Effect of Some Protic and Dipolar Aprotic Solvents on the H_- Function in Ethylene Glycol

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The effect of addition of some protic as well as some dipolar aprotic solvents to a 0·01M solution of sodium 2-hydroxyethoxide ($NaO{\cdot}C_2H_4{\cdot}OH$) in ethylene glycol on the H_- function of the system has been studied with some nitro-substituted amine indicators. The extent of enhancement of the $(H_-)^{EG}{}_{Am}$ function (*i.e.*, the H_- function of the system measured with the amine indicators) is in the order $Me_2SO > Me_2N{\cdot}CHO > Bu^tOH > Me_2CO > MeCN > MeOH$, whereas there is a small decrease in the function with the addition of water. The glycol–dimethylformamide–0·01M-$NaO{\cdot}C_2H_4{\cdot}OH$ system has also been studied with some t-butylphenol indicators in order to investigate the role played by the changes in the activity coefficients of the neutral indicator acid (HA) and its anion (A^-) with changes in the solvent media in enhancing the H_- function of the system. Attempts have been made to understand the relative order of the different solvent in enhancing the $(H_-)^{EG}{}_{Am}$ function.

THE addition of dipolar aprotic solvents such as dimethyl sulphoxide and dimethylformamide to basic solutions in water, methanol, ethanol, *etc.* causes a dramatic enhancement of the basicity of the system as indicated by studies on proton-transfer equilibria [1-8]

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[1] A. J. Parker, *Quart. Rev.*, 1962, **16**, 163.

[2] C. D. Ritchie, 'Solute–Solvent Interactions,' eds. J. F. Coetzee and C. D. Ritchie, Marcel Decker, New York, 1969.

[3] D. Dolman and R. Stewart, *Canad. J. Chem.*, 1967, **45**, 911.

[4] E. C. Steiner and J. D. Starkey, *J. Amer. Chem. Soc.*, 1967, **89**, 2751.

[5] R. Kuhn and D. Rewicki, *Annalen*, 1967, **704**, 9; 1967, **706**, 250.

[6] H. Fischer and D. Rewicki, *Progr. Org. Chem.*, 1968, **7**, 116.

[7] R. Stewart and J. P. O'Donnell, *J. Amer. Chem. Soc.*, 1962, **84**, 494.

[8] K. Bowden and A. F. Cockerill, *J. Chem. Soc.* (*B*), 1970, 173.

and the kinetics of various reactions.[9-15] The basicity of a system or its ability to abstract a proton from a weak acid (HA) referred to in most of these studies is the acidity function[11] H_-, as defined by equation (1),

$$H_- = -\log \frac{a_{H^+}f_{A^-}}{f_{HA}} = pK_a + \log \frac{c_{A^-}}{c_{HA}} \qquad (1)$$

where K_a is the ionization constant $[K_a = a_{H^+}a_{A^-}/a_{HA}]$ of the acid HA, f_{HA} and f_{A^-} are the activity coefficients and c_{HA} and c_{A^-}, the concentrations of the neutral acid HA and its anion A^- respectively. The effect of addition of dimethyl sulphoxide to the systems tetramethylammonium hydroxide in water,[3] sodium methoxide in methanol,[13,16] and sodium ethoxide in ethanol[14] on the H_- function of the respective system have been studied and the effect is always a sharp increase in H_-.

We now describe the effect of addition of some dipolar aprotic as well as some protic solvents to the basic system of 0·01M-sodium 2-hydroxyethoxide ($NaO{\cdot}C_2H_4{\cdot}OH$) in ethylene glycol upon the $(H_-)^{EG}{}_{Am}$ function[17] of the system. The dipolar aprotic solvents used are: dimethyl sulphoxide, acetone, dimethylformamide, and acetonitrile. The last two have special significance in the present study as they are 'isodielectric' with ethylene glycol (dielectric constant of glycol at 25 °C, 37·67; dimethylformamide, 36·7; acetonitrile, 37·5).[18] The protic solvents used are t-butyl alcohol, methanol, and water. In order to understand the importance of the changes in the activity coefficients of the neutral (HA) and anionic (A^-) forms of the indicator with changes in the medium in enhancing the H_- function of the system, we have also studied the dimethylformamide–glycol–0·01M-$NaO{\cdot}C_2H_4{\cdot}OH$ system with some t-butylphenols.

EXPERIMENTAL

Ethylene glycol was purified as reported.[17] Water was triply distilled. All other solvents were purified by standard methods and were used within two days.

The nitro-substituted amine indicators were 2,4,4′-trinitrodiphenylamine, 2,4,3′-trinitrodiphenylamine, 6-bromo-2,4-dinitroaniline, 2,4-dinitrodiphenylamine, and 4′-amino-2,4-dinitrodiphenylamine. The first four indicators were prepared as reported.[19] The fifth was prepared by coupling 1-chloro-2,4-dinitrobenzene with *p*-phenylenediamine and was purified by column chromatography. The phenol indicators used were 4- and 2-t-butylphenols (Aldrich Chemical Co.). They were purified as reported.[17]

Spectral measurements were as before.[19] The $\lambda_{max.}$ and ε values of the anion of the indicators used in each solvent along with the data for ethylene glycol are given in Table 1. There is not a large shift in $\lambda_{max.}$ except in the case of 2,4-dinitrodiphenylamine in dimethylformamide. Spectral measurements were made at suitable wavelengths intermediate between those of maximum absorption of the anion in pure glycol and in the pure dipolar aprotic solvent. For each solvent composition optical density measurements were made in three different solutions containing the indicator and (i) no $NaO{\cdot}C_2H_4{\cdot}OH$, to give optical density of the undissociated indicator (D_{HA}); (ii) 0·01M-$NaO{\cdot}C_2H_4{\cdot}OH$ to give the optical density of the required equilibrium of dissociated and undissociated forms of the indicator (D); and (iii) sufficient $NaO{\cdot}C_2H_4{\cdot}OH$ to give the optical density of the completely dissociated form (D_{A^-}). All solutions (for different compositions of a particular mixture) contained the same indicator concentration. For each measurement a reference solution of the same solvent composition and $NaO{\cdot}C_2H_4{\cdot}OH$ concentration, but without the indicator, was used. From such measurements the ratio of the concentration of ionized to un-ionized indicator $[R = c_{A^-}/c_{HA} = (D - D_{HA})/(D_{A^-} - D)]$ was obtained.

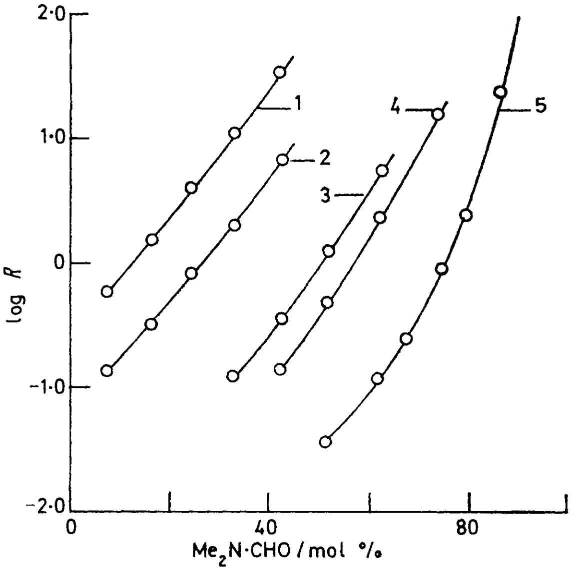

FIGURE 1 Plot of log *R* against percentage of dimethylformamide for the ethylene glycol–dimethylformamide–0·01M-$NaO{\cdot}C_2H_4{\cdot}OH$ system. Indicators are numbered as in Table 1

Calculations.—The reference indicator for which the pK_a is the same as that in pure glycol is 2,4,4′-trinitrodiphenylamine[19] in the case of the amine indicators and 4-t-butylphenol[17] in the case of the phenol indicators. The pK_a values of the other indicators in each system were obtained by comparing[3] the ionization of overlapping indicators in the same solution. The quantity log *R* was plotted against the solvent composition (mol % non-glycol component) for each system and smooth curves were obtained. Figure 1 gives such plots in the glycol–dimethylformamide system for the amine indicators. At the overlapping regions of two successive curves, differences were taken at regular intervals and the results averaged. These averages represent the differences between the pK_a values of the indicators. Table 2 gives the pK_a values of the indicators used in each solvent system. The H_- values for each system were then calcu-

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[9] A. J. Parker, *Chem. Rev.*, 1969, **69**, 1.

[10] A. J. Parker, *J. Chem. Soc.*, 1961, 1328.

[11] K. Bowdon, *Chem. Rev.*, 1966, **66**, 119.

[12] C. H. Rochester, *Quart. Rev.*, 1966, **20**, 511.

[13] R. Stewart, J. P. O'Donnell, D. J. Cram, and B. Rickborn, *Tetrahedron*, 1962, **18**, 917.

[14] R. Stewart and K. Bowden, *Tetrahedron*, 1965, **21**, 261.

[15] D. J. Cram, 'Fundamentals of Carbanion Chemistry,' Academic Press, New York, 1965, p. 289.

[16] D. J. Cram, B. Rickborn, C. A. Kingsbury, and P. Haberfield, *J. Amer. Chem. Soc.*, 1961, **83**, 3678.

[17] Lakshmi Aiyar, Amar Nath Dutta, and K. K. Kundu, *J.C.S. Perkin II*, in the press.

[18] R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' Butterworths, London, 2nd edn., 1965.

[19] K. K. Kundu and Lakshmi Aiyar, *J. Chem. Soc.* (*B*), 1971, 40.

lated from the pK_a and log R values in that system by use of equation (1). Assuming the accuracy in O.D. values to be $\pm 0{\cdot}002$, accuracy in log R and pK_a is $\pm 0{\cdot}01$ and that in H_- is $\pm 0{\cdot}02$.

RESULTS AND DISCUSSION

Table 3 gives the H_- values of the various glycol–aprotic and glycol–dipolar aprotic solvent systems containing 0·01M-NaO·C$_2$H$_4$·OH at selected mole % non-glycol component. Figure 2 compares the different H_- functions. The solid lines give the H_- function measured with the amine indicators and the broken line gives the H_- function of the glycol–dimethylformamide–0·01M-NaO·C$_2$H$_4$·OH system measured with the phenol indicators.

TABLE 1

Spectral data for the anions of the indicators used in ethylene glycol and in the other solvents

Indicator	$C_2H_4(OH)_2$ λmax./nm	ε	Me_2SO λmax./nm	ε	$Me_2N{\cdot}CHO$ λmax./nm	ε	Me_2CO λmax./nm	ε	MeCN λmax./nm	ε	Bu^{t}OH λmax./nm	ε	MeOH λmax./nm	ε	H_2O λmax./nm	ε
1 2,4,4′-Trinitrodiphenylamine	514	27,400	530	33,400	530	34,700	514	34,240	514	32,260	506	27,840	500	27,400	500	27,400
2 2,4,3′-Trinitrodiphenylamine	426	19,300	450	21,830	460	21,800	440	21,300			426	19,300				
3 6-Bromo-2,4-dinitroaniline	508	12,800	520	12,520	518	13,000										
4 2,4-Dinitrodiphenylamine	500	16,000			434	18,900										
5 4′-Amino-2.4-dinitrodiphenylamine	490	15,900			485	16,600										
6 4-t-Butylphenol	294	2620			299·5	3500										
7 2-t-Butylphenol	292	3640			303	8730										

TABLE 2

pK_a Values of the indicators used in the different mixed solvents, along with the values in ethylene glycol at 25 °C

Indicator	Glycol	$Me_2N{\cdot}CHO$ + glycol	Me_2SO + glycol	Acetone + glycol	Bu^{t}OH + glycol
1 2,4.4′-Trinitrodiphenylamine	14·35	14·35	14·35	14·35	14·35
2 2,4,3′-Trinitrodiphenylamine	14·95	15·04	15·10	15·07	15·07
3 6-Bromo-2,4-dinitroaniline	16·185	16·30	16·18		
4 2,4-Dinitrodiphenylamine	16·445	16·70			
5 4′-Amino-2,4-dinitrodiphenylamine	17·33	17·95			
6 4-t-Butylphenol	13·56	13·56			
7 2-t-Butylphenol	15·15	14·96			

TABLE 3

H_- Values at 25 °C of the different mixed solvent systems containing 0·01M-sodium glycoxide at selected mole % non-glycol component

Mol % Non-glycol component	Me_2SO + glycol	$Me_2N{\cdot}CHO$ + glycol Amine indicator	Phenol indicator	Me_2CO + glycol	MeCN + glycol	Bu^{t}OH + glycol	MeOH + glycol	H_2O + glycol
10	14·40	14·25	13·84	14·08	13·95	14·04	13·80	13·81
20	14·91	14·72	13·88	14·31	14·06	14·29	13·82	13·81
30	14·43	15·21	13·96	14·53	14·17	14·56	13·83	13·81
40	16·02	15·72	14·06	14·75	14·29	14·86	13·86	13·80
50	16·73	16·25	14·24	14·96	14·42	15·13	13·89	13·80
60		16·86	14·55	15·17	14·59	15·46	13·93	13·80
70		17·56	14·99	15·46	14·83	15·98	13·97	13·80
80		18·35	15·54	15·80	15·20		14·02	13·80
90		19·61	16·25	16·18			14·08	13·78

The enhancement of the H_- function of a basic hydroxylic system upon addition of a dipolar aprotic solvent is explained by Stewart and his co-workers[3] in the case of the tetramethylammonium hydroxide–water–dimethyl sulphoxide system from a consideration of the equilibrium between the hydroxide ion and the indicator acid HA [equation (2)] where the hydroxide ion

$$OH_{aq}^- + HA \rightleftharpoons A^- + (n+1)H_2O \qquad (2)$$

is considered to be intimately solvated by a number of water molecules. n Is the difference in solvation numbers between (OH$^-$ + HA) and A$^-$. According to these authors the shift of equilibrium (2) to the right, *i.e.*, an increase in the basicity of the system upon addition of dimethyl sulphoxide, is primarily due to the increase in the activity of the hydroxide ion caused by the poor anion-solvating capacity of dimethyl sulphoxide and decrease in the water activity caused by a dilution effect as well as a complex formation between dimethyl sulphoxide and water. Seemingly, they have not duly stressed the possible effect on equilibrium (2) of changes in the interactions, and hence on the activity coefficients, of the indicator acid, HA, and its anion, A$^-$, upon addition of dimethyl sulphoxide. Our results on the effect of addition of dimethylformamide on the H_- function of the system ethylene glycol–NaO·C$_2$H$_4$·OH (0·01M) with two different types of indicator indicate that perhaps the changes in the interactions of the indicator and its anion upon addition of a dipolar aprotic solvent to the system are no less important in enhancing the basicity of the system.

Although the two H_- functions measured for the system $NaO{\cdot}C_2H_4{\cdot}OH{-}C_2H_4(OH)_2$ by use of nitroamines $(H_-)^{EG}{}_{Am}$ and t-butylphenols $(H_-)^{EG}{}_{Ph}$ [17] deviate from each other at higher $NaO{\cdot}C_2H_4{\cdot}OH$ concentrations, they are identical up to *ca.* 0·2M. As Figure 2 shows, the effect of addition of dimethylformamide on the two H_- functions of the system is quite different. The magnitude of enhancement of the $(H_-)^{EG}{}_{Am}$ function at a particular mol % of dimethylformamide is much more than that of the $(H_-)^{EG}{}_{Ph}$ function. At a particular mol % of dimethylformamide the H_- functions measured with the two sets of indicators can be expressed by equations (3) and (4),[19,20] where K_{GOH} is the autoprotolysis constant of glycol, a_{GOH} is the activity of glycol, OG^- is $HO{\cdot}CH_2{\cdot}CH_2{\cdot}O^-$, and $f^{Am}{}_{AH}$ and $f^{Am}{}_{A^-}$ are the activity coefficients of the amine indicator and its anion respectively, the activity coefficient terms as well as the activity of glycol in the mixed solvents being referred to pure glycol as the standard state.

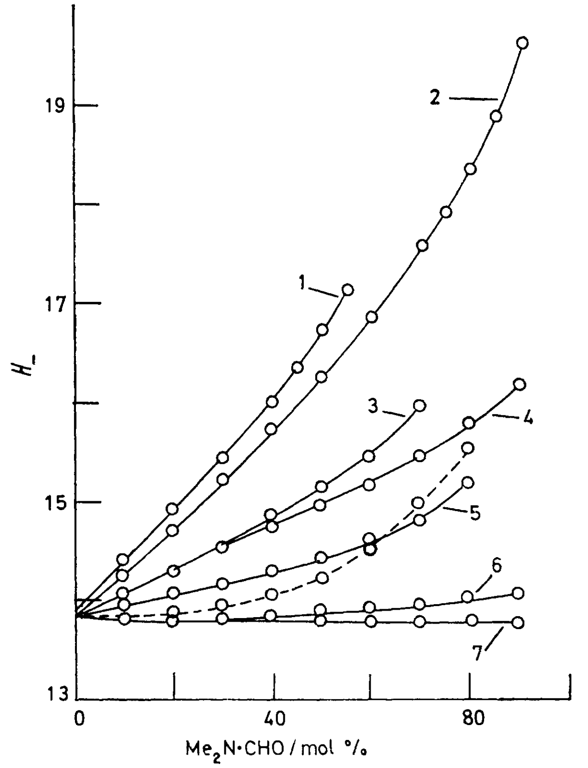

FIGURE 2 Solid lines: $(H_-)^{EG}{}_{Am}$ function for the system ethylene glycol–0·01M-$NaO{\cdot}C_2H_4{\cdot}OH$ with increasing mol % of 1, dimethyl sulphoxide; 2, dimethylformamide; 3, t-butyl alcohol; 4, acetone; 5, acetonitrile; 6, methanol; 7, water. Broken line: $(H_-)^{EG}{}_{Ph}$ function for the system ethylene glycol–0·01M-$NaO{\cdot}C_2H_4{\cdot}OH$ with increasing mol % of dimethylformamide

$$(H_-)^{EG}{}_{Am} = pK_{GOH} + \log c_{OG^-} - (n + 1)\log a_{GOH} + \log \frac{f^{Am}{}_{HA} f_{OG^-}}{f^{Am}{}_{A^-}} \qquad (3)$$

$$(H_-)^{EG}{}_{Ph} = pK_{GOH} + \log c_{OG^-} - (n + 1)\log a_{GOH} + \log \frac{f^{Ph}{}_{AH} f_{OG^-}}{f^{Ph}{}_{A^-}} \qquad (4)$$

If it is assumed that n is largely determined by the solvation number of OG^- and less significantly by the difference in solvation number of HA and A^-, at any solvent composition, n values are effectively equal in the cases of two sets of indicators. Thus equations (3) and (4) suggest that the difference in the two functions should arise from a difference in the activity coefficient ratios $f^{Am}{}_{HA}/f^{Am}{}_{A^-}$ and $f^{Ph}{}_{HA}/f^{Ph}{}_{A^-}$, *i.e.*, the interactions of the two types of indicator and their anions in the particular glycol–dimethylformamide mixture relative to that in pure glycol. From our earlier studies [17] on the behaviour of the activity coefficients of the neutral phenols and amines, f_{HA}, as well as that of the ratio of their anions $f^{Am}{}_{A^-}/f^{Ph}{}_{A^-}$ in concentrated $NaO{\cdot}C_2H_4{\cdot}OH$ solutions in ethylene glycol, we have seen that $f^{Am}{}_{A^-}/f^{Ph}{}_{A^-}$ becomes increasingly smaller than $f^{Am}{}_{HA}/f^{Ph}{}_{HA}$ as the basicity of the solution increases, *i.e.*, $f^{Am}{}_{HA}/f^{Am}{}_{A^-}$ becomes increasingly greater than $f^{Ph}{}_{HA}/f^{Ph}{}_{A^-}$ as the basicity increases. The same may hold in the present case where the basicity of the system is increased by adding more dimethylformamide. Thus the extent of enhancement brought about in the H_- function of a basic hydroxylic solvent system on the addition of a dipolar aprotic solvent is very much dependent on the type of indicators used to measure the H_- function. This again points to the error that may be incurred in the determination of the ionization constant of a weak acid by use of an H_- function of an aqueous dimethyl sulphoxide–base system set up with indicators structurally much different from the acid concerned. If this method of determination of ionization constant of a weak acid is to be employed, it is important to make sure that $\log_{10}(c_{A^-}/c_{HA})$ for the acid is a linear function with unit slope of the H_- scale used.[20]

As seen from Figure 2 the H_- function $(H_-)^{EG}{}_{Am}$ is exalted to different extents with the addition of different dipolar aprotic and protic solvents to the system. The H_- curves for the glycol–dipolar aprotic solvent systems generally lie above those of the glycol–protic solvent systems. The only exception is that of Bu^tOH, which though classed as a non-polar proton-donating solvent [15] behaves like a dipolar aprotic solvent in the present study. It is seen that all dipolar aprotic solvents do not enhance the H_- scale to the same extent, and that even such a protic solvent as Bu^tOH functions more effectively in this respect than the dipolar aprotic solvents acetone and acetonitrile. Although dimethylformamide and acetonitrile both have almost the same dielectric constants, their abilities to enhance the H_- scale of the $C_2H_4(OH)_2{-}NaO{\cdot}C_2H_4{\cdot}OH$ system are quite different.

Figure 2 suggests that the overall order of enhancement of the $(H_-)^{EG}{}_{Am}$ function is $Me_2SO > Me_2N{\cdot}CHO > Bu^tOH > Me_2CO > MeCN > MeOH$ and in the case of

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[20] C. H. Rochester, 'Acidity Functions,' Academic Press, New York, 1970, p. 257.

water there is a small decrease in the H_- function. It is, however, difficult at this stage to account for this order of enhancement of the H_- function of the system even qualitatively, for the overall effect is determined by several factors of solute–solvent interactions such as relative solvation and desolvation of the ions and neutral species through hydrogen bond, ion–dipole, dipole–dipole, and dispersion interactions as guided by the various chemical and physical properties of the solvents like basicity, dipole moment, dielectric constant, molecular polarizability, *etc.*, besides the effects of structure-making or -breaking of glycol accompanying the addition of a second solvent. Yet the consideration of the following possible factors should be of interest.

(*a*) The desolvation of the lyate anion $^{-}O{\cdot}C_2H_4{\cdot}OH$ as the hydroxylic solvent is replaced by a dipolar aprotic solvent is probably one of the important causes for the enhancement of the H_- function of the system. Now the relative hydrogen-bond stabilization of the glycoxide anion in the different glycol–dipolar aprotic solvent mixture should be largely dependent upon the relative acidities (availability of hydrogen atom with partial protonic character) of these mixtures and this in turn will presumably depend upon the relative acidities of the different dipolar aprotic solvents, if we assume that there is not much structure-breaking or -making by the addition of a dipolar aprotic solvent to glycol. The $(K_a)_{SH}$ values of the dipolar aprotic solvents used are given in Table 4. Hence, the extent of desolvation of $^{-}O{\cdot}C_2H_4{\cdot}OH$ ion or the increase in log f_{OG^-} is expected to be in the order $Me_2SO \gg MeCN \gg Me_2CO > Me_2N{\cdot}CHO$. But the observed order of enhancement of $(H_-)^{\mathrm{EG}}{}_{\mathrm{Am}}$ is $Me_2SO > Me_2N{\cdot}CHO \gg Me_2CO > MeCN$. This shows that there are other important factors.

TABLE 4

	Me_2SO	$Me_2N{\cdot}CHO$	MeCN	Me_2CO
$(K_a)_{SH}$	10^{-32} [a]	10^{-18} [b]	10^{-25} [c]	10^{-20} [c]
μ/D	4·3 [d]	3·82 [d]	3·37 [d]	2·72 [e]
$10^{-24}\alpha$/cm^3	7·97 [d]	7·91 [d]	4·45 [d]	6·39 [f]

[a] R. Stewart and J. R. Jones, *J. Amer. Chem. Soc.*, 1967, **89**, 5069. [b] $(K_a)_{SH}$ of dimethylformamide was calculated from the autoprotolysis constant $(K_S)_{SH} = ca.\ 10^{-18}$ (M. Tezé and R. Schaal, *Bull. Soc. chim. France*, 1962, 1372) and $p(K_a)_{SH_2^+} = -0{\cdot}01$ (ref. 2, ch. 4) by use of the relation $(K_a)_{SH} = (K_S)_{SH} \cdot (K_a)_{SH_2^+}$. [c] F. G. Bordwell, ' Organic Chemistry,' MacMillan, New York, 1963, p. 549. [d] Ref. 9. [e] Ref. 1. [f] Calculated from $\alpha = (n^2 - 1)/(n^2 + 2) \cdot M/d \cdot 3/4\pi N$.

(*b*) Ion–dipole interactions other than hydrogen-bonding on the relatively small anion $^{-}O{\cdot}C_2H_4{\cdot}OH$ may be considerable in dipolar aprotic solvents. But as the positive charge centres in dimethylformamide and dimethyl sulphoxide are well buried inside the molecule their interaction with the anion may be smaller than that of MeCN. Again, Me_2SO seems to have a highly associated form containing chains of sulphur and oxygen,[1] thus rendering the positive sulphur less available for interaction with the $^{-}O{\cdot}C_2H_4{\cdot}OH$ anion. Such association is also said to be present in the case of dimethylformamide. This may be partly responsible for the greater desolvation of $^{-}O{\cdot}C_2H_4{\cdot}OH$ and hence the much larger enhancement observed in the $(H_-)^{\mathrm{EG}}{}_{\mathrm{Am}}$ function in the case of these two solvents.

(*c*) The large polar HA molecule is much more soluble in dipolar aprotic solvents than in glycol (as our preliminary observations indicate) and the large dispersed anions A^- like the amide anions are also likely to be more solvated by dipolar aprotic solvents than by the hydroxylic solvents like glycol. Thus, both $f^{\mathrm{Am}}{}_{\mathrm{HA}}$ and $f^{\mathrm{Am}}{}_{\mathrm{A^-}}$ will decrease with the addition of a dipolar aprotic solvent to the system and to different extents depending upon the dipole moment (μ) and the molecular polarizability (α) values of the different dipolar aprotic solvents. These values are given in Table 4. A combined effect of the relative dipole moment and dispersion interactions of the solvents upon either log $f^{\mathrm{Am}}{}_{\mathrm{HA}}$ or log $f^{\mathrm{Am}}{}_{\mathrm{A^-}}$ would then be in the order $Me_2SO > Me_2N{\cdot}CHO > Me_2CO \approx MeCN$. It should, however, be pointed out that while the effect on log f_{HA} tends to decrease the $(H_-)^{\mathrm{EG}}{}_{\mathrm{Am}}$ values, that on log $f_{\mathrm{A^-}}$ tends to increase the same, thus balancing each other to some extent, but not completely, as indicated earlier in illustrating the specificity of indicators. It is difficult at this stage to guess the amalgamated effect of both the factors, *i.e.*, of the ratio log $f^{\mathrm{Am}}{}_{\mathrm{AH}}/f^{\mathrm{Am}}{}_{\mathrm{A^-}}$ towards the overall contribution to $(H_-)^{\mathrm{EG}}{}_{\mathrm{Am}}$ unless the relevant data in glycolic solvents be gathered.

(*d*) The decrease in glycol concentration due to the ' dilution effect ' accounts for some enhancement[3] of $(H_-)^{\mathrm{EG}}{}_{\mathrm{Am}}$ especially because the latter depends on $(n + 1)$ times the logarithm of the activity of free glycol[3] [*cf.* equation (3)]. It is of course common to all the mixed systems. But the possible complex formation of dimethyl sulphoxide and dimethylformamide with glycol as with other hydroxylic solvents[11] may be responsible for the larger enhancement of the $(H_-)^{\mathrm{EG}}{}_{\mathrm{Am}}$ function in these solvents.

(*e*) The degree of enhancement of the $(H_-)^{\mathrm{EG}}{}_{\mathrm{Am}}$ scale by a protic solvent will depend largely inversely upon its hydrogen-bond donating capability. The position of Bu^tOH in the series is interesting, for although containing a hydrogen atom attached to a strongly electronegative oxygen atom, it seems to solvate the $^{-}O{\cdot}C_2H_4{\cdot}OH$ ion to a far less extent. This may be because, owing to the hindering bulky methyl groups, the molecule cannot align itself suitably for electrostatic interaction with a solute anion to form a strong hydrogen bond. The order for methanol and water in the series is reasonable, for owing to the inductive effect of the methyl group the protonic character of the bridge-forming H-atoms in methanol, water, and glycol are in the decreasing order water > glycol > methanol.[21,22]

We thank C.S.I.R. (New Delhi) and U.G.C. (New Delhi) for financial assistance.

[1/1848 *Received, 11th October,* 1971]

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