What is Common-ion effect? Explain with example.

⇒ If there is no formation of complex ions to disturb the equilibrium, then solubility of any salt is less in a solution containing a common ion than in water alone. This effect is known as common-ion effect.

Let us consider a weak acid, HA the equilibrium between undissociated molecules and the produced ions is

$$HA \rightleftharpoons H^{\oplus} + A^{\ominus}$$

The dissociation constant, K_a of the weak acid in dilute solution is

$$K_a = \frac{C_{H^{\oplus}} \cdot C_{A^{\ominus}}}{C_{HA}}.$$

The addition of either $H^{\oplus}$ ion or $A^{\ominus}$ ion will affect the equilibrium. To keep K_a constant, some of the added ions will combine with opposite ions to produce undissociated HA molecule. The net result is a decrease in degree of dissociation. This is called common-ion effect.

Solubility of PbI_2 decreases in presence of $Pb(NO_3)_2$, common ion
but increases in presence of KNO_3. - Explain.
or,
uncommon ion
Solubility of a sparingly soluble salt decreases in presence of common ion, but increases in presence of uncommon ion. - Explain.

⇒ We consider the saturated solution of the sparingly soluble salt, PbI_2, if excess solid is added, then in aqueous medium the following equilibrium exists:

$$PbI_2(s) \rightleftharpoons Pb^{2\oplus}(aq) + 2I^{\ominus}(aq)$$

The solubility product is given by -

$$K_{sp} = a_{Pb^{2\oplus}} \cdot a^2_{I^{\ominus}}$$
$$= (c_{Pb^{2\oplus}} \cdot c^2_{I^{\ominus}}) \cdot (\gamma_\pm)^3 \qquad \gamma_\pm \simeq 1$$
so, neglected.

where 'c' is the concentration in moles per litre of the constituent ion and $\gamma_\pm$ is the mean ionic activity co-efficient of the electrolyte. At a given temperature K_{sp} remains constant.

If we add $Pb(NO_3)_2$ in PbI_2, then since there are already $Pb^{2\oplus}$ ion, so to keep K_{sp} constant concentration of $I^{\ominus}$ ion must decrease. But $I^{\ominus}$ ions are comming from PbI_2 alone, so solubility of PbI_2 will decrease.

But if we add KNO_3 in PbI_2 solution, then ionic strength of the solution will be increased. So from Debye - Hückel limiting law ($\log \gamma_{\pm} = -AZ_{\oplus}Z_{\ominus}\sqrt{\mu}$) $\gamma_{\pm}$ should decrease. To keep K_{sp} constant $C_{Pb^{\oplus}}$ and $C_{I^{\ominus}}$ should increase. So solubility should increase. Thus, the solubility of a salt decreases in presence of common ion, but increases in presence of uncommon ion.

The Solubility of AgCl decreases in presence of KCl solution, but increases in presence of ammonia solution. — Explain.

=> We consider the saturated solution of AgCl, if excess solid is added then following equilibrium exists:

$$AgCl(s) \rightleftharpoons Ag^{\oplus}(aq) + Cl^{\ominus}(aq)$$

The thermodynamic solubility product is

$$K_{sp} = (C_{Ag^{\oplus}} \cdot C_{Cl^{\ominus}}) \cdot (\gamma_{\pm})^2$$

Since K_{sp} is constant at a given temperature. If we add KCl solution in AgCl, then due to common ion $Cl^{\ominus}$, the solubility of AgCl decreases.

But if we add ammonia solution to AgCl, then a soluble complex $Ag(NH_3)_2Cl$ is produced. The various equilibrium involved in the dissolution of AgCl in aqueous ammonium solution are as follows:

$$AgCl(s) \rightleftharpoons Ag^{\oplus}(aq) + Cl^{\ominus}(aq)$$

$$Ag^{\oplus} + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^{\oplus}$$

$$AgCl(s) + 2NH_3 \rightleftharpoons \underbrace{[Ag(NH_3)_2]^{\oplus}}_{\text{stable soluble}} + Cl^{\ominus}$$

The equilibrium is shifted towards right and so solubility of AgCl increases in presence of ammonia solution.

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