

## Protonation of *p*- & *m*-Nitroanilinium Ions in Diethylene Glycol-Water Mixtures

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The thermodynamic ionization constants of *p*- and *m*-nitroanilinium ions have been determined spectrophotometrically at 25° in diethylene glycol and its aqueous mixtures. The *pK* of both the indicator ions decreases continuously with addition of diethylene glycol, passes through a minimum at about 80 wt % organic solvent and then increases in the pure solvent. The variation of  $\Delta pK$  ( $pK_s - pK_w$ ) with solvent composition was analysed in terms of the changes in transfer free energies of the different species involved in the ionization process in these solvent mixtures.

**S**TUDIES on the protonation equilibria of weak organic acids and bases in non-aqueous and mixed aqueous solvents as a function of solvent composition have provided<sup>1</sup> useful insight to an understanding of solute-solvent interactions in different media. Although such studies involving nitroanilinium ions have been made<sup>2</sup> in some amphiprotic solvent-water mixtures, no measurements have been reported in diethylene glycol or its aqueous mixtures. In this paper, which is in continuation of our earlier investigations<sup>3,4</sup> on the thermodynamic behaviour of electrolytes and ions in these media, the ionization constants of *p*- and *m*-nitroanilinium ions are reported in diethylene glycol and its aqueous mixtures of varying compositions in order to understand the solute-solvent interactions in these media.

### Materials and Methods

Diethylene glycol (BDH, LR) was purified as described<sup>3</sup> previously. The fraction boiling at 120°/10 mm was collected and stored out of contact with air. This sample had a refractive index 1.4445 at 27.5°. Doubly distilled water was used in the preparation of diethylene glycol-water mixtures.

*p*- and *m*-nitroanilines, recrystallized twice from aqueous ethanol (melting points 145° and 114°, respectively), were used in the spectral measurements. Hydrogen chloride used as the acid in these measurements was generated and purified as described earlier<sup>5</sup> and bubbled into the desired solvent. The strength of the stock acid was determined by titration against aq. sodium hydroxide which was standardized previously using a solution of potassium hydrogen phthalate.

**Indicator ratios** — All optical measurements were carried out at 25° on a PMQ II Carl Zeiss spectrophotometer. The indicator ratio,  $C_{BH^+}/C_B$ , was calculated<sup>6</sup> from relation (1)

$$\frac{C_{BH^+}}{C_B} = \frac{\epsilon_B - \epsilon}{\epsilon - \epsilon_{BH^+}} \quad \dots(1)$$

where  $\epsilon_B$  represents the molar extinction coefficient of the indicator in the basic form,  $\epsilon$  is the molar

extinction coefficient in the experimental solution, and  $\epsilon_{BH^+}$  is the extinction coefficient of the conjugate acid of the indicator at a given wavelength. In the present case, absorbance measurements were made at the wavelength of maximum absorption of the basic forms of the respective indicators and  $\epsilon_{BH^+}$  was found to be negligible in all cases. However,  $\epsilon_B$  was found to vary to a small extent with the solvent composition and was taken into account in calculating the indicator ratios in different mixtures. Further experimental details are similar to those given elsewhere<sup>5</sup>. The solubilities of the indicators in different solvent mixtures were determined spectrophotometrically at 25° in accordance with the procedure given earlier<sup>7</sup>.

### Results

The *pK* of the indicators, wherein equilibrium (2) operated,



was obtained by extrapolation of the plots of *pK'* against *C*, the concentration of acid, to  $C = 0$  in all solvent compositions. *pK'* is given by Eq. (3)

$$pK' = \log \frac{C_{BH^+}}{C_B} - \log C_{H^+} = pK + r(c) \quad \dots(3)$$

In calculating *pK'*, the acid was assumed to be completely dissociated in all solvent compositions. The plots were found to be linear in all cases. In the case of *m*-nitroaniline, a correction was applied<sup>8</sup> to the concentration of the acid at equilibrium taking  $BH^+$  formed into consideration. The *pK* and solubility data of the two indicators are recorded in Table 1. The transfer free energies of the neutral indicators [ $\Delta G_{(B)}^0$ ] in different solvent mixtures [ $\Delta G_i^0$  of a species *i* being defined by  $\Delta G_i^0 = G_{i(s)}^0 - G_{i(w)}^0$ , where  $G_{i(s)}^0$  and  $G_{i(w)}^0$  represent the standard free energies of *i* in the solvent and water, respectively] were calculated from expression (4)

$$\Delta G_B^0 = 2.303 RT \log \frac{S_w}{S_s} \quad \dots(4)$$

where  $S_w$  and  $S_s$ , representing the solubilities of the indicator in water and solvent respectively, are

TABLE 1 —  $pK$  AND SOLUBILITY DATA AT 25°

| Diethylene glycol (wt %) | <i>p</i> -Nitroaniline |   |  | <i>m</i> -Nitroaniline |   |  |
|--------------------------|------------------------|---|--|------------------------|---|--|
|                          | $pK^*$                 | Solubility $\times 10^3$ (mole kg <sup>-1</sup> ) | $-\Delta G_{(B)}^{\circ\dagger}$ (J mole <sup>-1</sup> ) | $pK^*$                 | Solubility $\times 10^3$ (mole kg <sup>-1</sup> ) | $-\Delta G_{(B)}^{\circ\dagger}$ (J mole <sup>-1</sup> ) |
| 0                        | (0.99) <sup>1</sup>    | (4.379) <sup>2</sup>                              | —  | (2.46) <sup>1</sup>    | (68.28) <sup>2</sup>                              | —  |
| 20                       | 0.64                   | 15.13   | 3104   | 2.22                   | 135.73  | 1703   |
| 40                       | 0.57                   | 37.70   | 5340   | 2.03                   | 320.60  | 3833   |
| 60                       | 0.24                   | 146.02  | 8695   | 1.84                   | 1095.80   | 6881   |
| 80                       | 0.18                   | 519.11  | 11840  | 1.79                   | 4306.50   | 10280  |
| 100                      | 1.89                   | 1163.67   | 13100  | 3.46                   | 14896.00  | 13360  |

\*Accurate to  $\pm 0.05$  unit.

†Accurate to  $\pm 80$  J mole<sup>-1</sup>.

also given in Table 1. The validity of Eq. (4) depends on the ratio of the activity coefficients of B in water and solvent being unity in the saturated solutions for which there is some evidence in the literature<sup>2,9</sup>. Considering the  $pK$  difference of an indicator between solvent and water,  $\Delta pK$  ( $pK_s - pK_w$ ), it is possible to write

$$2.303RT\Delta pK = \Delta G_{(diss)}^{\circ} = \Delta G_{(H^+)}^{\circ} + \Delta G_{(B)}^{\circ} - \Delta G_{(BH^+)}^{\circ} \quad \dots(5)$$

where  $\Delta G_{(H^+)}^{\circ}$  and  $\Delta G_{(BH^+)}^{\circ}$  represent the transfer free energies of H<sup>+</sup> and BH<sup>+</sup>, respectively. Eq. (5) may also be expressed as

$$2.303 RT\Delta pK = \Delta G_{(diss)}^{\circ} = \Delta G_{(HCl)}^{\circ} + \Delta G_{(B)}^{\circ} - \Delta G_{(BHC1)}^{\circ} \quad \dots(6)$$

where  $\Delta G_{(HCl)}^{\circ}$  and  $\Delta G_{(BHC1)}^{\circ}$  are the transfer free energies of hydrochloric acid and the nitroaniline hydrochloride, respectively. Using  $\Delta G_{(H^+)}^{\circ}$  obtained earlier<sup>4</sup> on the basis of ferrocene redox couple reference method,  $\Delta G_{(BH^+)}^{\circ}$  was evaluated from Eq. (5). Similarly,  $\Delta G_{(BHC1)}^{\circ}$  was calculated from Eq. (6) utilizing the transfer free energies of hydrochloric acid in these solvents determined previously<sup>3</sup>. All these results (molal scale) are recorded in Tables 2 and 3.

## Discussion

The  $pK$  values of both the indicators (Table 1) decrease continuously with the addition of diethylene glycol, pass through a minimum at about 80 wt % organic solvent and then sharply increases in the pure solvent. Since reaction (2) is isoelectric, change of dielectric constant of the solvent with addition of diethylene glycol should have negligible influence on this reaction. Thus, considering the variation of  $\Delta G_{(diss)}^{\circ}$  with solvent composition for the two indicators in terms of the transfer free energies of the various species involved in these equilibria, it is seen from the data in Tables 2 and 3 that this variation is due to two competing factors (i) the continuous increase of  $\Delta G_{(HCl)}^{\circ}$  with the addition of diethylene glycol which becomes very steep in the region of pure solvent and (ii) the continuous decrease of  $\Delta G_{(B)}^{\circ} - \Delta G_{(BHC1)}^{\circ}$  over the whole composition range. The increase of  $\Delta G_{(diss)}^{\circ}$  beyond 80 wt %

 TABLE 2 — THERMODYNAMIC QUANTITIES OF *p*-NITROANILINE (MOLAL SCALE)

(All values are in J mole<sup>-1</sup>)

| Diethylene glycol (wt %) | $\Delta G^{\circ}(HCl)$ | $\Delta G^{\circ}(diss)$ | $\Delta G^{\circ}(BHC1)$ | $\Delta G^{\circ}(BH^+)$ | $\Delta G^{\circ}(B) - \Delta G^{\circ}(BHC1)$ |
|--------------------------|-------------------------|--------------------------|--------------------------|--------------------------|--|
| 20                       | 1649                    | -2000                    | 545                      | -1744                    | -3649  |
| 40                       | 2598                    | -2397                    | -345                     | -6144                    | -4995  |
| 60                       | 4981                    | -4260                    | 546                      | -9675                    | -9241  |
| 80                       | 8665                    | -4623                    | 1448                     | -13005                   | -13288   |
| 100                      | 24540†                  | 5091                     | 6349                     | -24625                   | -19449   |

\*Also applicable to Table 3.

†Unpublished work.

 TABLE 3 — THERMODYNAMIC QUANTITIES OF *m*-NITROANILINE (MOLAL SCALE)

(All values are in J mole<sup>-1</sup>)

| Diethylene glycol (wt %) | $\Delta G^{\circ}(H^+)$ | $\Delta G^{\circ}(diss)$ | $\Delta G^{\circ}(BHC1)$ | $\Delta G^{\circ}(BH^+)$ | $\Delta G^{\circ}(B) - \Delta G^{\circ}(BHC1)$ |
|--------------------------|-------------------------|--------------------------|--------------------------|--------------------------|--|
| 20                       | -640                    | -1373                    | 1319                     | -970                     | -3022  |
| 40                       | -3201                   | -2456                    | 1221                     | -4578                    | -5054  |
| 60                       | -5240                   | -3540                    | 1640                     | -8581                    | -8521  |
| 80                       | -5788                   | -3824                    | 2209                     | -12244                   | -12489   |
| 100                      | -6434                   | 5711                     | 6089                     | -25505                   | -18829   |

\*Applicable also to Table 2.

organic solvent is due to a larger increase of  $\Delta G_{(HCl)}^{\circ}$  compared with the decrease of  $\Delta G_{(B)}^{\circ} - \Delta G_{(BHC1)}^{\circ}$  in both cases.

A comparison of  $\Delta G_{(BH^+)}^{\circ}$  and  $\Delta G_{(H^+)}^{\circ}$  for these indicators shows that  $\Delta G_{(BH^+)}^{\circ}$  decreases rapidly with the addition of diethylene glycol while the decrease in  $\Delta G_{(H^+)}^{\circ}$  is less marked under the same conditions. The negative values of the transfer free energies of the two ions indicate that they are solvated preferentially by the mixed solvent than by water. The large decrease of  $\Delta G_{(BH^+)}^{\circ}$  with the addition of organic solvent is most possibly due to the presence of the bulky hydrophobic benzene rings in the nitroanilinium ions which tend to get stabilized

through solvation by the organic solvent than by water. Further, the solvation of the nitroanilinium ions through the partially protonated hydrogen atoms attached to the nitrogen atom and the negatively charged oxygen centre of the solvent dipoles is also a contributing factor. This also explains the relatively less positive values of  $\Delta G_{\text{BHCl}}^{\circ}$  as compared with  $\Delta G_{\text{HCl}}^{\circ}$  over the whole range of solvent compositions. The negative values of  $\Delta G_{\text{(B)}}^{\circ}$  of the two nitroanilines and their increasing magnitude (in the negative direction) with increasing proportion of the organic component can be explained as due to the presence of the hydrophobic benzene rings in these molecules as stated above. Thus the overall variation of  $\Delta pK$  in these solvent mixtures is largely controlled by specific ion-solvent interactions as well as the basicity of the medium indicated by the proton medium effect.

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