Influence of Solvent on Polarographic Reduction of Acetophenone†

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The polarographic reduction of acetophenone in various water-ethanol mixtures (10-90% v/v) containing 0.1 mol dm⁻³ tetramethylammonium bromide and 0.03% gelatin has been studied at pH 10.3. The variation of diffusion current with the solvent composition has been explained on the basis of Stokes-Einstein equation. The shift of half-wave potential to more negative values with the increase in ethanol concentration has been discussed. The change of radius (r) of solvated depolarizer when the solvent composition is changed is found to be due to solute-solvent interaction. The various polarographic parameters such as the heterogeneous rate constant, $k_f$, $k_h$ and the free energy of activation, $\Delta G$ for the reduction process have been determined.

Though the polarographic reduction of a large number of ketones¹⁻³ in a variety of organic and aquo-organic media has been studied, much attention has not been paid to the effect of solvent on the polarographic characteristics of depolarizers. In the present investigation we report the influence of solvent on the mode of reduction of acetophenone in aqueous ethanol of varying compositions.

Materials and Methods

Acetophenone, fractionally frozen thrice, was distilled under reduced pressure, collecting the middle fractions only for the present study. Ethanol was purified as described in the literature and was found to be polarographically inactive in the range of potentials applied. Tetramethylammonium bromide (supporting electrolyte) and gelatin (maximum suppressor) used were AR grade reagents.

The viscosities of the solutions of different compositions were measured using Ostwald Viscometer taking the viscosity coefficient of water (0.7208 cP at 35°C) as reference. The densities of the solutions were measured using specific gravity bottle (10 ml capacity).

The temperature of the solutions was maintained at 35.0 ± 0.05°C by means of a thermostatically controlled water bath. In each case, dissolved oxygen was removed from the solution by bubbling purified nitrogen through it for 15-20 min. The polarograms of thoroughly deaerated solutions were recorded at 35 ± 0.05°C on an ELICO CL 25 automatic recording polarograph having LR 101 P recorder. The dropping mercury electrode (d.m.e) had the characteristics $m^{2/3}l^{1/6} = 1.4847$ mg²/³ s⁻¹/² at 1.77V (vs SCE) in a solution containing 50% (v/v) aqueous ethanol and 0.1 mol dm⁻³ tetramethylammonium bromide. Throughout the measurements, the current at the end of the drop life was taken instead of the average current because the determination of the kinetic parameters is based on the Koutecky's calculations which are more accurately reproduced by measuring the maximum current⁵.

Results and Discussion

In the present study the polarographic reduction of acetophenone was carried out at different compositions of ethanol (10-90%) v/v and the data obtained are recorded in Tables 1 and 2. In each of the solvent composition the reduction process was found to be irreversible as revealed by the higher slope values of the plots of $-E_d$ versus $\log(i/i_d)$ and also from the values of $k_f, k_h, D^{-1/2} < 0.05$ s⁻¹/².

The magnitude of the change in $I_d$ denotes a medium effect, without appreciable influence on the mode of reduction. The change of current is explained by changes in the effective diffusion coefficient due to changes in viscosity ($\eta$) and the effective size of depolarizer. The change of reduction current may be ascribed to the change in effective diffusion coefficient as a result of change in the volume of the reducible species, most probably due to the higher tendency of these species to be solvated by the molecules of ethanol than by water. The variation of diffusion coefficient with ethanol concentration may be due to changes in viscosity, thermodynamic factors and solvation.

Based on Stokes-Einstein equation it can be expressed that $D\eta$ should be constant provided the molar volume of the depolarizer remains the same. If $D\eta$ is a constant, the changes in diffusion coefficient may be expected to be due only to the viscosity of the medium. It is obvious that in the case of acetophenone the value of $D\eta$ is approximately constant when the concentration of ethanol is below 60% and distinctly varies at higher concentrations. It can therefore be

Table 1 — Radius \( r \) of Acetophenone in a Medium Containing Different Concentrations of Ethanol

<table>
<thead>
<tr>
<th>Ethanol ( w ) (v/v)</th>
<th>( I ) (( \mu A ) mol(^{-1}) dm(^{3}) mg(^{-2.3} ) s(^{-1/2}))</th>
<th>( D \eta \times 10^6 )</th>
<th>( I_d r^{1/2} )</th>
<th>( r \times 10^8 ) (cm)</th>
<th>( \Delta G ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>4.748</td>
<td>14.218</td>
<td>3.398</td>
<td>0.93</td>
<td>164.85</td>
</tr>
<tr>
<td>20</td>
<td>3.586</td>
<td>10.791</td>
<td>2.960</td>
<td>1.63</td>
<td>175.77</td>
</tr>
<tr>
<td>30</td>
<td>3.233</td>
<td>10.071</td>
<td>2.860</td>
<td>2.00</td>
<td>162.47</td>
</tr>
<tr>
<td>40</td>
<td>3.031</td>
<td>9.296</td>
<td>2.839</td>
<td>2.28</td>
<td>174.14</td>
</tr>
<tr>
<td>50</td>
<td>2.526</td>
<td>7.429</td>
<td>2.456</td>
<td>3.28</td>
<td>174.14</td>
</tr>
<tr>
<td>60</td>
<td>2.920</td>
<td>8.980</td>
<td>2.833</td>
<td>2.45</td>
<td>186.81</td>
</tr>
<tr>
<td>70</td>
<td>3.405</td>
<td>13.016</td>
<td>3.251</td>
<td>1.80</td>
<td>180.37</td>
</tr>
<tr>
<td>80</td>
<td>3.334</td>
<td>10.774</td>
<td>2.958</td>
<td>2.38</td>
<td>187.23</td>
</tr>
<tr>
<td>90</td>
<td>2.526</td>
<td>5.756</td>
<td>2.162</td>
<td>3.28</td>
<td>183.51</td>
</tr>
</tbody>
</table>

Table 2 — Polarographic Data of Acetophenone at Different Concentrations of Ethanol

<table>
<thead>
<tr>
<th>Ethanol ( w ) (v/v)</th>
<th>( -E' ) (V)</th>
<th>( n )</th>
<th>( k_{i, b} ) (cm s(^{-1}))</th>
<th>( D \times 10^6 ) (cm(^2) s(^{-1}))</th>
<th>( k_{i, x} D^{-1/2} ) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.632</td>
<td>0.875</td>
<td>1.367 \times 10^{-1}</td>
<td>15.298</td>
<td>3.495 \times 10^{-23}</td>
</tr>
<tr>
<td>20</td>
<td>1.639</td>
<td>0.945</td>
<td>1.922 \times 10^{-1}</td>
<td>8.729</td>
<td>6.507 \times 10^{-23}</td>
</tr>
<tr>
<td>30</td>
<td>1.647</td>
<td>0.840</td>
<td>3.505 \times 10^{-1}</td>
<td>7.092</td>
<td>1.316 \times 10^{-20}</td>
</tr>
<tr>
<td>40</td>
<td>1.651</td>
<td>0.879</td>
<td>3.747 \times 10^{-1}</td>
<td>6.233</td>
<td>1.501 \times 10^{-21}</td>
</tr>
<tr>
<td>50</td>
<td>1.654</td>
<td>0.918</td>
<td>3.528 \times 10^{-1}</td>
<td>4.328</td>
<td>1.696 \times 10^{-22}</td>
</tr>
<tr>
<td>60</td>
<td>1.659</td>
<td>1.009</td>
<td>2.592 \times 10^{-1}</td>
<td>5.784</td>
<td>1.078 \times 10^{-24}</td>
</tr>
<tr>
<td>70</td>
<td>1.666</td>
<td>0.960</td>
<td>3.171 \times 10^{-1}</td>
<td>7.865</td>
<td>1.131 \times 10^{-23}</td>
</tr>
<tr>
<td>80</td>
<td>1.672</td>
<td>1.005</td>
<td>2.194 \times 10^{-1}</td>
<td>7.542</td>
<td>7.990 \times 10^{-25}</td>
</tr>
<tr>
<td>90</td>
<td>1.684</td>
<td>0.965</td>
<td>9.330 \times 10^{-2}</td>
<td>4.328</td>
<td>4.484 \times 10^{-24}</td>
</tr>
</tbody>
</table>

concluded that the Stokes-Einstein equation is not applicable to acetophenone. Combination of the Ilkovic equation with Stokes-Einstein equation leads to the relationship

\[
I_d r^{1/2} = \text{Constant} \quad \ldots (1)
\]

The non-constancy of the product \( I_d r^{1/2} \) indicates that the change in diffusion coefficient which ultimately affects \( I_d \) is not solely due to viscosity changes. The variation in \( I_d r^{1/2} \) suggests a change in the size of the ion due to solvation. This is evidenced by the change in the value of ionic radius, \( r \), with increase in ethanol content. The change in current should accordingly, be the resultant effect of increased viscosity and the molecular volume which in turn lowers the diffusion coefficient. This is gathered from the Stokes-Einstein equation.

\[
D = \frac{3.32 \times 10^{-5}}{V_m^{1/3} \eta} \quad \ldots (2)
\]

Substituting for \( D \) in the Ilkovic equation, we get

\[
I_d = 607 nc m^2 s^4 10^{-6} \left( \frac{3.32 \times 10^{-5}}{V_m^{1/3} \eta} \right) \quad \ldots (3)
\]

Assuming that the diffusing particles are spherically symmetrical, one obtains the relation

\[
I_d = 607 nc m^2 s^4 10^{-6} \left( \frac{3.32 \times 10^{-5}}{4.3\pi^3 N \eta} \right)^{1/2} \quad \ldots (4)
\]

where \( I_d \) is the diffusion current (\( \mu A \)); \( n \), the number of electrons consumed in the reduction process; \( c \), the concentration of the depolarizer (mM); \( m \), the rate of flow of mercury (mg s\(^{-1}\)); \( t \), the drop-time (s); and \( N \), the Avogadro number.

Equation (4) can be given in the following form

\[
r = \frac{K^2}{I_d ^{1/2} \eta} \quad \ldots (5)
\]

where \( K = (2.996 nc m^2 s^4 10^{-6}) \).

The data presented in Table 1 indicate that the change in the radius \( r \) of the reducible species is a function of ethanol concentration in the medium, reflecting solute-solvent interaction.

Yet another factor that might be responsible for the variation of the diffusion coefficient is the activity factor. The following equation gives the relationship between diffusion coefficient and the activity factor of electrolytes and nonelectrolytes.

\[
D = D_0 \left(1 + C \frac{d \ln Y}{dC} \right) \quad \ldots (6)
\]

where \( C \) and \( Y \) are the concentration and activity factor respectively of the diffusing species. On the basis of the above equation it may be argued that when the activity factor is changed by changing the ionic strength of the medium, there should be consequent changes in the diffusion coefficient. In the present
work the concentration of the acetophenone (5.0 \times 10^{-4} \text{ mol dm}^{-3}) is kept constant. The total concentration of tetramethylammonium bromide is also kept at 0.1 \text{ mol dm}^{-3} while the concentration of ethanol is increased. The increase in ethanol concentration may be expected to bring about a decrease in the activity of tetramethylammonium bromide. Consequently the diffusion coefficient of acetophenone may also experience a change with progressive increase in ethanol concentration. This prediction has come out true in the case of acetophenone indicating qualitatively the dependence of diffusion coefficient of acetophenone on ethanol concentration in the base solution. In general, ketones (reactants) are less soluble in water than are the corresponding carbinols (products). In aqueous ethanol the solubilities of both the reactant and the product are assumed to be comparatively large. The half-wave potentials in aqueous ethanol should be approximately the same at a given \( \rho \text{H} \) value for a given compound. But the variation of half-wave potential of acetophenone with change in solvent composition can only be due to changes in the solubilities of the reactant and the product in various aqueous ethanol media.

If we take the pure substance as the reference state, the activity, \( A \), is nearly unity in a saturated solution. At any given concentration, \( C \), activity \( A \), and solubility \( S \), the following approximation holds

\[
AS = C
\]  

... (7)

If we let the subscripts \( r \) and \( p \) represent reactant and product molecules, then the difference in polarographic half-wave potentials (\( \Delta E_{1/2} \)) for aqueous and aqueous ethanol solutions at 35\(^\circ\) is given by the relation (8)

\[
\Delta E_{1/2} = -0.0611 \left( \log \frac{A_p}{A_r} - \log \frac{A_p}{A_r} \text{ ethanol} \right) \]  

... (8)

In Eq. (8) the first term in parenthesis can be assumed to be constant and therefore the change in half-wave potential with change of ethanol content is only due to the changes in the solubilities of the reactant and the product. According to Eqs. (7) and (8) the half-wave potential should decrease with increase of ethanol concentration, since the solubility of the product, phenylmethylcarbinol is more than that of acetophenone due to hydrogen-bonding with the solvent. But the observation is contrary to the expectation which can be explained as follows.

The values of \( E_{1/2} \) (Table 2) have been found to shift towards more cathodic direction as the percentage of ethanol increases. The observed shift in \( E_{1/2} \) with the variation of ethanol content can be attributed to several factors, namely dielectric constant (\( \epsilon \)), changes in solvation of ions and adsorption of organic solvent at the electrode surface. The variation of \( E_{1/2} \) with \( \epsilon \) is given by Takahashi relation\(^{12}\)

\[
E_{1/2}(S) = E_{1/2}(W) - K \left[ \frac{1}{d(W)} + \frac{1}{d(S)} \right] \]  

... (9)

where \( E_{1/2}(W) \) and \( E_{1/2}(S) \) are the half-wave potentials in pure aqueous solution and water-organic solvent mixtures respectively and \( K \) is a constant.

If the dielectric-constant change is the dominant factor, the shift in \( E_{1/2}(S) \) would be a linear function of \( \epsilon \cdot S \) (see ref. 12). This is not the case with acetophenone under investigation. The addition of organic solvent to water causes destruction of the normal structure of water. The destruction of the associated molecules readily influences the hydration layer surrounding the depolarizer leading to a shift of \( E_{1/2} \) to less negative values. However, the shift of \( E_{1/2} \) to more negative values, observed with acetophenone can be ascribed to the adsorption of the organic solvent molecules at the electrode surface. The accumulation of solvent molecules near the electrode surface retards the adsorption of the reducible species and also blocks the active centres on the electrode surface. Thus the reduction process requires higher energy and hence the \( E_{1/2} \) shifts to more negative potentials.

For irreversible systems the difference in half-wave potentials (\( \Delta E_{1/2} \)) due to transfer of the depolarizer from solvent 1 to solvent 2 as derived by Takahashi using Born equation and standard electrode potentials is given by Eq. (10).

\[
\Delta E_{1/2} = Z e \frac{v_2 - v_1}{2} \log \left( \frac{A_r}{A_r} \text{ ethanol} \right) \times 
\log \left( \frac{1.349 k_1^{2,1} \varepsilon_1^{1/2}}{D_1^{1/2}} \right) - \log \left( \frac{1.349 k_2^{2,2} \varepsilon_2^{1/2}}{D_2^{1/2}} \right) \]  

... (10)

The shift in \( E_{1/2} \) of an irreversible electrode reaction during the transfer from one solvent to another is governed not only by the dielectric constant, but also by the change in effective radius with change of solvent and the kinetic parameters of the reaction. Accordingly it is not easy to predict the magnitude of the shift in \( E_{1/2} \) of an irreversible process caused by changing the solvent. Irregular behaviour may also be due to the change of liquid junction potential, chemical nature of the solvent and ion-pair formation.

The kinetic parameters, viz., \( k_{r,b} \), \( z n_a \), \( I \) and \( \Delta G \) have been calculated using well known equations (Table 1). The values of heterogeneous rate constant \( k_{r,b} \), the free energy of activation, \( \Delta G \), for the reduction process and the diffusion current constant, \( I \) do not show any regular trend with the increase in ethanol content of the base medium.
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