Hammett Acidity Functions (H_-) of Lithium, Sodium, and Potassium Glycoxide Solutions in Ethylene Glycol at 25 °C

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H_- scales have been set up for solutions of lithium, sodium, and potassium glycoxides in anhydrous ethylene glycol at 25 °C by use of nitro-substituted anilines and diphenylamines as indicators. The order of increase of H_- with alkali concentration is Li < Na < K. This may be due to ion-pair formation which will be in the order Li > Na > K, and is reflected in the H_- being in the reverse order, as expected. The H_- scales for the three systems (i) NaOH in water, (ii) NaOMe in methanol, and (iii) Na glycoxide in ethylene glycol are compared. A comparison is also made of the aqueous and glycolic systems on a mole-fraction scale, which seems to indicate that, like the autoprotolysis constant, the H_- scale in any amphiprotic solvent is largely a composite function of bulk dielectric constant of the solvent, as well as the intrinsic acidity and basicity of the solvent molecules.

ALTHOUGH the Hammett acidity function has been studied exhaustively in several acid solutions, studies in basic solutions are comparatively few. Elaborate studies [1,2] have been made by several workers to set up H_- scales in methanol (aqueous or non-aqueous) with different indicators, to investigate the mechanisms of base-catalysed reactions, and to understand the physicochemical problems involved, but not much is known about other solvents. Glycols, which are widely used either alone or in mixtures with suitable 'co-

[1] C. H. Rochester, *Quart. Rev.*, 1966, **20**, 511.
[2] K. Bowden, *Chem. Rev.*, 1966, **66**, 119.

solvents ' as media for acid–base titrations,[3] are good amphiprotic solvents with dielectric constants (D) comparable with that of methanol (D for ethylene glycol at 25 °C = 37·67). The autoprotolysis constant of ethylene glycol and of its aqueous mixtures of various compositions are known.[4,5] Solutions of strong acids like HCl, H_2SO_4, and $HClO_4$ in ethylene glycol and its 50% aqueous mixture have been studied and acidity function (H_0) scales in the respective solvents have been set up.[6] These scales were also shown to be useful in the mechanistic consideration of some acid-catalysed reactions such as mutarotation of glucose and decomposition of paraldehyde.[6] Seemingly it would prove equally interesting and useful to set up acidity function (H_-) scales for strongly basic solutions of glycol using Li, Na, and K glycoxides as sources of glycoxide ions, as we have attempted.

We used nitro-substituted anilines and diphenylamines which have been amply proved to be true Hammett indicators. The spectra of the neutral (SH) and ionized (S^-) forms of these indicators were found to be similar in water and several alcoholic media.[7] In ethylene glycol also we obtained similar spectra with slight shifts of the maxima. In the case of 2,4-dinitrodiphenylamine there was a slow irreversible decomposition at higher alkali concentrations, but this difficulty was overcome by taking optical density values with time and extrapolating to zero time. In our work 2,4,4'trinitrodiphenylamine has been used as the basis of the H_- scale. This is a fairly strong acid with pK_a 12·35 in water and ionizes in the dilute pH region. The dissociation constant of this indicator in ethylene glycol (GOH) was determined by the ' extrapolation ' method described by More O'Ferrall and Ridd [7] by use of equation (1) where $({}_sK_b)_{S^-}$, the dissociation

$$p({}_sK_b)_{S^-} = \log R - \log C_{OG^-} + \log \frac{f_{S^-} \cdot f_{GOH}}{f_{SH} \cdot f_{OG^-}} \quad (1)$$

constant of the conjugate base of the indicator acid SH, is given by $a_{SH}.a_{OG^-}/a_{S^-}.a_{GOH}$ in this solvent, OG^- is $HO{\cdot}CH_2{\cdot}CH_2{\cdot}O^-$, and $R = C_{S^-}/C_{SH}$ is the ratio of the concentration of the indicator in the basic to acid form. The corresponding pK_a value is then obtained by subtracting the pK_b value from the autoprotolysis constant of ethylene glycol at 25 °C (15·75 on the molar scale).[4] For the other indicators a stepwise procedure is adopted. This method requires the basic postulate that for a series of indicators both $\partial \log_{10}(C_{S^-}/C_{SH})/\partial \log_{10} C_{MOG}$ (MOG = Na, Li, and K glycoxides) and H^- for a particular MOG concentration is independent of the indicator. The approximate constancy of the slopes of the graphs of ($\log R - \log C_{OG^-}$) against C_{OG^-} for different indicators at a given concentration of glycoxide ion (Figure 1) supports the above postulate.

EXPERIMENTAL

Ethylene glycol (E. Merck) was purified as described.[8] Sodium and potassium glycoxides were prepared by directly dissolving the respective metals in glycol under nitrogen, whereas lithium glycoxide was prepared under hydrogen. The glycoxides prepared (specially when they are of more than 2M concentration) could not be stored for more than 36 h as they tend to be coloured after this time. The solutions were titrated with standard HCl solutions with phenolphthalein as indicator.

2,4,4'-Trinitrodiphenylamine, 2,4,3'-trinitrodiphenylamine, and 2,4-dinitrodiphenylamine were prepared by coupling 1-chloro-2,4-dinitrobenzene with *p*-nitroaniline, *m*-nitroaniline, and aniline respectively. 6-Bromo-2,4-dinitroaniline was prepared by brominating 2,4-dinitroaniline with liquid bromine in presence of glacial acetic acid. The products were purified by column chromatography and crystallized from alcohol.

The spectral data for the indicators in glycol are in Table 1. The complete ionization of 2,4-dinitrodiphenylamine was not possible owing to decomposition and also because the glycoxide solutions become increasingly viscous with increasing concentration and difficult to handle above 4M concentration. The extinction coefficient for the anion of this indicator in other suitable alcoholic solvents have therefore been used in glycol, and this is justified as the medium effects on the position of the absorption maxima are found to be small.

TABLE 1

Spectral data for the indicators in ethylene glycol at 25 °C

	Neutral		Anion	
Indicator	$\lambda_{max.}$ (nm)	$\varepsilon_{max.}$	$\lambda_{max.}$ (nm)	$\varepsilon_{max.}$
(1) 2,4,4'-Trinitrodiphenylamine	378	21,900	514	27,400
(2) 2,4,3'-Trinitrodiphenylamine	357	17,800	426	19,300
(3) 6-Bromo-2,4-dinitroaniline	346	13,500	508	12,800
(4) 2,4-Dinitrodiphenylamine	362	16,800	500	16,000

The spectral measurements were made with a Beckman (Model DU) spectrophotometer in 1 cm stoppered silica cells. The cell compartment was thermostatted at 25 ± 0·1 °C. Reference solutions of exactly the same glycoxide concentrations were used in each case.

RESULTS AND DISCUSSION

The acid dissociation constants $p({}_sK_a)_{SH}$ on the molar scale for the indicators in ethylene glycol, determined as described earlier, with sodium glycoxide for the base are reported in Table 2 together with the $p({}_wK_a)_{SH}$ values in water and $\Delta pK_a[\equiv p({}_sK_a)_{SH} - p({}_wK_a)_{SH}]$. Figure 1 gives the plots of ($\log R - \log C_{OG^-}$) against C_{OG^-} for each indicator. At a given concentration of the glycoxide ion the slopes of the graphs for different

[3] S. R. Palit, M. N. Das, and G. R. Somayajulu, ' Non-Aqueous Titrations,' I.A.C.S., Calcutta, 1957.
[4] K. K. Kundu, P. K. Chatterjee, D. Jana, and M. N. Das, *J. Phys. Chem.*, 1970, **74**, 2633.
[5] S. K. Banerjee, K. K. Kundu, and M. N. Das, *J. Chem. Soc.* (*A*), 1967, 166.
[6] C. H. Kalidas and S. R. Palit, *J. Chem. Soc.*, 1961, 3998.
[7] R. A. More O'Ferrall and J. H. Ridd, *J. Chem. Soc.*, 1963, 5030.
[8] K. K. Kundu and M. N. Das, *J. Chem. Eng. Data*, 1964, **87**, 9.

indicators are approximately equal and this supports the validity of an acidity function H_- scale of the system established with the help of these indicators. Now, in spite of the inherent limitations of comparing $p(K_a)$ values in different solvents, the ΔpK_a values, following Brønsted's concept, are often taken to be a rough measure

TABLE 2

The acid dissociation constants on the molar scale of the indicators in ethylene glycol $p({}_sK_a)_{SH}$ compared with those in water $p({}_wK_a)_{SH}$ at 25 °C

Indicator (nos. as in Table 1)	$p({}_sK_a)_{SH}$	$p({}_wK_a)_{SH}$	$\Delta pK_a = p({}_sK_a)_{SH} - p({}_wK_a)_{SH}$
1	14·35	12·35	2·00
2	14·95	12·65	2·30
3	16·185	13·63	2·555
4	16·445	13·84	2·605

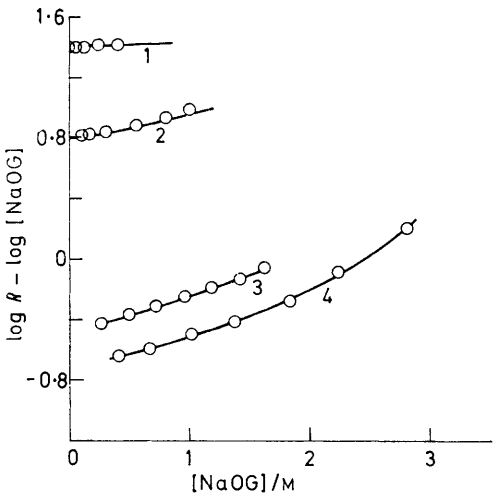


FIGURE 1 Plots for indicators numbered as in Table 1

of the relative basicities of the solvents with respect to that of water. But such measures are seldom found to be valid, being dependent on acid solutes.[7] The differences in the ΔpK_a values reported in Table 2 also show that the ' basicity ' of solutions of glycoxide in glycol cannot be related to the ' basicity' of aqueous media without reference to the indicator concerned. This necessitated the defining of the H_- scale in glycol with respect to glycol as the standard state, with use of pK_a values measured in glycol for its calculation. The H_- function has been calculated in this way from equation (2), where $({}_sK_a)_{SH} = a_{H^+} \cdot a_{S^-}/a_{SH}$ is the acid

$$H_- = p({}_sK_a)_{SH} + \log \frac{C_{S^-}}{C_{SH}} \qquad (2)$$

dissociation constant of the indicator SH, using $p({}_sK_a)_{SH}$ listed in Table 2. We propose to call this H_- scale in ethylene glycol $(H_-)^{Eg}$.

The variation of $(H_-)^{Eg}$ with concentration of glycoxide for the three systems, Li, Na, and K glycoxides in ethylene glycol is shown in Figure 2 and values of this function at selected molarities of glycoxide are listed in Table 3. The relationship of the $(H_-)^{Eg}$ function to the concentration of MOG (M = Li, Na, K) is given by equation (3), where pK_{GOH} is the autoprotolysis

$$(H_-)^{Eg} = \log C_{OG^-} + pK_{GOH} + \log \frac{f_{SH} \cdot f_{OG^-}}{f_{S^-} \cdot a_{GOH}} \qquad (3)$$

constant of ethylene glycol. The broken line in Figure 2

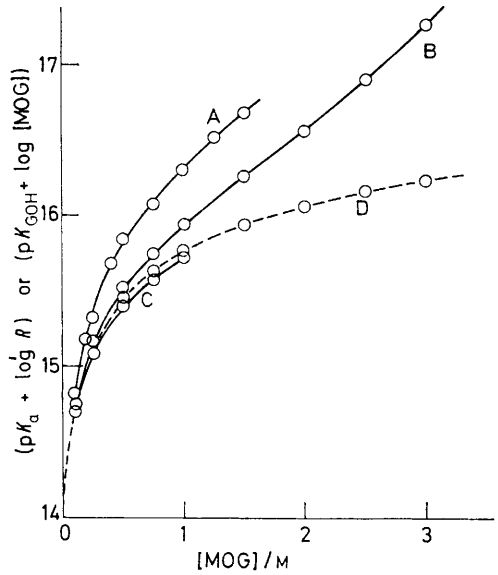


FIGURE 2 Variation of A, H_- of KOG in glycol; B, H_- of NaOG in glycol; C, H_- of LiOG in glycol; and D, the ideal pH function of the system

TABLE 3

The H_- acidity function scales for lithium, sodium, and potassium glycoxides in ethylene glycol $(H_-)^{Eg}$ at 25 °C

[MOG]/M	H_- for the system NaOG in glycol	H_- for the system LiOG in glycol	H_- for the system KOG in glycol
0·10	14·75	14·715	14·82
0·25	15·17	15·10	15·33
0·50	15·52	15·40	15·82
0·75	15·74	15·575	16·07
1·00	15·94	15·73	16·30
1·25	16·11	—	16·49
1·50	16·26	—	16·67
1·75	16·40		
2·00	16·56		
2·25	16·72		
2·50	16·89		
2·75	17·06		
3·00	17·25		

gives the ideal pH function for the system, *i.e.*, $(\log C_{OG^-} + pK_{GOH})$ against C_{OG^-}. The difference between the $(H_-)^{Eg}$ functions and the ideal pH function at higher alkali concentrations indicates the importance of the final term in equation (3) at such concentrations (*i.e.*, above 0·2M-glycoxide). Such deviations in the case of sodium and potassium glycoxides are positive whereas in the case of lithium glycoxide it is negative, at least in the region we have studied.

The positive deviations in the case of sodium and potassium glycoxides, which are analogous to pheno-

mena observed in the cases of sodium hydroxide in water [9] and sodium methoxide in methanol,[7] can be attributed in part to the greater solvation of the lyate ion than that of the indicator base,[9] as a result of which the ionization of the indicator sets free a number of solvent molecules as in equilibrium (4) where R =

$$SH + OR^- \rightleftharpoons S^- + (n + 1)ROH \qquad (4)$$

H, CH_3, or G (≡$HO{\cdot}CH_2{\cdot}CH_2$) and n is the difference in solvation numbers between ($SH + OR^-$) and S^-. The classical equilibrium constant, $K_c = C_{SH} \cdot C_{OR^-}/C_{S^-}$, should then be proportional to the concentration of free solvent molecules raised to the power $(n + 1)$.[10] With increase in lyate concentration, the concentration of free solvent molecules falls rapidly and the ionization of the indicator, therefore, takes place far more rapidly than is expected by the classical equilibrium constant.

The small negative deviation from ideality in the case of lithium glycoxide can be explained by the fact that although the difference in solvation between the glycoxide and the indicator anion plays a similar role here as well, lithium is a small ion, and an ion-pair formation analogous to the 'localized hydration' of Robinson and Harned [11] giving rise to ion groups like (I) pre-

$$Li^+ \cdots O - H \cdots O - G \qquad (I)$$
$$\quad\quad |$$
$$\quad\quad G$$

dominates, making the effective concentration of OG^- less. According to the size of the cation, such an effect should be in the order $Li^+ > Na^+ > K^+$, and this agrees with the observed order of increase of H_- with alkali concentration, *i.e.*, K > Na > Li. The H_- scales for alkali-metal hydroxides in water and alkali-metal methoxides in methanol also follow the same order.[2] Recently Jones [12] has pointed out that the apparent difference in the H_- scales for lithium, sodium, and potassium hydroxides in water is due to the different extent of association of the ions in the three systems. The same may apply to glycoxide solutions, but as the association constants of these glycoxides in ethylene glycol are not known, it is not possible yet to test that contention. The increased viscosity of the glycoxide solutions with increasing concentration of MOG, which is most pronounced in the case of LiOG solution, may be partly due to this type of ion association through the solvent.

Figure 3 compares the H_- scales for sodium hydroxide in water, sodium methoxide in methanol, and sodium glycoxide in ethylene glycol. The sharp rise in the H_- function with alkali concentration in the case of the glycol and methanol systems over that of the aqueous one, can be attributed to the smaller number of moles of the solvent per litre in the former cases than that for water. The concentration of the free solvent, and hence the equilibrium constant K_c, should then be more sensitive to the number of moles of solvent involved in solvating the OR^- ions. But if only as judged from the molecular weight of the solvent, H_- of the glycolic system should have fallen above that of methanol. The observed lower H_- values for the glycol system may be due to a lower n value for this system than for methanol. Owing to lack of data on the activity of ethylene glycol we could not calculate n for our system. An empirical calculation according to the method of Bascombe and Bell [10] shows that a value of $n = 2{\cdot}5$ fits well with the observed H_- value in the case of glycol whereas More O' Ferrall and Ridd have found that $n = 4$ suits their system (sodium methoxide–methanol) well. The decreased value of n in the case of the sodium

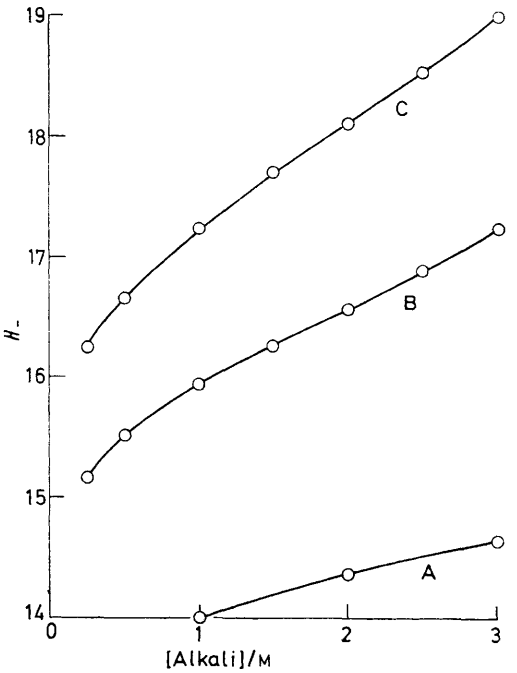
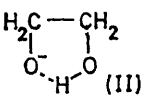


FIGURE 3 Variation of H_- with alkali concentration on the molar scale for A, NaOH in water; B, NaOG in glycol; and C, NaOMe in MeOH

glycoxide–glycol system may be due to the intramolecular solvation of the glycoxide ion as in (II). This may decrease the number of solvent molecules



(II)

attached to the glycoxide ion compared with that of the methoxide ion. However, in comparing the H_- values of different systems one should remember that a significant part of the apparent differences is due to the difference in the values of their autoprotolysis constants.

[9] J. T. Edward and I. C. Wang, *Canad. J. Chem.*, 1962, **40**, 399.
[10] K. N. Bascombe and R. P. Bell, *Discuss. Faraday Soc.*, 1957, **24**, 158.
[11] R. A. Robinson and H. S. Harned, *Chem. Rev.*, 1941, **28**, 419.
[12] J. R. Jones, *Chem. Comm.*, 1968, 513.

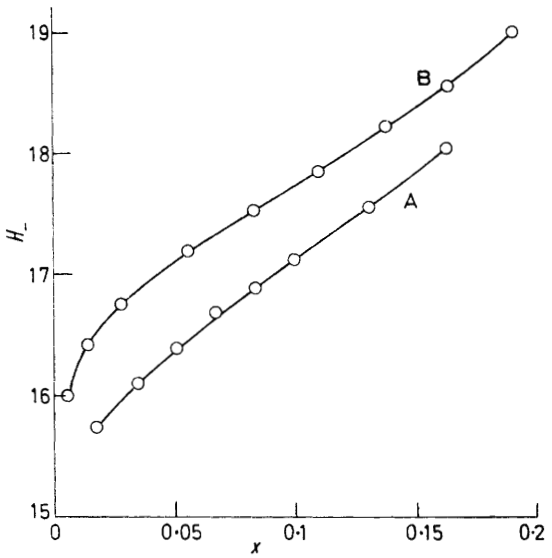


FIGURE 4 Variation of H_- with alkali concentration on the mole-fraction scale for A, NaOH in water and B, NaOG in ethylene glycol

A comparison of the variation of H_- with alkali concentration for the different systems on the mole-fraction scale will be better as it will exclude the concentration effect. Figure 4 gives such a comparison for water and glycol systems. As the densities of the methanolic NaOMe solutions were not available we could not convert the data on the molar scale for methanol into the mole-fraction scale, but Figure 4 shows that the differences between the H_- functions for different systems can almost wholly be accounted for by the difference in the autoprotolysis constants of the different media. This seems to indicate that like the autoprotolysis constant,[4,5] the H_- scale in any amphiprotic solvent is largely a composite function of bulk dielectric constant of the solvent, as well as the intrinsic acidity and basicity of the solvent molecules.

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