Delta H°$ 5.0), $-\Delta S°$	22.6	24.1	26.4	23.0	29.1	30.2	34.2	38.1
	22.5	24.0	25.7	27.9	29.2	30.6	34.1	38.9
p-C-NBHA $\Delta G°$	ins.	ins.	ins.	ins.	12.29	12.65	13.51	14.61
	ins.	ins.	ins.	ins.	12.43	12.89	13.73	14.89
($\Delta H°$ 8.5, $-\Delta S°$	ins.	ins.	ins.	ins.	12.71	13.92	16.80	20.48
	ins.	ins.	ins.	ins.	12.75	14.24	16.96	20.73

[a] $\Delta G°$ and $\Delta H°$ in kcal mol^{-1}, $\Delta S°$ in cal mol^{-1} K^{-1}, first value at 25 °C, second at 35 °C. Values in parentheses were calculated from extrapolated data, from Agrawal and Tandon (*3*); values extended up to 70% dioxane–water media. ins., insoluble. The values of $\Delta G°$ and $\Delta S°$ at 25 and 35 °C for BHA and PBHA are (12.15), (12.40), 22.4, 25.5 and (11.42), (11.69), 24.2, 24.3, respectively.

transfer $\Delta G°_{diss}$ may be split up in two distinct parts, electrostatic and nonelectrostatic.

$$\Delta G°_{diss} = \Delta G°_{el} + \Delta G°_{non} \qquad (9)$$

The electrostatic contribution to free energy change is often estimated by the Born equation (*12*).

$$\Delta G°_{el} = W = \frac{Ne^2}{2D}\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \qquad (10)$$

Where r_+ and r_- are radii of the solvated ions and D is the dielectric constant of the solvent (*33, 34*). Hence,

$$\Delta G°_{diss} = \Delta G°_{non} + \frac{Ne^2}{2D}\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \qquad (11)$$

Further, on substitution of $\Delta G°_{diss} = 2.303RT\ pK_a$ (*11*) becomes,

$$pK_a = \frac{\Delta G°_{non}}{2.303RT} + \frac{Ne^2}{4.606RTD}\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \qquad (12)$$

It is conventional to plot pK_a against $1/D$ assuming $\Delta G°_{non}$ to be independent of the solvent. In several cases nearly linear relations, especially in the water-rich portions of the medium, have been reported (*11, 29, 32, 39*) while instances of failure from linearity too have not been uncommon (*22*). When the pK_a of the hydroxamic acids is plotted against $1/D$ it is observed that the plots possess distinct curvature. This is illustrated by the typical plot shown in Figure 2. It seems evident that nonelectrostatic factors exert a considerable influence on the dissociation of hydroxamic acids.

Mole Fraction of Dioxane. For all hydroxamic acids the change in pK_a with mole fraction of dioxane is of considerable magnitude. In general, the difference in pK_a in water ($n_2 = 0$) and 70% dioxane water ($n_2 = 0.33$) is more than 4 pK_a units. When the pK_a of hydroxamic acids are plotted against the mole fraction of dioxane, linear relationships are observed (Figure 1). The experimental values of pK_a for almost all hydroxamic acids indicate a maximum deviation from linearity of the order of 0.05 or about 0.5% in pK_a.

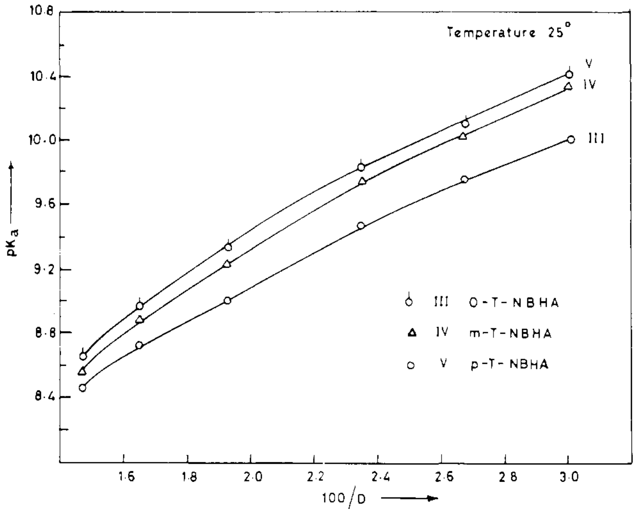

Figure 2. Variation of pK_a with the dielectric constant of the medium.

It is of interest to examine the accuracy of the extrapolated values of pK_a at zero dioxane concentration ($n_2 = 0$). Comparison with the experimentally determined values is possible for a few hydroxamic acids for which these data in aqueous medium are available. The data presented in Table VI show that there is an excellent agreement in two sets of values.

Thermodynamic Functions for Ionic Equilibria. The pK_a's have been determined with a precision of ±0.02 to ±0.03 and

Table VI. Ionization Constants of Hydroxamic Acids (in Aqueous Media)

Hydroxamic acid	pK_a extrapolated		pK_a experimental		p$K_a = mn_2 + c$, at 25 °C				p$K_a = mn_2 + c$, at 35 °C			
					Graphical		Least square		Graphical		Least square	
	25 °C	35 °C	25 °C	35 °C	*m*	*c*	*m*	*c*	*m*	*c*	*m*	*c*
BHA [a]	8.92	8.80	8.91	8.79	10.05	8.92	10.10	8.92	10.00	8.80	10.10	8.79
PBHA [b]	8.55	8.45	8.58	8.44	14.50	8.55	14.95	8.46	15.51	8.45	14.95	8.36
o-T-NBHA	8.17	8.05	8.15	8.03	11.04	8.17	11.14	8.14	11.00	8.05	11.20	8.01
m-T-NBHA	8.33	8.10	8.33	8.08	11.51	8.33	11.50	8.31	11.50	8.10	15.54	8.07
p-T-NBHA	8.37	8.26	ins. [c]	ins. [c]	11.66	8.37	11.69	8.36	11.57	8.26	11.61	8.24
p-c-NBHA	7.65	7.43	ins. [c]	ins. [c]	9.27	7.65	9.27	7.65	9.50	7.44	9.48	7.45

[a] Reference *3*, reported pK_a values are 8.75 (*37*) at 0.1 M KCl; computed pK_a values are 8.85 and 8.84, respectively. [b] References 3, 37. [c] ins, insoluble.

hence the error in $\Delta G°$ is estimated to be between ±0.03 and ±0.04 kcal.

The temperature coefficient method used here for the computation of $\Delta H°$ is subject to large error because (i) the enthalpy change involved in acid ionization is small, and (ii) the pK_a at a series of temperatures are not determined which, otherwise, would have enabled the adoption of a more precise graphical method (*31*) for its evaluations. In our case an error of 0.01 in pK_a causes an error of 0.42 kcal in $\Delta H°$ while the magnitude or error in ΔpK_a depends on the cancellation or addition of error of an individual set of pK_a determined at two temperatures.

Despite the relatively large errors in the value of $\Delta H°$ computed by the temperature coefficient method, the data are still of great significance for drawing certain valuable conclusions. In any case, the positive value of $\Delta H°$ found in all solvent media and for all hydroxamic acids implies that the ionization process at temperatures up to 25 °C is endothermic. Further it is certain that the magnitude of change in $\Delta H°$ with change in media is relatively small and is within the range of experimental error. It is because of this reason that the slopes of straight lines in the plots of pK_a vs. n_2 (Figure 1) are either the same or nearly the same at the two temperatures for individual hydroxamic acids (Table IV). In other words, the two lines are parallel.

In the light of above referred observation, it is justifiable, as a first approximation, to assume that $\Delta H°$ is independent of solvent media at least in the narrow range of the 0–0.33 mole fraction of dioxane. With this assumption, a fresh value of $\Delta H°$ for each hydroxamic acid was computed. Numerically this is equal to 42.07 times the difference in the intercepts of the parallel lines on the pK_a axis (Figure 1). The values of $\Delta H°$ computed in this manner are given in Table V, while the values calculated at each mole fraction of dioxane are deliberately omitted for the reasons advanced earlier. The $\Delta S°$ values were also assumed to be independent of solvent composition.

If the acid ionizes in two media the free energy change for the transfer reaction from one medium to other is given by $2.303RT$ ΔpK_a. For example with BHA, $\Delta G°$(aq) and $\Delta G°$ ($n_2 = 0.33$) is 12.15 and 16.72 kcal mol^{-1}, respectively, and $\Delta G°$ changes by 4.57 kcal/mol in the transfer reaction

$$\mathrm{HA_{(diox)} + H^+{}_{(aq)} + A^-{}_{(aq)} \rightleftharpoons HA^+{}_{(aq)} + H^+{}_{(diox)} + A^-{}_{(diox)}}$$

and this is essentially due to a change of 8.2 cal deg^{-1} mol^{-1} in $\Delta S°$.

Substituent Effects. In the present investigation the hydroxamic acids are nitro substituted (compound III–VI) with two parent acids (compound I and II). The nitro substituent is powerfully meta directing, indicating a pronounced electron attractive nature, which increased the strength of hydroxamic acid as pK_a's of PBHA > nitro substituted hydroxamic acids or the order of pK_a's as follows: compd II > V > IV > III > VI. The high strength of compound VI having the nitro and halogen substituent is explained on the basis, it is believed (*9, 21, 25, 26*), of a mesomeric effect arising from resonance of benzenoid forms and follows the order of pK_a's as: compd I, II, III, IV, and V > VI.

This order is valid in an aqueous and all-aqueous dioxane medium.

Further, an examination of the pK_a's of methyl substituted (in-N-phenyl ring) hydroxamic acids (compd III–V) follows the order of acidity of ortho, meta, and para positions. The order in aqueous and aqueous dioxane medium is

pK_a's compd *N-p*-tolyl-*m*-nitrobenzohydroxamic acid V > *N-m*-tolyl-*m*-nitrobenzohydroxamic acid IV >
N-o-tolyl-*m*-nitrobenzohydroxamic acid III

The electropositive methyl group in the meta and para position weaken the aromatic acid, whereas they strengthen the acid from the ortho position. The acid weaking of meta and para position isomers is generally explained by the positive inductive (electron repelling) and resonance effects. The unusual acid strengthing of the ortho isomer, which is stronger than the PBHA (compd II), the parent acid, can be explained on the basis of steric inhibition of resonance (*14*).

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Enthalpies of Mixing of Tributylphosphate with Hydrogen-Bonding Solvents[†]

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Excess enthalpies of mixing of tri-*n*-butyl phosphate with *tert*-butyl alcohol (303.15 K) are endothermic, but with chloroform (298.15 K) are exothermic, in spite of the fact that both solvents form hydrogen bonds with the proton acceptor phosphoryl oxygen of the ester. The results are discussed in terms of the apparent endothermic contribution of breaking the bonds in the self-associated solvents, and the apparent exothermic contribution from the newly formed hydrogen bonds between the ester and the solvent molecules.

Apart from the intrinsic interest in the thermodynamic functions of mixing of associated polar nonelectrolyte liquids, the information obtained here is relevant to the fundamental chemistry of solvent extraction processes. Namely, tributyl phosphate is one of the most powerful and most widely used extractants for inorganic compounds from aqueous solutions. Chloroform and water-immiscible alcohols are employed as diluent for the extractant, and the nature of the interaction between the extractant and its diluent—which together constitute the organic phase—has been studied by a variety of techniques in the past (*7*). Though much of that information is qualitative in nature, it clearly demonstrates that there is a reasonably strong H bonding between diluents containing a hydrogen atom capable of forming a hydrogen bridge and the phosphoryl oxygen of the ester.

Tri-*n*-butyl phosphate, $(C_4H_9O)_3PO$, has a dielectric constant of 8.05 and a dipole moment of about 3.1 D at room temperature (*10*). There is a variety of physicochemical evidence (*7*) to indicate that the ester is self-associated through a system of dipole–dipole bonds, when the predominating aggregate is the dimer. From infrared, vapor pressure, and dielectric measurements, the dimerization constant of the ester has been found to vary at 25 °C between $k_2 = 1.2$ and 2.9 $\mathrm{dm^3\ mol^{-1}}$, depending on the solvent used and the experimental method employed (*7, 10*). The energy of the bond was estimated (*7*) to be about 10 $\mathrm{kJ\ mol^{-1}}$.

Chloroform, dipole moment ~1.2 D, is only slightly dimerized. A dimerization constant of $k_2 = 0.013\ \mathrm{dm^3\ mol^{-1}}$ in dilute solutions of cyclohexane at room temperature has been calculated from spectral data (*6*). In the neat liquid, which is about 12 M, the fraction of dimers is likely to be higher than that calculated from this dimerization constant.

Literature data on the self-association of *tert*-butyl alcohol, dipole moment ~1.7 D, do not present a uniform picture. Reevaluation (*14*) of most of the existing spectral data shows that the importance of dimers in the self-association of the alcohol has been overestimated, and that other oligomers, trimers, tetramers, and perhaps even higher *n*-mers coexist in equilibrium. The major problem is frequently what oligomer can be identified and included in the set of mass-action law equilibria describing the process of polymerization of *tert*-butyl alcohol. Since this is a crucial factor affecting the calculation of equilibrium constants, it is not surprising that the reported numerical data are in poor agreement. The dimerization constant of *tert*-butyl alcohol in dilute solutions of cyclohexane or carbon tetrachloride at room temperature has been estimated to have a value ranging between $k_2 = 0.6$ and 1.0 $\mathrm{dm^3\ mol^{-1}}$ (*11*). The enthalpy of formation of a single hydrogen bond has been calculated to be about 10 ± 2 $\mathrm{kJ\ mol^{-1}}$ (*2, 11, 14*).

Experimental Section

Materials. Tri-*n*-butyl phosphate (Koch-Light) was dried, purified, and analyzed as described before (*13*). Its purity was better than 99.5 mole %. 2-Methyl-2-propanol, *tert*-butyl alcohol (BDH), melting point 25.8 °C, and chloroform (Schuchardt), both of the highest purity commercially available, were dried over Perlform molecular sieve for several days prior to fractional distillation. The middle fractions retained, and kept in dark over molecular sieve, gave a single peak in GLC analysis, indicating a purity of better than 99.6 and 99.9%, respectively. Densities of the liquids: tributyl phosphate, $d_{30} = 0.9687$; *tert*-butyl alcohol, $d_{30} = 0.7770$; and chloroform, $d_{25} = 1.4785$. The water content of all liquids was determined by Karl Fischer titration, and found to be less than 0.01 mole %.

Calorimeter. Heats of mixing were determined using a Tronac Model 1000A continuous titration calorimeter. The original commercial calorimeter was modified to operate as a dual-bath

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