

Determination of H_- Acidity Function for Glycolic Sodium Glycoxide by Use of t-Butylphenols as Indicators and a Comparison with that found by Use of Amine Indicators

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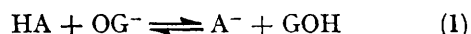
An H_- acidity scale, $(H_-)_{Ph}^{EG}$, for solutions of sodium glycoxide in ethylene glycol (EG) has been set up at 25 °C by use of t-butylphenols as indicator acids (HA). The value of H_- in this scale at a particular glycoxide concentration is lower than the corresponding value in the H_- scale, $(H_-)_{Am}^{EG}$, set up earlier for the same system with nitro-anilines and -diphenylamines as indicator acids (HA). In a bid to understand the observed differences in the two H_- values activity coefficients (f_{HA}) of a typical neutral phenol as well as an amine indicator in glycoxide solutions of increasing concentration in glycol (glycol being taken as the standard state) have been determined by solubility and partition experiments respectively. An attempt has been made to explain the observed variation of f_{HA} as a function of glycoxide concentration and to understand the corresponding variation of the activity coefficients of the anions (f_{A^-}) of the amine and phenol indicators in these solutions.

THE acidity function for a strongly acidic system has some specificity depending upon the class of indicator used to measure it, *i.e.*, a particular acidic system like aqueous sulphuric acid may have different acidity functions depending upon whether the indicators used to measure the acidity are primary anilines, tertiary amines, amides, arylmethanols, indoles, or azulenes.¹ Rochester² has shown that the H_- scale derived by him for methanolic sodium methoxide using t-butylphenols as indicators is somewhat different from the H_- scale set up earlier³ for the same system using amines as indicators. Recently Terrier *et al.*,⁴ using indoles as indicators, have derived an H_- scale for the same system which differs from the other two H_M functions. Thus we see that several H_- scales exist for methanolic NaOMe and this may be true for other basic systems as well. As acidity functions are being applied to kinetics involving different types of substrate and to find pK_a values of a wide variety of weak acids and bases, it is often essential to set up acidity functions for a particular acidic or basic system with use of different classes of indicator.

Earlier⁵ we reported an H_- function, $(H_-)_{Am}^{EG}$, for the basic system sodium glycoxide-ethylene glycol (along with those for the systems potassium glycoxide-ethylene glycol and lithium glycoxide-ethylene glycol) at 25 °C using nitro-substituted anilines and diphenylamines as indicators. We now describe an H_- function, $(H_-)_{Ph}^{EG}$, for the same system at 25 °C using t-butyl-substituted phenols as indicators and try to compare the two functions.

The ionization of several t-butylphenols has been studied by Rochester² in strongly basic solutions of methanolic sodium methoxide in order to set up an H_- scale for the medium. We have used phenol, 2- and 4-t-butylphenols, 2,4- and 2,6-di-t-butylphenols, and 2,4,6-tri-t-butylphenol. That phenols ionize in basic media by proton transfer has been supported by n.m.r.

studies.² Hence their ionization in glycolic sodium glycoxide can be represented by equation (1), where



HA is the phenol and GOH is $HO \cdot CH_2 \cdot CH_2 \cdot OH$. Phenol, 2- and 4-t-butylphenols, and 2,4-di-t-butylphenol are fairly strong acids and their acid dissociation constants $(K_a)_{HA}$ have been obtained by the extrapolation method.³ $(K_a)_{HA}$ Of the other two phenols were determined by

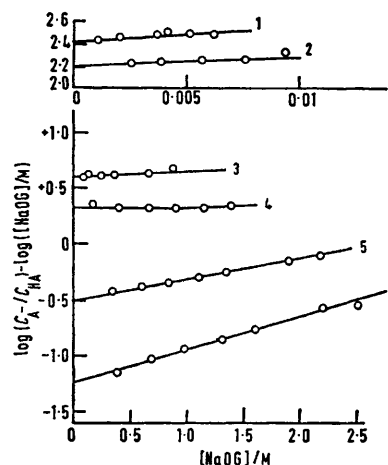


FIGURE 1 Plots of $\log(C_{A^-}/C_{HA}) - \log[NaOG]$ against $[NaOG]$ for the phenols numbered as in Table I

the stepwise procedure. The basic requirement for the stepwise procedure, namely that for the series of indicators both $\partial \log_{10}(C_{A^-}/C_{HA})/\partial C_{NaOG}$ and H_- for a particular NaOG (sodium glycoxide) concentration should be independent of indicator, is met with by the approximate constancy of the slopes of the plots of $\log(C_{A^-}/C_{HA}) - \log C_{OG^-}$ against C_{OG^-} for different indicators at a given glycoxide concentration (Figure 1).

In an effort to account for the differences in the two acidity functions, $(H_-)_{Am}^{EG}$ and $(H_-)_{Ph}^{EG}$, we also deter-

¹ R. H. Boyd, in 'Solute-Solvent Interactions,' eds., J. F. Coetzee and C. D. Ritchie, Marcel Dekker, New York, 1969, ch. 3.

² C. H. Rochester, *J. Chem. Soc.*, 1965, 676.

³ R. A. More O'Ferrall and J. H. Ridd, *J. Chem. Soc.*, 1963, 5030.

⁴ F. Terrier, F. Millot, and R. Schaal, *Bull. Soc. chim. France*, 1969, 3002.

⁵ K. K. Kundu and Lakshmi Aiyar, *J. Chem. Soc. (B)*, 1971, 40.

mined the activity coefficients f_{HA} in glycolic solutions of sodium glycoxide (ethylene glycol being taken as the standard state) for one amine and one phenol indicator by methods similar to those utilized by Vinnik *et al.*⁶ in concentrated H_2SO_4 solutions in water.

EXPERIMENTAL

Determination of the $(H_{-})_{\text{Ph}}^{\text{EG}}$ Scale.—Ethylene glycol, purified as earlier,⁷ was unsuitable for the present work for when sodium was dissolved in it the sodium glycoxide had a strong absorption band near 270 nm which overlapped with the absorption bands of the neutral phenols and their anions. We suspected some impurities in the solvent and purified it further as follows: glycol, distilled and kept over anhydrous sodium sulphate for *ca.* 1 week as described,⁷ was decanted off and refluxed with sodium for 2–3 h and was finally distilled through a long fractionating column. Sodium glycoxide thus purified was optically clear.

The phenols (Aldrich) were purified by microdistillation. 2,4,6-Tri-*t*-butylphenol was crystallized from benzene. Their purity was checked by measuring their extinction coefficients in methanol and by comparing these with literature values.³ Immediately after purification of a phenol, a stock solution was made in ethylene glycol which could be stored in the dark for two days during which the ionization measurements were made.

The spectral data for the indicators in ethylene glycol are in Table 1. The indicators are all stable in glycoxide

TABLE 1

The acid dissociation constants on the molar scale of the phenol indicators and spectral data for the neutral phenols and their anions in ethylene glycol at 25 °C

No.	Indicator	$p(K_{\text{a}})_{\text{HA}}$	Neutral		Anion	
			$\lambda_{\text{max.}}/\text{nm}$	ϵ	$\lambda_{\text{max.}}/\text{nm}$	ϵ
1	Phenol	13.34	217	5626	237	10,150
			272	1396	287	2595
2	4-Butylphenol	13.56	222	8700	239	12,100
			277	2100	294	2618
3	2- <i>t</i> -Butylphenol	15.15	215	6300	244	8420
			272	2240	292	3640
4	2,4-Di- <i>t</i> -butylphenol	15.43	277	2290	245	10,800
					296	3380
5	2,6-Di- <i>t</i> -butylphenol	16.18	271	1600	252	9000
					298	5200
6	2,4,6-Tri- <i>t</i> -butylphenol	16.73	274	1580	302 ^a	4400

^a Ref. 2.

solutions during the period of ionization measurements. Complete ionization of 2,4,6-tri-*t*-butylphenol was not possible as sodium glycoxide solutions could be handled only up to a concentration of 4M.⁵ Hence we have used the value of ϵ 4400 at λ 302 nm in methanol for this anion from ref. 2, for our $\lambda_{\text{max.}}$ and ϵ values of the neutral indicator as well as the $\lambda_{\text{max.}}$ value of the anion tallied exactly with the corresponding values in methanol given in this reference.

The spectral measurements were made as reported for the amine indicators in the system.⁵

Determination of Activity Coefficients f_{HA} in Sodium Glycoxide Solutions.—The activity coefficients of the neutral acids (f_{HA}) in solutions of increasing sodium glycoxide

⁶ M. I. Vinnik and N. B. Librovich, *Tetrahedron*, 1966, 2945.

⁷ K. K. Kundu and M. N. Das, *J. Chem. Eng. Data*, 1964, 87, 9.

concentration in ethylene glycol (with ethylene glycol as standard state) were determined either by solubility or by partition experiments. In both cases the solutions had to be shaken for several days to reach equilibrium. As sodium glycoxide solutions of more than *ca.* 1.5M concentration would not keep for more than two days we had to limit our activity coefficient study to sodium glycoxide solutions of *ca.* 1.5M concentration.

2,4,6-Tri-*t*-butylphenol is solid (m.p. 131 °C) and in 1.5M-sodium glycoxide is dissociated only up to 20%. Its solubility in glycol is 2.167×10^{-3} mol l⁻¹ at 25 °C, which is suitable for solubility experiments for determining activity coefficients. Hence it was chosen to represent the class of phenol indicators. On prolonged standing in concentrated sodium glycoxide solutions this phenol undergoes some decomposition. The rate of decomposition was slow and a correction could be made. Several solutions of indicator in glycolic sodium glycoxide were prepared with C_{NaOG} kept constant and with varying indicator concentration and *vice versa*. These solutions were studied spectrophotometrically with time (for a few days), thus giving the rate of decomposition as a function of indicator as well as of sodium glycoxide concentration.

Of the amine indicators used to set up the $(H_{-})_{\text{Am}}^{\text{EG}}$ scale, 2,4,4'- and 2,4,3'-trinitrodiphenylamines are completely dissociated in *ca.* 0.5 and 1.0M-sodium glycoxide respectively, whereas 2,4-dinitrodiphenylamine decomposes rather rapidly in concentrated sodium glycoxide solutions rendering a study over a period of four or more days impossible. 6-Bromo-2,4-dinitroaniline is dissociated to *ca.* 50% in 1.5M-sodium glycoxide. Although it undergoes some decomposition in glycoxide solutions on prolonged standing, similar corrections as described for 2,4,6-tri-*t*-butylphenol could be applied. The solubility of the indicator in ethylene glycol is 2.044×10^{-2} M (at 25 °C) which is rather high for the determination of activity coefficients by solubility measurements, for the solubility further increases in the glycoxide solutions. Hence, partition experiments had to be made for the determination of $f_{\text{HA}}^{\text{Am}}$.

The solvent chosen for partition measurements is xylene. The sample used (AnalaR) was a mixture of *o*-, *m*-, and *p*-xylenes. It was distilled, b.p. 139 °C, and its density was 0.873 g cm⁻³ at 25 °C. It has three u.v. absorption bands, $\lambda_{\text{max.}}$ 265.5 (ϵ 309), 268.5 (282), and 272 nm (232). Beyond 300 nm, *i.e.*, in the visible region where 6-bromo-2,4-dinitroaniline and its anion absorb, xylene does not. It dissolves to some extent (*ca.* 2%) in ethylene glycol. The solubility of xylene in glycol and glycolic sodium glycoxide is given in Table 2.

TABLE 2

Solubility of xylene in ethylene glycol and glycolic sodium glycoxide solutions at 25 °C

[NaOG]/M	Solubility (mol l ⁻¹)	Solubility (ml l ⁻¹)
0	0.1909	23.18
0.25	0.1675	20.33
0.50	0.1552	18.85
0.75	0.1463	17.76
1.00	0.1387	16.85
1.25	0.1322	16.05
1.50	0.1263	15.33
1.75	0.1208	14.67

Owing to this varying solubility of xylene in ethylene glycol and sodium glycoxide solutions, a correction is

necessary without which the activity coefficients determined in the different solutions will be affected to different extents. Assuming tentatively that the solubility of the indicator HA in xylene dissolved in glycol (or sodium glycoxide solutions) will be approximately the same as that in free xylene, we have made the following correction for the concentration of the indicator in the glycol (with or without glycoxide) and xylene phases by means of equations (2) and (3) respectively, where $(C_a)_{\text{True}}$ and $(C_{xy})_{\text{True}}$ are the

$$(C_a)_{\text{True}} = \left\{ C_a - \frac{C_{xy}S_{xy}}{1000} \right\} \frac{1000}{1000 - S_{xy}} \quad (2)$$

$$(C_{xy})_{\text{True}} = C_{\text{Total}} - (C_a)_{\text{True}} \quad (3)$$

actual concentrations of indicator in the glycol (with or without glycoxide) and xylene phase respectively, C_a and C_{xy} are the corresponding observed concentrations of indicator and S_{xy} is the solubility of xylene in ml/l in the glycol or glycolic sodium glycoxide solution concerned.

RESULTS AND DISCUSSION

Table 1 gives the $p(K_a)_{\text{HA}}$ values of the indicators in ethylene glycol. The $(H_-)_{\text{Ph}}^{\text{EG}}$ values were calculated from these $p(K_a)_{\text{HA}}$ values and the measured ionization ratios.⁵ Table 3 gives values of $(H_-)_{\text{Ph}}^{\text{EG}}$ at selected glycoxide concentrations and $(H_-)_{\text{Am}}^{\text{EG}}$ values for

TABLE 3

$(H_-)_{\text{Ph}}^{\text{EG}}$ and $(H_-)_{\text{Am}}^{\text{EG}}$ at selected glycoxide concentrations

[NaOG]/M	$(H_-)_{\text{Ph}}^{\text{EG}}$	$(H_-)_{\text{Am}}^{\text{EG}}$ ^a	$\Delta H_- [= (H_-)_{\text{Am}}^{\text{EG}} - (H_-)_{\text{Ph}}^{\text{EG}}]$
0.1	14.75	14.75	0.00
0.25	15.15	15.17	0.02
0.50	15.48	15.52	0.04
0.75	15.68	15.74	0.06
1.00	15.85 ₅	15.94	0.08 ₅
1.25	16.00	16.11	0.11
1.50	16.12	16.26	0.14
1.75	16.23	16.40	0.17
2.00	16.36	16.56	0.20
2.25	16.49	16.72	0.23
2.50	16.62	16.89	0.27

^a Ref. 5.

comparison. Figure 2 gives a plot of $(H_-)_{\text{Ph}}^{\text{EG}}$ against [NaOG]. A plot of $(H_-)_{\text{Am}}^{\text{EG}}$ against [NaOG] is included. The two plots are almost identical up to ca. 0.5M-sodium glycoxide, but with increasing glycoxide concentration they diverge more and more from each other so that at a concentration of ca. 2.5M-sodium glycoxide the difference is more than 0.25 unit of H_- . A similar phenomenon, namely the H_- function set up with phenol indicators becoming increasingly lower than the H_- function set up with aniline indicators for the same system, was noted by Rochester in methanolic sodium methoxide solutions.² A plot of $(H_-)_{\text{Ph}}^{\text{EG}}$ against $(H_-)_{\text{Am}}^{\text{EG}}$ would furnish a slope of ca. 0.8 (comparable with that in methanol²).

The difference between the two functions, $\Delta H_- [= (H_-)_{\text{Am}}^{\text{EG}} - (H_-)_{\text{Ph}}^{\text{EG}}]$, is given by equation (4).

$$H_- = -\log \left(\frac{a_{\text{H}^+} f_{\text{A}^-} / f_{\text{HA}}}{f_{\text{HA}}^{\text{Am}}} \right)^{\text{Am}} + \log \left(\frac{a_{\text{H}^+} f_{\text{A}^-} / f_{\text{HA}}}{f_{\text{HA}}^{\text{Ph}}} \right)^{\text{Ph}} \\ = \log f_{\text{HA}}^{\text{Am}} / f_{\text{HA}}^{\text{Ph}} - \log f_{\text{A}^-}^{\text{Am}} / f_{\text{A}^-}^{\text{Ph}} \quad (4)$$

Thus, a determination of the activity coefficient ratios in equation (4) will enable us to account for the ΔH_- observed. But, though the determination of the activity coefficients of neutral species like HA is possible, that for individual ions is intrinsically unfeasible.⁸ Besides, it is known from the work of Boyd *et al.*¹ that the determination of the activity-coefficient ratio of the type $f_{\text{A}^-}^{\text{Am}} : f_{\text{A}^-}^{\text{Ph}}$ as a function of sodium glycoxide concentration should be formidably difficult. So the

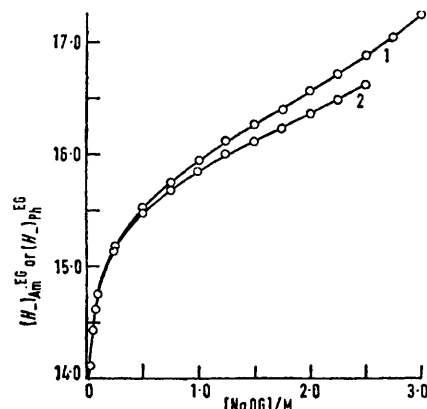


FIGURE 2 Variation of $(H_-)_{\text{Am}}^{\text{EG}}$ and $(H_-)_{\text{Ph}}^{\text{EG}}$ with glycoxide concentration 1, $(H_-)_{\text{Am}}^{\text{EG}}$; 2, $(H_-)_{\text{Ph}}^{\text{EG}}$

direct approach of observing the ΔH_- values in increasing concentration of glycoxide is somewhat difficult at this stage. Nevertheless, it would be equally meaningful if we could explain the variation of the activity-coefficient ratio $f_{\text{A}^-}^{\text{Am}} : f_{\text{A}^-}^{\text{Ph}}$, found from the observed ΔH_- values and the experimentally determined quantities f_{HA} for phenols and amines, from the consideration of structural and molecular properties of the individual acids and their anions and their relative interactions in the glycoxide solutions.

The activity coefficients of the neutral indicators in glycolic sodium glycoxide solutions (with glycol as standard state) have been determined by solubility and partition experiments from equations (5) and (6),

$$f_{\text{HA}} = \frac{S_0}{S} \left[1 + \frac{(K_a)_{\text{HA}}}{h_-} \right] \quad (5)$$

$$f_{\text{HA}} = \frac{\gamma_0}{\gamma} \left[1 + \frac{(K_a)_{\text{HA}}}{h_-} \right] \quad (6)$$

where S_0 and S are the solubilities of the phenol indicator in glycol and glycolic sodium glycoxide solutions respectively, and γ_0 and γ are the distribution ratios of the aniline indicator between pure glycol and xylene and between glycolic NaOG and xylene respectively. $(K_a)_{\text{HA}}$ is the acidic dissociation constant of the indicator acid (phenol or aniline), HA, and h_- is the antilog of the $-(H_-)_{\text{Ph}}^{\text{EG}}$ or $-(H_-)_{\text{Am}}^{\text{EG}}$ values at the particular glycoxide concentration. γ_0 and γ are given by equations (7)

$$\gamma_0 = C_a^0 / C_i \quad (7)$$

$$\gamma = C_a / C_i \quad (8)$$

⁸ E. A. Guggenheim, *J. Phys. Chem.*, 1929, **33**, 842.

and (8), where C_a^0 , C_a , and C_1 are the concentrations of the indicators in glycol, glycoxide, and xylene phases respectively after application of correction for the solubility of xylene in glycol.

Table 4 gives the observed solubilities of 2,4,6-tri-*t*-butylphenol in glycol and sodium glycoxide solutions

TABLE 4

Solubility of 2,4,6-tri-*t*-butylphenol in ethylene glycol and sodium glycoxide solutions at 25 °C and activity coefficients f_{HA}^{Ph} (ethylene glycol being taken as the standard state). (K_a)_{HA} = 1.862×10^{-17}

[NaOG]/M	$10^3 \times$ Solubility (mol l ⁻¹)	(H^-) _{Ph} ^{EG}	f_{HA}^{Ph}
0.0	2.167		1.000
0.105	2.395	14.80	0.915
0.260	2.640	15.19	0.845
0.520	2.861	15.53	0.806
0.885	2.752	15.79	0.878
1.105	2.582	15.92	0.969
1.335	2.506	16.04	1.042
1.685	2.484	16.21	1.136

and the calculated f_{HA}^{Ph} values. Table 5 gives the observed distribution ratios for 6-bromo-2,4-dinitroaniline between glycol and xylene and glycoxide solutions and xylene, and the calculated f_{HA}^{Am} values.

TABLE 5

Partition coefficients of 6-bromo-2,4-dinitroaniline between ethylene glycol and xylene and between glycolic sodium glycoxide and xylene at 25 °C and activity coefficients f_{HA}^{Am} (ethylene glycol being taken as the standard state). (K_a)_{HA} = 6.531×10^{-17} (ref. 5)

[NaOG]/M	γ	(H^-) _{Am} ^{EG}	f_{HA}^{Am}
0.0	0.206		1.000
0.290	0.302	15.21	0.754
0.580	0.343	15.57	0.745
0.890	0.371	15.845	0.808
1.235	0.381	16.085	0.969
1.595	0.448	16.315	1.080

Figure 3 shows the variation of f_{HA}^{Ph} and f_{HA}^{Am} with glycoxide concentration. Included is the activity-coefficient variation of xylene (f_{xy}) in these solutions. The values of f_{xy} (pure glycol being taken as the standard

TABLE 6

Calculated ratios $f_{A}^{-Am} : f_{A}^{-Ph}$ and f_{xy} at selected concentrations of sodium glycoxide

[NaOG]/M	$f_{A}^{-Am} : f_{A}^{-Ph}$	f_{xy}
0.10	0.929	1.07
0.25	0.881	1.14
0.50	0.838	1.23
0.75	0.808	1.31
1.00	0.760	1.38
1.25	0.742	1.44
1.50	0.699	1.51

state) in different concentrations of glycoxides have been computed from the ratio of solubility of xylene in mol l⁻¹ in pure glycol to that in the respective concentrations of glycoxide, and are in Table 6. In the case of xylene we see a clear salting-out which is presumably

⁹ A. Eucken and G. Hertzberg, *Z. phys. Chem. (Leipzig)*, **1950**, **195**, 1.

¹⁰ F. A. Long and W. F. McDevit, *Chem. Rev.*, **1952**, **51**, 119.

due to the decreased availability of 'free glycol'⁹ because of the solvation of Na⁺ and glycoxide ions. In the case of f_{HA}^{Ph} and f_{HA}^{Am} there is an initial salting-in followed by a salting-out. According to Long and McDevit¹⁰ (also several other workers¹¹⁻¹³) large molecules with relatively large molar volumes are salted-in in electrolyte solutions. According to Bergen and Long,¹³ salts with either large anions or large cations generally cause salting-in; salts with large anions cause increased salting-in of acidic solutes relative to benzene and the effect increases with the acid strength of the solute. Glycoxide ions, being comparatively large, may be responsible for the observed (initial) salting-in of the acidic indicator molecules. But as there is no such initial salting-in in the case of xylene, probably the acidity of the phenol and aniline molecules plays an important role in causing their salting-in in the

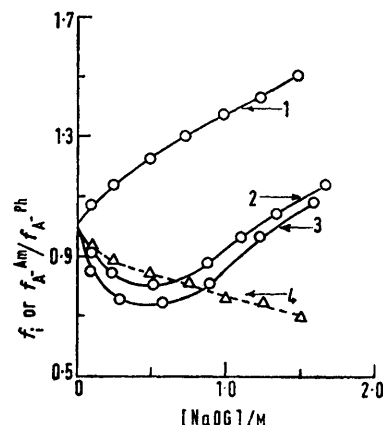


FIGURE 3 Variation of the activity coefficients of 1, xylene (f_{xy}); 2, 2,4,6-tri-*t*-butylphenol (f_{HA}^{Ph}); 3, 6-bromo-2,4-dinitroaniline (f_{HA}^{Am}); and 4, that of $f_{A}^{-Am} : f_{A}^{-Ph}$

glycoxide solutions. Interactions of the glycoxide anion with the acidic indicator molecules may be a decisive factor. At higher concentrations of glycoxide, the salting-out effect due to the decreased availability of 'free glycol' presumably predominates.

Regarding the relative position of the two curves for f_{HA}^{Ph} and f_{HA}^{Am} , the greater polarity of the aniline molecule may be responsible for the greater salting-in in this case. According to Saylor *et al.*,¹¹ a particular electrolyte causes more salting-in of polar solutes such as nitrobenzene than the non-polar benzene. Another important factor for the greater solvation of the aniline is the greater protonic character of the amino-hydrogen than of the phenolic hydrogen atom, for several reasons. The negative charge density of oxygen in phenol is greater than that of nitrogen in amine. The charge delocalization in the highly resonating nitroanilines also increases the protonic character of the amino-hydrogen

¹¹ J. H. Saylor, A. I. Whitton, I. Claiborne, and P. M. Gross, *J. Amer. Chem. Soc.*, **1952**, **74**, 1778.

¹² N. C. Deno and C. H. Spink, *J. Phys. Chem.*, **1963**, **67**, 1347.

¹³ R. L. Bergen, jun., and F. A. Long, *J. Phys. Chem.*, **1956**, **60**, 1131.

atom. Further, solvation of phenols may also be hindered by the bulky t-butyl groups.

The activity coefficient ratios $f_{A^{-Am}} : f_{A^{-Ph}}$ are calculated from the observed H_- and $f_{HA^{Am}} : f_{HA^{Ph}}$ values by equation (4). Table 6 gives the calculated $f_{A^{-Am}} : f_{A^{-Ph}}$ ratios at selected sodium glycoxide concentrations. The broken line in Figure 3 gives the variation of $f_{A^{-Am}} : f_{A^{-Ph}}$ with glycoxide concentration.

Although much information about salt effects on non-electrolytes is available very little is known about salt effects on ions, or the activity coefficients of individual ions in the presence of swamping electrolytes, especially in non-aqueous media. Recently Boyd¹⁴ has determined the relative activity coefficient f^* of some cations and anions in aqueous sulphuric acid solutions using large anions and cations for reference. He finds that the $f_{A^{-*}}$ of anions decrease with increasing H_2SO_4 concentration. It is also found that the more polarizable the anion, the larger is the negative deviation of $f_{A^{-*}}$.^{1,15} It is probable that in our system the anions interact with the Na^+ ions in solution resulting in a

salting-in of the anions of both phenols and amines. But as the amine anions are much more polarizable than the phenolate anions (extinction coefficients of the amine anions are of the order of 10^5 and those of the phenolates are of the order of 10^8) the negative deviation in the former case should be much more than in the latter and hence the decrease of $f_{A^{-Am}} : f_{A^{-Ph}}$ with increase in concentration of sodium glycoxide.

Thus the above analysis indicates that the observed ΔH_- values are seemingly consistent with what is expected from the consideration of the effects of structural and molecular properties of the neutral as well as the anionic forms of the two classes of indicator on their respective interactions in the glycoxide solutions.

We thank the C.S.I.R., New Delhi, for financial support.

[1/1573 Received, 1st September, 1971]

¹⁴ R. H. Boyd, *J. Amer. Chem. Soc.*, 1963, 1555.

¹⁵ E. Grunwald and E. Price, *J. Amer. Chem. Soc.*, 1964, **86**, 4517.