697. *The Depolymerisation of Paraldehyde in Ethanol–Water Mixtures. The H_0 Acidity Function in this Solvent.*

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Acidity-function data are presented for solutions of hydrochloric acid in 24·4 moles % ethanol–water up to a concentration of 6·20M. Their usefulness is discussed. The rate of the acid-catalysed depolymerisation of paraldehyde correlates with the results. This result, together with earlier data, leads to the conclusion that the mixed medium in question is a promising one from the Zucker–Hammett viewpoint.

THE rate of the acid-catalysed iodination of acetone in a 24·4 moles % ethanol–water solvent is determined[1] much more nearly by the stoicheiometric acid concentration than by the H_0 acidity function [2] for the medium as measured by the base *p*-nitroaniline. This behaviour is the same as that found in water and, if we follow Zucker and Hammett's arguments,[3] is that expected from the known mechanism of the reaction. This being so, a 24·4 moles % ethanol–water mixture seemed likely to prove, in contrast to more ethanolic media,[1] a suitable solvent in which to conduct experiments of the Zucker–Hammett design, which distinguish between different acid-catalysed reaction mechanisms according to whether the reaction rate is determined by the stoicheiometric acid concentration or by the value of H_0 for the medium. The limited H_0 data available for this solvent were therefore extended, and experiments conducted to discover whether a reaction rate known to parallel H_0 in water also did so in the ethanolic mixture. The reaction chosen in the latter connection was the acid-catalysed depolymerisation of paraldehyde.[4]

EXPERIMENTAL

Materials.—" AnalaR " ethanol was used. The concentrated aqueous hydrochloric acid was the B.D.H. reagent, suitable for analysis. The paraldehyde was a redistilled sample, b. p. 124°. *o*-Nitroaniline and 4-chloro-2-nitroaniline were recrystallised samples with m. p. 70·5° and 116° respectively. The alcohol–water–acid mixtures were made up from amounts calculated to keep the ethanol–water ratio constant.

Acidity-function Measurements.—Values of H_0, as measured by the indicator *p*-nitroaniline, for 24·4 moles % ethanol–water containing hydrochloric acid in concentrations up to *ca.* 2·4M have been reported.[1] These data were extended by similar measurements with the indicators *o*-nitroaniline and 4-chloro-2-nitroaniline at *ca.* 18°. The results (see discussion) are given in Table 1 and plotted against the stoicheiometric acid concentration in Fig. 1, which also contains the data for aqueous solutions.

TABLE 1. *Acidity function in 24·4 moles % ethanol–water as determined by (a)* p-nitroaniline, *(b)* o-nitroaniline, *and (c)* 4-chloro-2-nitroaniline.

HCl (M)	0·047	0·141	0·430	0·950	1·44	1·90	2·37	3·51	4·39	5·80	6·20
H_0 (by *a*)	2·45	1·95	1·36	0·85	0·51	0·25	−0·02				
H_0 (by *b*)	—	—	(1·29)	0·84	0·51	0·25	0·01	−0·59	−1·07	—	—
H_0 (by *c*)	—	—	—	—	—	0·26	−0·01	−0·59	−1·06	−1·79	−2·10
H_0 (aver.)	2·45	1·95	1·36	0·85	0·51	0·25	−0·01	−0·59	−1·07	−1·79	−2·10

Kinetics of the Depolymerisation of Paraldehyde.—The reaction was followed by a titration method [5] similar to that used by Bell and Brown.[4] A particular acidic medium (*ca.* 80 ml.) was placed in a 100 ml. stoppered flask and the flask and contents brought to 25° in a thermostat bath. The reaction was started by adding a small (*ca.* 0·2 ml.) known quantity of paraldehyde.

[1] Satchell, *J.*, 1957, 2878.
[2] Hammett, " Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, 1940.
[3] Zucker and Hammett, *J. Amer. Chem. Soc.*, 1939, **61**, 2791.
[4] Bell and Brown, *J.*, 1954, 774.
[5] Friedemann, Contonio, and Shaffer, *J. Biol. Chem.*, 1927, **73**, 342.

At appropriate intervals 5 ml. samples were withdrawn and run into sufficient cooled aqueous 5N-sodium hydroxide almost to neutralise the acid, thus stopping the reaction. An excess (*ca.* 15 ml.) of concentrated (0·5M) sodium hydrogen sulphite was now added to convert the free acetaldehyde into its bisulphite compound. After not less than 15 min., during which the vessel was kept tightly corked, most of the excess of hydrogen sulphite was removed with a concentrated iodine solution and the rest with *ca.* N/30-iodine (starch indicator). Just enough sodium hydrogen carbonate to decolorise the indicator was added and the liberated

TABLE 2. *First-order rate constant k for depolymerisation of paraldehyde at 25°.*

| HCl (M)	3·51	2·37	1·90	1·44	0·95	0·43
$10^4 k$ (sec.$^{-1}$)	24·8	5·52	3·50	1·61	0·63	0·19

hydrogen sulphite was titrated with standard (*ca.* N/30) iodine. (The use of too much hydrogen carbonate causes the iodine to react with the liberated acetaldehyde.) By this method the infinity titres corresponded to about 97% completion of the reaction.

The rate of depolymerisation was measured at six different acidities covering the range 0·43—3·51M-hydrochloric acid. In all cases the first-order plots were linear over at least the first 70% of the reaction. The first-order constants are collected in Table 2.
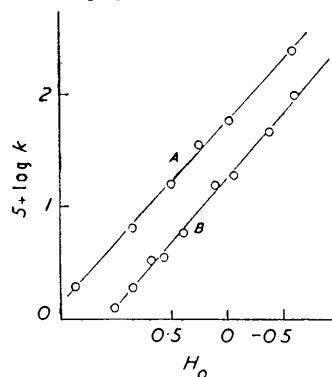
DISCUSSION

Table 1 shows that in the regions where the data for the different indicators overlap there is good agreement between the measured H_0 values. H_0 values given by *p*-nitro-

FIG. 1. *Acidity functions for hydrochloric acid solutions.*
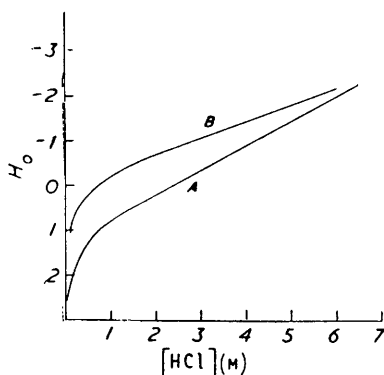
A, 24·4 moles % ethanol–water. *B*, water.

FIG. 2. *Depolymerisation of paraldehyde.*

A, 24·4 moles % ethanol–water. *B*, water.[4]

aniline were derived [1] by assuming that the pK_a value for that indicator is 0·99 (the value in water [6]). To obtain the agreement shown in Table 1 it is then necessary to take the pK_a values for *o*-nitroaniline and 4-chloro-2-nitroaniline to be −0·37 and −1·26 respectively, whereas the " best " values drawn by Long and Paul,[6] mainly from data concerning aqueous media, are −0·29 and −1·03 respectively.

These facts imply that on moving from an infinitely dilute solution of acid in water to an infinitely dilute solution of acid in the alcohol–water medium, the values of pK_a for the different indicators (B) change by different amounts, but that for variation of the acid concentration in the ethanolic medium the various activity-coefficient ratios f_B/f_{BH^+} change to roughly the same extent.

For a given indicator,

$$(pK_a{}^B)_S - (pK_a{}^B)_W = \log f_B{}^\circ . f_{H^+}{}^\circ / f_{BH^+}{}^\circ = \Delta pK_a{}^B \qquad . \quad . \quad . \quad (1)$$

[6] Paul and Long, *Chem. Rev.*, 1957, **57**, 1.

where the activity coefficients represent their limiting values at infinite dilution in the solvent S relative to their values at infinite dilution in water (W). Also in the solvent S for any two indicators B and C,

$$(pK_a{}^C)_S - (pK_a{}^B)_S = \log [CH^+]/[C] - \log [BH^+]/[B] - \log [(f_C.f_{BH^+})/(f_{CH^+}.f_B)] \qquad \ldots \ldots (2)$$

The H_0 scale is defined by the equation

$$H_0 = (pK_a)_W - \log [BH^+]/[B] \qquad \ldots \ldots (3)$$

If the ΔpK_a values for a series of indicators are the same, and if the variation of the ratios of the type f_B/f_{BH^+} with acid concentration is the same for them all in solvent S, then the activity-coefficient term in equation (2) vanishes and the usual stepwise calculation [2] will produce pK_a values equal to those in water, if the calculation is started from an aqueous value. In this case also, H_0 values obtained from eqn. (3) will imply the same amount of ionisation as they do in water and values calculated for different indicators will overlap exactly.

If, however, the ΔpK_a values for a series of indicators are not the same, then even if terms such as f_B/f_{BH^+} should vary with acidity in solvent S in the same way, the activity-coefficient term in eqn. (2) will not vanish, but will be constant for each pair of indicators. Hence a stepwise calculation of pK_a based on a given aqueous value as a starting point will not reproduce the aqueous pK_a values for the rest of the sequence. Also H_0 values calculated from eqn. (3) will not coincide where data for successive indicators overlap. To make them do so a constant must be added, as here found. Such circumstances are envisaged by Gutbezahl and Grunwald [7] when they state that the H_0 scale as defined in eqn. (3) will not exist in some solvents. This fact, however, does not defeat the usefulness of the concept provided that terms such as $f_C.f_{BH^+}/f_{CH^+}.f_B$ remain constant with changes in acid concentration for, if this is so, then appropriate acid-catalysed reaction rates will correlate with values obtained as were those in Table 1. Fig. 2 shows that the data for paraldehyde in fact do so. Fig. 2 also contains Bell and Brown's data refering to aqueous hydrochloric acid solutions. The slope of the plot of the logarithm of the first-order rate constant against $-H_0$ is 1·09 in the mixed solvent compared with 1·16 in the aqueous media. At a given H_0 value the reaction rate in water is about three-fold slower than that in the alcoholic medium. This discrepancy is probably mainly due to the inconstancy of ΔpK_a values between aqueous and ethanolic media already mentioned.

Thus for solutions of hydrochloric acid in a 24·4 moles % ethanol–water solvent it has been shown (a) that activity-coefficient ratios such as $f_C.f_{BH^+}/f_{CH^+}.f_B$ remain constant for the three indicators used, (b) that a reaction rate known to depend on the acidity function behaves in the expected manner, and (c) that a reaction rate known to depend on the hydrogen-ion concentration in aqueous media continues to follow this concentration fairly accurately in the mixed solvent.[1] Hence this particular ethanol–water mixture seems a promising medium from the Zucker–Hammett viewpoint.

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[7] Gutbezahl and Grunwald, *J. Amer. Chem. Soc.,* 1953, **75**, 559, 565.