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Studies in Isodielectric Media. Part IV. Thermodynamics of Protonation of *p*-Nitroaniline in Ethylene Glycol—Diethylene Glycol Mixtures at 25 °C

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The thermodynamic ionisation constant of *p*-nitroanilinium ion was determined spectrophotometrically at 25 °C in the near isodielectric mixtures of ethylene glycol (*EG*) and diethylene glycol (*DEG*) over the complete range of solvent compositions. The *pK* of the ion decreases continuously with the addition of diethylene glycol, passes through a minimum around 80 wt% of the same solvent and then increases. The variation of ΔpK ($pK_{\text{mixed solvent}}$—$pK_{EG}$) with solvent composition was analyzed in terms of the changes in *Gibbs* energies of transfer of the different species involved in the ionisation process in these mixtures.

(Keywords: Diethylene glycol; Ethylene glycol; p-Nitroaniline, ionisation)

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Die thermodynamischen Ionisierungskonstanten des *p*-Niroanilinium-Ions wurde spektrophotometrisch bei 25 °C in den annähernd isodielektrischen Mischungen von Ethylenglykol—Diethylenglykol (*EG*—*DEG*) über den gesamten Bereich der Lösungsmittelzusammensetzungen gemessen. Der *pK* des Ions sinkt kontinuierlich mit der Zugabe von Diethylenglykol und geht bei etwa 80 Gew.% *DEG* durch ein Minimum. Die Änderung von ΔpK ($pK_{\text{Lösungsm.-Gemisch}}$—$pK_{EG}$) mit der Lösungsmittelzusammensetzung wird als Wechsel in den *Gibbs*-Energien des Transfers der verschiedenen in den Ionisierungsprozess verwickelten Spezies erklärt.

Introduction

Recent studies on protonation equilibria of weak organic acids and bases in binary mixed solvents have provided valuable information[1–3]

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towards an understanding of solute—solvent interactions in different media. In particular, the use of isodielectric media has been been helpful towards an elucidation of the chemical effects of the solvent components on the thermodynamics of transfer of the various species participating in the equilibria. In continuation of our earlier work on this subject[4–6] this paper deals with the protonation behaviour of *p*-nitroaniline in ethylene glycol (*EG*)—diethylene glycol mixtures (*DEG*) at 25 °C over the complete range of solvent compositions by employing a spectrophotomeric method.

Experimental

Ethylene glycol and diethylene glycol (BDH, LR) were purified as described earlier. *p*-nitroaniline (*PNA*), recrystallised twice from aqueous ethanol (m.p. 145 °C), was used in the spectral measurements. Hydrochloric acid generated by adding conc. sulfuric acid to A.R. conc. Hydrochloric acid was purified as described earlier[7] and bubbled into the desired solvent. The strength of the stock acid solution was determined by titration against aqueous sodium hydroxide which was standardised previously using a standard solution of potassium hydrogen phthalate. In the determination *pK*, i.e., the dissociation constant of the protonated species of *p*-nitroaniline ($PNAH^+$) a spectrophotometric method was employed for the determination of the indicator ratio c_{BH^+}/c_B. All optical measurements were carried out at 25 °C using a PMQ II Carl Zeiss Spectrophotometer. The indicator ratio was calculated from the relation[8]

$$\frac{c_{BH^+}}{c_B} = \frac{\varepsilon_B - \varepsilon}{\varepsilon - \varepsilon_{BH^+}} \tag{1}$$

where ε, ε_B and ε_{BH^+} represents the molar extinctions in the experimental solution, of the basic form B, and of the protonated species, BH^+ respectively, all being measured at a given wavelength. In the present case, ε_{BH^+} was found to be negligible. All absorbance measurements were carried out at the wavelength of maximum absorption of the basic form of the indicator and ε_{BH^+} was found to be negligibly small at this wavelength in all compositions. The solubility of *p*-nitroaniline was determined by shaking an excess of the compound with the solvent mixture of the desired composition for 72 hours using a mechanical shaker. The solution was then kept in a thermostat maintained at 25 °C for 24 hours with occasional shaking. Aliquots of the saturated solution were suitably diluted, their absorbance measured at the wavelength of maximum absorption of the basic form of the indicator and from these data the solubility was calculated. Further experimental details are given elsewhere[7].

Results and Discussion

The dissociation of $PNAH^+$ may be represented by

$$BH^+ \rightleftharpoons B + H^+ \tag{2}$$

and the dissociation constant pK for the above equilibrium was obtained by extrapolation of the plots of pK' against the concentration of the acid c, to $c \to 0$ in the various solvent mixtures. The function pK' is defined by

$$pK' = \log \frac{c_{BH^+}}{c_B} - \log c_{H^+} = pK + f(c) \tag{3}$$

The plots of pK' vs. c were found to be fairly linear in all cases. In calculating pK', the acid was assumed to be completely dissociated in all solvent compositions. The solubility and the pK data are given in Table 1. The *Gibbs* transfer energy of the neutral base B is defined by

$$\Delta G^{\circ}_{(B)} = 2.303\,RT \log \frac{S_{B(EG)}}{S^{\circ}_{B(S)}} \tag{4}$$

where $S_{B(EG)}$ and $S_{B(S)}$ represent the solubilities of *p*-nitroaniline in ethylene glycol and in mixed solvent respectively. The validity of equation (4) depends on the ratio of activity coefficients in the reference and in the experimental solvent being unity in the saturated solutions for which there is some evidence in literature[6,10]. The pK difference of an indicator between the solvent under consideration and the reference solvent (*EG* in the present case) ΔpK may be written as

Table 1. pK_{BH^+} of PNAH$^+$ ion and ΔpK_{BH^+} (molal scale), *solubility and Gibbs transfer energy data of p-nitroaniline in EG—DEG mixtures at 25 °C*

Wt % *DEG*	$pK^m_{BH^+}$	$\Delta pK^m_{BH^+}$	Solubility of *PNA* mol kg^{-1}	ΔG° (*PNA*) J mol^{-1}
0[a]	2.06	0	0.3429	0
20	1.89	—0.17	0.4344	—586
40	1.79	—0.27	0.5408	—1130
60	1.69	—0.37	0.8183	—2156
80	1.81	—0.25	1.0769	—2837
100	1.88	—0.18	1.1637	—3029

[a] *K. K. Kundu* et al., J. Chem. Soc., Perkin II, **1972**, 2063.

$$\begin{aligned} 2.303\,RT\,\Delta pK &= \Delta G^{\circ}_{(\mathrm{diss})} \\ &= \Delta G^{\circ}_{(\mathrm{H^+})} + \Delta G^{\circ}_{(B)} - \Delta G^{\circ}_{(BH^+)} \end{aligned} \tag{5}$$

where $\Delta G^\circ_{BH^+}$ and $\Delta G^\circ_{H^+}$ represent the transfer energies of H^+ and BH^+ respectively. It is also possible to represent equation (5) in a different form

$$2.303\,RT\,\Delta pK = \Delta G^\circ_{(\mathrm{diss})} = \Delta G^\circ_{(\mathrm{HCl})} + \Delta G^\circ_{(B)} - \Delta G^\circ_{(B\mathrm{HCl})} \qquad (6)$$

where $\Delta G^\circ_{(B\mathrm{HCl})}$ and $\Delta G^\circ_{(\mathrm{HCl})}$ represent the transfer energies of the hydrochloride salt and hydrochloric acid respectively. Using the *Gibbs* energies of transfer of the proton and the hydrochloric acid from our earlier work[11], $\Delta G^\circ_{(BH^+)}$ and $\Delta G^\circ_{(B\mathrm{HCl})}$ were evaluated from equations (5) and (6) and all these data (molal scale) are recorded in Table 2. An examination of Table 2 shows that the $\Delta G^\circ_{(\mathrm{diss})}$ passes through a minimum at about 60 wt% diethylene glycol and subsequently increases upon further addition. A better insight into the variation of the *pK* with solvent composition can be obtained by considering the variation of the transfer parameters associated with the equilibrium process with the solvent composition. It is seen that $\Delta G^\circ_{(\mathrm{diss})}$ is negative over the entire range of solvent compositions and thus the equilibrium is more favoured in the mixed solvent than in pure *EG*. While $\Delta G^\circ_{\mathrm{HCl}}$ continuously increases with the addition of *DEG*, $\Delta G^\circ_{(B)} - \Delta G^\circ_{(B\mathrm{HCl})}$ continuously decreases and thus the minimum observed in $\Delta G^\circ_{(\mathrm{diss})}$ around 60 wt.% *DEG* can be explained as arising from the opposite variation of both of these factors, the dominating factor being $\Delta G^\circ_{(B)} - \Delta G^\circ_{(B\mathrm{HCl})}$.

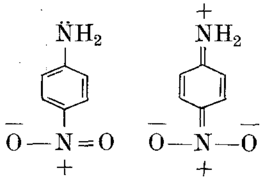
Table 2. *Thermodynamic parameters*[a] *of various species involving p-nitroaniline in EG—DEG mixtures at 25 °C (molal scale)*

Wt% *DEG*	$\Delta G^\circ_{(\mathrm{diss})}$	$\Delta G^\circ_{B\mathrm{HCl}}$	$\Delta G^\circ_{BH^+}$	$(\Delta G^\circ_{(B)} - \Delta G^\circ_{(B\mathrm{HCl})})$	$\Delta G^\circ_{H^+}$[b]	$\Delta G^\circ_{(\mathrm{HCl})}$[b]
0	0	0	0	0	0	0
20	—971	366	342	—952	—43	—19
40	—1541	894	289	—2024	—112	+ 483
60	—2112	1943	—225	—4099	—181	1987
80	—1427	2749	—1439	—5586	—529	4159
100[b]	—1027	3286	—3558	—6315	—1556	5288

[a] All values in J mol^{-1}.

[b] Ref.[11]; $\Delta G^\circ_{H^+}$ on ferrocene-ferricinium ion assumption.

The transfer energy of neutral base decreases continuously with the addition of *DEG* (Table 1) indicating that the transfer of the base from *EG* to the mixed solvent is a favourable process. Noting that *DEG* is more basic and less acidic compared to ethylene glycol in view of the continuously decreasing values of $\Delta G^{\circ}_{(\mathrm{H}^+)}$ with the addition of *DEG* $\delta^+_{EG} > \delta^+_{DEG}$ and $\Delta^-_{DEG} > \Delta^-_{EG}$ where δ^+ and Δ^- represent the protonic character and the negative charge density of oxygen atom on the OH groups of the two solvents respectively. It is well known that in one of the mesomeric forms of *PNA* there exists a partial quinonoid structure (**b**) such that



(**a**) (**b**)

it is likely that *PNA* is solvated through the positively charged amino function by *DEG* molecules as $\Delta^-_{DEG} > \Delta^-_{EG}$ and that at the same time *PNA* molecules are solvated by *EG* through the negatively charged oxygen atoms of $—\mathrm{NO}_2$ function because $\delta^+_{EG} > \delta^+_{DEG}$. Keeping in view the above two competing factors and the experimental results, it may be inferred that the affinity of *PNA* for *DEG* seems to be greater than that for *EG*. Interestingly, an opposite variation is observed[3] in the case of the neutral base (Tris hydroxy methyl amino methane) which was explained in terms of the specific ion solvent interactions.

The continuous increase of $\Delta G^{\circ}_{(B\mathrm{HCl})}$ for the hydrochloride of *PNA* with increasing additions of *DEG* may be attributed to the large increase[11] of $\Delta G^{\circ}_{(\mathrm{Cl}^-)}$. Also it is likely that $PNA\mathrm{H}^+\mathrm{Cl}^-$ is better solvated in *EG* due to the interactions between the negatively charged oxygen atoms of the $—\mathrm{NO}_2$ function and the solvent dipoles of *EG* where $\delta^+_{EG} > \delta^+_{DEG}$.

It is seen from Table 2 that $\Delta G^{\circ}_{(B\mathrm{H}^+)}$ passes through a maximum at about 20 wt% *DEG* and subsequently decreases (becomes more negative). It may be expected that in $PNA\mathrm{H}^+$ the $—\overset{+}{\mathrm{N}}\mathrm{H}_3$ group will be better solvated through the hydrogen atoms attached to the —N atom and the negatively charged oxygen atoms of the solvent dipoles in *DEG* since $\Delta^-_{DEG} > \Delta^-_{EG}$ (interaction type I). Also solvation of $PNA\mathrm{H}^+$ can occur through negatively charged oxygen atoms of $—\mathrm{NO}_2$ function and the molecules of *EG* as $\delta^+_{EG} > \delta^+_{DEG}$ (interaction type II). Also the solvophilicity of the phenyl group is an important factor (interaction type III). At higher compositions of *EG*, the above mentioned interactions of the types II and III appear to predominate over the type I while at higher compositions of *DEG*, the type I interaction dominates thus resulting in the observed behaviour.

Thus the overall variation of ΔpK with solvent composition is controlled by specific solute—solvent interactions of the above mentioned nature.

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