Subing (17)→(15) gives $\mu_{\pm} = \frac{\mu_{solute}}{\nu} = \frac{\nu_{+}\mu_{+} + \nu_{-}\mu_{-}}{\nu}$ (15)

$$\begin{aligned}\mu_{solute} &= \nu\mu_{\pm} = \nu(\mu_{\pm}^{o} + RT\ln a_{\pm}) \\ &= \nu\mu_{\pm}^{o} + RT\ln a_{\pm}^{\nu}\end{aligned} \qquad (23)$$

Subing (22)→ (23) using (19) and (21) gives,

$$\begin{aligned}\mu_{solute} &= \nu\mu_{\pm}^{o} + RT\ln(\frac{m_{\pm}}{m^{o}})^{\nu}\gamma_{\pm}^{\nu} \\ &= \nu\mu_{\pm}^{o} + RT\ln[\frac{(\nu_{+}^{\nu_{+}}\nu_{-}^{\nu_{-}})^{\frac{1}{\nu}}m}{m^{o}}]^{\nu} + \nu RT\ln\gamma_{\pm} \\ &= [\nu\mu_{\pm}^{o} + RT\ln\nu_{+}^{\nu_{+}}\nu_{-}^{\nu_{-}}] + \nu RT\ln\frac{m}{m^{o}} + \nu RT\ln\gamma_{\pm}\end{aligned} \qquad (24)$$

1st term in bracket ≡ Normal standard state (Henry's std state)

2nd term in bracket comes from the chemical formula of the solute.

[1st term + 2nd term] ≡ New standard state

$\equiv \mu^{oo}$

Then (24) becomes

$$\mu_{solute} = \mu_{solute}^{oo} + \nu RT\ln\frac{m}{m^{o}} + \nu RT\ln\gamma_{\pm} \qquad (25)$$

►For ideal ionic solution $\gamma_{\pm} = 1$, and the 1st two terms are left.

►The last term describes deviation from the ideal behavior and most important here. It is obtained through experiments as follow;

1) Measure $\gamma_{\pm}$ for solvent from bpe and fpd as follow.

→ Use Gibbs-Duhem eq ($d\mu_2 = -\frac{n_1 d\mu_1}{n_2}$) calculate $\gamma_{\pm}$ for solute!

2) Measure the electrochemical cell (to be treated in 11.8).

3) Use $Debye-H\ddot{u}ckel$ model for dilute electrolytes solution (beliw).

10.4 Calculating $\gamma_{\pm}$ using Debye-Hückel model

Solute ions in solvent causes a electrostatic potential, $\varphi(r)$← Can be calculated if the spatial distribution of ions is known.

In dilute electrolyte solution the energy change experienced by an ion of charge $\pm ze$ is much smaller than the thermal energy (kT), i.e.,

$$\pm ze\phi << kT \qquad (26)$$

e=charge on a proton
k=Boltzmann constant (=R/AN)

In this limit (viz. 26) the dependence of ϕ on spatial distribution of ions around an arbitrary central ion can be calculated as follow.

Electrical potential around an isolated ion in a dielectric medium;

$$\Phi_{isolatedion(r)} = \frac{\pm ze}{4\pi\epsilon_r\epsilon_0 r} \qquad (27)$$

And in the dilute electrolyte solution;

$$\Phi_{solution}(r) = \frac{\pm ze}{4\pi\epsilon_r\epsilon_0 r}exp(-\kappa r) \qquad (28)$$

Due to the exponential decrease, (28) falls off much more rapidly than (27), called "Potential of an ion is screened by other ions". The κ (Debye length=$1/\kappa$) is related to the individual charges and molality (m) by

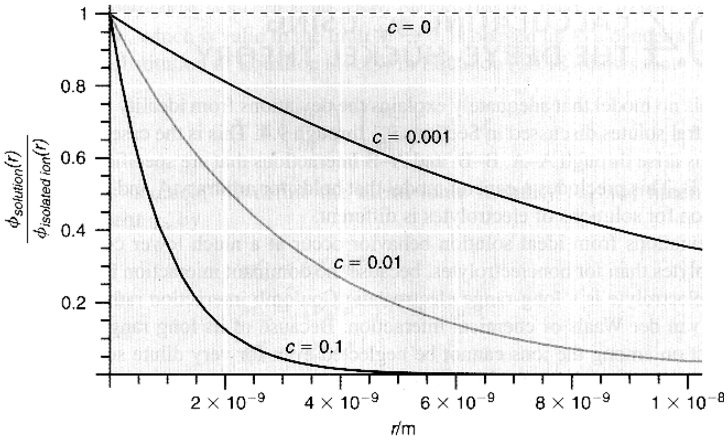
$$\kappa^2 = e^2 N_A (1000Lm^{-3}) m \left(\frac{\nu_+ z_+^2 + \nu_- z_-^2}{\epsilon_0\epsilon_r kT}\right)\rho_{solvent} \qquad (29)$$

It is noted that screening is more effective with solute concentration, multiple charged ions, and with larger value of ν_+ and ν_-.

See the ratio of the two potentials in Figure 10.3 with different values of molality for an aqueous solution of 1-1 electrolyte.

FIGURE 10.3

The ratio of the falloff in the electrostatic potential in the electrolyte solution to that for an isolated ion is shown as a function of the radial distance for three different molarities, c of a 1−1 electrolyte such as NaCl.



$$\frac{\phi_{solution}(r)}{\phi_{isolated\,ion}(r)} = e^{-\kappa r}$$

Note: Potential fall off much more rapidly with r in electrolyte solution than in dielectric.
Rapid falls off the ratio with increasing electrolyte concentration→ The central ion is surrounded by the oppositely charged ions forming a diffuse ion cloud to reduce the net charge of the central ion. (Figure 10.4). The net effect is to screen the central ion from the rest of solution at a screening length of 1/κ. At κr≃8, the net charge becomes zero. Larger value of κ corresponds to smaller diffuse cloud (r) and more effective screening.

Figure 10.4
Concentration dependent terms is defined as ionic strength (I) ;

$$I = \frac{m}{2}\sum_i (\nu_{i+} z_{i+}^2 + \nu_{i-} z_{i-}^2) = \frac{1}{2}\sum_i (m_{i+} z_{i+}^2 + m_{i-} z_{i-}^2) \qquad (30)$$

EXAMPLE PROBLEM 10.2

Calculate I for (a) a 0.050 molal solution of NaCl and for (b) a

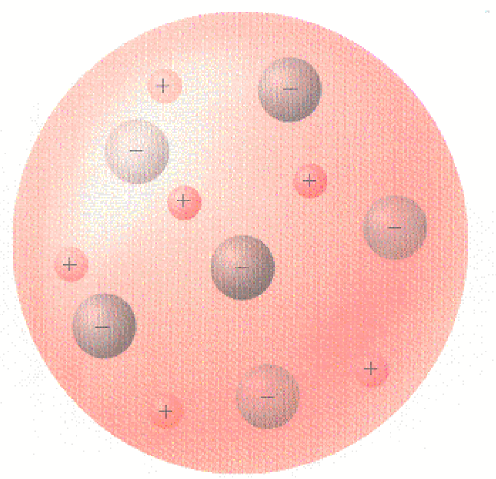


FIGURE 10.4

Pictorial rendering of the arrangement of ions about an ion in an electrolyte solution. The negatively charged central ion is more likely to have oppositely charged ions as neighbors. The large circle represents a sphere of radius $r \sim 8/\kappa$. From a point outside of this sphere, the charge on the central ion is essentially totally screened.

Na_2SO_4 solution of the same molality.

Solution

a. $I_{NaCl} = \frac{m}{2}(\nu_+ z_+^2 + \nu_- z_-^2) = \frac{0.050\,mol\,kg^{-1}}{2} \times (1+1) = 0.050\,mol\,kg^{-1}$

b. $I_{Na_2SO_4} = \frac{m}{2}(\nu_+ z_+^2 + \nu_- z_-^2) = \frac{0.050\,mol\,kg^{-1}}{2} \times (2+4) = 0.15\,mol\,kg^{-1}$

Subing (30) into (29) gives,

$$\kappa = \sqrt{\frac{2e^2 N_A}{\epsilon_0 k T}(1000\,L m^{-3})}\sqrt{(\frac{I}{\epsilon_r})\rho_{solvent}}$$

$$= 2.91 \times 10^8 \sqrt{\frac{I/mol\,kg^{-1}\rho_{solvent}}{\epsilon_r \qquad kg\,L^{-1}}}\,m^{-1} \quad \text{at } 298\text{K} \qquad (31)$$

(Note the numerator of the second bracket in eq 29 is replaced by 2I/m)

1st term=fundamental constants independent of solvent and solute.

2nd term= ionic strength of solution and relative permittivity of solute

---

EX) Calculate the Debye-Hückel screening length $\frac{1}{\kappa}$ at 298 K in a 0.00100m solution of NaCl.

$$\kappa = 9.211\times10^{8}\sqrt{\frac{{}^{I}\!/_{\mathrm{mol\,kg^{-1}}}}{\varepsilon_r}}\ \mathrm{m^{-1}} = 9.211\times10^{8}\sqrt{\frac{0.00100}{78.54}}\ \mathrm{m^{-1}} = 3.29\times10^{6}\,\mathrm{m^{-1}}$$

$$\frac{1}{\kappa} = 3.04\times10^{-7}\,\mathrm{m} = 304\ \mathrm{nm}$$

In terms of conventional unit of mol/L, and ε_r=78.5 for water,

$\kappa = 3.29\mathrm{x}10^{9}\sqrt{I}\ \mathrm{m^{-1}}$ @298K.

By calculating charge distribution and work for charging to z_+ and z_- from neutral state, Debye-H$\ddot{u}$ckel obtained the mean activity coeff called Debye-H$\ddot{u}$ckel limiting law (Only obeyed for small I);

$$\ln\gamma_\pm = -\,|\,z_+z_-\,|\,\frac{e^2\kappa}{8\pi\epsilon_0\epsilon_r kT} \qquad (32)$$

►Negative (-) sign ► $\gamma_\pm < 1$

→ Chemical potential of electrolyte solutions<Uncharged solution (25)

$$\mu_{solute} = \mu^{oo}_{solute} + \nu RT\ln\frac{m}{m^o} + \nu RT\ln\gamma_\pm$$

→ Debye-H$\ddot{u}$ckel model describes lowering of enengy.

►$\ln\gamma_\pm \propto (-)\kappa$ (32), $\kappa \propto \sqrt{I}$ → $\ln\gamma_\pm \propto -\sqrt{I}$ (See Figure 10.5)

►$\ln\gamma_\pm$ decreases with increased ionic strength.

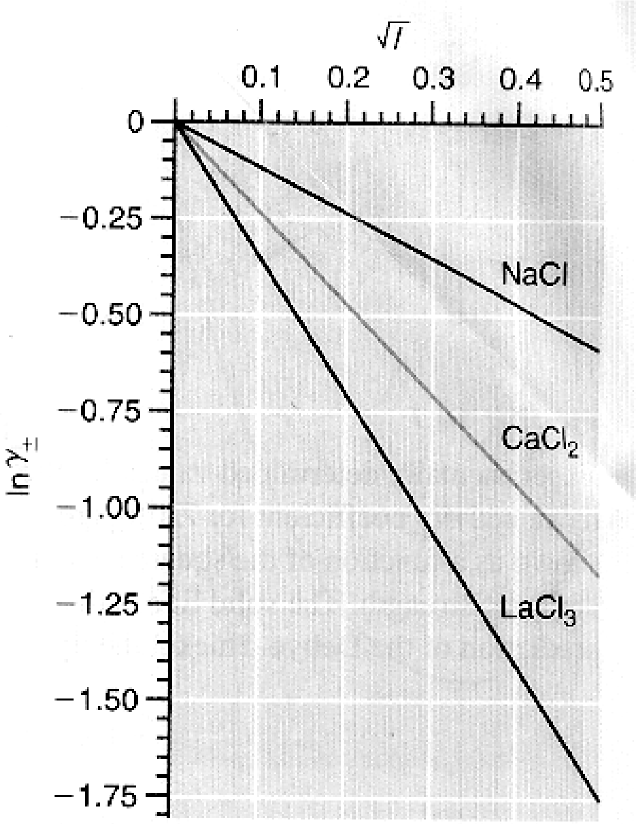


FIGURE 10.5

The decrease in the Debye–Hückel mean activity coefficient with the square root of the ionic strength is shown for a 1−1, a 1−2, and a 1−3 electrolyte, all of the same molality in the solute.

Figure 10.5

See different slopes for the same solute concentration is due to the different z_+ and z_-.

Eq 32 is simplified for aqueous solution @ 298K to

$$\log\gamma_\pm = -0.5092\,|\,z_+z_-\,|\,\sqrt{I} \quad \text{or} \quad \ln\gamma_\pm = -1.173\,|\,z_+z_-\,|\,\sqrt{I} \qquad (33)$$

Figure 10.6 compares D-H model with experimental data. Deviation from the model is seen from $\sqrt{I}$=0.1 ($AgNO_3$) and $\sqrt{I}$=0.06 ($CaCl_2$).

See as I→0, data obey D-H model (limiting law).

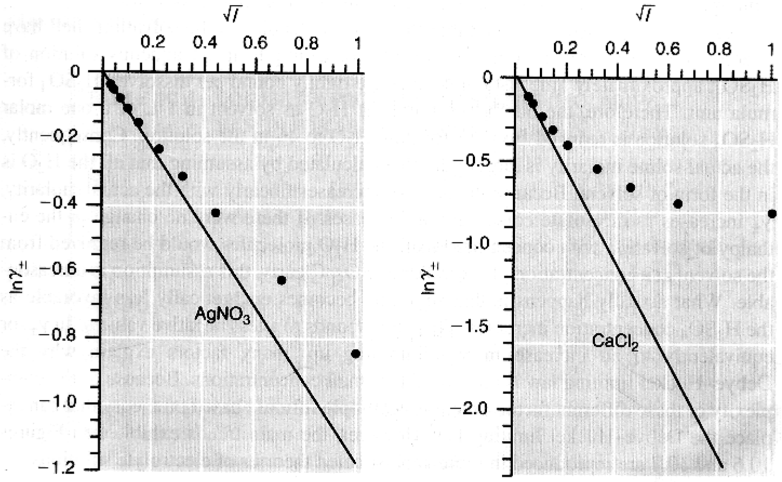


FIGURE 10.6

The experimentally determined activity coefficients for $AgNO_3$ and $CaCl_2$ are shown as a function of the square root of the ionic strength. The solid lines are the prediction of the Debye–Hückel theory.

EX) Calculate I, $\gamma_\pm$, and $a_\pm$ for a 0.0250m solution of $AlCl_3$ at 298K. Assume complete dissociation.

$$AlCl_3 \Rightarrow v_+ = 1,\ v_- = 3,\ z_+ = 3,\ z_- = 1$$

$$I = \frac{0.0250}{2}(9+3) = 0.1500 \text{ mol kg}^{-1}$$

$$\ln\gamma_\pm = -1.173\times 3\times\sqrt{0.1500} = -1.3629$$

$$\gamma_\pm = 0.2559$$

$$a_\pm = \left(\frac{m_\pm}{m^\circ}\right)\gamma_\pm$$

$$m_\pm^4 = (0.025)(0.025\times 3)^3 = 1.0546875\times 10^{-5}$$

$$m_\pm = 0.05699 \text{ mol kg}^{-1}$$

$$a_\pm = 0.05699\times 0.2559 = 0.0146$$

Empirical model for high concentration (Davis eq)

$$\log_{10}\gamma_\pm = -0.51\,|\,z_+z_-\,|\left[\frac{(\frac{1}{m^o})^{1/2}}{1+(\frac{1}{m^o})^{1/2}} - 0.20(\frac{1}{m^o})\right] \qquad (34)$$

Better agreement with experimental data (Figures 6, 7) at high solute concentrations is seen (See dotted lines of D-H and solid line for

Davis model)-but (34) has no theoretical background.

10.5 Chemical equilibrium in electrolyte solutions

From eq 9.67,

$$K=\prod_i (a_i^{eq})^{\nu_i} \qquad (35)$$

Activity is defined as

$$a_i=\gamma_i \frac{c_i}{c_o} \qquad (36)$$

where $\frac{c_i}{c_o}$ is the reduced (dimensionless) concentration of malarity.

Consider the degree of dissociation of MgF_2 in water.

K_{sp}: Equilibrium constant in terms of molarity for ionic salt (sp=solubility product).

$$MgF_2(s) \rightarrow Mg^{2+}(aq) + 2F^-(aq) \qquad (37)$$

K_{sp} = $6.4\text{x}10^{-9}$ (See Table 4 for selected substance).

Activity of pure solid = 1, then (35) can be written as:

$$K_{sp}=a_{Mg^{2+}}a_{F^-}^2=(\frac{c_{Mg^{2+}}}{c^o})(\frac{c_{F^-}}{c^o})^2\gamma_\pm^3=6.4\times 10^{-9} \qquad (38)$$

From the stoichiometry: $C_{F^-} = 2C_{Mg}^{2+}$ (38)'

For (38) and (38)':

\# of variables(M=3): $\gamma_\pm$, C_{F^-}, C_{Mg}^{2+}

\# of Equations(N=2): (38), (39)

→The degree of freedom: F=M-N=1.

→Not directly solvable.

→Solution is obtained by iteration.

Assign arbitrary value for $\gamma_{\pm}$ (1 is a good start.)

→Calculate C_{F^-} (and $C_{Mg^{2+}}$) from (38).

→Calculate the ionic strength from (30)

$$I = \frac{m}{2}\sum_i (\nu_{i+}z_{i+}^2 + \nu_{i-}z_{i-}^2) = \frac{1}{2}\sum_i (m_{i+}z_{i+}^2 + m_{i-}z_{i-}^2) \qquad (30)$$

→Calculate $\gamma_{\pm}$ from (33) as 0.870

$$\log \gamma_{\pm} = -0.5092\ |\ z_+z_-\ |\ \sqrt{I} \qquad (33)$$

→Not agreed with the assigned value of 1.

⇒Repeat the same procedure with the calculated value until satisfied (Direct substitution).