Standard electrode potentials of \( \text{Br}_3^-/\text{Br}^- \), \( \text{Br}_2^-/\text{Br}_3^- \) and \( \text{Br}_2^-/\text{Br}^- \) redox couples and related formation constants of \( \text{Br}_3^- \) in some dipolar aprotic solvents

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Standard potentials of \( \text{Br}_3^-/\text{Br}^- \) and \( \text{Br}_2^-/\text{Br}_3^- \) redox couples have been determined in dipolar aprotic solvents like acetonitrile (AN), N,N-dimethylformamide (DMF) and propylene carbonate (PC) at 25°C by potentiometric method. The standard potentials of the redox couple \( \text{Br}_2^-/\text{Br}^- \) as well as the related formation constants \( (K_f) \) of \( \text{Br}_3^- \) in the solvents have also been derived thereof. These values help derive transfer free energies, \( \Delta G^\circ \), of \( \text{Br}_3^- \) and \( \text{Br}_2^- \) from water to the solvents, as the corresponding values of \( \text{Br}^- \) based on TATB reference electrolyte are already known in the literature. \( \Delta G^\circ \) values of different Br-species have also been examined in the light of various types of interactions, such as cavity, Born, ion-dipole, ion-induced dipole and the rest ‘chemical’ as guided chiefly by dispersion-type soft-soft interactions.

Results and Discussion

The overall half-cell reaction in cell (A) is essentially represented by Eq. (1)

\[
\text{Br}_3^- + 2e \rightarrow 3\text{Br}^- \quad \ldots (1)
\]

The observed emf \( (E_A) \), of the cell is given by Eq. (2)
DATTA et al.: STANDARD ELECTRODE POTENTIALS OF Br$_3^+$/Br$^-$, Br$_2$/Br$_3^+$ & Br$_2$/Br$^-$ REDOX COUPLES

As before, the extrapolation of the observed linear plots of $E^0$ versus $\mu$ to $\mu = 0$ yielded $E^0_{Br_2/Br_3^+}$ relative to $[E_{sHE(W)} + E_j]$. The $E^0_{Br_2/Br_3^+}$ values relative to $E_{sHE(W)}$ were obtained in a similar manner as described above.

The values of the formation constant ($K_f$) of Br$_3^+$ being essentially the equilibrium constant of the reaction (7)

Br$_3^+(s) + Br^-(s) = Br_3^-(s) \quad \ldots (7)$

were obtained using Eq. (8)

$$\log K_f(\text{Br}_3^+) = \frac{2}{3} \frac{F}{2.3RT} [E^0_{Br_2/Br_3^+} - E^0_{Br_2/Br_3}] \quad \ldots (8)$$

The $E^0_{Br_2/Br_3^-}$ values of the redox couple Br$_2$/Br$^-$ in these solvents relative to $E_{sHE(W)}$ were obtained by proper coupling of $E^0_{Br_2/Br_3^+}$ and $E^0_{Br_2/Br_3^-}$ relative to $E^0_{sHE(W)}$ with the help of the relation (9)

$$E^0_{Br_2/Br^-} = 1/3[2E^0_{Br_3/Br^-} - E^0_{Br_2/Br_3^+}] \quad \ldots (9)$$

The values of $E^0_{Br_3^+/Br^-}, E^0_{Br_2/Br_3}$ and $E^0_{Br_2/Br^-}$ so obtained are summarized in Table 1 along with the $K_f(\text{Br}_3^+)$ values. The estimated uncertainties in $E^0$ values are about ±1 mV and those in $pK_f$ are about ±0.02.

The $K_f$ values in AN and DMF reported earlier are fairly comparable to those obtained in the present study and are given in Table 1.

Moreover, $E^0$ values of the Br$_3^+/Br^-$ redox couple relative to $E^0_{sHE(W)}$, tacitly denoted as $E^0_{Br_3^+/Br^-}$, when multiplied by $-2F$ stands for the free energy change $\Delta G^r_{Br_3^+/Br^-}$ of the galvanic reaction (10)

Br$_3^+(s) + H_2(g, 1 \text{ atm}) = 3Br^-(s) + 2H^+(w) \quad \ldots (10)$

where (s) and (w) refer to the standard state in the solvent and water respectively. Similarly, the corresponding $-2F^2E^0_{Br_3^+/Br^-}$ stands for $\Delta G^r_{Br_3^+/Br^-}$ of the galvanic reaction (11)

Br$_3^-(w) + H_2(g, 1 \text{ atm}) = 3Br^-(w) + 2H^+(w) \quad \ldots (11)$

Table 1 – Standard electrode potentials [$E^0$ (in V)] of Br$_3^+/Br^-$, Br$_2$/Br$_3^+$ and Br$_2$/Br$^-$ redox couples relative to $[E_{sHE(W)} + E_j]$ as well as to $E^0_{sHE(W)}$ and the values of $K_f(\text{Br}_3^+)$ in pure solvents AN, DMF and PC at 25°C

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$E^0_{Br_3/Br^-}$</th>
<th>$E^0_{Br_2/Br_3^+}$</th>
<th>$E^0_{Br_2/Br^-}$</th>
<th>$E^0_{Br_2/Br_3}$</th>
<th>$E^0_{Br_2/Br_3^-}$</th>
<th>$K_f(\text{Br}_3^+)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AN</td>
<td>0.385</td>
<td>0.985</td>
<td>0.585</td>
<td>0.532</td>
<td>0.732</td>
<td>6.8(7.0)</td>
</tr>
<tr>
<td>DMF</td>
<td>0.375</td>
<td>0.845</td>
<td>0.532</td>
<td>0.418</td>
<td>1.888</td>
<td>5.3(6.0)</td>
</tr>
<tr>
<td>PC</td>
<td>0.390</td>
<td>0.755</td>
<td>0.512</td>
<td>0.501</td>
<td>0.866</td>
<td>0.623</td>
</tr>
</tbody>
</table>

Values in parantheses are obtained from ref. 8.
Table 2—Various free energy transfer parameters (in kJ mol⁻¹) for Br⁻, Br₂ and Br₃ from water to pure solvents such as AN, DMF and PC at 25°C

<table>
<thead>
<tr>
<th>Solvent</th>
<th>ΔG°&lt;sub&gt;total&lt;/sub&gt;</th>
<th>ΔG°&lt;sub&gt;cav&lt;/sub&gt;</th>
<th>ΔG°&lt;sub&gt;Born&lt;/sub&gt;</th>
<th>ΔG°&lt;sub&gt;i-d&lt;/sub&gt;</th>
<th>ΔG°&lt;sub&gt;i-id&lt;/sub&gt;</th>
<th>ΔG°&lt;sub&gt;int&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br⁻</td>
<td>Br₂</td>
<td>Br₃</td>
<td>Br⁻</td>
<td>Br₂</td>
<td>Br₃</td>
<td>Br⁻</td>
</tr>
<tr>
<td>ACN</td>
<td>31.8</td>
<td>-4.9</td>
<td>-4.7</td>
<td>-10.2</td>
<td>-12.7</td>
<td>-29.5</td>
</tr>
<tr>
<td>PC</td>
<td>29.7</td>
<td>-30.2</td>
<td>-17.0</td>
<td>-11.8</td>
<td>-14.6</td>
<td>-33.0</td>
</tr>
<tr>
<td>DMF</td>
<td>30.1</td>
<td>-38.6</td>
<td>-31.8</td>
<td>-7.4</td>
<td>-8.9</td>
<td>-19.3</td>
</tr>
</tbody>
</table>

(a) Values are taken from ref. 17.

So we have

\[ -2F\left[ E_{\text{Br}_2/\text{Br}_3} - W_{\text{Br}_2/\text{Br}_3} \right] = 3\Delta G°_{t}(\text{Br}^{-}) \]

\[ -\Delta G°_{t}(\text{Br}_3) \]  \hspace{1cm} (12)

Similarly

\[ -2F\left[ E_{\text{Br}_2/\text{Br}_3} - W_{\text{Br}_2/\text{Br}_3} \right] = 2\Delta G°_{t}(\text{Br}_3) \]

\[ -3\Delta G°_{t}(\text{Br}_2) \]  \hspace{1cm} (13)

Using the literature values of ΔG°<sub>t</sub>(Br⁻) based on widely used Ph₄AsPh₄B reference electrolyte assumption, we have computed ΔG°<sub>cav</sub> values of Br⁻ from Eq. (12) and those of Br₂ from Eq. (13), and the values are listed in Table 2.

The observed nearly equal positive values of ΔG°<sub>cav</sub> for Br⁻ for each of the solvents reflect the well known anion destabilizing effect of the dipo­lar aprotic solvents AN, DMF and PC. The other two bromine species namely Br₂ and Br₃ however get more stabilized in these solvents than in water, the solvating capacity being in the order DMF > PC > AN. The observed order of destabilization of Br⁻ and stabilization of Br₂ and Br₃ in each of the solvents is Br⁻ > Br₂ > Br₃.

This relative order is apparently indicative of the fact that Br⁻ gets destabilized chiefly due to the well known aprotic character of these organic solvents as well as the Born-type electrostatic interactions. But the increased stabilization of Br₂ and Br₃ in comparison to that of Br⁻ in any solvent, however, reflects that whereas solvation of Br₂ molecule is guided by dispersion-type soft-soft interactions, that of Br₃ is guided by the superimposed interactions of larger stabilizing effect of dispersion interaction and the smaller destabilizing effect of Born-type interactions. Moreover, as the dielectric constants of AN, DMF, PC and water are 35.95, 36.5, 64.4 and 78.32 respectively, the Born-type interactions of Br⁻ and Br₂ in these solvents would be in the order of ACN≈DMF > PC. But as the order of dispersion-type interaction is chiefly guided by the polarizability of the solvent molecules and those are being in the order H₂O < ACN < PC < DMF, the relative stabilization of Br₂ is expected to be in the same order as has been observed. But relatively less stabilization of Br₃ does not seem to conform to what is expected from the superimposed Born-type destabilization effects alone. Evidently solvation of these species in these solvents are somewhat involved.

In fact, as is now increasingly recognised, ΔG°<sub>cav</sub>(i) values in general are guided by various types of interactions; (i) cavity effect arising from the difference of free energy change in accommodating the ionic and non-ionic species in the solvents (s) and the reference solvent, water (w); and (ii) electrostatic effect, ΔG°<sub>el</sub>(i) arising from the difference of Born-type (ΔG°<sub>Born</sub>(i)), ion-dipole (ΔG°<sub>i-d</sub>(i)), ion-induced dipole (ΔG°<sub>i-id</sub>(i)) and ion-quadrupole (ΔG°<sub>i-qd</sub>(i)) interactions in the two solvents and the rest, ΔG°<sub>cav</sub>(i) guided by the difference in dispersive-type soft-soft interactions as well as of the chemical nature of the two solvents. Thus

\[ \Delta G°(i) = \Delta G°_{cav}(i) + \Delta G°_{el}(i) + \Delta G°_{ch}(i) \]  \hspace{1cm} (14)

where

\[ \Delta G°_{el}(i) = \Delta G°_{t,Born}(i) + \Delta G°_{i-d}(i) + \Delta G°_{i-id}(i) + \Delta G°_{i-qd}(i) \]  \hspace{1cm} (15)

So in order to have better insight into the chemical effect of solvents towards relative stabilization of species in different solvents relative to that in water, evaluation ΔG°<sub>t</sub>(i) is in order.

Thus, following the procedure similar to that adopted in our previous paper, we computed ΔG°<sub>cav</sub>(i) using the formulations of scale particle theory (SPT) and the different electrostatic contributions using Born and Buckingham formul-
Table 3—Various free energy transfer parameters (in kJmol\(^{-1}\)) for I\(^{-}\), I\(_2\) and I\(_3\) from water to pure solvents such as AN, DMF and PC at 25°C

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(\Delta G_{i,\text{total}}^0)</th>
<th>(\Delta G_{i,\text{cav}}^0)</th>
<th>(\Delta G_{i,\text{Born}}^0)</th>
<th>(\Delta G_{i,i-d}^0)</th>
<th>(\Delta G_{i,i-d}^0)</th>
<th>(\Delta G_{i,\text{int}}^0)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(I^{-})</td>
<td>(I_2)</td>
<td>(I_3)</td>
<td>(I^{-})</td>
<td>(I_2)</td>
<td>(I_3)</td>
</tr>
<tr>
<td>ACN</td>
<td>18.8</td>
<td>-13.9</td>
<td>11.1</td>
<td>-16.2</td>
<td>-37.5</td>
<td>4.7</td>
</tr>
<tr>
<td>PC</td>
<td>17.6</td>
<td>-11.6</td>
<td>18.3</td>
<td>-13.6</td>
<td>-42.1</td>
<td>9.0</td>
</tr>
<tr>
<td>DMF</td>
<td>18.8</td>
<td>-16.4</td>
<td>20.9</td>
<td>-8.4</td>
<td>-24.0</td>
<td>4.6</td>
</tr>
</tbody>
</table>

(a) Values taken from ref. 17.

The dielectric constant, dipole moment, polarizability and radius of solutes and solvents were obtained from our previous paper\(^5\) as well as from literature\(^{29}\). All these values are presented in Table 2 and the rest, \(\Delta G_{i,\text{ch}}^0(i)\) as obtained from the Eq. (14) are also presented in Table 2. Despite certain possible uncertainties involved in computing various contributions, and the fact that the term \(\Delta G_{i,i-qd}(i)\) remains yet unresolved, \(\Delta G_{i,\text{ch}}^0(i)\) values being free from most of the major electrostatic contributions and the non-electrostatic cavity contributions, are expected to reflect the true chemical characteristic of the ion-solvent interactions and also of other specific interactions like acid-base, complex formation etc. if any, provided the relative extent of the dispersion-type soft-soft interactions can be estimated or at least predicted, from the polarizability of the solvents and the solute concerned.

Interestingly enough while \(\Delta G_{i,\text{Born}}^0(i)\) and \(\Delta G_{i,i-id}^0(i)\) contributions are positive and relatively small, those of \(\Delta G_{i,\text{cav}}^0(i)\) and \(\Delta G_{i,i-qd}(i)\) are negative and fairly large (vide Table 2). And the combined effects of these when subtracted from the respective \(\Delta G_{i}(i)\) values, make \(\Delta G_{i,\text{ch}}^0(i)\) values fairly large and positive for Br\(^{−}\) which however get diminished by the superimposed dispersion as well as other chemical type interactions in the cases of Br\(_2\) and less so in the case of Br\(_3\) due to the influence of aprotic character of the solvents. The anionophobicity of solvents resulting from the aproticity of these organic solvents, i.e. weak H-bonding ability due to location and charge distribution of positive end in an unapproachable position for the anions. This is all the more vivid in the case of small-sized Br\(^{−}\) as the \(\Delta G_{i,\text{ch}}^0(\text{Br}^{−})\) values are found to be fairly large positive. Had the dispersion-type soft-soft interactions been negligi-
than \( \text{Br}_3 \) the order of stabilization in DMF is reversed since the solvents become more approachable by \( \text{Br}_3 \) than the bulkier \( \text{I}_3 \).

Thus, though the analysis of individual ionic contribution of \( \Delta G_i \) is not so precise, or free from possible uncertainties, a qualitative idea on the solvation behaviour of the individual halogen species \( X_2 ^+, X^-, X_3 ^- \) becomes possible and their comparative analysis in these solvents is also found to be more or less consistent with what is expected from the molecular picture of the solutes and solvents.

Acknowledgement

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References