65. *The Parallelism of the Acidity Functions H_0 and H_+.*

By T. G. Bonner and J. C. Lockhart.

The Hammett acidity functions H_0 and H_+ are shown to be parallel functions of medium composition in aqueous sulphuric acid over the ranges 30—55% and 75—95% sulphuric acid.

Hammett[1] has suggested that while the value of the acidity function H_0, given by

$$H_0 = -\log a_{\mathrm{H}^+}\,.\,f_{\mathrm{B}}/f_{\mathrm{BH}^+} = \mathrm{p}K_a^{\mathrm{BH}^+} + \log\,[\mathrm{B}]/[\mathrm{BH}^+] \quad . \;\; . \;\; . \quad (1)$$

measures the tendency of a solution to transfer a proton to a neutral indicator base, B, to form the conjugate acid BH^+, it does not at all measure the tendency to do the same thing to a base of any other electrical charge. A proton transfer to a univalent cation base AH^+ to form the conjugate acid AH_2^{++} corresponds to an acidity function H_+ defined by

$$H_+ = -\log a_{\mathrm{H}^+}\,.\,f_{\mathrm{AH}^+}/f_{\mathrm{AH}_2^{++}} = \mathrm{p}K_a^{\mathrm{AH}_2^{++}} + \log\,[\mathrm{AH}^+]/[\mathrm{AH}_2^{++}] \quad . \;\; . \quad (2)$$

The difference between H_+ and H_0

$$H_+ - H_0 = \log f_{\mathrm{B}}f_{\mathrm{AH}_2^{++}}/f_{\mathrm{BH}^+}f_{\mathrm{AH}^+} \quad . \;\; . \;\; . \;\; . \;\; . \;\; . \;\; . \quad (3)$$

has been calculated[2] for pure sulphuric acid and is only *ca.* 0·28 log unit; H_0 in this medium is $-10{\cdot}60$, and since the value of the acidity function changes rapidly with medium composition in this region, the difference may not be significant.

Coryell and Fix[3] state that all Hammett acidity functions are parallel functions of medium composition, and refer to the constant difference of 0·8 log unit between H_0 and H_- found in the range of 4—6M-sulphuric acid and to the close parallelism[4] between H_0 and the Michaelis acidity function *G* (measured up to 11M-sulphuric acid with substituted thiazine indicators which take up variously from one to three protons). Any two acidity functions will be parallel functions of medium composition if the activity-coefficient ratio corresponding to eqn. (3) is unity or constant over the range of media studied. It would follow for H_+ and H_0 that

$$\log\,[\mathrm{B}]/[\mathrm{BH}^+] - \log\,[\mathrm{AH}^+]/[\mathrm{AH}_2^{++}] = \mathrm{p}K_a^{\mathrm{BH}^+} - \mathrm{p}K_a^{\mathrm{AH}_2^{++}} = \text{const.} \quad . \quad (4)$$

since the *K*'s are thermodynamic acidity constants.

Hammett and Deyrup[5] demonstrated the parallelism of the plots of the log ionisation ratios $[B]/[BH^+]$ against medium composition for different neutral indicator bases and concluded that the ratio f_B/f_{BH^+} has the same value for all bases of this type in the same medium. In the course of measurements of H_0 for H_2SO_4–SO_3 media, the *m*-nitroanilinium ion was used[2] as one of the indicators and the plot of the log ionisation ratio for this cation base and its conjugate acid against medium composition was parallel to those for neutral indicator bases in the same range of media, indicating that, for oleum, eqn. (4) is valid. The present work has shown that this validity holds for aqueous sulphuric acid media. The indicators used were 4-nitro-1 : 2-phenylenediamine over the range 30—55% sulphuric acid and 4-aminoacetophenone over the range 75—95% acid, and the ratios $[AH^+]/[AH_2^{++}]$ for these indicators were determined from spectrophotometric data.

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[1] Hammett, " Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, 1940, p. 267.
[2] Brand, Horning, and Thornley, *J.*, 1952, 1374.
[3] Coryell and Fix, *J. Inorg. Nuclear Chem.*, 1955, **1**, 119.
[4] Michaelis and Granick, *J. Amer. Chem. Soc.*, 1942, **64**, 1861.
[5] Hammett and Deyrup, *ibid.*, 1932, **54**, 2721.
[6] Kehrmann, *Ber.*, 1895, **28**, 1707.

EXPERIMENTAL

Materials.—4-Nitro-1 : 2-phenylenediamine was obtained by reduction of 2 : 4-dinitroaniline with aqueous ammonium polysulphide [6] (some 2-nitro-1 : 4-phenylenediamine was also formed but this remained dissolved in the aqueous medium); it was recrystallised from water to a constant spectrum $\varepsilon_{max.} = 7920$ at 2470 Å in 72% perchloric acid and had m. p. 204°. 4-Aminoacetophenone was boiled in aqueous solution with charcoal and recrystallised from water to a constant spectrum $\varepsilon_{max.} = 16470$ at 3110 Å in water; m. p. 106°.

FIG. 1. *A*, *4-Nitro-*1 : *2-phenylenediamine at* 3600 Å. *B*, *4-Aminoacetophenone at* 2440 Å.

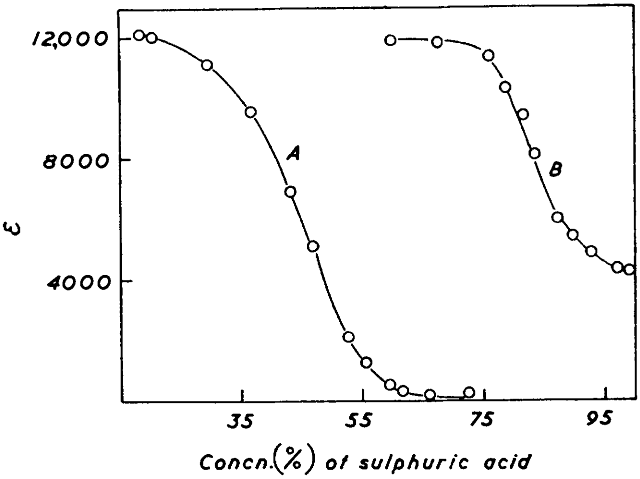


FIG. 2. 4-*Nitro-*1 : 2-*phenylenediamine in* 20·0% H_2SO_4 (*C*), 43·2% H_2SO_4 (*D*), *and* 73·0% H_2SO_4 (*E*).

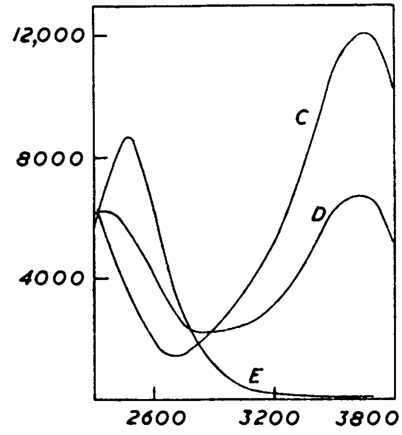
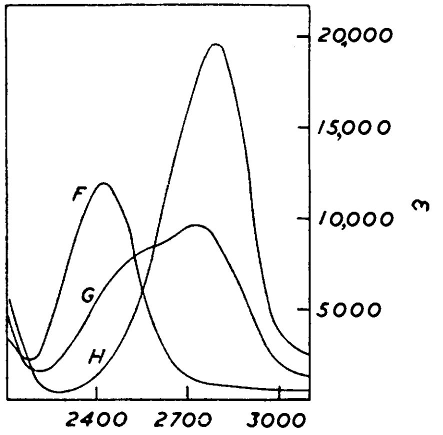


FIG. 3. 4-*Aminoacetophenone in* 59·9% H_2SO_4 (*F*), 83·8% H_2SO_4 (*G*), *and* 98·5% H_2SO_4 (*H*).



Ultraviolet Absorption Measurements.—These were made on a Hilger Uvispek spectrophotometer. Solutions were prepared separately by weight and diluted to give the optimum range of absorption for measurement. The ionisation ratio was obtained from the equation

$$[AH^+]/[AH_2^{++}] = (\varepsilon_{AH_2^{++}} - \varepsilon)/(\varepsilon - \varepsilon_{AH^+})$$

where $\varepsilon_{AH^{++}}$ and ε_{AH^+} are the extinction coefficients at the selected wavelength for the diprotonated and monoprotonated form as indicated by the curves in Fig. 1 (for 4-nitro-1 : 2-phenylenediamine at 3600 Å, $\varepsilon_{AH_2^{++}} = 150$ and $\varepsilon_{AH^+} = 12{,}010$, and for 4-aminoacetophenone at

2440 Å $\varepsilon_{AH_2^{++}} = 4210$ and $\varepsilon_{AH^+} = 11{,}900$), and ε is the extinction coefficient corresponding to the presence of both forms of the given indicator in a particular medium. The isobestic-point method [7] was used for 4-aminoacetophenone.

RESULTS

Spectra of the Indicators in Sulphuric Acid–Water Media.—(a) *4-Nitro-1 : 2-phenylenediamine.* The absorption curves corresponding to the pure monoprotonated form (curve *C*) and pure diprotonated form (curve *E*) are shown in Fig. 2. As expected, curve *C* resembles that of *p*-nitroaniline in water [8] ($\varepsilon_{max.}$ *ca.* 11,500 at 3850 Å, taken from the graph in ref. 8), and curve *E* that of *p*-nitroaniline in acid solution ($\varepsilon_{max.}$ *ca.* 7600 at 2580 Å also taken from ref. 8).

(b) *4-Aminoacetophenone.* The absorption curve of the monoprotonated form (curve *F*, Fig. 3) is similar to that of acetophenone ($\varepsilon_{max.}$ 11,700 at 2500 Å, from ref. 7) and that of the diprotonated form (curve *H*, Fig. 3) resembles that of the conjugated acid of acetophenone ($\varepsilon_{max.}$ 10,500 at 2900 Å, from ref. 7).

The Parallelism of H_+ and H_0.—The log ionisation ratios $[AH^+]/[AH_2^{++}]$ for both indicators in their respective ranges of media are plotted in Fig. 4 against concentration of sulphuric acid, together with the corresponding figures reported by Hammett and Deyrup [5] for the ratios of $[B]/[BH^+]$ for neutral indicator bases ionising in the same ranges of media. The parallelism of the two types of curves is evident and it can be concluded that H_+ and H_0 either differ by a small constant value or are identical. H_0 as defined is identical with pH in very dilute aqueous acids and this identity should also apply to H_+. Any divergence between these acidity functions, if it occurs at all, must therefore appear in the lower ranges of acidity and the difference would have to reach a constant value in order to attain the parallelism found above 30% sulphuric acid.

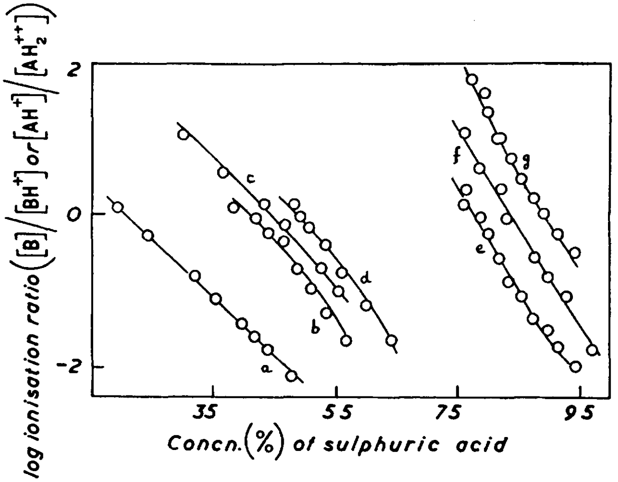


FIG. 4. *a, 4-Chloro-2-nitroaniline; b, 4-nitrodiphenylamine; d, 2 : 4-dichloro-6-nitroaniline; e, 6-bromo-2 : 4-dinitroaniline; g, anthraquinone (results of Hammett and Deyrup* [5]*); c, 4-nitro-1 : 2-phenylenediamine; f, 4-aminoacetophenone (this paper).*

If the identity of H_+ and H_0 is assumed, the pK_a values for the diprotonated forms of 4-nitro-1 : 2-phenylenediamine and 4-aminoacetophenone can be calculated by means of eqn. (3); they are $-2{\cdot}67 \pm 0{\cdot}07$ and $-7{\cdot}36 \pm 0{\cdot}06$ respectively.

Acidity Function and Reaction Mechanism.—The relation

$$\log k + H_0 = \text{Constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

between rate constant and H_0 has hitherto only been applied to test whether a reaction in strongly acidic media proceeds through a reacting species formed in relatively small amount by a single proton uptake on an uncharged molecule. Since H_0 can now be replaced by H_+ in equation (5) without affecting the constancy of the quantities indicated, the equation can be used to decide if a reaction proceeds through a diprotonated form present in relatively small

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[7] Flexser, Hammett, and Dingwall, *J. Amer. Chem. Soc.*, 1935, **57**, 2103.

[8] Dede and Rosenberg, *Ber.*, 1934, **67**, 147.

amount, provided that all of the remaining substrate is in the monoprotonated form. An example of this use of eqn. (5) is provided by the denitration of the univalent nitroguanidinium cation in sulphuric acid solution.[9] The plot of log k against H_0 has a gradient of $-1{\cdot}4$, which is sufficiently far removed from unity to indicate that the denitration is not likely to proceed through the relatively small amount of the conjugate acid of the nitroguanidinium ion which may be present.

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[9] Simkins and Williams, *J.*, 1953, 1386; Hardy, unpublished work.