771. *Determination of the Ionization Constant of Hydrocyanic Acid at 25° by a Spectrophotometric Indicator Method.*

By K. P. Ang.

Spectrophotometric measurements of the spectrum of *m*-bromophenol in buffers of hydrocyanic acid and sodium cyanide have been used to give p*K* $9{\cdot}21_6$ for hydrocyanic acid. *m*-Bromophenol has p*K* $9{\cdot}00_4$.

When the spectrophotometric method is used to determine the ionization constant of a weak acid, *e.g.*, by measurement of the absorption spectrum of *p*-nitrophenol in phosphate buffers,[1] the buffer constituents are necessarily in comparatively high concentration but are optically transparent (or at least have small optical densities); it is the weak acid added at low concentration to the buffer which affords the optical absorption whose change with pH gives the ionization constant of the acid. The method can, however, be used in reverse if the ionization constant of the " coloured " acid is known, to give the ionization constant of the acid in the buffer mixture; it now becomes essentially a quantitative indicator method extended to the ultraviolet region of the spectrum.

[1] Robinson and Biggs, *Trans. Faraday Soc.*, 1955, **51**, 901.

The equilibria in a buffer solution containing a " coloured " acid are governed by two equations:

$$\mathrm{p}K_{\mathrm{R}} = \mathrm{pH} - \log\,([\mathrm{Salt}]/[\mathrm{Acid}]) - \log \gamma_{\mathrm{R}} \quad . \; . \; . \; . \; . \quad (1)$$

where K_{R} is the ionization constant of the buffer acid, γ_{R} the activity coefficient of its anion and the [Salt]/[Acid] ratio is corrected for hydrogen-ion concentration if the buffer acid is only moderately weak and for the hydroxyl-ion concentration if it is very weak. Eqn. (2) relates the ionization constant of the " coloured " acid to the optical densities of its solution:

$$\mathrm{p}K = \mathrm{pH} - \log\,(D_1 - D)/(D - D_2) - \log \gamma_{\mathrm{B}} \quad . \; . \; . \; . \quad (2)$$

where γ_{B} is the activity coefficient of its anion, D_1 is the optical density in a solution of low pH where all the " coloured " acid is present in the undissociated form, D_2 that in a solution of high pH containing only the dissociated species, and D that in the buffer solution. If the anion of the " coloured " acid and that of the buffer acid are of the same valency type, a good approximation is:

$$\mathrm{p}K = \mathrm{p}K_{\mathrm{R}} + \log\,([\mathrm{Salt}]/[\mathrm{Acid}]) - \log\,(D_1 - D)/(D - D_2) \quad . \; . \; . \quad (3)$$

Thus either pK or pK_{R} can be determined if the other is known.

In previous work[2] on *p*-iodobenzoic acid it was noted that the apparent pK values from measurements in formate and succinate buffers differed by some 0·02 unit. This was not a favourable example to which to apply the method because the separation between the spectra of the undissociated and the dissociated form was not wide, and to resolve doubts about the use of these buffers, the method has now been checked in the more favourable case of barbituric acid, with the results given in Table 1. As the mean values

TABLE 1.

Barbituric acid, $9{\cdot}32 \times 10^{-6}$M; wavelength, 258 mμ; 4 cm. cells; temperature, 25°; D_1 (in M-HCl) 0·014; D_2 (in 0·001M-NaOH) 0·785.

Molality of acid	D	log ([Salt]/[Acid])	log $(D_1 - D)/(D - D_2)$	pK
Formic acid, 1 mol.	Sodium formate, 1·923 mol.			
0·001733	0·427	0·321	0·062	4·011
0·003466	0·423	0·304	0·053	4·003
Formic acid, 1 mol.	Sodium formate, 1·504 mol.			
0·001989	0·375	0·222	−0·055	4·029
0·003978	0·364	0·201	−0·080	4·033
Formic acid, 1 mol.	Sodium formate, 1 mol.			
0·002533	0·311	0·059	−0·203	4·014
0·005066	0·300	0·033	−0·229	4·014
			Mean	4·017
Succinic acid, 1 mol.	Sodium hydrogen succinate, 0·5 mol.		Sodium chloride, 1 mol.	
0·02	0·343	−0·315	−0·128	4·020
0·03	0·337	−0·321	−0·142	4·028
0·04	0·338	−0·326	−0·140	4·021
0·05	0·339	−0·328	−0·138	4·017
Succinic acid, 1 mol.	Sodium hydrogen succinate, 0·5 mol.		Sodium chloride, 0·5 mol.	
0·02	0·340	−0·318	−0·135	4·024
0·03	0·343	−0·322	−0·128	4·013
0·04	0·339	−0·324	−0·137	4·020
0·05	0·340	−0·327	−0·135	4·015
Succinic acid, 1 mol.	Sodium hydrogen succinate, 0·5 mol.			
0·02	0·343	−0·321	−0·128	4·014
0·03	0·343	−0·323	−0·128	4·012
0·04	0·338	−0·322	−0·140	4·025
0·05	0·343	−0·326	−0·128	4·009
			Mean	4·018

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[2] Robinson and Ang, *J.*, 1959, 2314.

from the formate and the succinate buffer are in good agreement, it is now believed that the difficulties encountered with iodobenzoic acid were due to the limited accuracy which could be achieved in this unfavourable case.

The mean of the 18 determinations is $4{\cdot}01_8$, but a higher value, $4{\cdot}03_5$, has been derived from measurements in succinate buffers.[3]

Having demonstrated that the formate and succinate buffers give the same result, the reverse determination can be illustrated with hydrocyanic acid. In this method the "coloured" acid should have about the same pK; *m*-bromophenol was chosen. In Table 2 are recorded the data necessary for the determination of its pK in borax buffers for which pH values have already been reported;[4] γ_B in equation (2) was calculated as before[3] by the equation $-\log \gamma_B = 0{\cdot}5092\sqrt{I}/(1 + \sqrt{I}) - 0{\cdot}2I$. A small correction[5] was applied to allow for the effect of bromophenol on the pH of the buffer mixture, giving pK $9{\cdot}00_4$. From this, the extent of dissociation of the bromophenol in hydrocyanic acid–sodium cyanide buffers was measured as shown in Table 3. Application of equation (3) gave pK $9{\cdot}21_6$ for hydrocyanic acid, a value considerably lower than many which have been reported[6] based on potentiometric titration: what have been recorded are probably "concentration" ionization constants with pK 9·3; any correction to give thermodynamic ionization constants would raise pK to about 9·4. The value now reported depends on the well-substantiated pH values of borax solutions, and the only uncertainty is in the value of γ_B used in calculating the pK of *m*-bromophenol; arbitrary to some extent as this is, it is not believed that it can influence the pK of hydrocyanic acid by more than ±0·01.

TABLE 2. *Ionization constant of* m-*bromophenol.*

m-Bromophenol, $2{\cdot}28 \times 10^{-4}$M; wavelength, 294 m$\mu$; 1 cm. cells; temperature, 25°;
D_1 (in 0·01M-HCl) 0·019; D_2 (in 0·01M-NaOH) 0·715.

Molality of borax	D	$\log (D_1 - D)/(D - D_2)$	pH	$-\log \gamma_B$	pK
0·010	0·456	0·227	9·177	0·059	9·009
0·025	0·464	0·249	9·172	0·083	9·006
0·050	0·480	0·293	9·196	0·102	9·005

Corrected pK = 9·004.

TABLE 3. *Ionization constant of hydrocyanic acid.*

m-Bromophenol, $2{\cdot}28 \times 10^{-4}$M; wavelength, 294 m$\mu$; 1 cm. cells; temperature, 25°.

Molality of HCN	D	log ([Salt]/[Acid])	$\log (D_1 - D)/(D - D_2)$	pK
HCN, 1 mol. NaCN, 0·8411 mol.				
0·005435	0·421	−0·077	0·136	9·217
0·01087	0·421	−0·076	0·136	9·216
0·02174	0·418	−0·076	0·128	9·208
HCN, 1 mol. NaCN, 1·032 mol.				
0·004919	0·456	0·011	0·227	9·220
0·009838	0·455	0·012	0·224	9·216
0·01968	0·456	0·013	0·227	9·218
				Mean 9·216

Experimental.—Measurements of the optical density of barbituric acid solutions were made with a Uvispek instrument in an air-conditioned room at 25°; other measurements were made with a Beckman Model DU instrument at 25°.

Barbituric acid was purified by three recrystallisations from water (m. p. 250°), and *m*-bromophenol by distillation under reduced pressure (b. p. 86°/0·5 mm.); samples taken before

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[3] Biggs, *J.*, 1956, 2485.

[4] Manov, DeLollis, Lindvall, and Acree, *J. Res. Nat. Bur. Stand.*, 1946, **36**, 543.

[5] Robinson and Kiang, *Trans. Faraday Soc.*, 1955, **51**, 1398.

[6] Britton and Robinson, *J.*, 1931, 458; *Trans. Faraday Soc.*, 1932, **28**, 531; Britton and Dodd, *J.*, 1931, 2332.

and after distillation gave the same p*K* values, but those recorded in Table 2 refer to a distilled sample.

Hydrocyanic acid was prepared by slow distillation of a potassium cyanide solution acidified with dilute sulphuric acid, and buffer mixtures were prepared from it by partial neutralisation of the acid with carbonate-free sodium hydroxide. The concentration of the acid, determined by silver nitrate titration,[7] was checked at the end of the experiment and no change was detected. Measurements made on potassium cyanide solutions partially neutralised with hydrochloric acid gave the same p*K* value.

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[7] Diehl and Smith, " Quantitative Analysis," Wiley, New York, 1952.