779. *The Acidity Function, H_0, in Ethylene Glycol and Ethylene Glycol–Water Mixtures.*

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Acidity functions have been measured with the indicators, *p*- and *o*-nitroaniline and 4-chloro-2-nitroaniline, for hydrochloric acid in ethylene glycol up to 2M-acid concentration. Similar measurements have been made for hydrochloric and perchloric acid up to 4M-concentration in 50% (v/v) aqueous glycol; H_0 values for perchloric acid up to M-concentration in 10% (v/v) aqueous glycol with two indicators, *p*- and *o*-nitroaniline, are also presented. The results suggest that the H_0 concept is applicable to all the media studied and indicate the greater acidic character of ethylene glycol than of methanol and ethanol. The rates of hydrolysis of sucrose, depolymerisation of paraldehyde, and iodination of acetone have been measured at various acid concentrations in 50% (v/v) aqueous glycol. The rate of the iodination of acetone at different acid concentrations was extended to 1 : 9 (v/v) aqueous glycol. The applicability of Zucker–Hammett hypothesis to these media is discussed.

RECENT interest in acidity functions has been confined [1] mainly to the mechanism of acid-catalysed reactions. Bascombe and Bell [2] have, however, shown that the acidity function can be of use in interpreting the behaviour of concentrated acid solutions. Further, the ease of measurement of acidity function in non-aqueous media offers a simple method for the comparison of solvent basicities.

Comparatively few indicator data are available for non-aqueous media, particularly for alcohols. Braude [3] reported H_0 data in different solvents with a single indicator, *p*-nitroaniline, and Satchell [4] investigated various ethanol–water mixtures extensively. The results suggest that the acidity function has no generality in these media. Eaborn [5] studied methanol–water mixtures and recently showed that in 27% aqueous methanol the plot of the logarithm of the indicator ratio for *p*-nitroaniline against that for *o*-nitroaniline does not give unit slope. Bunton and his co-workers [6] established the H_0 scale in two aqueous dioxan media, one containing 40% and the other 60% (v/v) of dioxan.

Application of the acidity function to mechanistic investigations of acid-catalysed reactions is well known. Zucker and Hammett [7] have suggested on the basis of this application that *A*-1 and *A*-2 reactions (in Ingold's terminology) can be distinguished according to whether the rate increases in proportion to h_0 (antilog $-H_0$) or acid concentration. The advantages of mixed and non-aqueous media in these investigations, as pointed out by Paul and Long,[1] are two-fold: the kinetic investigations can be extended to substances insoluble in water and there is a possibility that $-\log C_{H^+}$–H_0 plots may be

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[1] Long and Paul, *Chem. Rev.*, 1957, **57**, 1, 935.
[2] Bascombe and Bell, *Discuss. Faraday Soc.*, 1957, **24**, 158.
[3] Braude, *J.*, 1948, 1971.
[4] Satchell, *J.*, 1957, 3524.
[5] Eaborn, *J.*, 1953, 3148.
[6] Bunton, Ley, Rhind-Tult, and Vernon, *J.*, 1957, 2327.
[7] Zucker and Hammett, *J. Amer. Chem. Soc.*, 1939, **61**, 2779.

significant at lower acid concentrations than in water. Although the limitations of the Zucker–Hammett hypothesis were shown in recent communications,[8] the present investigations were made with a view to understanding the solvent basicity of ethylene glycol and its mixtures, and to see whether H_0 data in these media are useful for kinetic investigations of the Zucker–Hammett type. This is of interest as glycol mixtures have been lately used extensively for non-aqueous acid–base titrations.

Results of acidity-function measurements in ethylene glycol and two aqueous glycol media, and the application of these data to a few acid-catalysed reactions are here presented.

RESULTS

The acidity function, H_0, is defined by $\mathrm{p}K_{\mathrm{BH^+}} - \log (C_{\mathrm{BH^+}}/C_{\mathrm{B}})$ or $-\log (a_{\mathrm{H^+}} . f_{\mathrm{B}}/f_{\mathrm{BH^+}})$, where the activity coefficients of all the species are referred to a value of unity at infinite dilution in

TABLE 1. *H_0 of hydrogen chloride in ethylene glycol.*

Acid (M)	log I	H_0	Acid (M)	log I	H_0	Acid (M)	log I	H_0
p-Nitroaniline, $\mathrm{p}K_{\mathrm{BH^+}}$ 0·99			*o*-Nitroaniline, $\mathrm{p}K_{\mathrm{BH^+}}$ −0·29			4-Chloro-2-nitroaniline, $\mathrm{p}K_{\mathrm{BH^+}}$ −1·03		
0·050	0·61	0·38	0·200	0·07	−0·36	0·500	−0·43	−0·60
0·100	0·985	0·005	0·500	0·38	−0·68	0·800	−0·12	−0·91
0·200	1·34	−0·35	0·700	0·58	−0·87	1·000	−0·01	−1·02
0·392	1·58	−0·59	1·000	0·76	−1·05	1·500	0·22	−1·25
0·600	1·76	−0·77	1·300	0·95	−1·24	2·000	0·48	−1·51
0·741	1·83	−0·84						
1·000	1·98	−0·99						

TABLE 2. *H_0 of perchloric acid in 50% (v/v) aqueous ethylene glycol.*

Acid (M)	log I	H_0	Acid (M)	log I	H_0	Acid (M)	log I	H_0
p-Nitroaniline			*o*-Nitroaniline			4-Chloro-2-nitroaniline		
0·060	−0·44	1·43	0·500	−0·86	0·57	2·563	0·05	−1·08
0·100	−0·23	1·22	1·000	−0·29	0·00	3·280	0·43	−1·46
0·400	0·42	0·57	1·700	0·20	−0·49	3·582	0·59	−1·62
0·800	0·85	0·14	2·563	0·63	−0·92	3·894	0·81	−1·84
1·000	0·99	0·00	3·000	0·90	−1·19	4·100	0·94	−1·97
1·500	1·32	−0·33	3·582	1·31	−1·60			
2·000	1·57	−0·58						

TABLE 3. *H_0 of hydrogen chloride in 50% (v/v) aqueous ethylene glycol.*

Acid (M)	log I	H_0	Acid (M)	log I	H_0	Acid (M)	log I	H_0
p-Nitroaniline			*o*-Nitroaniline			4-Chloro-2-nitroaniline		
0·060	−0·24	1·23	0·500	−0·73	0·44	2·500	−0·42	−0·61
0·100	−0·08	1·07	1·000	−0·30	0·01	3·200	−0·06	−0·97
0·400	0·46	0·53	1·700	0·03	−0·32	3·500	0·07	−1·10
0·800	0·81	0·18	2·500	0·37	−0·66	3·800	0·22	−1·25
1·000	0·96	0·03	3·000	0·62	−0·91	4·000	0·30	−1·33
1·500	1·24	−0·25	3·500	0·81	−1·10			
2·000	1·44	−0·45						

TABLE 4. *H_0 of perchloric acid in 1 : 9 (v/v) aqueous ethylene glycol.*

Acid (M)	log I	H_0	Acid (M)	log I	H_0
p-Nitroaniline			*o*-Nitroaniline		
0·100	0·07	0·92	0·200	−1·26	0·97
0·300	0·62	0·37	0·400	−0·63	0·34
0·400	0·79	0·20	0·600	−0·27	−0·02
0·500	0·97	0·02	0·800	0·01	−0·30
0·600	1·09	−0·10	1·000	0·25	−0·54
0·700	1·22	−0·22	1·14	0·35	−0·64
0·900	1·43	−0·44			
1·000	1·55	−0·55			

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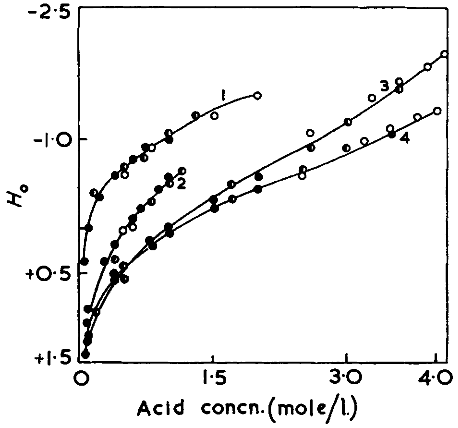
[8] Whalley, *Trans. Faraday Soc.*, 1959, **55**, 798.

FIG. 1. *Plot of H_0 against concentration in* (1) *ethylene glycol and* (2—4) 50% v/v *aqueous ethylene glycol for* (1,4) *hydrogen chloride and* (2,3) *perchloric acid.*



● p-*Nitroaniline.* ◐ o-*Nitroaniline.* ○ 4-*Chloro-2-nitroaniline.*

FIG. 2. *Plot of log I against concentration of hydrogen chloride in ethylene glycol for* (1) p-*nitroaniline,* (2) o-*nitroaniline, and* (3) 4-*chloro-2-nitroaniline.*

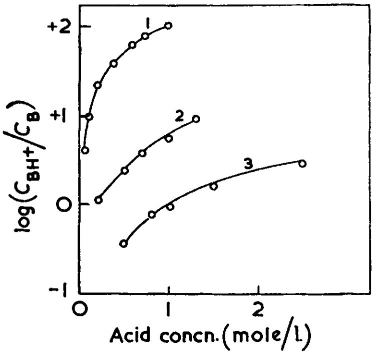


FIG. 3. *Plot of log I against concentration of hydrogen chloride in* (1—3) 50% v/v *and* (4,5) 1 : 9 v/v *aqueous ethylene glycol for* (1,4) p-*nitroaniline,* (2,5) o-*nitroaniline, and* (3) 4-*chloro-2-nitroaniline.*

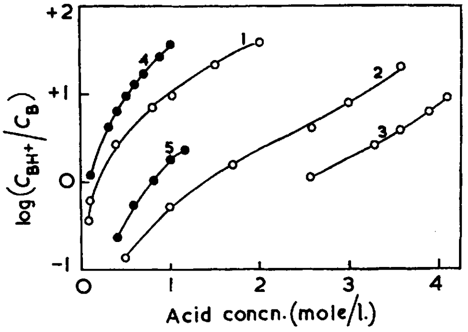


FIG. 4. *Plot of log I against concentration of hydrogen chloride in* 50% v/v *aqueous ethylene glycol for* (1) p-*nitroaniline,* (2) o-*nitroaniline, and* (3) 4-*chloro-2-nitroaniline.*

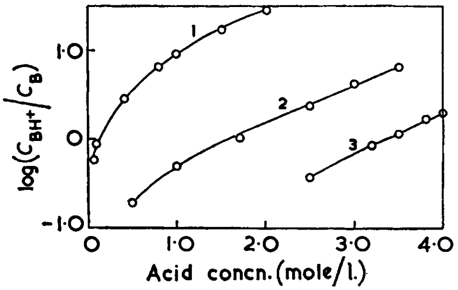


FIG. 5. *Plot of log k against* (1,3,4) *log* [HClO$_4$] *or* (2,5,6) H_0 *for the iodination of acetone in* (1,2) 1 : 9 v/v *and* (3,5) 50% v/v *aqueous ethylene ethylene or* (4,6) *water.*

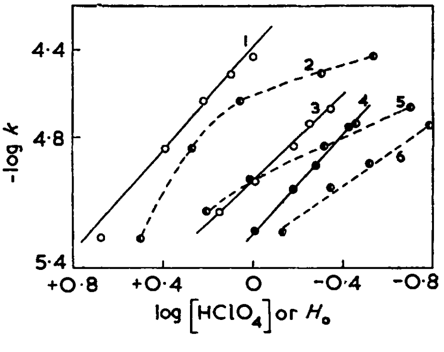
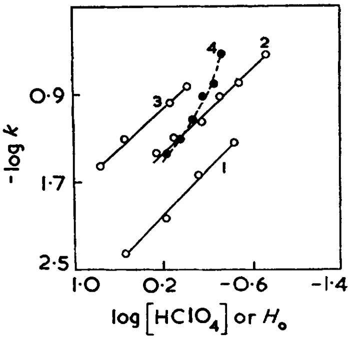


FIG. 6. *Plot of log k against* (1—3) H_0 *and* (4) *log* [HClO$_4$] *for the hydrolysis of sucrose in* (1,2,4) 50% v/v *aqueous ethylene glycol and* (3) 40% *aqueous dioxan.*



water. The pK_{BH^+} values used in the calculation of H_0 are thus those reported by Paul and Long[1] for water. The indicator ratio, I ($=C_{BH^+}/C_B$), can be calculated by employing a formula details of which are given in the Experimental section.

Table 1 gives the H_0 values for hydrochloric acid in pure ethylene glycol. Tables 2 and 3 give H_0 values for perchloric and hydrochloric acid in 50% (v/v) aqueous glycol. Table 4 gives H_0 values for perchloric acid in 1 : 9 (v/v) aqueous glycol. While all the three indicators were used in measurements in glycol and 50% (v/v) aqueous glycol, only *p*- and *o*-nitroaniline were used in measurements in 1 : 9 aqueous glycol. These results are illustrated in Figs. 1—4.

By plotting ($\log I - \log C_A$) against C_A at a series of acid concentrations (I = indicator ratio and C_A = acid concn.) and extrapolating the graphs to zero concentration, approximate $pK_{BH^+}{}^S$ values (*i.e.*, the indicator constants when the activity coefficients are referred to a value of unity at infinite dilution in the particular solvent) have been obtained. These values are listed in Table 5.

Tables 6 and 7 list results for hydrolysis of sucrose and depolymerisation of paraldehyde at various acid concentrations in 50% (v/v) aqueous glycol. Tables 8 and 9 give the results for iodination of acetone at a series of acid concentrations in 50% (v/v) and 1 : 9 (v/v) aqueous glycol respectively.

The rate of iodination of acetone is proportional to the stoicheiometric acidity in both the media and log *k* plotted against $-\log C_{HClO_4}$ in Fig. 5 gives a slope of unity in 50% (v/v) aqueous glycol and 1·16 in 1 : 9 aqueous glycol. The results for this reaction in water are plotted for comparison.

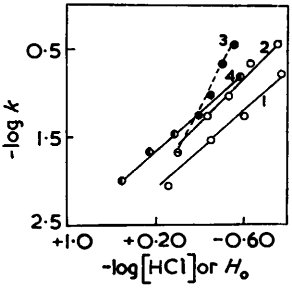


FIG. 7. *Plot of log k against* (1,2,4) H_0 *and* (3) [HCl] *in* (1) *water,* (2,3) 50% v/v *aqueous ethylene glycol, and* (4) 75·6 mole % *aqueous ethanol.*

The rates of hydrolysis of sucrose and of depolymerisation of paraldehyde increase much faster than the stoicheiometric acidity, and log *k* plotted against H_0 in Figs. 6 and 7 give slopes of 0·98 and 1·22, respectively. For both the reactions, results in water and a mixed aqueous

TABLE 5. $pK_{BH^+}{}^S$ *values of the indicators.*

Indicator	Ethylene glycol	1 : 9 (v/v) aqueous glycol	50% (v/v) aqueous glycol
p-Nitroaniline	2·00	0·98	0·76
o-Nitroaniline	0·76	−0·42	−0·63
4-Chloro 2-nitroaniline	−0·10	—	−1·33

TABLE 6. *Hydrolysis of sucrose in* 50% (*v/v*) *aqueous ethylene glycol.*

Acid (M)	10^2k (min.$^{-1}$)	log *k*	H_0	$\log k + H_0$	$\log k - \log C_{H^+}$
0·700	3·55	−1·45	0·25	−1·20	−1·30
0·900	4·85	−1·31	0·08	−1·23	−1·26
1·200	7·19	−1·14	−0·15	−1·29	−1·22
1·500	10·96	−0·96	−0·33	−1·29	−1·14
1·782	14·13	−0·85	−0·50	−1·35	−1·10
2·200	31·62	−0·50	−0·75	−1·25	−0·84

TABLE 7. *Depolymerisation of paraldehyde in* 50% (*v/v*) *aqueous ethylene glycol.*

Acid (M)	10^2k (min.$^{-1}$)	log *k*	H_0	$\log k + H_0$	$\log k - \log C_{H^+}$
1·000	2·14	−1·67	0·00	−1·67	−1·67
1·500	5·754	−1·24	−0·26	−1·50	−1·42
2·000	9·55	−1·02	−0·46	−1·48	−1·32
2·500	21·73	−0·663	−0·66	−1·32	−1·06
3·000	35·48	−0·45	−0·90	−1·35	−0·93

TABLE 8. *Iodination of acetone in* 50% (*v*/*v*) *aqueous ethylene glycol.*

Acid (M)	10^6k (mole l.$^{-1}$ min.$^{-1}$)	log *k*	H_0	log $k + H_0$	log $k -$ log C_{H^+}
0·709	7·244	−5·14	0·20	−4·94	−4·99
1·014	10·00	−5·00	0·00	−5·00	−5·00
1·503	14·45	−4·84	−0·32	−5·16	−5·02
1·800	18·20	−4·74	−0·45	−5·19	−5·00
2·210	21·38	−4·67	−0·70	−5·37	−5·01

TABLE 9. *Iodination of acetone in* 1 : 9 (*v*/*v*) *aqueous ethylene glycol.*

Acid (M)	10^6k (mole l.$^{-1}$ min.$^{-1}$)	log *k*	H_0	log $k + H_0$	log $k -$ log C_{H^+}
0·210	5·495	−5·26	0·50	−4·76	−4·56
0·406	14·13	−4·85	0·27	−4·58	−4·45
0·603	23·99	−4·62	−0·06	−4·68	−4·42
0·805	30·20	−4·52	−0·30	−4·82	−4·45
1·000	35·48	−4·45	−0·54	−4·99	−4·45

medium (40% dioxan for hydrolysis of sucrose and a 24·4 moles % aqueous ethanol for depolymerisation of paraldehyde) are plotted for comparison. In all cases the reactions were studied in the acidity ranges where $-\log C_{H^+}$ and H_0 differ considerably.

DISCUSSION

For the acidity function to obtain in a solvent, two conditions must be fulfilled: (i) f_B/f_{BH^+} should be independent of the indicator used; and (ii) $\log (C_{CH^+}/C_C) - \log (C_{BH^+}/C_B)$ for a pair of indicators B and C should be the same in different solvents and should equal the value in water. Satchell,[9] in a detailed survey of the results for mixed and non-aqueous media, concluded that, while the first condition is generally fulfilled, it is in the second that deviations occur for many solvents. He also showed that the ΔpK_{BH^+} values (the difference in the values for an indicator in water and the medium in question) for an indicator should be the same and, if f_B/f_{BH^+} remains constant for a series of indicators in that solvent, then stepwise calculations based on a p*K* value of an indicator in water will afford p*K* values equal to those in water for other indicators. Under these conditions, H_0 values calculated from p*K* values (in water) of a pair of indicators coincide in the overlap region.

The results for all the present media satisfy both the conditions within the limits of experimental error. From Figs. 2 and 3 it is seen that log *I* plots for the three indicators in the different media are fairly parallel. A more critical test of such a parallelism is as follows. If from one curve X of Fig. 2 or 3 one plots the slopes at points corresponding to concentrations *a*, *b*, *c* . . . against the slopes of a second curve Y severally at the same concentrations, then this new plot is a straight line with slope unity if the curves X and Y are parallel. For the pair, *o*/*p*-nitroaniline, these slopes are 1·10 in ethylene glycol, 1·05 in 50% v/v aqueous glycol, and 1·08 in 1 : 9 v/v aqueous glycol; for the pair, 4-chloro-2-nitroaniline/*o*-nitroaniline, the slopes are 0·97 and 1·00 in the pure glycol and 50% v/v aqueous glycol, respectively. These values are probably within the limits of experimental error since *I* values include those in the low protonation range as well. The difference between the logarithms of indicator ratios for pairs of indicators is thus constant and also equals the value in water. This means that the relative basicity of a pair of indicators is unchanged on changing the medium from glycol or glycol–water mixture to water, which is the basic assumption underlying the development of acidity function. It can thus be concluded that the H_0 concept is valid for these media.

Basicity of Ethylene Glycol and its Mixed Media.—The H_0 values in glycol are more negative at a given acid concentration than in water, ethanol, or methanol, although the H_0 data in methanol were obtained with methanesulphonic acid. The conclusion is that

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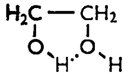
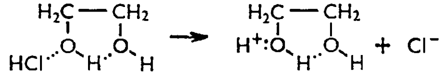
[9] Satchell, *J.*, 1958, 1916.

ethylene glycol is much less basic than the other hydroxylic solvents named. This is in agreement with Palit's surmise[10] from studies of the solubility of soaps in glycols and the applicability of glycol mixtures as titration media for weak bases and with results obtained by Hine and Hine[11] and lately by Ballinger and Long[12] by other methods.

The greater acidity of ethylene glycol than of alcohols possibly arises from its capacity to form hydrogen bonds (intra- and inter-molecular) between the two hydroxyl groups so that the hydrogen atoms of these groups become more positive (cf. A). One oxygen atom is then more basic than the other, so that an acid, *e.g.*, HCl, tends to become attached to this more basic oxygen atom (cf. B), a process that is followed by ionisation (C).


(A)


(B) (C)

Now in the ion (C), a result of the three groups attached to each oxygen atom is to increase the *B* strain. Since ethylene glycol contains more CH_2 groups, this effect may be greater than in the conjugate acid cations of methyl or ethyl alcohol. The net result of the *B* strain effect is to decrease the electron-releasing powers of the CH_2 groups attached to the oxygen atoms by increasing the steric and dipolar repulsions between the groups attached to oxygen. This in turn increases the C–O–H bond angle. (The *B* strain hypothesis was employed by Hine and Hine[11] to explain the relative basicities of water, alcohols, and ethers.) It is thus likely that the electron-releasing capacity of the CH_2 groups is much diminished in the acid cation of ethylene glycol which results in a lower electron-density on both the oxygen atoms, facilitating removal of a proton.

Bunton and his co-workers[6] believed that, as the variation of $-\log C_{H^+}$ and H_0 in methanol is the same when methanesulphonic acid was employed, it was not permissible to compare solvent basicities at fixed acid concentrations. A similar result can be observed from our H_0 values for hydrochloric acid in ethylene glycol. We believe that, so long as the same acid is used and provided that the ionisation of the acid is also large, a comparison of solvent basicities can still be made since it was shown by Hammett[13] that the effect of dielectric constant of the solvent will be small in highly ionised systems.

The basicity of the mixed media increases with increasing amounts of water and is characterised by substantial increase in H_0 values, when comparison is made at a single acid concentration up to about 50% (v/v) aqueous glycol. Further additions of water tend to increase acidity. Similar observations were made by Braude[3] for ethanol–water mixtures. It is likely that the explanation given by Paul and Long[1] holds also in the present case.

The rates of hydrolysis of sucrose and of depolymerisation of paraldehyde depend on H_0 in 50% (v/v) aqueous glycol. This is also the correlation obtained for both the reactions in water. Applying Brönsted's equation for the effects of the medium on the heterolysis of the conjugate acid of the substrate as the rate-determining step and substituting for a_{H^+}, we get

$$\log k = -H_0 + \log \frac{f_{BH^+} f_S}{f_B f_{T^+}} + \text{Constant.}$$

If, as found in Figs. 6 and 7, the plot of log k against H_0 is linear with slope unity, the activity coefficient factor in the above equation remains constant with changing acidity. This is quite plausible since f_S/f_{T^+} can be expected to behave in the same way as f_B/f_{BH^+} because of the similar nature of the transition state (T^+) and of the conjugate acid BH^+.

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[10] Palit, *J. Amer. Chem. Soc.*, 1947, **69**, 3120; *Ind. Eng. Chem., Analyt.*, 1946, **18**, 246.
[11] J. Hine and M. Hine, *J. Amer. Chem. Soc.*, 1952, **74**, 5266.
[12] Ballinger and Long, *J. Amer. Chem. Soc.*, 1960, **82**, 795.
[13] Hammett, *J. Amer. Chem. Soc.*, 1928, **50**, 2666.

While a true correlation requires that the log k–H_0 graph should be of slope unity, in the present case, the slope for the depolymerisation of paraldehyde is somewhat higher, which in terms of the above equation means that f_S/f_{T^+} is increasing faster than f_B/f_{BH^+}. Such small departures from the essential requirement of unit slope, as pointed by Paul and Long,[1] are to be expected since the indicators used in establishing the H_0 scale are very different from the substrates in the kinetic experiments.

For both the reactions, Figs. 6 and 7 show that the rate is considerably faster (about three times) than that in water at corresponding values of H_0. If log k were to depend only on H_0, then the activity-coefficient factors in the above equation should be equal and the rates in water and the mixed medium will also be equal. But inequality of rates in water and 50% (v/v) aqueous glycol thus indicates that these ratios are not equal but that their first derivatives with acid concentration remain approximately equal, an observation in agreement with those of Bunton and his co-workers.[6]

The rate of iodination of acetone in 50% (v/v) and 1 : 9 aqueous ethylene glycol is proportional to the stoicheiometric acidity. Applying Brönsted's equation for the rate-determining step, which in this case involves the bimolecular reaction of the conjugate acid of the substrate and a nucleophile, and simplifying, we get

$$\log k = \log C_{H^+} + \log (f_S f_{H^+} a_Y / f_{T^+}) + \text{Constant},$$

where a_Y is the activity of the solvent and the other terms retain their usual significance. Since, as shown in Fig. 5, a plot log k against log C_{H^+} is linear, the activity-coefficient term in the above equation remains constant with changing medium. But it was pointed out by Long and Paul [1] that this condition cannot be expected to be general since the behaviour of the transition state on change in the medium is uncertain because of its structural difference from the conjugate acid of the substrate. It is not surprising then that different results were obtained in a number of cases for reactions which are known to proceed by an A-2 mechanism. Satchell [14] found that iodination of acetone in a series of ethanol–water mixtures does not follow the stoicheiometric acidity (as the Zucker–Hammett hypothesis predicts for an A-2 reaction) once a certain composition of ethanol–water is reached, but in our work increasing additions of ethylene glycol do not affect the essential dependence of log k on log (acid concn.). Archer and Bell [15] reported rate data for the iodination of acetone in acid up to 8M-concentration and the interpretation of their data, in a recent modification suggested by Bell,[16] is that the rate depends only on acid concentration, the correction for the protonation of acetone being negligible. The rate, however, is found to be somewhat higher than in water at equal acid concentrations in both the media and also shows a slight increase with increasing glycol content of the medium at constant acid concentration. Similar observations [14] were made for ethanol–water mixtures.

EXPERIMENTAL

Materials.—Ethylene glycol. Reagent-grade ethylene glycol supplied by Fisher Scientific Co., U.S.A., was used. It contained no trace of acid or basic impurity. Anhydrous sodium sulphate was added in sufficient quantity to remove any water. The material was then distilled. Drying was repeated. Then several distillations through a long column gave a fraction, b. p. 195—196°, that was stored out of contact with air; it had n^{26} 1·4300.[17]

Water. Water was doubly distilled in an all-glass apparatus.

Perchloric acid. 60% and 70% (w/v) Perchloric acid supplied by E. Merck was employed throughout.

Hydrochloric acid. For measurements in ethylene glycol, hydrogen chloride was generated

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[14] Satchell, *J.*, 1957, 2878.

[15] Archer and Bell, *J.*, 1959, 3228.

[16] R. P. Bell, personal communication.

[17] Cf. Weissberger, " Organic Solvents, Physical Properties and Methods of Purification," Interscience Publ., Inc., New York, 1955.

from sulphuric acid and " AnalaR " hydrochloric acid and was passed through sulphuric acid directly into the glycol. For studies in 50% (v/v) aqueous glycol, " AnalaR " hydrochloric acid was used.

Indicators. *p*-Nitroaniline, *o*-nitroaniline, and 4-chloro-2-nitroaniline were recrystallised twice from aqueous alcohol and checked for purity by their m. p.s.

Other materials for kinetic investigations. All were of " AnalaR " quality or were purified by the recommended methods.

Preparation and Standardisation of Acid Solutions.—In studies with hydrogen chloride in pure glycol, the gas was bubbled into the glycol until the concentration was about 2M. This solution was standardised by aqueous 0·1N-sodium hydroxide. This solution retained constant strength on storage. Appropriate portions of this stock acid in glycol were added from a micro-burette to give solutions of the desired acid concentration.

Solutions of perchloric and hydrochloric acid in 50% (v/v) aqueous glycol were prepared from a stock 2M- or 5M-aqueous acid.

Indicator Solutions.—These solutions (0·0005M) were prepared in pure glycol by weight and aliquot parts were then used.

Procedure.—Optical measurements were carried on a Hilger ultraviolet spectrophotometer. The temperature in the cell compartment was not controlled but fluctuations were not sufficient to introduce significant error. The temperature was always 30° ± 2° during measurements.

The indicator ratio was calculated by the formula $C_{BH^+}/C_B = (\varepsilon_B - \varepsilon_S)/\varepsilon_S - \varepsilon_{BH^+})$, where ε_B is the extinction coefficient of the indicator in the purely basic form at a particular wavelength, ε_S is the extinction coefficient at the same wavelength in the test solution, and ε_{BH^+} is the extinction coefficient of the conjugate acid of the indicator.

The molar extinctions coefficients (ε_B) of the indicators were determined by the usual procedure in all the media under study. Beer's law was obeyed for all the three indicators at the wavelength of maximum absorption of the basic forms. The extinction coefficient in the acid solution was next determined as follows: A known volume of the stock indicator solution in glycol was added to the test solution so that the optical density of the solution was in the range 0·30—0·70 (a preliminary experiment was usually necessary) (cf. Braude [3] and Lemaire and Lucas [18]). The pure solvent was employed as control. The acid forms of the indicators gave negligible absorptions at the wavelengths of maximum absorptions of their basic forms. Extinction coefficients in test solutions were checked at two or three indicator concentrations to see whether they were reasonably independent of concentration; they were generally so to an accuracy of ±5%. The volume of glycol introduced during addition of the indicator solution to the test solution was taken into account in keeping the ratio of glycol to water constant in measurements in glycol–water mixtures.

The optical density of the test solution was measured for a few wavelengths near the absorption peak to detect any shift in the wavelength of maximum absorption of an indicator due to changing medium: except for *p*-nitroaniline, where a considerable shift to lower wavelengths occurred at higher acid concentrations in all media, no such shift was observed. In calculating the indicator ratio, the extinction coefficient only at the wavelength of maximum absorption of the basic form was considered.

While this shift, due to changing medium, in the wavelength of maximum absorption of the test solution in 50% (v/v) aqueous glycol is not large enough to introduce considerable error in the calculated values of H_0, this is not so in studies in ethylene glycol. Here, a gradual shift of the maximum to lower wavelengths was noted with increasing acid concentration. When the extinction coefficient at changing wavelength was used in the calculations, rather than the method of the present work, the H_0 values differed by about 0·10 unit in the concentration range 0·80—1·00M. Below this concentration range, the difference between the two methods of calculation is negligible.

Kinetic Experiments.—(a) *Hydrolysis of sucrose.* The rate of hydrolysis of sucrose (5 g. per 100 c.c.) at different concentrations of perchloric acid in 50% (v/v) aqueous glycol was followed polarimetrically. Calculated amounts of ethylene glycol and aqueous sucrose were mixed such that when the acid was added at a later stage the ratio of glycol to water was 50 : 50. The appropriate amount of acid was added to this mixture to start the kinetic experiment and the solution immediately transferred to the polarimeter tube maintained at 30°. The rotatory power was determined at convenient times. Infinity readings were taken the next day and

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[18] Lemaire and Lucas, *J. Amer. Chem. Soc.*, 1951, **73**, 5198.

were fairly constant. Good linear plots were obtained when log ($x_t - x_\infty$) was plotted against time. The rate constant was calculated from the slope of the plot.

(b) *Iodination of acetone.* The rate of iodination of acetone at different perchloric acid concentrations in 50% (v/v) and 10% (v/v) aqueous glycol was studied at 30° with a Hilger spectrophotometer. The method adopted was that of Satchell[14] with slight modifications. The concentration of acetone was maintained at 0·003M while the iodine concentration was varied from 3 to 8 × 10^{-4}M, the range in which Beer's law was obeyed for iodine solutions. The rate of the iodination was found to be of zero order for the concentrations of the halogen used, this being verified by varying the iodine concentration by nearly a factor of two in all cases. Sodium nitrite was employed as the oxidising agent to reoxidise the iodide ions formed in the reaction to iodine (the advantages thereof are described elsewhere[14]). For media richer in glycol addition of nitrite itself decolorised the iodine to a slight extent: the resulting error was minimised (i) by adding the nitrite immediately before the kinetic experiment and (ii) by keeping the nitrite concentration equal to the concentration of iodine employed in the particular experiment. Use of potassium iodate as oxidising agents gave the same results as use of nitrite. Good zero-order plots were obtained for both media.

(c) *Depolymerisation of paraldehyde.* The rate of depolymerisation of paraldehyde in hydrochloric acid solutions in 50% (v/v) aqueous glycol was studied at 30° by a method similar to that used by Bell and Brown[19] and by Satchell.[4] Good first-order plots were obtained for about 70% reaction by plotting log ($x_\infty - x_t$) against time.

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[19] Bell and Brown, *J.*, 1954, 774.