Study of the Proton Transfer Equilibria of BH\(^+\)-type Acids in Propylene Glycol-Water Mixtures

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The thermodynamic dissociation constants, \((K)_m\), of two BH\(^+\) type cationic acids, \(m\)-nitroanilinium ion and \(p\)-nitroanilinium ion, have been determined spectrophotometrically at 25°C in propylene glycol (PG)-water mixtures containing 30, 50, 70 and 90 wt % PG. Standard Gibbs energies of transfer, \(\Delta G_{(B)}\), of the nitroanilines from water to the mixed solvents have been determined at 25°C from the measurement of their solubilities. Solvent effect on the proton transfer equilibria of the acids \[\Delta G_{(diss)}=2.303 \, RT \, \log \left( \frac{[B]}{[H_+]} \right)\] has been discussed in terms of the standard Gibbs energy of transfer of the base (B) from water to the mixed solvent, \(\Delta G_{(B)}\), and the relative values of the standard Gibbs energies of transfer of \(H^+\), \(\Delta G_{(H^+)}\) and of \(BH^+\), \(\Delta G_{(BH^+)}\) in this solvent system. Difference in the \(\Delta G_{(diss)}\) of the nitroanilinium ions is primarily attributed to the difference in the \(\Delta G_{(B)}\) values of the two nitroanilines.

This note reports the dissociation constants of \(m\)- and \(p\)-nitroanilinium ions (BH\(^+\)) in a series of aqueous mixtures of propylene glycol (PG) at 25°C. The study of two isomers is interesting as it can reveal the change in the effect of solvent on the dissociation of acids due to change in the position of the substituent group.

Purification of propylene glycol (LR, BDH), has been described earlier\(^4\). Dissociation constants \((K)_m\) of the nitroanilinium ions in the aqueous mixtures of PG were determined spectrophotometrically in a manner similar to that described earlier\(^2-4\). p\((K)_m\) values in the molal scale were obtained by the extrapolation of the plots of p\((K)_m\)'s of Eq. (1) against \(m_{HCl}\) to \(m_{HCl}=0\).

\[
p_{(K)_m} = -\log m_{SH^+} - \log \frac{x}{1-x} - \log \frac{\gamma_{SH^+}}{\gamma_{BH^+}} = p_{(K)_m} - \log \frac{\gamma_{SH^+}}{\gamma_{BH^+}} \ldots (1)
\]

where \(x\) and \(1-x\) are the fractions of the indicator species present in the neutral form B and the ionic form BH\(^+\) respectively and \(m_{SH^+}\) is the effective molality of \(H^+\) in the solution. \(p_{(K)_m}\) values are summarized in Table 1. The uncertainties in the \(p_{(K)_m}\) values are of the order of 0.01 unit.

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**Table 1** Values of \(p_{(K)_m}\), \(\Delta G_{(diss)}\) for Nitroanilinium Ions in Propylene Glycol-Water Mixtures at 25°C

<table>
<thead>
<tr>
<th>Wt % PG</th>
<th>(p_{(K)_m}) m-NA</th>
<th>(p_{(K)_m}) p-NA</th>
<th>(\Delta G_{(diss)}) m-NA</th>
<th>(\Delta G_{(diss)}) p-NA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.46(^a)</td>
<td>1.00(^b)</td>
<td>4.204(^a)</td>
<td>2.744(^b)</td>
</tr>
<tr>
<td>30</td>
<td>2.15 0.66</td>
<td>3.782</td>
<td>2.297</td>
<td>-2.41</td>
</tr>
<tr>
<td>50</td>
<td>1.83 0.26</td>
<td>3.366</td>
<td>1.796</td>
<td>-4.79</td>
</tr>
<tr>
<td>70</td>
<td>1.75 0.18</td>
<td>3.163</td>
<td>1.593</td>
<td>-5.95</td>
</tr>
<tr>
<td>90</td>
<td>2.06 0.45</td>
<td>3.301</td>
<td>1.691</td>
<td>-5.16</td>
</tr>
<tr>
<td>100</td>
<td>—</td>
<td>2.04(^a)</td>
<td>—</td>
<td>3.159(^a)</td>
</tr>
</tbody>
</table>

\(^{a}\)Ref. 4; \(^{b}\)ref. 2; \(^{c}\)ref. 1.

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**Table 2** Solubilities and \(\Delta G_{(B)}\) for Nitroanilines in Propylene Glycol-Water Mixtures at 25°C

<table>
<thead>
<tr>
<th>Wt % PG</th>
<th>(10^4 x^a)</th>
<th>(\Delta G_{(B)}) Retrieval</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>30</td>
<td>0.7686(^b)</td>
<td>-2.71</td>
</tr>
<tr>
<td>50</td>
<td>9.414</td>
<td>-5.51</td>
</tr>
<tr>
<td>70</td>
<td>36.97</td>
<td>-8.75</td>
</tr>
<tr>
<td>90</td>
<td>131.22</td>
<td>-12.74</td>
</tr>
</tbody>
</table>

\(^a\)Mole fraction of the base in the saturated solution, \(^b\)ref. 5; \(^c\)ref. 2.

The standard Gibbs energies of transfer of the uncharged bases (B), the nitroanilines, from water to the mixed solvents were computed by the method described earlier\(^2,5,6\) using the relation \(\Delta G_{(B)}=RT \ln \left( \frac{x_{w}}{x_{s}} \right)\) where \(x_{w}\) and \(x_{s}\) are the solubilities of the base in water and respective solvents in the mole fraction scale. The solubilities of B and \(\Delta G_{(B)}\) values for both the nitroanilines at 25°C are recorded in Table 2. The maximum uncertainties in the \(\Delta G_{(B)}\) values are ±0.05 kJ mol\(^{-1}\).

The solvent effect on the dissociation of BH\(^+\) ion, \(\Delta G_{(diss)}\), in the mole fraction scale\(^2\) has been calculated using Eq. (2).

\[\Delta G_{(diss)} = \Delta G_{(\text{water})} - \Delta G_{(\text{solvent})} = 2.303 \, RT \left[ p_{(\text{water})} - p_{(\text{solvent})} \right] \]

which can be expressed\(^2,7,8\) in the form of Eq. (3).

\[\Delta G_{(i)} = \Delta G_{(H^+)} + \Delta G_{(B)} - \Delta G_{(BH^+)} \]

where \(\Delta G_{(i)}\) is the Gibbs energy change accompanying the transfer of one mole of species \(i\) from the...
NOTES

![Graph](image)

Fig. 1—Variation of $\Delta G_{i}(\text{diss})$, $\Delta G_{i}(\text{B})$, and $\Delta G_{i}(\text{BH}^+)$ $-$ $\Delta G_{i}(\text{BH}^+)$ at 298.15 K with weight % propylene glycol [●, p-nitroaniline; X, m-nitroaniline]

The values of $\Delta G_{i}(\text{diss})$ are summarized in Table 1. Mole fraction scale value, $p_f(K)_x$, was obtained from molal scale value by the usual relation $^9$.

Figure 1 illustrates the variation of $\Delta G_{i}(\text{diss})$ for both the BH$^+$ ions with wt % PG. In both cases $\Delta G_{i}(\text{diss})$ decreases as proportion of PG in the solvent increases and passes through a minimum at about 75 wt % PG.

Figure 1 shows that $\Delta G_{i}(\text{B})$ becomes increasingly negative with increase in PG content in the solvent which may primarily be attributed to the larger stabilization of the base due to the dispersion interaction of the benzene nucleus of the nitroaniline with the organic component of the solvent mixture. As p-nitro group can enter into resonance with the unshared electron pair of the N atom of the amino group, which is not possible for the m-nitro group, the charge densities on the atoms of the substituent groups are different in the two nitroanilines, leading to a difference in the extent of interaction of the substituent groups with the solvent dipoles. These differences are reflected in the relative positions of the two $\Delta G_{i}(\text{B})$ curves.

The variations in the values of the combined term $\Delta G_{i}(\text{H}^+)$ $-$ $\Delta G_{i}(\text{BH}^+)$, obtained from Eq. (3) by substituting known values of $\Delta G_{i}(\text{diss})$ and $\Delta G_{i}(\text{B})$, are shown in Fig. 1 for the two nitroanilines. The two curves almost coincide. It is evident that whereas interactions of the two bases are somewhat different, these are almost same for the two BH$^+$ ions. Now, unlike the free base, protonated form of p-nitroaniline can not show resonating structure (lone pair of :NH$_2$ group becomes tagged with H$^+$ of NH$_3^+$ group) and hence nature of interaction of both the BH$^+$ ions would be the same, and this, in fact, is reflected in the coincidence of the two $\Delta G_{i}(\text{H}^+)$ $-$ $\Delta G_{i}(\text{BH}^+)$ curves.

Since both H$^+$ and BH$^+$ ions are monopositively charged ions, electrostatic contribution $^7$ to $\Delta G_{i}(\text{H}^+)$ $-$ $\Delta G_{i}(\text{BH}^+)$ due to change in dielectric constant values of the solvent should be very small. The overall positive $\Delta G_{i}(\text{H}^+)$ $-$ $\Delta G_{i}(\text{BH}^+)$ value indicates that $\Delta G_{i}(\text{BH}^+)$ $>$ $\Delta G_{i}(\text{H}^+)$ and reflects the dispersion interaction of the benzene ring of BH$^+$ ion with organic component of the solvent which is absent for H$^+$. The minimum in the $\Delta G_{i}(\text{diss})$ curve is the result of an increase in $\Delta G_{i}(\text{H}^+)$ $-$ $\Delta G_{i}(\text{BH}^+)$ as the organic component is added, and the simultaneous decrease in $\Delta G_{i}(\text{B})$.

It appears from Eq. (3) that, $\Delta G_{i}(\text{H}^+)$ being common and $\Delta G_{i}(\text{BH}^+)$ being almost same, the small differences in the effect of solvent on the dissociation of the two nitroanilinium ion acids, reflected in $\Delta G_{i}(\text{diss})$ values, are primarily due to small difference in $\Delta G_{i}(\text{B})$ values of the two nitroanilines.

References