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Salt and Medium Effects on H_- Indicators

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The activity coefficients of the molecular forms of a few nitrodiphenylamine indicators were determined by a solubility method in basic solutions of ethylene and propylene glycols. The medium effects on the ions of these indicators were also obtained by determination of the medium effects of their molecular forms separately by solubility measurements. Variation of the activity coefficients and the medium effects on the ions of the indicators are discussed.

In earlier papers on this subject,[1,2] it was shown that the validity of the acidity function concept is based on two conditions. For a pair of successive indicators B and B_1 in the overlapping range, the equality of the activity coefficient ratios

$$\frac{f_{B^{0,-}}}{f_{A^{+,0}}} = \frac{f_{B_1{}^{0,-}}}{f_{A_1{}^{+,0}}} \qquad (1)$$

must be satisfied where A, B and A_1, B_1 are the indicator acid-base pairs. The superscripts $B^{0,-}$ indicate an uncharged or a negatively charged basic indicator used in H_0 or H_- measurements, respectively. The charges on the other species can be explained in a similar manner. The relative strengths of a pair of indicators must remain unchanged on changing the medium. Although the equality of the ratios of the above type has approximately been shown to hold by indirect methods for indicators of similar structure in water and some non-aqueous solvents of fairly high dielectric constant, the recent work of Boyd[3] has clearly established that there are quite large variations in the individual values of the activity coefficient for both the neutral bases and their conjugate acids. A direct determination of the activity coefficients of the indicators is, therefore, necessary not only for an evaluation of the relative contributions of the various terms in the appropriate acidity function but also to understand[4] the dependence of the acidity function on the indicator structure and in particular on the site of ionisation. Although several classes of indicators have been employed[5-7] for H_- measurements in aqueous and non-aqueous solutions of bases, no data are hitherto available on the variation of their activity coefficients with changing medium. The present work deals with the determination of the activity coefficients of the molecular forms of a few nitrodiphenylamines (which have earlier been employed for H_- measurements in glycols[2]) in sodium glycollate solutions of ethylene and propylene glycols and also their medium effects.

Experimental

Preparation of Solvents, Indicators, and Base. The purification of ethylene and propylene glycols has been described elsewhere.[2] The indicators 2,4,3′-trinitrodiphenylamine (2,4,3′-TNDA), 2,4-dinitrodiphenylamine (2,4-DNDA), and 2,4-dinitro-4′-aminodiphenylamine (2,4-DN-4′-amino-DA) were employed. They were prepared and purified according to standard methods in literature.[8] The preparation and standardization of sodium glycollate in ethylene and propylene glycols has been described.[2]

Solubility Measurements. The solubility measurements of the indicators at various concentrations of the base in the two glycol were carried out at 30±0.5°C. Their saturated solutions were obtained by shaking mixtures of the solid with the appropriate base solution for about 48 hr in a thermostat maintained at a fixed temperature. Known volume of the saturated solution was diluted suitably with the appropriate solvent (the pure solvent or a base solution of the desired concentration) to get convenient values of optical density. The optical densities were measured at the wavelength of maximum absorption of the molecular forms in a P.M.Q. II Carl Zeiss Spectrophotometer and the concentrations were calculated using the known extinction coefficients of the indicators in these solvents at this wavelength. In addition, solubility measurements of the various indicators in water at the same temperature were carried out to compute the medium effects. All solubility measurements were carried out at least in duplicate to confirm the reproducibility of results.

Results

The activity coefficients were calculated from

$$f_{\mathrm{HA}} = \frac{S_0}{S}\left(1+\frac{K_{\mathrm{HA}}}{h_-}\right) \qquad (2)$$

where S_0 and S refer to the solubilities of the given indicator in the pure glycol and the base solution, respectively. K_{HA} is the thermodynamic dissociation constant of the indicator, the activity coefficients being referred to a value of unity at infinite dilution in the given solvent and $\log h_- = -H_-$ on the solvent standard state.

Table 1 gives the solubility and activity coefficient data for different indicators in the two solvents. The medium effects on the molecular and ionic forms of these indicators are presented in Table 2. The medium effect on the ions was calculated by adding the medium effect of the corresponding molecular acids to the overall medium effect which is given by $\mathrm{p}K^{s}_{\mathrm{HA}}$—$\mathrm{p}K^{w}_{\mathrm{HA}}$ where $\mathrm{p}K^{s}_{\mathrm{HA}}$ and $\mathrm{p}K^{w}_{\mathrm{HA}}$ refer to the negative logarithm of thermodynamic ionisation constants of a given indicator in solvent "S" and water, respectively.

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TABLE 1. ACTIVITY COEFFICIENT DATA OF THE MOLECULAR FORM OF THE VARIOUS INDICATORS

Solvent: Ethylene glycol
Indicator: 2,4,3'-TNDA

Base concn. (mol/l)	Solubility × 10^4 (mol/l)	log f_{HA}
0.00	4.27	—
5.00×10^{-4}	3.50	+0.088
1.00×10^{-3}	4.25	+0.008
1.00×10^{-2}	5.28	−0.037
1.10×10^{-1}	7.68	+0.041

Solvent: Propylene glycol
Indicator: 2,4,3'-TNDA

Base concn. (mol/l)	Solubility × 10^4 (mol/l)	log f_{HA}
0.00	4.79	—
2.50×10^{-4}	5.05	−0.017
5.00×10^{-4}	5.99	−0.096
1.00×10^{-3}	6.48	−0.109
5.00×10^{-3}	6.69	−0.049

Indicator: 2,4-DNDA

Base concn. (mol/l)	Solubility × 10^3 (mol/l)	log f_{HA}
0.00	2.21	—
5.00×10^{-4}	1.93	+0.060
1.00×10^{-3}	2.24	−0.005
5.00×10^{-3}	2.30	−0.015
1.00×10^{-2}	1.93	+0.061
1.00	1.97	+0.160

Indicator: 2,4-DNDA

Base concn. (mol/l)	Solubility × 10^3 (mol/l)	log f_{HA}
0.00	3.98	—
2.50×10^{-4}	3.53	+0.053
5.00×10^{-4}	4.57	−0.060
1.00×10^{-3}	4.80	−0.081
5.00×10^{-3}	4.81	−0.080
5.00×10^{-2}	3.88	+0.032

Indicator: 2,4-DN-4'-amino-DA[a]

0.00	3.97	—
5.00×10^{-4}	3.83	+0.016
1.00×10^{-3}	3.66	+0.035
5.00×10^{-3}	3.39	+0.069
5.00×10^{-1}	3.33	+0.081
1.25	4.03	+0.033

a) The tabular columns have the same headings as for the above indicator.

TABLE 2.

Indicator	ΔpK in E.G.	ΔpK in P.G.	log f^o_{HA} in E.G.	log f^o_{HA} in P.G.	log $(f^o_{H^+}\cdot f_{A^-})$ in E.G.	log $(f^o_{H^+}\cdot f_{A^-})$ in P.G.
2,4,6-TNDA[a]	2.01	2.53	−2.27	−2.11	−0.26	+0.42
2,4,2',4'-TNDA[b]	1.90	2.27	−2.13	−1.78	−0.23	+0.49
2,4,3'-TNDA	1.91	2.53	−1.83	−1.88	+0.08	+0.65
2,4-DNDA	2.25	3.02	−2.54	−2.79	−0.29	+0.23
2,4-DN-4'-amino-DA	2.07	—	−2.47	—	−0.40	—

E.G. = Ethylene glycol; P.G. = Propylene glycol.
a) 2,4,6-trinitrodiphenylamine
b) 2,4,2',4'-tetranitrodiphenylamine

The medium effect of the molecular acid was calculated from

$$\log f^o_{HA} = \log \frac{S_w}{S_g} \tag{3}$$

where S_w and S_g are the solubilities of the indicator in water and the glycol, respectively. The results of Table 1 are plotted in Fig. 1.

Discussion of the Activity Coefficients. We see from Table 1 as well as from Fig. 1 that the activity coefficients of all the indicators vary considerably in the range of base concentrations employed contrary to general assumption. Generally, the indicator molecules are 'salted in' in the presence of the base except in the case of 2,4-DN-4'-amino-DA. There is, however, a tendency for the activity coefficients to increase *i.e.* show a 'salting out effect' at low base concentrations as well as at higher base concentrations.

A similar variation of the activity coefficients of some nitroanilines and amides was noted by others[3,4,9] in acid solutions although no attempt was made to explain the variation. Qualitatively this can be explained in terms of three types of hydrogen bonded interactions when base concentration is increased. At low concentrations, the base, being a strong hydrogen bond acceptor, removes the solvent molecules bonded to the indicator thus decreasing its solubility. At intermediate concentrations, the increased indicator ionization coupled with the solvation of the indicator ion increases its solubility. At higher concentrations, this is opposed by hydrogen bonding between the base molecules, the effect being less on the sol-

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[9] M. I. Vinnik and N. Librovich, *Tetrahedron*, **22**, 2945 (1966).

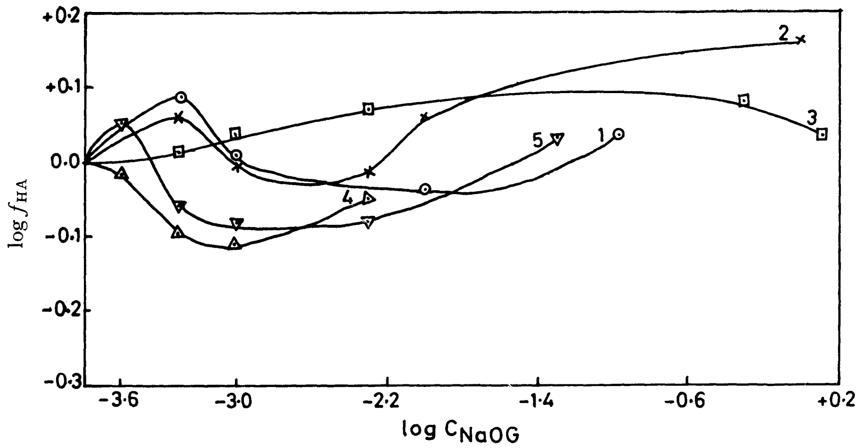

Fig. 1. Plot of log f_{HA} against log C_{NaOG} for various indicators in ethylene and propylene glycols. Curves 1,2,3 are in ethylene glycol and 4,5 are in propylene glycol. ⊙,△ refer to 2,4,3′-TNDA. ×,▽ refer to 2,4-DNDA. ▣ refers to 2,4-DN-4′-amino-DA.

vation of the indicator ion thus decreasing its solubility. In the case of 2,4-DN-4′-amino-DA the ionization of the indicator being much less, predominantly salting out effect is observed.

Our results show that the ratio of the activity coefficients of two successive indicators in the overlap region decreases from unity at higher base concentrations in ethylene glycol while it increases in propylene glycol. Since it was shown[2] that Eq. (1) is applicable for nitrodiphenylamines in basic solutions of ethylene and propylene glycols, a similar variation should be expected in the case of the activity coefficient ratio of the anionic forms of the indicators. An increase in the number of nitro groups leads to a greater "salting in" effect presumably due to the strong hydrogen bond interactions between these groups and the solvent, the effect being much more pronounced in propylene glycol than in ethylene glycol.

Discussion of Medium Effects. The medium effects for the ions of the various indicators in ethylene glycol are smaller than those in propylene glycol, and the free energy change for the transfer of the ions from water to ethylene glycol is negative while it is positive for propylene glycol.

Application of the Born equation reveals that the free energy change associated with the transfer of the indicator ions (the proton and the indicator anion) from a solvent of high to a low dielectric constant should be positive. Although the results in propylene glycol are in qualitative agreement with that predicted by the Born equation, the results in ethylene glycol are contradictory. This is not surprising since the Born equation takes into account only the electrostatic contribution to the free energy change of transfer while other factors, such as ion-solvent interactions, which depend on solvent basicity and contribute to the nonelectrostatic part of the free energy change are ignored. The opposite signs of the medium effects of the indicator ions in the two solvents are undoubtedly due to the differences[2,10] in their solvent basicities. The differences in the medium effects of the ions of the various indicators in a given solvent most possibly arise from the changes in the delocalization of charge caused by the introduction of nitro or amino groups in various positions in the benzene ring. Such differences in charge delocalization affect the ion-solvent interactions considerably.

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[10] R. G. Bates, "Determination of pH. Theory and Practice," John Wiley & Sons Inc., New York (1964), p. 194.