1.4 Ionic Reaction : Salt effects

Due to electrostatic interactions, the kinetics of reaction between ions deviate from those observed in reaction between non-electrolytes. The velocity constants of ionic reactions , it will be seen, depend upon the charges of the reacting ions and also the ionic strength of the solution. The effect of ionic strength (μ) on the rate constant is called the **Primary kinetic salt effect.** A very satisfactory treatment of this matter was first made by Bronsted (1922) and later on by Bjerrum. It has been postulated that the ions, say A^{Z_A} and B^{Z_B} first form an activated complex $(A.B)^{Z_A+Z_B}$ which subsequently decomposes to yield the products. The complex formed at any time has a small concentration and it is in equilibrium with the reactant ions, i.e,

$$A^{Z_A}+B^{Z_B} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [A.B]^{Z_A+Z_B} \xrightarrow{k_3} Products$$
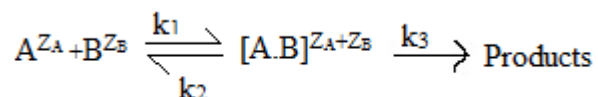
Where Z_A, Z_B, etc are the charges of the respective species; k-terms are velocity constants.

The equilibrium constant is given by

(1)

$$K^{\neq} = \frac{a_x}{a_A b_B} = \frac{C_x f_x}{(C_A f_A)(C_B f_B)}$$

in which a's represent activities , C's concentrations and f's activity coefficients ; the suffix 'x' indicates the complex formed. Rewriting , we have

(2)

$$C_x = K^{\neq} C_A C_B \frac{f_A f_B}{f_x}$$

Now the rate of formation of the product, i.e, rate of reaction is

$$\frac{dC_P}{dt} = k_3 C_x = k_3 K^{\neq} C_A C_B \frac{f_A f_B}{f_x}$$

(3) or

$$\frac{dC_P}{dt} = k_0 \frac{f_A f_B}{f_x} C_A C_B \quad (\text{Putting } k_3 k^{\neq} = k_0 \text{ constant})$$

But for the biomolecular reaction between A and B ions, the experimental rate of recation may be expressed as

(4)

$$\frac{dC_P}{dt} = k\, C_A C_B$$

Where k is the experimentally evaluated rate constant.

Comparing (3) and (4), we have, $k = k_0(f_A f_B / f_x)$

(5) or $\qquad\qquad\qquad \log k = \log k_0 + \log f_A + \log f_B - \log f_x$

Applying Debye-Huckel's relation, the activity coefficients may be expressed in terms of ionic strength i;

$\qquad\qquad \log f = -0.509 z^2 \sqrt{i}$ at $25^0 C$,in dilute solutions

Hence, $\log k = \log k_0 - [-0.509 z^2_A + 0.509 z^2_B - 0.509\,(Z_A + Z_B)^2]\,\sqrt{i}$

Or $\quad \log k = \log k_0 + 1.018\, Z_A Z_B \sqrt{i}$ $\qquad$ ……………………………. (1.4.1)

This is known as Bronsted –Bjerrum equation. A plot of log k against $\sqrt{i}$ for aqueous solution ($25^0 C$) would be linear and its slope would be $1.018\, Z_A Z_B$ and its intercept $\log k_0$.

The plot of $\log k/k_0$ vs $\sqrt{i}$ would be linear, the slop of the line depending on $Z_A Z_B$, i.e, the charges of the reacting ions. Three special cases may arise:

(i) when Z_A and Z_B are of the same sign, $Z_A Z_B$ is positive, the rate constant would increase with $\sqrt{i}$.

(ii) when Z_A and Z_B are of opposite sign, $Z_A Z_B$ is negative, the rate constant would decrease with $\sqrt{i}$.

(iii) When one of the reactants is unchanged, $Z_A Z_B$ is zero, the rate constant would be independent of i.

These predictions have been confirmed from experimental results. In Fig.2 plots of $\log(k/k_0)$ against $\sqrt{i}$ are given for reactions of ions with different $Z_A Z_B$ values. These lines indicate the theoretical predictions from equation (1.4.1)
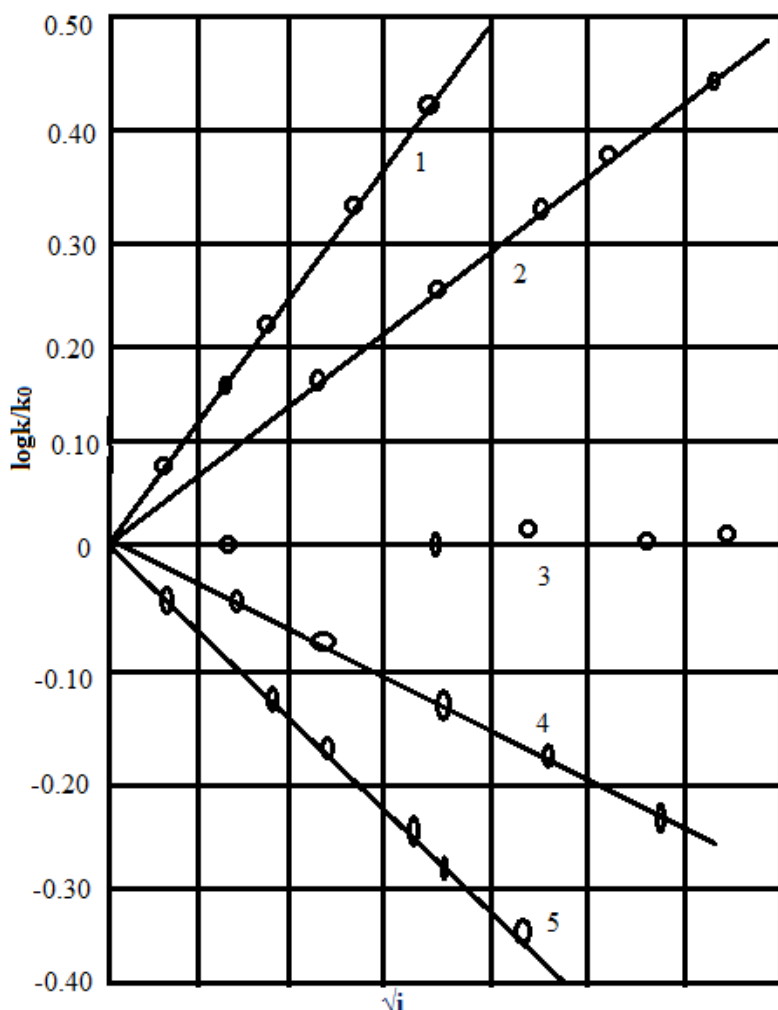
Fig 2: Rate constant variation with ionic strength

1. $2[Co(NH_3)_5Br]^{+++} Hg^{++} +2H_2O \rightarrow 2[Co(NH_3)_5 H_2O]^{+++} +HgBr_2$

2. $2I^- +S_2O_8^{--} \rightarrow I_2 +2SO_4^{--}$

3. Inversion of sucrose solution

4. $H_2O_2 +2Br^- +2H^+ \rightarrow 2H_2O +Br_2$

5. $[Co(NH_3)Br]^{++} + OH^- \rightarrow [Co(NH_3)_5 OH]^{++} + Br^-$

Secondary salt effect: The influence of ionic strength on the activity coefficients called the '**Primary salt effect**' and in the above the affects of the velocity constant has been discussed. When H^+ or OH^- ions produces from a weak acid or weak base acts as the catalyzing agent, the addition of salts i.e, variation in ionic strength influences the conc. of H^+ or OH^- ions. Since the rate of reaction depends upon the conc of H^+ or OH^- ions, it is clear the rate constant will be

affected by the salt concentration. The phenomenon is quite independent of primary salt effect and is known as the *Secondary salt effect.* For a weak acid,

$$HA \rightleftharpoons H^+ + A^-$$, the dissociation constant,
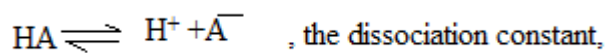
$$K_a = \frac{C_{H^+} \cdot C_{A^-}}{C_{HA}} \cdot \frac{f_{H^+} f_{A^-}}{f_{HA}}$$

$$C_{H^+} = K_a \frac{C_{HA}}{C_{A^-}} \cdot \frac{f_{HA}}{f_{H^+} f_{A^-}} = K \frac{f_{HA}}{f_{H^+} f_{A^-}}$$

for a given acid-salt mixture , i.e, $C_{HA}/C_{A^-} =$ constant

Since the rate depends on the conc. of H^+ ions, hence for a given acid –salt ratio, the rate constant would be,

$k = k_0 \, f_{HA}/f_{H^+} \cdot f_{A^-}$, (where k_0 includes the primary salt effect)

$\log k = \log k_0 + 1.018\sqrt{i}$ (at 25^0 C)