

7. Debye-Huckel limiting law

1 Review

→ Reference electrode (CE, WE, RE)

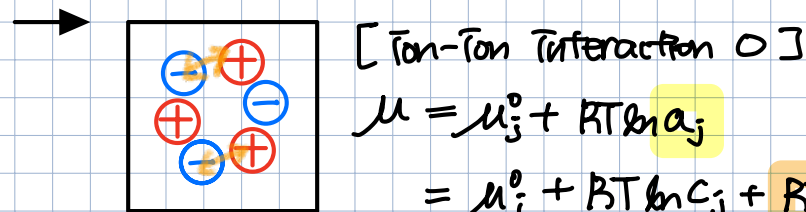
2 Ion-Ion Interaction & activity

→ Activity : 특정 성분의 양 (농도, 몰분율) & 그 성분의 종류 (불가역적인 상호작용)에 영향을 받는, 이온들의 "유효농도"

→ $a_i = \gamma_i \cdot c_i$ (activity coefficient : $\gamma_i = \frac{a_i}{c_i}$)

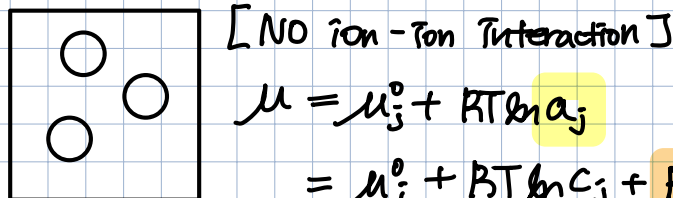
→ 순수한 물질일 때 (혼합물 X) $\gamma = 1$, but 혼합될수록 (이온화될수록) $\gamma < 1$

→ Why? : 불가역적인 상호작용 & Ion-solvent 상호작용



$$\mu = \mu_j^0 + RT \ln a_j$$

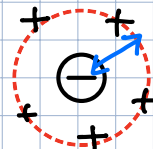
$$= \mu_j^0 + RT \ln c_j + RT \ln \gamma_j \rightarrow \text{농도가 커질수록 (c ↑) 값이 (↓) → stabilized (Gibbs free E ↓)}$$



$$\mu = \mu_j^0 + RT \ln a_j$$

$$= \mu_j^0 + RT \ln c_j + RT \ln \gamma_j \rightarrow = 0 \rightarrow \text{less stabilized (Gibbs free E ↑)}$$

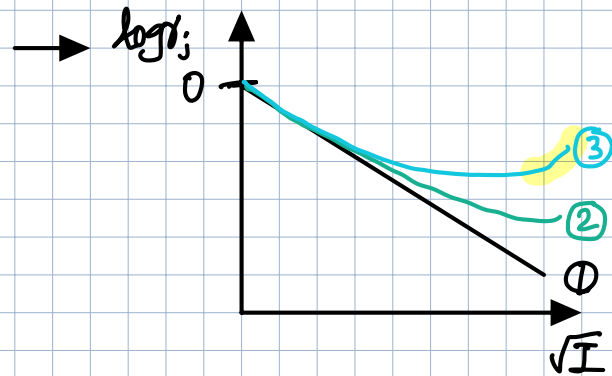
→ Ionic strength : $I = \frac{1}{2} \sum c_j z_j^2$ & Debye length $\propto \frac{1}{\sqrt{I}}$



→ Ionic concentration = Ionic strength ↑
 = Stabilization ↑
 = Debye length ↓
 = γ ↓

③ Debye-Huckel limiting law

→ Ionic strength (이온 강도) : 전체 이온들의 농도를 합친다!



① Debye-Huckel limiting law (DHL) : $\log \gamma_j = -A z_j^2 \sqrt{I}$

↳ $< 10^{-2} M$ & point charge (real: hydration & point charge x)

② Extended Debye-Huckel limiting law (EDHL) : $\log \gamma_j = \frac{-A z_j^2 \sqrt{I}}{1 + B a \sqrt{I}}$

↳ only consider "Ion-Ion Interaction"

③ Robinson - Stokes (R-S) : $\log \gamma_j = \frac{-A z_j^2 \sqrt{I}}{1 + B a \sqrt{I}} + C I$

↳ Ion-dipole Interaction (즉, Ion-solvent Interaction)

↳ 용액 농도가 높을수록 water 분자 끌어들임, 즉 stabilize 시켜 분자 끌어들임, ∴ γ 가 증가