Ionization Constants of Water & Related Transfer Free Energies of Hydroxide Ion in Aqueous Acetonitrile & Dimethylformamide Based on TATB Assumption

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The ionization constants \( K_w \) of water have been determined in aqueous mixtures (20, 40, 60 wt %) of acetonitrile and dimethylformamide at 25°C from emf measurements of cells comprising glass and Ag-AgCl electrodes. Transfer free energies, \( \Delta G^\circ_{\text{OH}^-} \) have been evaluated therefrom using \( \Delta G^\circ_{\text{H}^+} \) values based on TATB assumption. These are explained in the light of ion-solvent interactions as guided by physicochemical properties of the solvents.

The rates of nucleophilic reactions including base-catalyzed reactions, are often dramatically enhanced on the addition of dipolar aprotic solvents to protic solvents like water, alcohols, glycols etc.\(^1\)–\(^3\). It is believed since long that nucleophiles and the Brønsted bases like OH\(^-\) etc. get increasingly 'activated' due to the decreased solvation of the ions in these solvents. These views are substantiated by the observed increasingly positive magnitudes of transfer free energies, \( \Delta G^\circ_{\text{i}} \) of nucleophiles like halide ions (X\(^-\)) etc. from water to some aqueous dipolar aprotic solvents\(^4\)–\(^6\), as recently determined using widely known\(^4\) tetraphenylarsonium tetraphenylboride (TATB) assumption: \( \Delta G^\circ_{\text{i}}(\text{Ph}_4\text{As}^+) = \Delta G^\circ_{\text{i}}(\text{Ph}_4\text{B}^-) = \frac{1}{2} \Delta G^\circ_{\text{i}}(\text{Ph}_4\text{AsPh}_4\text{B}) \).

Although \( \Delta G^\circ_{\text{i}}(\text{OH}^-) \) values of various ions based on TATB assumption are known in aqueous mixtures of some aprotic and dipolar aprotic solvents\(^4\)–\(^6\) including acetonitrile (ACN)\(^6\) and N,N-dimethylformamide (DMF)\(^6\), those for OH\(^-\) are known only in a limited number of solvents, other than ACN and DMF. As part of our studies on the rates of alkaline hydrolysis of crystal violet cation (CV\(^+\)) in aqueous mixtures of various protic, aprotic and dipolar aprotic solvents including ACN and DMF\(^1\), it was considered essential to determine \( \Delta G^\circ_{\text{i}}(\text{OH}^-) \) values in the latter two cosolvent systems. In this communication we report the \( \Delta G^\circ_{\text{i}}(\text{OH}^-) \) values by measuring the ionization constants \( K_w \) of water in aq. ACN and aq. DMF (20, 40 and 60 wt %), and then evaluating \( \Delta G^\circ_{\text{i}}(\text{OH}^-) \) using \( \Delta G^\circ_{\text{i}}(\text{H}^+) \) values based on TATB assumption\(^6\), as reported earlier\(^5\)–\(^6\).

Materials and Methods

Since Pt, H\(_2\) (g, 1 atm)/H\(^+\) electrode was found to behave irreversibly in these solvent systems, cell (A) GE – H\(^+\)/NaOH(m\(_1\)), NaCl(m\(_2\)), solvent/AgCl – Ag

... (A)

was used for the determination of \( K_w \) values in these solvents. In cell (A) GE – H\(^+\) stands for H\(^+\)-reversible glass electrode. The \( \varepsilon_{\text{cell}}^0 \) values of cell (A), were determined using the cell (B) GE – H\(^+\)/HCl(m), solvent/AgCl – Ag ...

in an auxiliary experiment for each of the solvent mixtures before the use of cell (A) in the corresponding solvent mixtures.

The reagent grade solvents were purified as described earlier\(^5\)–\(^6\). All other chemicals were of AR grade and used after usual pretreatment. Concentrations of the electrolytes were determined by standard procedures. GE – H\(^+\) electrodes used were of Elico model EL-52. Ag-AgCl electrodes were prepared by the method described earlier\(^5\). Keithley digital electrometer (model 616) was used for measuring the emf of the cells. Other experimental details were essentially the same as described earlier\(^7\). Emf values were correct to ±.001 V.

Results

The emfs of the cells (A) and (B) are given by

\[
E_{\text{A,n}} = \varepsilon_{\text{cell}}^0 - k \log a_{\text{H}^+} a_{\text{Cl}^-}
\]

... (1)

where \( k = 2.303 \) \( RT/F \) and \( \varepsilon_{\text{cell}}^0 \) represents the standard emfs of the cells (A) and (B). Assuming complete ionization of HCl, an extrapolation function, \( E_{\text{cell}}^0 \) defined by Eq. (2)

\[
E_{\text{cell}}^0 = E_a + 2 k \log a_{\text{Cl}^-} - 2 k S_t c^{1/2} = \varepsilon_{\text{cell}}^0 + h_{\text{Cl}^-} \]

... (2)

was constructed, where \( S_t \) is the Debye-Hückel constant (values were taken from earlier papers\(^5\)–\(^6\)) and \( h_{\text{Cl}^-} \) is an empirical constant depending upon the nature of the solute, solvent and temperature. The plots of \( E_{\text{cell}}^0 \) versus \( c_{\text{HCl}} \) were linear which on extrapolation to \( c = 0 \) furnished \( E_{\text{cell}}^0 \) values on molar scale.
Table 1—Values of $p,K^*$ and Related Transfer Free Energies Accompanying Ionization of Water in Aqueous Mixtures of ACN and DMF at 25°C

<table>
<thead>
<tr>
<th>Wt% cosolvent</th>
<th>$p,K^*$</th>
<th>$\delta(\Delta G^0_{\text{ion}})$</th>
<th>$\Delta G^0(H^+)^*$</th>
<th>$\Delta G^0(OH^-)^{\text{app}}$</th>
<th>$\Delta G^0(H_2O)$</th>
<th>$\Delta G^0(OH^-)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACN + water mixtures</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>14.33</td>
<td>1.10</td>
<td>-3.1</td>
<td>4.2</td>
<td>0.56</td>
<td>4.8</td>
</tr>
<tr>
<td>40</td>
<td>15.05</td>
<td>4.30</td>
<td>-4.8</td>
<td>9.1</td>
<td>0.83</td>
<td>9.9</td>
</tr>
<tr>
<td>60</td>
<td>16.68</td>
<td>12.57</td>
<td>-4.9</td>
<td>17.5</td>
<td>0.96</td>
<td>18.5</td>
</tr>
<tr>
<td>DMF + water mixtures</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>12.95</td>
<td>-6.80</td>
<td>-3.0</td>
<td>-3.8</td>
<td>0.15</td>
<td>-3.6</td>
</tr>
<tr>
<td>40</td>
<td>13.06</td>
<td>-7.14</td>
<td>-9.4</td>
<td>2.3</td>
<td>0.38</td>
<td>2.7</td>
</tr>
<tr>
<td>60</td>
<td>13.04</td>
<td>-8.44</td>
<td>-16.5</td>
<td>8.1</td>
<td>0.78</td>
<td>8.9</td>
</tr>
</tbody>
</table>

$^*\Delta G^0(H^+)$ values were taken from references 5c and 5d, but slightly modified due to the involved computational errors in the previously reported data.

The emf, $E_A$ of cell (A), given by Eq. (1), can be correlated with $p,K^*$, defined by Eq. (3)

$$
p,K^* = E - sE_{\text{cell}}/k + \log(c_{\text{cell}}/c_{\text{OH}}) = p,K^* + f(\mu) \quad \ldots (3)
$$

Where $s$ and $w$ refer to the solvent and the reference solvent water respectively, and other terms have usual significance. These values are given in Table 1. The estimated uncertainties in $p,K^*$ values are of the order $\pm 0.02$ unit.

The solvent effects, $\delta(\Delta G^0_{\text{ion}})$, on the ionization of water were computed on mole fraction scale using Eq. (4)

$$
\delta(\Delta G^0_{\text{ion}}) = \delta G^0_{\text{ion}} - w\Delta G^0_{\text{ion}} = 2.303 RT[p,K^* - p_wK^*] + 2.303 RT \log(d_wM_w/d_sM_s) \quad \ldots (4)
$$

where the subscripts $s$ and $w$ refer to the solvent and the reference solvent water respectively, and other terms have usual significance. These values are given in Table 1.

Since the solvent effects on $p,K^*$ are related to $\Delta G^0(H^+)$, $\Delta G^0(OH^-)^{\text{app}}$ and $\Delta G^0(OH^-)$ by Eq. (5)

$$
\delta(\Delta G^0_{\text{ion}}) = \delta G^0_{\text{ion}} + \Delta G^0(OH^-)^{\text{app}} - \Delta G^0(H_2O) \quad \ldots (5)
$$

$\Delta G^0(OH^-)^{\text{app}}$ values were computed by subtracting $\Delta G^0(H^+)$ values based on TATB assumption for these solvent mixtures, as reported by us earlier. $\Delta G^0(OH^-)$ values were estimated by adding $-RT$ in $\sigma_{H_2O}$ to $\Delta G^0(OH^-)^{\text{app}}$ in the case of ACN + water mixtures and $-RT$ in $\sigma_{H_2O}$ in the case of DMF + water mixtures, as the corresponding $\sigma_{H_2O}$ data activity of water in the solvent) to the best of our knowledge are not known: $\sigma_{H_2O}$ is the mol fraction of water and can approximately be equated to $\sigma_{H_2O}$. All these values are listed in Table 1. It is evident from Table 1 that the contributions of $RT \log \sigma_{H_2O}$ or $RT \log \sigma_{H_2O}$ in $\Delta G^0(OH^-)^{\text{app}}$ and hence $\Delta G^0(OH^-)$ values differ slightly from the corresponding $\Delta G^0(OH^-)^{\text{app}}$. Similar is the case in DMSO-water mixtures, although experimental values of $\sigma_{H_2O}$ were used.

Discussion

Interestingly enough, while $\delta(\Delta G^0_{\text{ion}})$-wt% profile for ACN-water mixtures (Fig. 1) becomes increasingly positive that for DMF-water mixtures (Fig. 2) exhibits a sharp downward trend up to 20 wt% DMF followed by a slight 'roller-coaster' type behaviour in 20-60 wt% aq DMF. Since these profiles are chiefly guided by the combined effects of transfer free energies of $H^+$ and $OH^-$ from water to the respective solvents, the observed opposing behaviour of $\delta(\Delta G^0_{\text{ion}})$ obviously reflects the involved nature of the relative behaviour of these two ions in the two solvent systems.

The $\Delta G^0(H^+)$-composition profile in DMF-water mixtures becomes increasingly negative with a slight hump around 20 wt% DMF (Fig. 2), which is chiefly due to the combined effects of intrinsic protophilicity of DMF and the possible hydrates of DMF at lower compositions where the basicity is lying intermediate between pure water and DMF and the Born-type electrostatic interactions. Similarly, in ACN-water mixtures the observed slight minimum in $\Delta G^0(H^+)$-composition profile (Fig. 2) is the result of the possible breakdown of three dimensional (3D) ice-like water structures releasing more basic monomeric
profile in DMF-water mixtures exhibits a distinct minimum around 20 wt % DMF and then assumes an increasingly positive trend, as is expected from the destabilizing effect of the aproticity of DMF, besides the Born-type electrostatic effect. The observed initial minimum or increased stabilization of OH\(^-\) compared to pure water is possibly indicative of the effect of the possible stable hydrates of DMF\(^{10-13}\) imparting more proticity, H\(^+\), to the H-bonded intercomponent complex as shown in (D).

Thus (D) is likely to be more effective for solvation of protophilic anions like OH\(^-\) which can undergo 'localized hydrolysis' type interaction\(^{18}\) as in (E) than that for non-protophilic anion like Cl\(^-\) as in (F). This is also evident from the parallel behaviour of both OH\(^-\) and Cl\(^-\) in this solvent system (vide Fig. 2). This explains why \(\Delta G_\text{w}^o(\text{OH}^-)\)-composition profile is lying below that for Cl\(^-\) in the solvents. On the contrary, as in DMSO-water mixtures\(^3\) the observed reverse behaviour of Cl\(^-\) and OH\(^-\) in ACN-water mixtures seemingly results from the combined effects of larger Born-type electrostatic effect of OH\(^-\) compared to Cl\(^-\) and the opposing soft-soft interactions\(^{19}\) on the soft Cl\(^-\). Besides, because of the structural akinness of OH\(^-\) in pure water, OH\(^-\) gets more stabilized in pure water than does Cl\(^-\), thus augmenting more destabilization of OH\(^-\) than Cl\(^-\).

Acknowledgement

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References


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(c) *J phys Chem*, 71 (1975) 2604.


