Influence of Structure Breaking and Structure Forming Ions on the Dissociation Mechanism of Acetic Acid in Aqueous Solutions

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Dedicated to Professor W. Vielstich on the Occasion of his 65th Birthday.

Using a rotating disc electrode, the dissociation rate of acetic acid in various aqueous electrolyte solutions is studied. Li\(^+\), Cs\(^+\) and (CH\(_3\))\(_4\)N\(^+\) at 1 M concentration considerably modify the activation enthalpy and entropy of the reaction. Evidently the interaction between the cations and water molecules influences the dissociation mechanism of the weak acid. In the presence of 1 molar Li\(^+\) the activated complex of acetic acid seems to contain only one water molecule instead of two in the other cases.

**Keywords**: Dissociation mechanism, weak acids, structure breaking and structure forming ions.

**Introduction**

The dissociation of weak acids in aqueous solutions has already been studied in previous papers [1, 2]. The dissociation seems to take place after formation of an activated complex [3, 4] in which two orientated water molecules allow for the formation of long-distance ion pairs. If the ionic strength is close to zero, the critical charge separation seems to be 7.5 Å [5], i.e. about three times the length of a hydrogen bond in water. This charge separation enables the dissociation of the ion pair. Thus, the dissociation step requires the previous orientation of two water molecules, this orientation being a process competing with the tendency of the water molecules to acquire their usual short range order.

Introduction of ions influences the ordering of the water molecules. Some ions are structure-breaking, others, such as ions with hydrophobic groups [6] are structure-forming.

Thus, when the solution contains structure-breaking ions, e.g., Na\(^+\) or K\(^+\), the orientation of the two water molecules needed for the formation of the activated complex should become easier. The contrary should be the case if the ions are structure-promoting.

In our work we have studied with a rotating disc electrode, how the formation of long-range activated complex seems to be a process competing with the tendency of the water molecules to acquire their usual short range order.

**Experimental**

The cell (glass, 500 cm\(^3\) capacity) consisted of three compartments, one for the PINE INST. Co, rotating Pt disc electrode, one for the SCE reference electrode, which communicates with a Luggin capillary, and one
for the Pt counter electrode (a 1 cm$^2$ Pt plate). The disc electrode had an area of 0.5 cm$^2$ and was inserted in a Teflon cylinder of 1.83 cm diameter. An MS 120 Model Fabelle potentiostat for the potential control and a PAR Mo. 175 Universal Programmer as function generator were used. The voltammograms and limiting currents were recorded on a Hewlett-Packard Mod. 7047A X-Y Recorder. The viscosity was measured with a Pobel glass pycnometer and the $K_1$ value of acetic acid with a Beckman Expandomatic pH meter-Potentiometer. A Heto thermostat and a Colora Tauchkühler served for controlling the temperature. The Na$^+$, K$^+$, Cs$^+$ and (CH$_3$)$_4$N$^+$ chlorides were from Merck (p.a.) and the Li$^+$ chloride from Carlo Erba (p.a.).

The concentrations of acetic acid and sodium acetate were $3 \times 10^{-3}$ M and $3 \times 10^{-2}$ M, respectively, and the chloride concentrations were 0.5 and 1 M.

The measurements of the diffusion coefficient for the free proton were made for a $3 \times 10^{-3}$ M HCl solution at 0.5 or 1.0 M concentrations of the electrolytes used.

The solutions were prepared with bidistilled water cleansed through a Millipore System and deaired by stirring with N$_2$ previous to each experiment. The

Table 1. Diffusion coefficients of undissociated acetic acid molecules obtained from the intercepts of $I_L/\sqrt{\omega}$ vs. $I_L^2$ plots in the presence of 0.5 M and 1.0 M MCl solutions.

<table>
<thead>
<tr>
<th>$t$ (°C)</th>
<th>LiCl</th>
<th>NaCl</th>
<th>KCl</th>
<th>CsCl</th>
<th>(CH$_3$)$_4$NCl</th>
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<td>5.68</td>
<td>6.46</td>
<td>6.27</td>
<td>6.01</td>
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<tr>
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<td>7.45</td>
<td>7.31</td>
<td>7.58</td>
<td>6.73</td>
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<td>11.90</td>
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<td>9.05</td>
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<td>9.58</td>
<td>11.80</td>
<td>10.60</td>
<td>10.90</td>
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</table>

Pt disc working electrode was activated by application of triangular potential sweeps between hydrogen and oxygen evolution until the same voltammogram, taken as a reference, was obtained. Before every experiment and before activation, the working electrode was polished with 0.05 μ alumina powder.

Results

Figure 1 shows the limiting currents obtained in a special case. The potential sweep rate was 50 mV sec$^{-1}$. 

![Figure 1](image_url)

**Fig. 1.** Limiting current for H$_3$O$^+$ reduction at increasing rotation rate in solution of 1 M KCl, 3 $\times$ 10$^{-2}$ M NaAc and 3 $\times$ 10$^{-3}$ M HAc. $T$ = 5°C, $v$ = 50 mV sec$^{-1}$. 

![Figure 2](image_url)

**Fig. 2.** $I_L\sqrt{\omega}$ vs. $I_L^2$ for solution of 1 M LiCl, 3 $\times$ 10$^{-2}$ M NaAc and 3 $\times$ 10$^{-3}$ M HAc.
Table 2. Values of $k_f$ (sec$^{-1}$) and $k_d$ (1 mol$^{-1}$ sec$^{-1}$) for the dissociation of acetic acid in the presence of 0.5 M and 1.0 M MCI.

Reaction: $\text{CH}_3\text{-COOH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{-COO}^- + \text{H}_3\text{O}^+$.

<table>
<thead>
<tr>
<th>Cation</th>
<th>$T$ (°C)</th>
<th>0.5 M MCI</th>
<th>NaCl</th>
<th>KCl</th>
<th>CsCl</th>
<th>(CH$_3$)$_4$NCl</th>
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<tr>
<td></td>
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<td>$k_f$ (sec$^{-1}$)</td>
<td>$k_d$ (1 M$^{-1}$ sec$^{-1}$)</td>
<td>$k_f$ (sec$^{-1}$)</td>
<td>$k_d$ (1 M$^{-1}$ sec$^{-1}$)</td>
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<td>2.0 - 10$^{10}$</td>
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</tr>
<tr>
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<td>1.4 - 10$^{10}$</td>
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<td>1.5 - 10$^{10}$</td>
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<tr>
<td>(CH$_3$)$_4$NCl</td>
<td>5</td>
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<td></td>
<td>3.35 - 10$^{10}$</td>
<td>7.2 - 10$^{10}$</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3. In $k_f$ vs. $1/T$ for 1 M CsCl and 1 M (CH$_3$)$_4$NCl solutions.
and perhaps in the diffuse double layer [12]. Mihelic and Vielstich [13] studied the influence of the field effect on the acetic acid dissociation. They showed that \( k_r \) for acetic acid dissociation and, therefore, \( k_r \) is a function of \( \delta_R \) (reaction layer thickness) only when \( \delta_R \) is smaller than a critical value of around 30 Å. Taking a value for \( k_r \) of \( 2.1 \times 10^{10} \) (of the same order of magnitude as the \( k_r \) values shown in Table 2), application of the equation

\[
\delta_R (\text{cm}) = \frac{D}{\sqrt{k_r (\text{Ac}^-)}} \tag{3}
\]

gives a \( \delta_R \) value of around 34.8 Å (13).

At 25 °C the layer is already so thick that with further increase of \( \delta \), the constant \( k_r \) does not change any more. Furthermore, the fact that [Ac\(^-\)] was maintained constant means that the field effects on the acetic acid dissociation were the same, so that no influence on the reaction kinetics could be expected.

**Discussion**

Provided two water molecules are necessary to obtain an activated complex, the dissociation process of any weak acid takes place according to the following steps:

\[
\begin{align*}
\text{I} & \quad \text{II} \\
\text{R} - \text{COOH} + \text{H}_2\text{O} \quad \text{R} - \text{COO}^- + \text{H}_3\text{O}^+ \\
\end{align*}
\]

Configuration II corresponds to the activated complex; the positive and negative charges are separated by 7.5 Å [5].

The number of hydrogen bridges which must be broken for the formation of an activated complex depends on the structure of the solvent, i.e. on the type and concentration of the ions present [6].

**Activation Enthalpy Values**

Table 3 and Fig. 4 show that the most significant effect on \( \Delta H^\ddagger \) is brought about by (CH\(_3\))\(_4\)N\(^+\) and Li\(^+\) at 1.0 M concentration. For the other ions at 1.0 M and all ions at 0.5 M \( \Delta H^\ddagger \) has a value around 18 kJ mol\(^{-1}\), i.e. about for times the value 1.32 kcal mol\(^{-1}\) = 5.52 kJ mol\(^{-1}\) calculated [8] for the breaking of one of the four distorted hydrogen bonds with which a water molecule is bound in liquid water. This corresponds to the breaking of about 2 hydrogen bonds for each of the two water molecules in the activated complex. Only the Li\(^+\) ions show also at 0.5 M a little effect (\( \Delta H^\ddagger \approx 24 \text{ kJ mol}^{-1} \)), due to the high capacity of these small ions for orientating water molecules in their solvation shells.

**Effect of Structure Forming Ions on the \( \Delta H^\ddagger \) Value**

In case of the structure promoting ion (CH\(_3\))\(_4\)N\(^+\) the big size and the methyl hydrophobic group give rise to a high structuration of the solvent. The presence of such ions in a 1.0 M solution requires breaking of almost 2 hydrogen bonds of an "icelike" structure (in ice the energy per hydrogen bond is twice that in liquid water) for every water molecule entering the activated complex.

**Effect of Structure Breaking Ions on the \( \Delta H^\ddagger \) Value**

The small Li\(^+\) ions have the greatest Stokes radius [7]. In the case of the 1.0 M Li\(^+\) solution, the two water molecules necessary for the formation of the activated complex have to be snatched from the solvation shells of the Li\(^+\) ions, so that coulombic interac-
tions beside hydrogen bond breaking must be overcome.

On the other hand, in the presence of highly orientating ions, possibly, dissociation of acetic acid via a complex containing only one water molecule could be preferred. The dissociation of such a structure, gives rise to two electrical charges close to each other, so that their coulombic interaction would be determining the dissociation step:

\[
\text{CH}_3 - C = \cdots O - H + ^+ O - H
\]

For 0.5 M and 1.0 M solutions of Na\(^+\) and K\(^+\) ions the obtained \(\Delta H_f^{\neq}\) values agree with the small hydration capacity of both ions, or, according to Samallov’s ideas [7] to their slight positive (Na\(^+\) ions) or negative (K\(^+\) ions) hydration. As for the Cs\(^+\) ions, their negative hydration [7] can explain their low Stokes radius. Their large size contributes significantly to the structuring of water, whenever the concentration is high enough. This explains the high \(\Delta H_f^{\neq}\) value obtained in the presence of 1 M Cs\(^+\) ions.

It is clear that the Cl\(^-\) ions cannot affect the \(\Delta H_f^{\neq}\) or \(\Delta S_f^{\neq}\) values since they were the common counter-ions. Only a specific adsorption could play a role, but not in the used potential range in which they have to compete with H atoms for the Pt sites.

**Activation entropy values**

The obtained activation entropies are given in Table 3 and Figure 5. For the 0.5 M solutions \(\Delta S_f^{\neq} = -75 \text{ J mol}^{-1} \text{ K}^{-1}\) with the exception of the Li\(^+\) ions \(\Delta S_f^{\neq} = -56 \text{ J mol}^{-1} \text{ K}^{-1}\). The negative values of \(\Delta S_f^{\neq}\) indicate an increase of order on activated complex formation. This increase can be attributed: a) to the conversion of translational and rotational degrees of freedom in the reactants into vibrational degrees of freedom in the activated complex: and/or b) to the separated electrical charges in the activated complex which bring about an additional orientation of water dipoles around them.

In the 1.0 M solutions \(\Delta S_f^{\neq}\) is negative for the Cs\(^+\), K\(^+\) and Na\(^+\) ions. The value \(- 59 \text{ J mol}^{-1} \text{ K}^{-1}\) for the Cs\(^+\) ions may be due to their big size, which has an ordering effect on the water structure making the orientation of the water dipoles more difficult. The value \(- 100 \text{ J mol}^{-1} \text{ K}^{-1}\) for the K\(^+\) ions could be a consequence of their negative hydration [7], which also lowers the value for \(\Delta H_f^{\neq}\) (Table 3). The most significant effect, is shown by the (CH\(_3\))\(_4\)N\(^+\) and Li\(^+\) ions at 1.0 M concentration. For the (CH\(_3\))\(_4\)N\(^+\) ions \(\Delta S_f^{\neq}\) is slightly positive. It seems that the water molecules pass from one to an other structure with a balance of almost no entropy change. The above discussed \(\Delta H_f^{\neq}\) value agrees with this interpretation.

The Li\(^+\) ions at 1.0 M show a high positive \(\Delta S_f^{\neq}\) value: If only one water molecule takes part in the activated complex, the electrical charges in the complex remain close to each other so that their interaction could partly hinder water dipole orientation around them. These ideas are in agreement with the high \(\Delta H_f^{\neq}\) value obtained.

**Acknowledgement**

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