

CH. 9 Electrolyte Solutions

9.1 Activity Coefficient of a Nonvolatile Solute in Solution and Osmotic Coefficient for the Solvent

As shown in Ch. 6, the chemical potential is

$$\mu_i = \mu_i^0 + RT \ln a_i = \mu_i^0 + RT \ln(\gamma_i \xi_i) \quad (9-1)$$

where μ_i^0 is the chemical potential in the standard state and ξ is a measure of concentration.

For a nonvolatile solute, its pure liquid is often not a convenient standard state because a pure nonvolatile solute cannot exist as a liquid.

For the dissolved solute,

$$\mu_i = \mu_i^* + RT \ln a_i = \mu_i^* + RT \ln(\gamma_i \xi_i) \quad (9-2)$$

μ_i^* is the chemical potential of i in a hypothetical ideal solution at unit concentration ($\xi_i = 1$).

In the ideal solution $\gamma_i = 1$ for all compositions

In real solution, $\gamma_i \rightarrow 1$ as $\xi_i \rightarrow 0$

A common misconception:

The standard state for the solute is the solute at infinite dilution. (×)

At infinite dilution, the chemical potential of the solute approaches $-\infty$.

Thus, the standard state should be at some non-zero concentration.

A standard state need not be physically realizable, but it must be well-defined.

For convenience, unit concentration $\xi_i = 1$ is used as the standard state.

Three composition scales:

Molarity (moles of solute per liter of solution, c_i)

$$\mu_i = \mu_i^\ominus + RT \ln(\gamma_i^{(c)} c_i) \quad (9-3)$$

The standard state of the solute is a hypothetical ideal 1-molar solution of i .

In real solution, $\gamma_i^{(c)} \rightarrow 1$ as $c_i \rightarrow 0$

Molality (moles of solute per kg of solvent, m_i)

// commonly used for

electrolytes

// density of solution not needed

$$\mu_i = \mu_i^\ominus + RT \ln(\gamma_i^{(m)} m_i) \quad (9-4)^2$$

The standard state is hypothetical ideal 1-molal solution of i .

In real solution, $\gamma_i^{(m)} \rightarrow 1$ as $m_i \rightarrow 0$

Mole fraction x_i

Molality is an inconvenient scale for concentrated solution, and the mole fraction is a more convenient scale.

$$\mu_i = \mu_i^* + RT \ln(\gamma_i^{(x)} x_i) \quad (9-5)$$

The standard state is hypothetical ideal solution of $x_i = 1$.

In real solution, $\gamma_i^{(x)} \rightarrow 1$ as $x_i \rightarrow 0$

For the solvent, the pure liquid is used as the standard state.

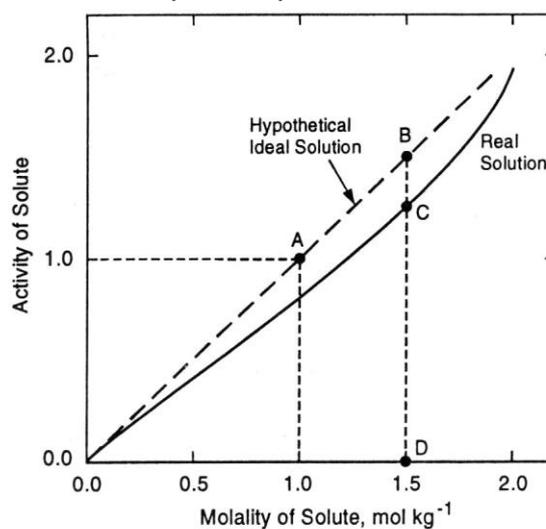


Figure 9-1 Schematic representation of the activity of a nondissociating solute as a function of its molality. Point A shows the standard state. When the solute's molality is 1.5, its activity coefficient is given by $\overline{CD} / \overline{BD}$.

The activity and the activity coefficient are affected by the choice of standard state and also by the choice of concentration scale.

Relationships to convert activity coefficients:

$$\gamma_2^{(x)} = \gamma_2^{(m)}(1 + 0.001M_s m_2) \quad (9-6)$$

$$\gamma_2^{(m)} = \gamma_2^{(c)} c_2 / (m_2 d_s) \quad (9-7)$$

$$\gamma_2^{(x)} = \gamma_2^{(c)} [d + 0.001c_2(M_s - M_2)] / d_s \quad (9-8)$$

where d is the mass density (g cm^{-3}) of the solution, d_s the mass density of pure solvent, M_2 the molar mass of the solute, and M_s the molar mass of the solvent.

At constant temperature and pressure, the activity of the solvent is obtained by the Gibbs-Duhem equation.

$$n_s d\mu_s + n_i d\mu_i = 0$$

$$\mu_s = \mu_s^0 + RT \ln a_s \quad \mu_i = \mu_i^\ominus + RT \ln a_i^{(m)} = \mu_i^\ominus + RT \ln \gamma_i^{(m)} m_i$$

$$RT d \ln a_s = -\frac{n_i}{n_s} RT d \ln \gamma_i^{(m)} m_i$$

For 1 kg of solvent, $n_s = 1000/M_s$, $n_i = m_i$

Integrating from pure solvent to solution at constant T, P

$$\ln a_s = -\int_0^{m_i} \frac{M_s}{1000} m_i \frac{d \ln \gamma_i^{(m)} m_i}{dm_i} dm_i$$

$$\ln a_s = -\frac{M_s}{1000} m_i - \frac{M_s}{1000} \int_0^{m_i} m_i \left(\frac{\partial \ln \gamma_i^{(m)}}{\partial m_i} \right)_{T,P} dm_i \quad (9-9)$$

The osmotic pressure π of the solution is

$$\pi = -\frac{RT}{v_s} \ln a_s \quad (9-10)$$

Eq (4-41)

The osmotic coefficient is defined by

$$\phi^{(m)} = \frac{\pi(\text{real})}{\pi(\text{ideal})} = \frac{\ln a_s(\text{real})}{\ln a_s^{(m)}(\text{ideal})} = 1 + \frac{1}{m_i} \int_0^{m_i} m_i \left(\frac{\partial \ln \gamma_i^{(m)}}{\partial m_i} \right)_{T,P} dm_i \quad (9-11)$$

$$\ln a_s^{(m)}(\text{ideal}) = -\frac{M_s}{1000} m_i \quad \text{from (9-9) with } \gamma_i^{(m)} = 1 \text{ for ideal solution}$$

Experimentally, the osmotic coefficient is often obtained from vapor-pressure measurement.

The activity of the solvent at modest pressure is

$$a_s = \frac{P_s}{P_s^{\text{sat}}} \quad (9-12)$$

P_s is the partial pressure of the solvent, and P_s^{sat} is the vapor pressure of the pure solvent.

From (9-10) and (9-12),

$$\phi^{(m)} = \frac{\pi(real)}{\pi(ideal)} = \frac{\ln a_s}{\ln a_s^{(m)}(ideal)}$$

$$\phi^{(m)} = -\frac{1000}{M_s m_i} \ln \frac{P_s}{P_s^{sat}} \quad (9-11a)$$

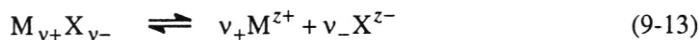
9.2 Solution of an Electrolyte. Electroneutrality

Cations and anions are not independent components because of electroneutrality.

The electroneutrality imposes the condition that the number of moles of the individual ionic species cannot be varied independently.

In aqueous NaCl, there are three species but only two components.

Electrolyte dissociation is represented by



Electroneutrality requires that

$$v_+ z_+ + v_- z_- = 0 = v_+ z_+ - v_- |z_-| \quad (9-14)$$

For example,



$v_+ = 2$, $z_+ = 1$, $v_- = 1$, and $z_- = -2$.

The criterion for chemical equilibrium is

$$\mu_{M_{v_+} X_{v_-}} = v_+ \mu_{M^{z_+}} + v_- \mu_{X^{z_-}} \quad (9-15)$$

Using the molality scale, Eq (9-4), we have

$$\mu_{M_{v_+} X_{v_-}} = \mu_{M_{v_+} X_{v_-}}^\ominus + v_+ RT \ln(m_+ \gamma_+) + v_- RT \ln(m_- \gamma_-) \quad (9-16)$$

and

$$\mu_{M_{v_+} X_{v_-}}^\ominus = v_+ \mu_{M^{z_+}}^\ominus + v_- \mu_{X^{z_-}}^\ominus \quad (9-17)$$

Rewriting (9-16) in a more convenient form

$$\begin{aligned} \mu_{MX} &= \mu_{MX}^\ominus + RT \ln(m_+^{v_+} m_-^{v_-}) + RT \ln(\gamma_+^{v_+} \gamma_-^{v_-}) \\ &= \mu_{MX}^\ominus + RT \ln(a_+^{v_+} a_-^{v_-}) \end{aligned} \quad (9-16a)$$

The mean ionic molality m_{\pm} and the mean ionic activity coefficient γ_{\pm} are

defined by

$$m_{\pm} = (m_+^{v_+} m_-^{v_-})^{1/v} \quad (9-18)$$

$$\gamma_{\pm} = (\gamma_+^{v_+} \gamma_-^{v_-})^{1/v} \quad (9-19)$$

where $v = v_+ + v_-$

γ_{\pm} is a measurable quantity while γ_+ and γ_- are not independently measurable.
// We cannot vary moles of cations alone due to electroneutrality

Eq (9-16a) becomes

$$\begin{aligned} \mu_{MX} &= \mu_{MX}^{\ominus} + vRT \ln(m_{\pm} \gamma_{\pm}^{(m)}) \\ &= \mu_{MX}^{\ominus} + vRT \ln(a_{\pm}^{(m)}) \end{aligned} \quad (9-20)$$

with

$$a_{\pm} = [(a_+)^{v_+} (a_-)^{v_-}]^{1/v} = m_{\pm} \gamma_{\pm}^{(m)} \quad (9-21) \quad \text{the mean ionic activity}$$

For strong electrolyte, dissociation is essentially complete

$$m_+ = v_+ m_{MX} \quad \text{and} \quad m_- = v_- m_{MX}$$

The mean ionic activity coefficient is

$$\gamma_{\pm}^{(m)} = \frac{a_{\pm}}{m_{MX} (v_+^{v_+} v_-^{v_-})^{1/v}} \quad (9-22)^{10}$$

For NaCl (1-1 electrolyte)

$$m_{\pm} = m_{MX} \quad \text{and} \quad \gamma_{\pm}^{(m)} = [(\gamma_{Na^+})(\gamma_{Cl^-})]^{1/2}$$

For 2-1 (or 1-2) electrolyte (e.g. CaCl₂)

$$m_{\pm} = 4^{1/3} m_{MX} \quad \text{and} \quad \gamma_{\pm}^{(m)} = [(\gamma_{Ca^{2+}})(\gamma_{Cl^-})]^{1/3}$$

Table 9-1 Mean ionic molality (m_{\pm}) for several electrolytes.

| Type of Solute | Example | m_{\pm} |
|----------------|---|--------------------|
| Electrolyte | $M_{v_+} X_{v_-}$ | m_{MX} |
| 1-1; 2-2; 3-3 | NaCl; ZnSO ₄ | m_{MX} |
| 2-1; 1-2 | CaCl ₂ | $4^{1/3} m_{MX}$ |
| 3-1; 1-3 | AlCl ₃ | $27^{1/4} m_{MX}$ |
| 4-1; 1-4 | Th(NO ₃) ₄ | $256^{1/5} m_{MX}$ |
| 3-2 | Al ₂ (SO ₄) ₃ | $108^{1/5} m_{MX}$ |

Activity coefficient as a function of concentration

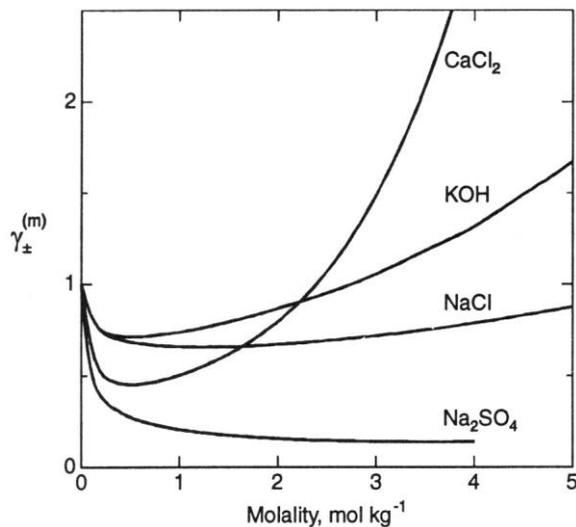


Figure 9-2 Mean ionic activity coefficients (Robinson and Stokes, 1970) for some electrolytes in aqueous solution at 25°C.

In dilute solution, $\gamma_{\pm}^{(m)}$ decreases rapidly with increasing concentration. For a given valence type, $\gamma_{\pm}^{(m)}$ at low concentrations ($m < 0.01$) is independent of its chemical nature of the ions. (explained by the Debye-Hückel theory)

Activity data for electrolytes are obtained from measurements of the potentials of electrochemical cells, from solubility and colligative-property measurements and from vapor-pressure measurements.

The standard state for dissociating solute is at $m_{\pm} = 1$ (unit molality), not at $m_{MX} = 1$.

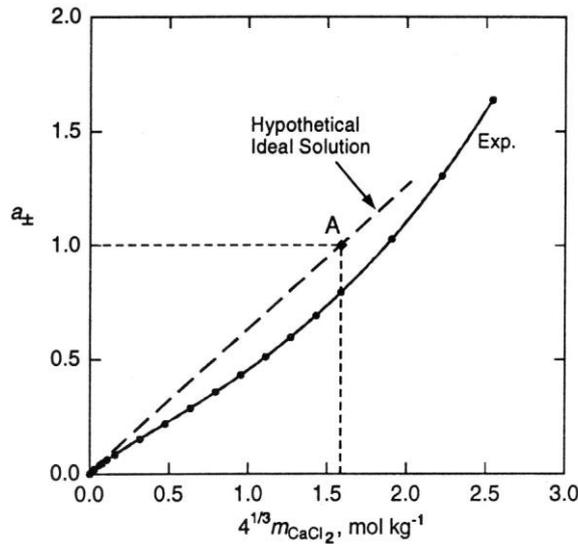


Figure 9-3 Mean ionic activity of aqueous CaCl_2 at 25°C as a function of its molality (Robinson and Stokes, 1970). Point A shows the standard state. The (ideal solution) straight line goes through coordinates (0, 0) and $(1, 4^{1/3})$. When $m_{\text{CaCl}_2} = 1 \text{ mol kg}^{-1}$, $4^{1/3}m_{\text{CaCl}_2} = 1.587 \text{ mol kg}^{-1}$.

$$m_{\pm} = 4^{1/3} m_{\text{CaCl}_2}$$

9.3 Osmotic Coefficient in an Electrolyte Solution

The chemical potential of the solvent using the molality scale is

$$\mu_s = \mu_s^0(T, P) + RT \ln a_s = \mu_s^0(T, P) + RT \phi^{(m)} \ln a_s^{(m)}(\text{ideal}) \quad (9-23)$$

$\phi^{(m)}$ is the osmotic coefficient. $\phi^{(m)} = \frac{\pi(\text{real})}{\pi(\text{ideal})} = \frac{\ln a_s}{\ln a_s^{(m)}(\text{ideal})}$

If MX dissociates into ν ions, the ideal-solution activity of the solvent is

$$\ln a_s^{(m)}(\text{ideal}) = -\frac{M_s}{1000} \nu m_{\text{MX}} \quad (9-24)$$

For real solution, substitution of (9-12) into (9-23) gives

$$\phi^{(m)} = -\left(\frac{1000}{\nu m_{\text{MX}} M_s}\right) \ln a_s \quad (9-25)$$

In the mole fraction scale, the chemical potential of the solvent is

$$\mu_s = \mu_s^0(T, P) + RT \ln a_s = \mu_s^0 + RT \ln(\gamma_s x_s) \quad (9-23a)$$

The mole fraction of the electrolyte is defined as

$$x_{\text{MX}} = \frac{n_{\text{MX}}}{n_w + \nu n_{\text{MX}}} = \frac{m_{\text{MX}}}{55.51 + \nu m_{\text{MX}}} \quad (9-26)^{12}$$

account

taking ionic species into

Table 9-2 Activity coefficients (γ), and rational (g) and molal osmotic (ϕ) coefficients of aqueous sulfuric acid solutions at 25°C.*

| $m_{\text{H}_2\text{SO}_4}$ | $\gamma_{\pm}^{(m)}$ | $\gamma_{\text{H}_2\text{O}}$ | $g_{\text{H}_2\text{O}}$ | $\phi_{\text{H}_2\text{O}}$ |
|-----------------------------|----------------------|-------------------------------|--------------------------|-----------------------------|
| 0.1 | 0.266 | 1.000 | 0.749 | 0.680 |
| 0.3 | 0.183 | 1.005 | 0.686 | 0.668 |
| 0.5 | 0.156 | 1.008 | 0.708 | 0.676 |
| 1.0 | 0.132 | 1.014 | 0.745 | 0.721 |
| 1.5 | 0.126 | 1.015 | 0.828 | 0.780 |

* Robinson and Stokes (1970). The activity coefficient of the solute, $\gamma_{\pm}^{(m)}$, is based on the molality scale, whereas the activity coefficient of the solvent, $\gamma_{\text{H}_2\text{O}}$, is based on the mole-fraction scale.

9.4 Relation of Osmotic Coefficient to Mean Ionic Activity Coefficient

The mean ionic activity coefficient of the solute and the osmotic coefficient of the solvent are related to each other through the Gibbs-Duhem equation.

At constant temperature and pressure,

$$x_s d \ln a_s + x_{MX} d \ln a_{MX} = 0 \quad (9-31)$$

where x_i is the mole fraction in accord to Eq (9-26).

Rewriting

$$d \ln a_s = -(x_{MX} / x_s) d \ln a_{MX} = -\frac{m}{1000} d \ln a_{MX} \frac{M_s}{M_s}$$

Substituting (9-21)

$$a_{\pm} = [(a_+)^{v_+} (a_-)^{v_-}]^{1/v} = m_{\pm} \gamma_{\pm}^{(m)}$$

We obtain

$$d \ln a_s = -\frac{M_s}{1000} m d \ln a_{MX} = -\frac{M_s}{1000} v m d \ln a_{\pm} = -\frac{M_s}{1000} v m d \ln (m_{\pm} \gamma_{\pm}^{(m)})$$

Note that $d \ln m_{\pm} = d \ln m$ since $m_{\pm} = \text{const} * m_{MX}$

$$\gamma_{\pm}^{(m)} = \frac{a_{\pm}}{m_{MX} (v_+^{v_+} v_-^{v_-})^{1/v}} \quad \text{and (9-25)} \quad \phi^{(m)} = -\left(\frac{1000}{v m_{MX} M_s}\right) \ln a_s$$

From (9-22)

$$d \ln \gamma_{\pm}^{(m)} = d\phi + \frac{1}{m} (\phi - 1) dm \quad (9-32)$$

Integration from pure solvent to the solution of interest gives

$$\ln \gamma_{\pm}^{(m)} = \phi - 1 + \int_0^m \frac{\phi - 1}{m} dm \quad (9-33)$$

the integrand $(\phi - 1) / m$ diverges to $-\infty$ as $m \rightarrow 0$.
changing the independent variable from m to $m^{1/2}$.

$$\ln \gamma_{\pm}^{(m)} = \phi - 1 + 2 \int_0^m \frac{\phi - 1}{m^{1/2}} dm^{1/2} \quad (9-34)$$

The integrand approaches $(-A_{\phi})$ as $m \rightarrow 0$, the Debye-Hückel coefficient of the osmotic coefficient.

In summary,

The experimental activity of solvent gives osmotic coefficient ϕ by Eq (9-25).

$$\phi^{(m)} = -\left(\frac{1000}{v m_{MX} M_s}\right) \ln a_s \quad (9-25)$$

The activity coefficient of the solute is then calculated from Eq (9-34).

$$\ln \gamma_{\pm}^{(m)} = \phi - 1 + 2 \int_0^m \frac{\phi - 1}{m^{1/2}} dm^{1/2} \quad (9-34)$$

9.7 Debye-Hückel Limiting Law

The ionic strength of the solution, I is defined by

$$I(\text{mol kg}^{-1}) = \frac{1}{2} \sum_i m_i z_i^2 \quad (9-45)$$

a measure of concentration of ions

For seawater, $I = 0.72 \text{ mol kg}^{-1}$

Table 9-3 Concentrations of major ions in oceanic seawater (Clegg and Whitfield, 1991).

| Component | Molality (mol kg ⁻¹) |
|-------------------------------|----------------------------------|
| Na ⁺ | 0.486 |
| Mg ²⁺ | 0.055 |
| Ca ²⁺ | 0.011 |
| K ⁺ | 0.010 |
| Cl ⁻ | 0.566 |
| SO ₄ ²⁻ | 0.029 |

Solutions of electrolytes depend on both long-range electrostatic interactions and on short-range interactions between ions and between ions and solvent molecules.

At infinite dilution, the ions are too far apart to exert any influence on each other.

The mean ionic activity coefficient is unity.

For dilute solutions, Coulombic forces become important; the local concentration of positive ions is slightly higher than that for the bulk solution (ionic atmosphere).

The Debye-Hückel theory shows that the Coulomb's potential is shielded by the ionic atmosphere, which is

$$(r^{-1}) \exp(-r\kappa) \quad (9-46)$$

where κ^{-1} is called the Debye length (a characteristic distance of interaction).

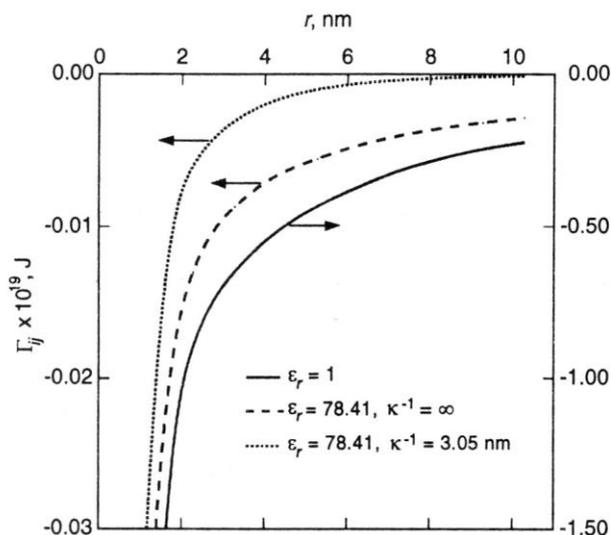


Figure 9-4 Coulomb potential for Cl^- and Na^+ as a function of their (center-to-center) separation distance: in vacuo, $\epsilon_r = 1$; in an infinitely-dilute aqueous solution at 25°C , $\epsilon_r = 78.41$, $\kappa^{-1} = \infty$; shielded Coulomb potential in water at 25°C , $\epsilon_r = 78.41$ and $\kappa^{-1} = 3.05$ nm. Debye length 3.05 nm is that of a 0.01 mol kg^{-1} aqueous NaCl solution at 25°C .

The Debye length is defined by

$$\kappa^{-1} = \left(\frac{\epsilon_0 \epsilon_r RT}{2d_s N_A^2 e^2 I} \right)^{1/2} \quad (9-47)$$

$$\epsilon_0 = 8.85419 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}, \quad e = 1.60218 \times 10^{-19} \text{ C}$$

ϵ_r the relative permittivity or dielectric constant, d_s the solvent density

The Debye length decreases with increasing concentration.

E.g., for a 1-molal solution of 1-1 electrolyte at 25°C , $\kappa^{-1} = 0.03 \text{ nm}$

When $m = 0.001 \text{ mol kg}^{-1}$, $\kappa^{-1} = 9.64 \text{ nm}$.

Electrolyte solutions are nonideal even at low concentration because of long-range Coulombic forces.

From the Debye-Hückel theory, the activity coefficient γ_i of an ion with charge z_i in a dilute solution of ionic strength I is

$$\ln \gamma_i^{(c)} = -z_i^2 \frac{e^2 N_A}{8\pi \epsilon_0 \epsilon_r RT} \kappa \quad (9-48)$$

(For further details, see McQuarrie's book, Statistical Mechanics)

There is no significant difference between molality and molarity for dilute aqueous solution near ambient temperature. (density of water $\approx 1.0 \text{ kg/L}$)

$$\ln \gamma_i^{(m)} = -A_\gamma z_i^2 I^{1/2} \quad (9-48a) \quad \text{activity coefficient of ions}$$

where

$$A_\gamma = \left(\frac{e^2}{\epsilon_0 \epsilon_r RT} \right)^{3/2} \frac{N_A^2}{8\pi} (2d_s)^{1/2} \quad (9-49)$$

Substituting into the definition of the mean ionic activity coefficient (9-19), we obtain

$$\ln \gamma_{\pm}^{(m)} = -A_{\gamma} |z_+ z_-| I^{1/2} \quad (9-50) \quad \text{Debye-Hückel limiting law}$$

The osmotic coefficient is

$$\phi - 1 = -A_{\phi} |z_+ z_-| I^{1/2} \quad (9-51)$$

$$A_{\phi} = \frac{1}{3} A_{\gamma} \quad (9-49a)$$

For aqueous solution at 25°C,

$$\log \gamma_{\pm}^{(m)} (25^\circ \text{C, aqueous}) = -0.510 |z_+ z_-| I^{1/2} \quad (9-50a) \quad \log_{10}$$

The Debye-Hückel limiting law is exact at low concentrations.

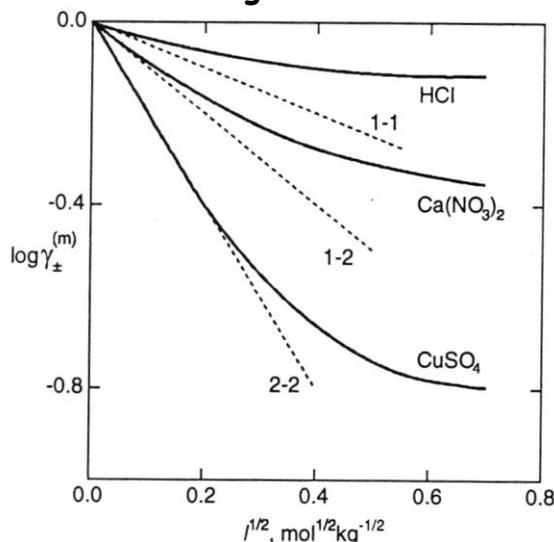


Figure 9-5 Mean ionic activity coefficients as a function of concentration for some aqueous strong electrolytes (Robinson and Stokes, 1970). Full lines show experimental data. Dashed lines are calculated from the Debye-Hückel limiting law [Eq. (9-50a)].

$\gamma_{\pm}^{(m)}$ depends on the valence but not on the chemical nature of the electrolyte.

The Debye-Hückel equation is applicable only at low concentration ($I < 0.01 \text{ mol kg}^{-1}$)

Deviation from the Debye-Hückel law at high concentration is due to nonelectrostatic ion-ion interactions (repulsion and dispersion forces), ion-solvent solvation forces.

Semi-empirical corrections for concentrated electrolyte solutions

For $I < 0.1 \text{ mol kg}^{-1}$,

$$\ln \gamma_{\pm}^{(m)} = \frac{-A_{\gamma} |z_+ z_-| I^{1/2}}{1 + I^{1/2}} \quad (9-52)$$

For $I < 0.1 \text{ mol kg}^{-1}$,

$$\ln \gamma_{\pm}^{(m)} = \frac{-A_{\gamma} |z_+ z_-| I^{1/2}}{1 + I^{1/2}} + bI \quad (9-53)^{19}$$

b is an adjustable parameter

Table 9-4 Mean-ionic activity coefficients of aqueous sodium chloride at 25°C (Robinson and Stokes, 1970).

| m (mol kg ⁻¹)* | $\gamma_{\pm}^{(m)}$ [Experiment] | $\gamma_{\pm}^{(m)}$ [Eq. (9-50)] | $\gamma_{\pm}^{(m)}$ [Eq. (9-52)] | $\gamma_{\pm}^{(m)}$ [Eq. (9-53) with $b = 0.37 \text{ kg mol}^{-1}$] |
|---------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|--|
| 0.001 | 0.965 | 0.964 | 0.965 | 0.965 |
| 0.005 | 0.927 | 0.920 | 0.925 | 0.927 |
| 0.01 | 0.902 | 0.889 | 0.899 | 0.902 |
| 0.05 | 0.819 | 0.769 | 0.807 | 0.822 |
| 0.1 | 0.778 | 0.690 | 0.755 | 0.783 |

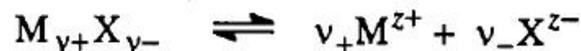
* For a 1:1 electrolyte, molality of the electrolyte is equal to ionic strength.

9.8 Weak Electrolytes

Weak Electrolytes are compounds (such as acetic acid) that are only partially dissociated in aqueous solutions.

At equilibrium, in addition to the ions, there exists a significant concentration of the molecular (undissociated) electrolyte.

The dissociation constant of the weak electrolyte (that depends only on temperature) relates the concentration of the undissociated electrolyte to the concentrations of the ions formed by partial dissociation.



The dissociation (or ionization) equilibrium constant is

$$K = \frac{a_+^{v_+} a_-^{v_-}}{a_{MX}} = \frac{m_+^{v_+} m_-^{v_-} (\gamma_+^{(m)})^{v_+} (\gamma_-^{(m)})^{v_-}}{m_{MX} \gamma_{MX}^{(m)}} = \frac{m_+^{v_+} m_-^{v_-} (\gamma_{\pm}^{(m)})^v}{m_{MX} \gamma_{MX}^{(m)}} \quad (9-54)$$

m_{MX} and $\gamma_{MX}^{(m)}$ are, respectively, the molality and the activity coefficient of the molecular (undissociated) part of the electrolyte.

E.g., Dissociation constant of acetic acid (HAc) into H⁺ and acetate (Ac⁻) ions,

$$K = \frac{m_{H^+} m_{Ac^-} (\gamma_{\pm}^{(m)})^2}{m_{HAc} \gamma_{HAc}^{(m)}}$$

9.9 Salting-out and Salting-in of Volatile Solutes

When the appreciable amount of salt dissolves in a liquid, it significantly affects that liquid's vapor pressure. Further, the dissolved salt affects the solubility of a gas (liquid) in that solvent and finally, if the solvent is mixture of two (or more) volatile components, the dissolved salt influences the composition of the vapor in equilibrium with the solvent mixture.

The solubility of a gas in a salt solution is usually less than that in salt-free water; this solubility decrease is called **salting-out**.

Hydration forces (A simplistic but incomplete explanation)

: Ions like to form complexes with water (hydration), thereby leaving less "free" water available to dissolve the gas.

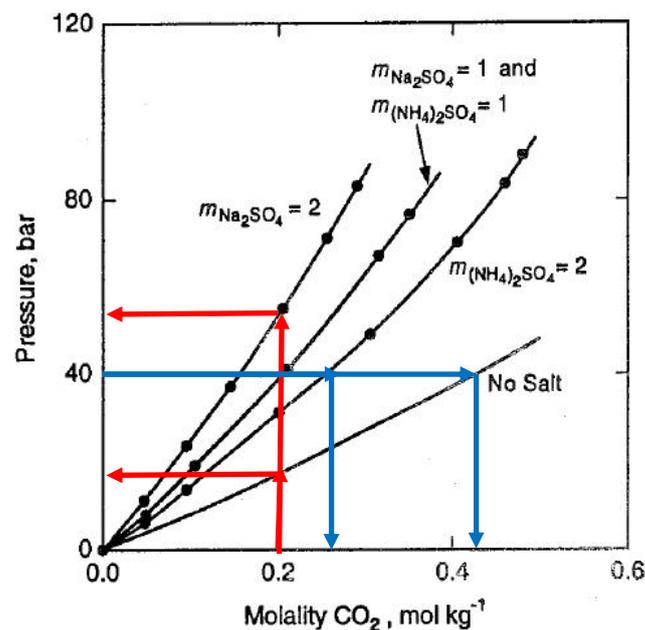


Figure 9-6 Solubility of carbon dioxide in aqueous solutions of sodium sulfate and ammonium sulfate at 80°C (Rumpf and Maurer, 1993). For the salt-containing solutions the ionic strength is 6 mol kg⁻¹.

Setchenov equation (Setchenov, 1889)

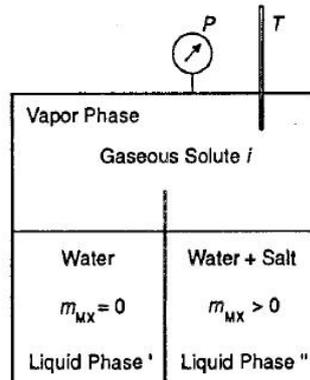


Figure 9-7 Three-phase system consisting of a gaseous solute in equilibrium with two aqueous liquid phases: phase ' contains only water; phase '' contains water and a salt with molality m_{MX} . It is assumed that water is nonvolatile.

Three-phase system consisting of a gas phase and two aqueous phases.
 One aqueous phase(') contains no salt.
 The Other aqueous phase contains salt with molality m_{MX}
 Temperature is sufficiently low so that water is essentially nonvolatile.

For solute *i*, at equilibrium,

$$\mu_i^G = \mu_i' = \mu_i''$$

$$\mu_i^G = \mu_i^{0'} + RT \ln m_i' = \mu_i^{0''} + RT \ln m_i''$$

Where, m_i' and m_i'' are, respectively, the molalities of solute *i* in the liquid phase ' (no salt) and in the liquid phase '' (with salt)

Assume, $\mu_i^{0''} - \mu_i^{0'} = RT \ln(k_{MX} m_{MX}) + \text{higher terms}$ (a power series of the salt concentration)

As an approximation, consider only the first term in the series.

$$\ln \frac{m_i'}{m_i''} = k_{MX} m_{MX} \quad (9-55)$$

(Setchenov equation)

: for low concentrations

k_{MX} : the salting parameter

m_{MX} : the molality of the salt in the aqueous solution

Strictly, Setchenov's constant, k_{MX} , is independent of m_{MX} only in the limit of infinite dilution of the electrolyte.

Constant k_{MX} depends on the salt, the solute, and the temperature.

Table 9-5 Molality Setchenov constants for volatile solutes in aqueous electrolyte solutions at 25°C (Krishnan and Friedman, 1974).

| Salt | Gas | k_{MX} (mol kg ⁻¹) |
|-------------------------------------|--------------------------------|----------------------------------|
| NaCl | H ₂ | 0.220 |
| | N ₂ | 0.309 |
| | CH ₄ | 0.319 |
| | C ₂ H ₆ | 0.399 |
| KCl | O ₂ | 0.298 |
| | SO ₂ | -0.051 |
| (CH ₃) ₄ NBr | CH ₄ | -0.039 |
| | C ₂ H ₆ | -0.092 |
| | C ₄ H ₁₀ | -0.170 |

Constant k_{MX} can be either positive or negative.

If it is positive, the solubility of the gas decreases with rising salt concentration (the gas is salted-out)

If it is negative, the solubility of the gas increases with rising salt concentration (the gas is salted-in)

* Several empirical models (estimation of Setchenov constant)

The model of Schumpe (1993)

: The most general model because it can also be applied to mixed electrolyte solutions.

Lang (1996) showed that the Setchenov equation and the Schumpe model can also be applied to aqueous solutions containing ionogenic organic compounds, such as amino acids, zwitterions peptides, proteins, and bases.

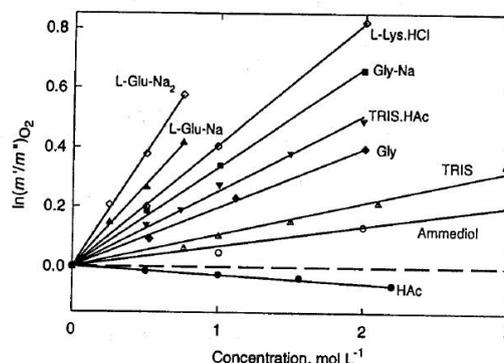


Figure 9-8 Setchenov plot of oxygen in aqueous solutions of some bio-organic compounds at body temperature (37°C).²⁸ HAc, acetic acid; Ammediol, 2-amino-2-methyl-1,3-propan-diol; TRIS, Tris(hydroxymethyl)amino-methane; Gly, glycine; TRIS.HAc, Tris(hydroxymethyl)amino-methane acetate; Gly-Na, glycine-sodium salt; L-Lys.HCl, L-lysine-monohydrochloride; L-Glu-Na, L-glutamic acid-monosodium salt; L-Glu-Na₂, L-glutamic acid-disodium salt. (Lang, 1996).

A dissolved salt can also have a large effect on the composition of a vapor in equilibrium with an aqueous solution of a volatile liquid. (Furter and Cook, 1967; Furter, 1976, 1977) When the dissolved salt solvates preferentially with the molecules of one component, the salt can have a selective effect on the volatilities of the two liquids, and hence on the composition of the equilibrium vapor.

The effect of salt on vapor-liquid equilibria can be described by a Setchenov-type equation. For a single salt in a binary mixed-solvent at fixed (salt-free) composition,

$$\ln \frac{\alpha}{\alpha^0} = k'_{MX} x_{MX} \quad (9-56)$$

Where, α and α^0 are the relative volatilities with and without salt, respectively
 k_{MX} is the salt-effect parameter
 m_{MX} is the mole fraction of the salt in the liquid phase

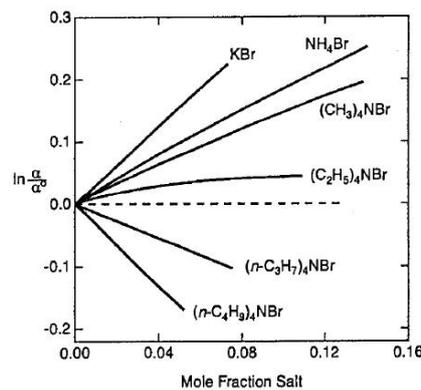


Figure 9-9 Salt effects in ethanol/water system at constant liquid composition $x_{\text{ethanol}} = 0.206$ (salt-free basis).

Another example, Fig. 9-10 (\circ : azeotrope)

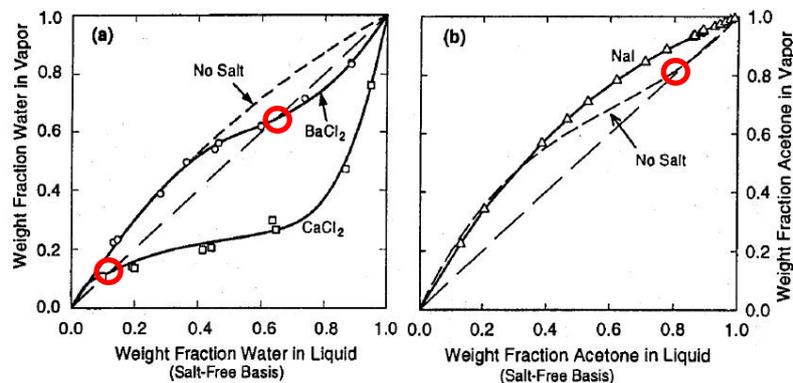


Figure 9-10 A salt may invert relative volatility or eliminate an azeotrope. Vapor-liquid equilibrium at 1 bar for: (a) Acetic acid/water system with no salt (---), saturated (about 1.8 mol kg^{-1}) with BaCl_2 (o), and saturated (about 7.5 mol kg^{-1}) with CaCl_2 (□) (Ramalho *et al.*, 1964). (b) Acetone/methanol system with no salt (---), and saturated (about 3.8 mol kg^{-1}) with NaI (Δ) (Iliuta and Thyron, 1995).

9.10 Models for Concentrated Ionic Solutions

When ions concentrations are low, the average distance between ions is large; in that case, only long-range electrostatic forces are important. As ion concentration rises ions begin to interact also with hard-core repulsive forces (leading to excluded-volume effects) and with short-range (van der Waals) attraction forces.

To correlate activity coefficients in aqueous electrolyte solutions, semi-empirical models can be divided into three broad categories.

- **Physical models.**
: Deviations from the Debye-Hückel limiting law are attributed to physical interactions between ions (excluded-volume and van der Waals-attraction effects)
- **Chemical models.**
: Nonideal behavior of an electrolyte solution is attributed to chemical reactions that lead to the formation of semi-stable chemical species, particularly solvated ions.
- **Local-composition models.**
: The local-composition concept is used to account for nonrandomness. These models use the NRTL equation, or the Wilson equation, or the UNIQUAC equation.

In all these models, the key adjustable parameters for the excess Gibbs energy are determined by regression of experimental data for the binary mixture.

9.11 Fundamental Models

With few exceptions, theoretical descriptions of electrolyte solutions have been based on the primitive model where the solvent is a dielectric continuum and the ions are considered to be charged hard sphere.

This crude approximation is satisfactory for dilute solutions or else for solutions of particles that are much larger than the solvent molecules. Nevertheless, it is a bad approximation for concentrated ionic solutions where the size of the solute ion is comparable to that of the solvent molecule.

Henderson et al. (1986) developed a non-primitive model where a perturbation expansion is applied to a mixture of dipolar hard spheres (the solvent) and charged hard spheres (the ions) of the same diameter.

Using perturbation theory, Jin and Donohue (1988, 1988a, 1991) derived a four-parameter equation of state for aqueous solutions containing strong or volatile weak electrolytes, including multisalt systems

The mean spherical approximation (MSA) has also been used to correlate activity coefficients in aqueous electrolyte solutions. This approximation uses the primitive model of aqueous electrolyte solutions but it takes serious account of the finite sizes of the charged particles (ions).

9.12 Semi-Empirical Models

Numerous semi-empirical models correct the Debye-Hückel theory through additional terms that account for ion-ion interactions and, at high concentrations, for incomplete dissociation.

$$g^{E*} = g_{LR}^{E*} + g_{SR}^{E*} \quad (9-57)$$

Where, Long-range (LR) coulombic forces, short-range forces (SR)

$$\ln \gamma_{\pm}^{(x)} = \ln \gamma_{\pm,LR}^{(x)} + \ln \gamma_{\pm,SR}^{(x)} \quad (\text{from sec. 9.3})$$

$$\ln \gamma_{\pm}^{(x)} = \frac{1}{\nu} (\nu_+ \ln \gamma_+^{(x)} + \nu_- \ln \gamma_-^{(x)}) \quad (\text{from Eq. *.19})$$

Although almost all semi-empirical models use a Debye-Hückel-type term for the long-range contribution, several choices are available to account for the short-range contribution.

Local-composition expressions (UNIQUAC, NRTL, Wilson)

Van Laar equations

Margules equations

Long-range forces between ions dominate at dilute electrolyte concentrations while short-range forces between all species dominate at high electrolyte concentrations.

9.13 Models Based on the Local-Composition Concept

1. Cruz and Renon

For the long-range contribution, Cruz and Renon use an expression obtained from the Debye-Hückel theory, For the short-range contribution, they use the NRTL model

2. Chen et al.

The NRTL model of Chen et al. Uses Eq. (9-57) with a Debye-Hückel long-range term and a short-range interaction term of the NRTL form.

Chen makes two assumptions to define local composition:

Like-ion repulsion assumption

Local electroneutrality assumption

For single salt systems, \rightarrow Two adjustable parameters ($\tau_{MX,S}$ and $\tau_{S,MX}$)

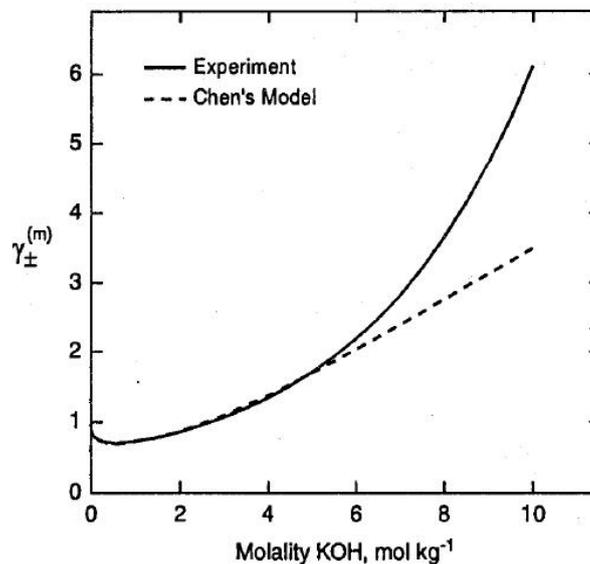


Figure 9-11 Mean ionic activity coefficients for aqueous KOH at 25°C. — Experiment (Zemaitis *et al.*, 1986); - - - - - Chen's model.

For multisalt systems, \rightarrow binary parameters for solvent-salt pairs and binary salt-salt energy parameters

3. Haghtalab and Vera

Hanhtalab and Vera use the NRTL equation [as modified by Panayiotou and Vera] for short-range interactions, whereas long-range Coulombic interactions are obtained from the Debye-Hückel theory.

For multisalt solutions, → not successful

4. Liu et al.

Liu et al. propose that The first term of Eq. (9.57) is obtained from an extended Debye-Hückel theory, and the second term of Eq. (9.57) is obtained from a local-composition expression of the Wilson type.

$$g^{E*} = g_{LR}^{E*} + g_{SR}^{E*} \quad (9-57)$$

Liu does not assume additivity of long-range and short-range contributions.

Liu's model successfully fits data $(\gamma_{\pm}^{(x)})$ for a variety of concentrated electrolyte solutions.

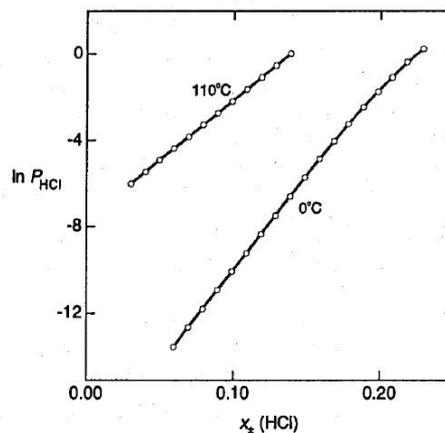


Figure 9-12 Partial pressures of HCl (with pressure in bar) in the HCl/H₂O system as a function of the mean ionic mole fraction x_{\pm} of HCl [defined by Eq. (9-26)].
 ○ Experiment; — Liu's model with parameters in Table 9-6.

Table 9-6 Parameters obtained by Liu and Grén (1991) from fitting $\gamma_{\pm}^{(x)}$ data converted from partial pressure data for the HCl/H₂O system in the temperature range 0-110°C and for HCl concentrations to 21.55 M. Temperature T is in Kelvin.*

| $(g_{H^+,H_2O})/RT$ | $(g_{H^+,Cl^-})/RT$ | $(g_{Cl^-,H_2O})/RT$ | r_{H^+} |
|---------------------|---------------------|----------------------|-----------------------------------|
| -1.92597 | 2.63355 | -0.39037 | $0.72649 + 0.0019624(T - 273.15)$ |

* The significance of g here is not to be confused with that used in Eq. (9-27)

5. Sander et al.

Sander et al. proposed a method to correlate and predict salt effects in vapor-liquid equilibria for water+cosolvent mixtures.

This model combines a term of the Debye-Hückel type with a modified UNIQUAC equation with concentration-dependent parameters.

9.14 The Model of Pitzer

Since about 1973, the ion-interaction model of Pitzer has achieved wide acceptance.

For an electrolyte solution containing w_s kilograms of solvent, with molalities m_i, m_j, \dots , of solute species I, j, \dots , Pitzer assumed that the excess Gibbs energy is given by

$$\frac{G^{E*}}{RTw_s} = f(I) + \sum_i \sum_j m_i m_j \lambda_{ij}(I) + \sum_i \sum_j \sum_k m_i m_j m_k \Lambda_{ijk} + \dots \quad (9-58)^{32}$$

Function $f(I)$ depends on ionic strength I , temperature and solvent properties; it represents long-range electrostatic forces and includes the Debye-Hückel limiting law.

$\lambda_{ij}(I)$ represents the short-range interaction between two solute particles in the solvent.

$\Lambda_{ijk}(I)$ terms account for three-body ion interactions; they are important only at high salt concentrations.

Pitzer assumed that the λ and Λ matrices are symmetric, i.e., $\lambda_{ij} = \lambda_{ji}$ and $\Lambda_{ijk} = \Lambda_{ikj} = \Lambda_{jik}$

Applying Eq.(9-42) and (9-43) to Eq. (9-58),
For a binary (i.e. single electrolyte) solution,

$$\ln \gamma_{\pm}^{(m)} = |z_+ z_-| f^{\gamma} + m \left(\frac{2\nu_+ \nu_-}{\nu} \right) B_{MX}^{\gamma} + m^2 \left[\frac{2(\nu_+ \nu_-)^{3/2}}{\nu} \right] C_{MX}^{\gamma} \quad (9-59)$$

$$\phi - 1 = |z_+ z_-| f^{\phi} + m \left(\frac{2\nu_+ \nu_-}{\nu} \right) B_{MX}^{\phi} + m^2 \left[\frac{2(\nu_+ \nu_-)^{3/2}}{\nu} \right] C_{MX}^{\phi} \quad (9-60)$$

Pitzer found that the best general agreement was obtained when terms f , B_{MX} , and C_{MX} have the form

$$f^{\gamma} = -A_{\phi} \left[\frac{I^{1/2}}{1+bI^{1/2}} + \frac{2}{b} \ln(1+bI^{1/2}) \right] \quad (9-61)$$

$$B_{MX}^{\gamma} = 2\beta_{MX}^{(0)} + \frac{2\beta_{MX}^{(1)}}{\alpha^2 I} \left[1 - \left(1 + \alpha I^{1/2} - \frac{\alpha^2 I}{2}\right) \exp(-\alpha I^{1/2}) \right] \quad (9-62)$$

$$C_{MX}^{\gamma} = \frac{3}{2} C_{MX}^{\phi} \quad (9-63)$$

$$f^{\phi} = -A_{\phi} \frac{I^{1/2}}{1+bI^{1/2}} \quad (9-64)$$

$$B_{MX}^{\phi} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} \exp(-\alpha I^{1/2}) \quad (9-65)^{33}$$

$$C_{MX}^{\phi} = \frac{3}{(v_+ v_-)^{1/2}} (v_+ \Lambda_{MMX} + v_- \Lambda_{MXX}) \quad (9-66)$$

- A_{ϕ} is the Debye-Hückel constant for the osmotic coefficient given by Eq. (9-49a)
- b is a universal parameter equal to $1.2 \text{ kg}^{1/2} \text{ mol}^{-1/2}$
- α is another universal parameter equal to $2.0 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ for most electrolytes.
- Adjustable binary parameters $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, and C_{MX}^{ϕ} are specific for each salt
- Parameters C_{MX}^{ϕ} depend on triple-ion interactions
- All parameters (except α and β) are temperature-dependent.

Table 9-7 Deviations for estimated versus experimental mean ionic activity coefficients ($\ln \gamma_{\pm}^{(m)}$) at 25°C. Calculations from Pitzer's equation with binary parameters obtained at different conditions: Pitzer and Mayorga from data regression to the lower concentration shown for each electrolyte; Kim and Frederick from data regression to the higher concentration shown for each electrolyte.

| Electrolyte | Maximum molality (mol kg ⁻¹) | Deviation* | |
|-------------------|---|-----------------|----------------|
| | | Pitzer, Mayorga | Kim, Frederick |
| HCl | 16.00 | 0.22031 | 0.02854 |
| | 6.00 | 0.00311 | 0.02956 |
| LiBr | 20.00 | 0.06099 | 0.07224 |
| | 2.50 | 0.00286 | 0.06780 |
| CaBr ₂ | 7.66 | 0.46557 | 0.08760 |
| | 2.00 | 0.00773 | 0.00732 |

* Root-mean-square deviation.

For mixed electrolytes, Pitzer uses additional terms in Eq. (9.58) that require additional interaction parameters, θ_{ij} and ψ_{ijk} , obtained from experimental data for aqueous mixed-electrolyte solutions with a common ion.

However, for a multi-electrolyte solution, the principal contributions to GE^* usually come from the single-electrolyte parameters; parameters θ_{ij} and ψ_{ijk} have only a small effect.

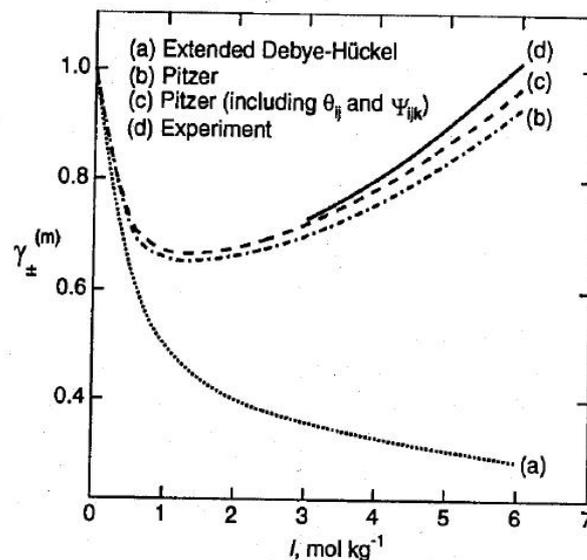


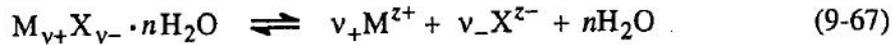
Figure 9-13 Mean ionic activity coefficient of NaCl, $\gamma_{\pm}^{(m)}$, in water at 25°C as a function of ionic strength: (a) Extended Debye-Hückel term [Eq. (9-61)]; (b) Pitzer equation for a multi-electrolyte system with electrolytes as in seawater [Eq. (9-58)], with $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$ and C_{MX} , but omitting mixed-salt parameters θ_{ij} and ψ_{ijk} ; (c) All terms including mixed-salt parameters θ_{ij} and ψ_{ijk} . For comparison, the solid line (d) gives experimental $\gamma_{\pm}^{(nl)}$ of NaCl (in the range $3 \leq I \leq 6 \text{ mol kg}^{-1}$) in aqueous NaCl at the same ionic strength as that of the multi-electrolyte system. Line (d), based on data for the single-solute solution, closely approximates line (c) for seawater.

→ The like-sign interactions have little effect on mean ionic activity coefficient of NaCl; they account for only 3.5% of the total.

All parameters can be evaluated from measurements for single electrolytes and common-ion two-salt solutions.

→ With Pitzer-model parameters and with solubility products of salts available from the experimental solubility in single-salt solutions, Pitzer's model can be used to predict solid solubilities in mixed-salt systems.

For a solid electrolyte $M_{v+}X_{v-} \cdot nH_2O$ the solubility equilibrium in water is



If the activity of the pure solid electrolyte is taken as unity, the solubility product is defined as

$$\begin{aligned} K_{sp} &= (a_+)^{v+} (a_-)^{v-} (a_{H_2O})^n \\ &= (m_+ \gamma_+^{(m)})^{v+} (m_- \gamma_-^{(m)})^{v-} (a_{H_2O})^n \\ &= (m_+)^{v+} (m_-)^{v-} (\gamma_{\pm}^{(m)})^v (a_{H_2O})^n \end{aligned} \quad (9-68)$$

The solubility product, K_{sp} , can be calculated if the standard-state Gibbs energy of the solid and aqueous species are available at the temperature of interest.

For the aqueous ions and electrolytes, the standard state is the ideal, molal solution at fixed pressure and temperature.

For the solid and solvent, the standard state is the pure phase at the pressure and temperature of interest.

At reference temperature $T_r = 298.15$ K and standard pressure, K_{sp} can be calculated from tabulated standard-state values of $\Delta_f g_i^0$

$$\ln K_{sp}(T_r) = -\frac{\Delta g^0(T_r)}{RT_r} \quad (9-69)$$

$$\Delta g^0(T_r) = \Delta_f g_M^0 + \Delta_f g_X^0 - \Delta_f g_{MX}^0$$

With

Using the Gibbs-Helmholtz equation, the temperature dependence of K_{sp} is

$$\ln K_{sp}(T) = \ln K_{sp}(T_r) - \frac{\Delta h^0(T_r)}{R} \left(\frac{1}{T} - \frac{1}{T_r} \right) + \frac{1}{R} \int_{T_r}^T \left[\frac{\int_{T_r}^T \Delta c_p^0(T) dT}{T^2} \right] dT \quad (9-70)$$

Where, $\Delta h^0(T_r) = \Delta_f h_M^0 + \Delta_f h_X^0 - \Delta_f h_{MX}^0$, $\Delta c_p^0(T) = c_{p,M}^0(T) + c_{p,X}^0(T) - c_{p,MX}^0(T)$

If the temperature dependence of $c_{p,i}^0$ is not known or if the difference between T and T_r is not large, Δc_p^0 may be assumed constant, in that case, Eq. (9-70) simplifies to

$$\ln K_{sp}(T) = \ln K_{sp}(T_r) - \frac{\Delta h^0(T_r)}{R} \left(\frac{1}{T} - \frac{1}{T_r} \right) + \frac{\Delta c_p^0(T_r)}{R} \left(\ln \frac{T}{T_r} + \frac{T_r}{T} - 1 \right) \quad (9-70a)$$

Figure 9-14 and 9-15 present two examples comparing experimental and calculated solubilities of two solid salts in an aqueous ternary mixture. The system NaCl/KCl in fig. 9-14 is simple with no intermediate solid phase but the system NaCl/Na₂SO₄ exhibits an intermediate solid phase due to the formation of hydrate Na₂SO₄·10H₂O. In both examples the two salts have a common ion thereby simplifying the calculations.

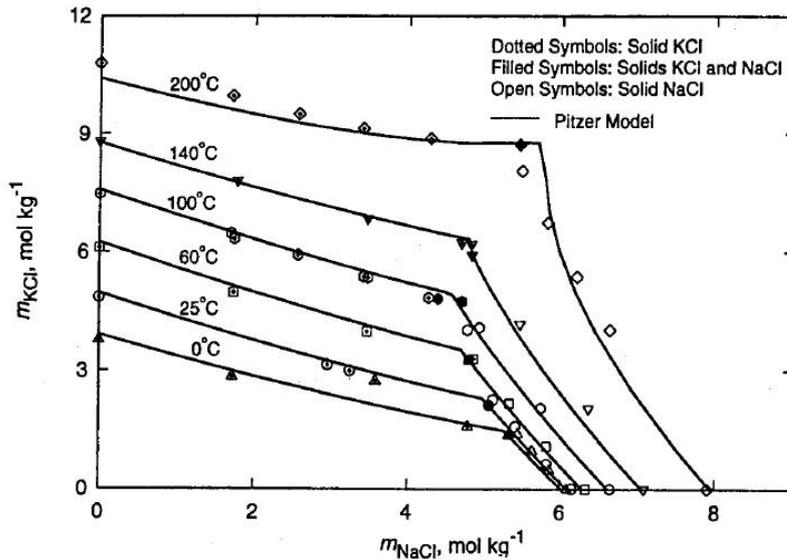


Figure 9-14 Experimental (Linke and Seidell, 1958, 1965) and calculated solubilities in the ternary mixture NaCl/KCl/H₂O at several temperatures. Intersections of isothermal curves represent calculated ternary invariant points, where three phases are in equilibrium: solid NaCl, solid KCl, and aqueous solution.

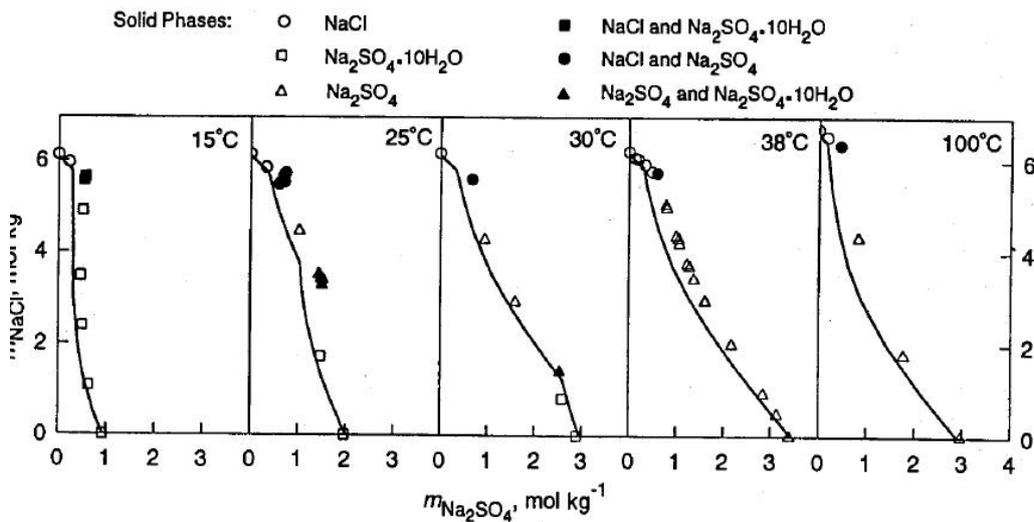


Figure 9-15 Experimental and calculated solubilities in the ternary mixture NaCl/Na₂SO₄/H₂O at several temperatures. Hydrate Na₂SO₄·10H₂O is stable only at temperatures below about 38°C. Symbols: experiment (Linke and Seidell, 1958, 1965); — Pitzer model. Intersections of isothermal curves represent calculated ternary invariant points where three phases are in equilibrium: aqueous solution, solid NaCl, and solid Na₂SO₄ or solid hydrate; or aqueous solution, solid Na₂SO₄ and solid hydrate.

Another example of application of Pitzer's model to multi-salt mixtures is provided by studies of mineral solubilities in brines by Weare and collaborators. To illustrate Weare's results, Fig. 9-16 compares experimental with calculated solubilities of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in $\text{Na}_2\text{SO}_4/\text{NaCl}$ solutions.

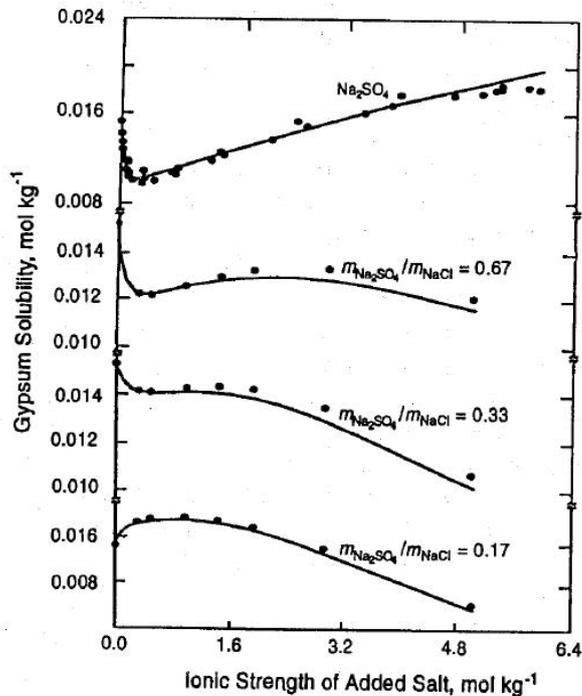


Figure 9-16 Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) solubilities in aqueous $\text{Na}_2\text{SO}_4/\text{NaCl}$ solutions at 25°C. ● Experiment; — Pitzer's model (Harvie *et al.*, 1982).

Calculated gypsum solubilities are in good agreement with experimental data at all ionic strengths. However, for this ternary system the model requires 12 single electrolyte parameters and 5 mixed-electrolyte parameters. The large number of parameters required in Pitzer's model for multi-salt mixtures is its major disadvantage.

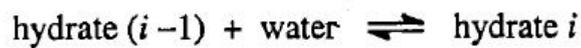
9.15 The "Chemical" Hydration Model of Robinson and Stokes

In a manner similar to that for chemical theories described in Chap. 7, it is possible to relate the activity of the water to the equilibrium constant (or constants) which characterize hydration equilibria.

A particularly successful example for a single solvent solution is provided by the work of Stokes and Robinson (1973)

Consider an aqueous solution of a strong electrolyte, containing n_w moles of free water, n_0 moles of anhydrous cations, n_1 moles of singly-hydrated cations, n_i moles of i -hydrated cations and n_A moles of anions, at temperature T and total volume V . We neglect hydration of anions. This solution was prepared by adding c moles of anhydrous salt to water to give a final volume of 1 liter.

The hydration equilibrium is



And the corresponding equilibrium constant K_i is

$$K_i = \frac{a_i}{a_{i-1} a_w} \quad (9-71)$$

For fixed i , K_i depends only on temperature. In general, however, K_i also depends on i . To reduce the number of adjustable parameters, Stokes and Robinson suggest that

$$\begin{aligned} K_1 &= K \\ K_2 &= kK \\ &\vdots \\ K_i &= k^{i-1}K \end{aligned}$$

Stokes and Robinson also assume that in a mixture of hydrated cations and anhydrous anions, there is a Flory-Huggins-type contribution to the entropy of mixing because the various dissolved species do not all have the same size.

The molar volumes of the hydrates are assumed linear functions of i according to

$$v_i = v_0 + i v_w \quad (9-72)$$

Where v_0 is the molar volume of anhydrous cation and v_w is the molar volume of water.

Stokes and Robinson obtained an expression for the activity based on the theory of ion-ion interactions given by Waisman and Lebowitz (1970) which, in effect, is a higher-order Debye-Hückel theory

The activity of water is given by

$$\ln a_w = \ln(1 - c v_h) + c(v_h - v v_w) + \frac{v_w k^3}{24\pi N_A} S(\kappa d) \quad (9-73)$$

Where, $v_h = v_+ v_0 + v_- v_A + h v_w$

Here h , the average hydration number, is found from a known function of the maximum hydration number, K , k , a_w and Y where

$$\ln Y = c(v_h - v v_w)$$

In Eq.(9-70), k_{-1} is the Debye length; d is the average diameter of the anhydrous cation and anion; N_A is Avogadro's constant; and function S is given by the Waisman-Lebowitz theory:

$$S(t) = \left(\frac{6}{t^3}\right) \left[\frac{2}{3}(1+2t)^{3/2} - \frac{2}{3} - t - t(1+2t)^{1/2} \right] \quad (9-74)$$

Volumetric data give v_0 , v_A , and v_w . Crystallographic data give diameter d . The Debye length is found from Eq. (9-47). The important adjustable binary parameters are K and k .

Fig. 9-17 shows calculated and observed (molality) osmotic coefficients for water in three aqueous systems; NaOH and LiBr[Fig. (9-17a); and CaCl₂[Fig.(9-17b)]

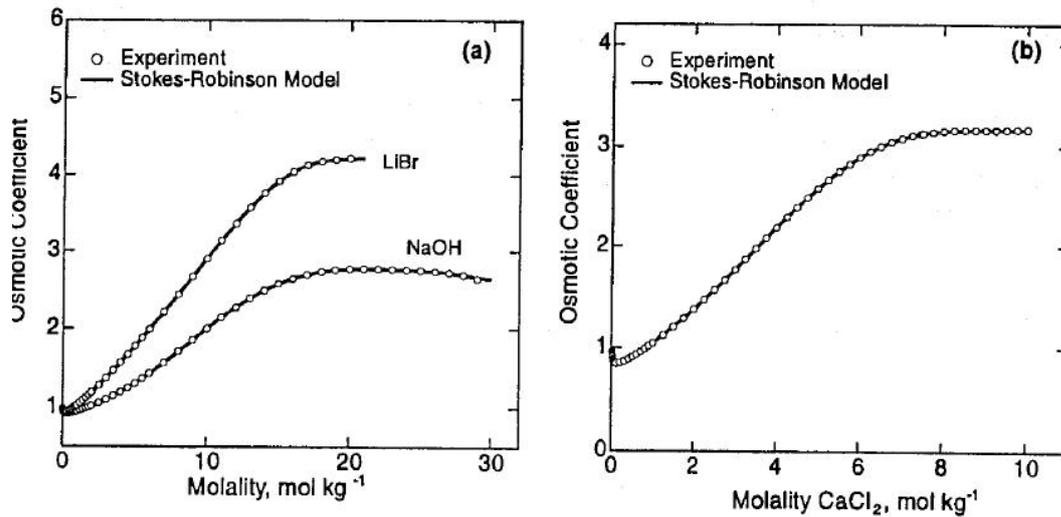


Figure 9-17 Osmotic coefficients for aqueous electrolyte solutions at 25°C: (a) NaOH and LiBr; (b) CaCl₂. ○ Experiment (Hamer and Wu, 1972; Staples and Nuttall, 1977); — Stokes and Robinson chemical theory using parameters in Table 9-8.

Table 9-8 gives parameters for several binary aqueous systems. Results are not sensitive to ion diameter d and to the maximum hydration number, provided that reasonable values are used. However, results are sensitive to adjustable binary parameters K and k .

Table 9-8 Parameters in the Stokes-Robinson model and maximum molality of fit. Aqueous solutions at 25°C. For all solutes, $d = 0.4$ nm.

| Solute | Maximum hydration number | K | k | Maximum molality |
|-------------------|--------------------------|-------|-------|------------------|
| NaOH | 4 | 77.6 | 0.375 | 29 |
| HCl | 6 | 135 | 0.338 | 16 |
| LiCl | 5 | 81.6 | 0.414 | 20 |
| LiBr | 5 | 492 | 0.290 | 20 |
| CaCl ₂ | 9 | 48.7 | 0.678 | 10 |
| CaBr ₂ | 9 | 804.6 | 0.595 | 8 |

The law of mass action suggests that, when water is present in excess, cations tend to hydrate with large hydration numbers. However, as the ratio of water to electrolyte declines, hydration numbers decrease.

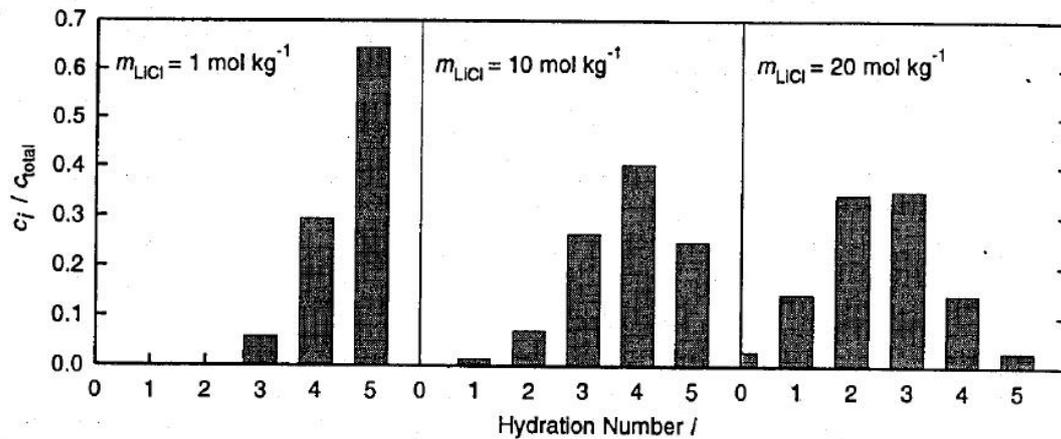


Figure 9-18 Distribution of hydration numbers for aqueous lithium chloride at 1, 10, and 20 mol kg⁻¹.

9.16 Conversion from McMillan-Mayer to Lewis-Randall Formalisms

In the semi-empirical models briefly described in Sec.9.12, the excess Gibbs energy G^{E^*} is written as the sum of two contributions:

First, a long-range contribution described by a Debye-Hückel-type electrostatic expression

Second, a short-range contribution from another model (NRTL, Wilson, UNIQUAC, virial expansion, expression based on a chemical theory)

However this simple addition of two contributions gives rise to an inconsistency because it combines an electrostatic contribution derived from the framework of MacMillan and Mayer with a contribution due to short-range forces calculated in the customary framework of Lewis and Randall.

In the Lewis-Randall framework,

The independent variables are temperature T , pressure P , and the mole numbers of all species n_i .

In the McMillan-Mayer framework,

The independent variables are temperature T , volume V , the mole numbers of the solute species n_k , and the chemical potential of the solvent μ_s .

Thermodynamic properties obtained from the McMillan-Mayer formalism are not identical to those obtained from the Lewis-Randall formalisms.

To maintain consistency, it is necessary to convert the activity coefficients from the McMillan-Mayer to the Lewis-Randall frame work.

9.17 Phase Equilibria in Aqueous solutions of Volatile Electrolytes

Design of operations to remove volatile weak electrolytes from aqueous solutions requires representation of pertinent vapor-liquid equilibria.

In aqueous solution, volatile electrolytes exist in ionic and molecular form. At ordinary temperatures and pressure only the molecular form exists in the vapor.

Calculation of vapor-liquid equilibria requires simultaneous solution of phase-equilibrium equations (for the molecular species), chemical-equilibrium equations for the liquid phase, and material balances.

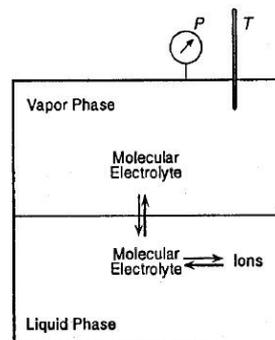


Figure 9-19 Schematic representation of vapor-liquid equilibria for an aqueous solution containing a single volatile weak electrolyte.

A molecular-thermodynamic framework proposed by Edwards et al. has been successfully used for calculating vapor-liquid equilibria in aqueous solutions containing one or more weak volatile electrolytes for temperatures from 0 to 200°C for the total ionic strengths to more than 6 molal.(Figure9-19)

For some solute i at low concentration of i , the phase equilibrium is primarily determined by Henry's constant, H_i , and the molality of molecular (not ionic) solute i . This molality is strongly influenced by the chemical dissociation equilibrium, characterized by the dissociation constant, K .

At higher concentration of i , Henry's constant H_i must be multiplied by an activity coefficient that depends on the concentration of all solute species and on temperature.

First consider the single-solute case;

Since ions are not volatile, the phase equilibrium is governed only by the molecular concentration of the electrolyte in the liquid phase. Vapor liquid equilibria for the solvent(water) and for the solute(molecular electrolyte) are described by

$$f_w^V = f_w^L \quad (9-75)$$

$$f_i^V = f_i^L \quad (9-76)$$

Equation (9-75) is rewritten (see Sec. 3.3)

$$\phi_w^V y_w P = a_w P_w^s \phi_w^s \exp \frac{v_w (P - P_w^s)}{RT} \quad (9-77)$$

For the electrolyte, phase equilibrium considers only molecular electrolyte (designated with subscript M); therefore, Eq. (9-76) is rewritten

$$\phi_{MX,M}^V y_{MX,M} P = \gamma_{MX,M}^{(m)} m_{MX,M} H_{MX,M} \quad (9-78)$$

In Eq. (9-78), $y_{MX,M} P$ is the partial pressure of the molecular weak electrolyte and $\phi_{MX,M}^V$ is the vapor-phase fugacity coefficient; $m_{MX,M}$ is the molality of the electrolyte in molecular form, $\gamma_{MX,M}^{(m)}$ is the activity coefficient and $H_{MX,M}$ is Henry's constant for the molecular solute.

From a mass balance for the weak electrolyte in the liquid phase, we relate the overall electrolyte concentration (stoichiometric), m_{MX} , to that in molecular form, $m_{MX,M}$, and in chemically reacted form. For example, when NH_3 is dissolved in water,

$$m_{NH_3} = m_{NH_3,M} + m_{NH_4^+} \quad (9-79)$$

In addition, the bulk electroneutrality condition of the liquid phase relates the concentration of cations to those of anions:

$$\sum_i z_i m_i = 0 \quad (9-80)$$

Finally, using Eq. (9-54) the chemical equilibrium relates the molecular concentration of the undissociated electrolyte and the ionic concentrations of the weak electrolyte; for example, for the reaction $MX \rightleftharpoons v_+ M^{z+} + v_- X^{z-}$,

$$K = \frac{m_+^{v_+} m_-^{v_-} (\gamma_{\pm}^{(m)})^v}{m_{MX,M} \gamma_{MX,M}^{(m)}} \quad (9-81)$$

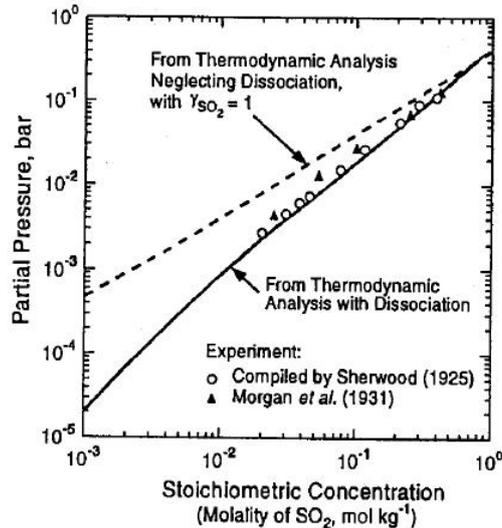
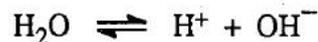


Figure 9-20 Solubility of sulfur dioxide in water at 10°C. Comparison with experiment of the calculated (Edwards *et al.*, 1978) results considering (—) or neglecting (---) ionization of SO₂ in water.

For aqueous solutions of sulfur dioxide, Fig. 9-20 compares experiment with results calculated using the method of Edwards. Dissociation of sulfur dioxide in the liquid phase was taken into account through the chemical equilibria



Each of these chemical equilibria is characterized by a chemical-equilibrium constant, defined according to Eq. (9-81). Vapor-phase fugacity coefficients were calculated using the method of Nakamura *et al.* Henry's constants as a function of temperature were obtained from binary-data reduction. Activity coefficients for the electrolyte and the activity of water were obtained from Edward's extension of Pitzer's model. Because SO₂ is a weak electrolyte with a low dissociation constant, the concentration of ions is so small that Eq.(9-59) reduces to

$$\ln \gamma_{\text{SO}_2, \text{M}}^{(\text{m})} = 2\beta_{\text{SO}_2, \text{SO}_2}^{(0)} m_{\text{SO}_2, \text{M}} \quad (9-82)$$

And for water

$$\ln a_w = -\frac{M_w}{1000} (m_{\text{SO}_2, \text{M}} + \beta_{\text{SO}_2, \text{SO}_2}^{(0)} m_{\text{SO}_2, \text{M}}^2) \quad (9-83)$$

Combining Eqs. (9-78) and (9-82), the equation for the phase equilibrium of SO_2 is

$$\ln \frac{y_{\text{SO}_2} \phi_{\text{SO}_2} P}{m_{\text{SO}_2, \text{M}}} - \frac{\bar{v}_{\text{SO}_2}^{\infty} (P - P_w^s)}{RT} = \ln H_{\text{SO}_2, \text{M}}^{(P_w^s)} + 2\beta_{\text{SO}_2, \text{SO}_2}^{(0)} m_{\text{SO}_2, \text{M}} \quad (9-84)$$

Where, $H_{\text{SO}_2, \text{M}}^{(P_w^s)}$ stands for Henry's constant of molecular SO_2 in water at infinite dilution.

Plotting the left-hand side of Eq.(9-84) as a function of the molecular concentration of SO_2 , the slope gives the molecule-molecule interaction parameter, $\beta_{\text{SO}_2, \text{SO}_2}^{(0)}$, and the intercept gives Henry's constant, $H_{\text{SO}_2, \text{M}}^{(P_w^s)}$.

The thermodynamic framework described above for a single-solute system can be extended to multisolite systems. The necessary parameters are obtained primarily from binary-data reduction but at high salt concentration, some ternary data are required.

Figure 9-21 compares calculated and experimental results (Rumpf et al., 1993a) for a two-solute system: ammonia and sulfur dioxide in water, from 40 to 100°C at two overall molalities of ammonia (302 or 6.1 mol kg⁻¹ of water) and at pressures to 22bar

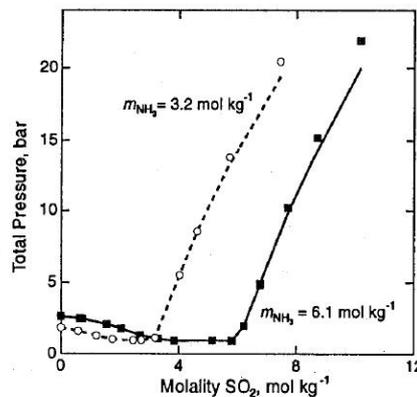


Figure 9-21 Experimental and calculated results for the simultaneous solubilities of ammonia and sulfur dioxide in water at 100°C. Experiment: o, ■; Calculated from model of Edwards and Maurer: --- $m_{\text{NH}_3} = 3.2 \text{ mol kg}^{-1}$; — $m_{\text{NH}_3} = 6.1 \text{ mol kg}^{-1}$.

This example is qualitatively different from the previous one because there is strong chemical interaction between the two solutes: acidic sulfur dioxide and basic ammonia. In this example, in addition to water, the liquid phase contains molecular ammonia, molecular sulfur dioxide, ammonium ion, hydrogen ion, hydroxyl ion, sulfite ion, and bisulfate ion, as indicated in Fig. 9-22.

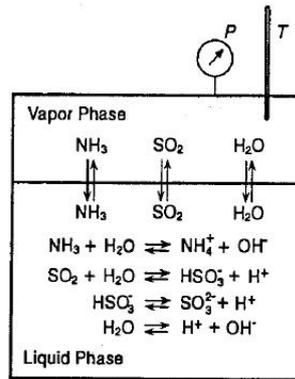


Figure 9-22 Vapor-liquid equilibria and chemical equilibria in the ammonia/sulfur dioxide/water system.

Details of Rumpf et al. work (See 562p)

Coal-gasification and sweetening of natural gases often require removal of acid gases such as carbon dioxide and hydrogen sulfide from gaseous fuels. Such removal is best accomplished by absorption with aqueous alkanolamine solutions. Proper design of absorption equipment requires information on vapor-liquid equilibria, caloric effects and also on the kinetics of mass transfer and of chemical reactions

Numerous models have been proposed to describe vapor-liquid equilibria for such systems.

Silkenbäumer et al. (1998) used a similar correlation(Kuranov et al. 1996) for the solubility of carbon dioxide in aqueous solutions containing 2-amino-2-methyl-1-propanol (AMP) and the alkanolamines MDEA and AMP, Due to chemical reactions in the liquid phase, carbon dioxide dissolves in both neutral and (non-volatile) ionic forms.(Figure 9-23)

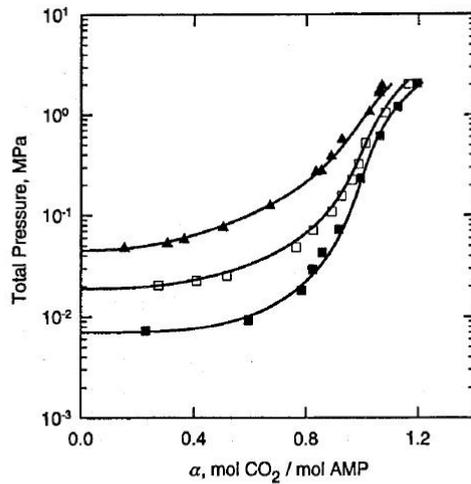


Figure 9-23 Solubility of carbon dioxide in aqueous solutions of 2-amino-2-methyl-1-propanol (AMP). Experiment: \blacktriangle $m_{\text{AMP}} = 2.44 \text{ mol kg}^{-1}$ at 353.15 K; \square $m_{\text{AMP}} = 2.45 \text{ mol kg}^{-1}$ at 333.15 K; \blacksquare $m_{\text{AMP}} = 2.43 \text{ mol kg}^{-1}$ at 313.15 K. — Pitzer model. (Silkenbäumer *et al.*, 1998).

The good agreement between calculation and experiment is achieved only by taking into account all the chemical reactions possible in the liquid phase. In the system $\text{CO}_2/\text{AMP}/\text{H}_2\text{O}$, in addition to the solvent (water), 8 species are present: CO_2 , RNH_2 , RNH_3^+ , RNHCOO^- , HCO_3^- , CO_3^{2-} , H^+ , and OH^- .

Details of Silkenbäumer *et al.* (1998) work (See 563~564p)

Figure 9-24 show predicted molalities of the major molecular species present in the liquid phase as a function of the overall molality of carbon dioxide for a 2.43 molal AMP aqueous solution at 313.15K.

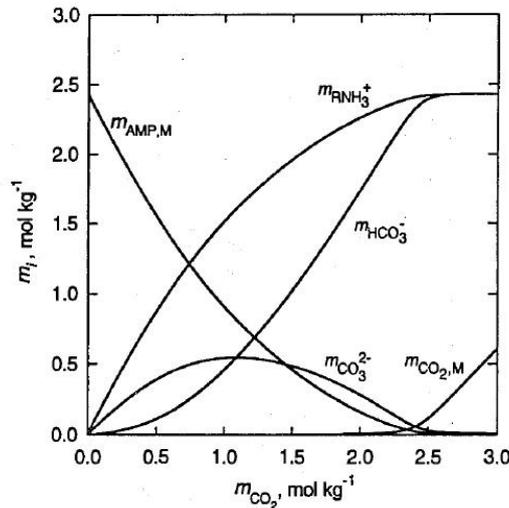


Figure 9-24 Predicted molalities (Pitzer's model) of major species present in aqueous 2.43 molal AMP solutions at 313.15 K as a function of the overall molality of CO_2 (Silkenbäumer *et al.*, 1998).

Silkenbäumer et al. (1998) also demonstrated that the solubility of carbon dioxide can be predicted reliably in solutions containing two alkanolamines, MDEA and AMP, using parameters of the Pitzer model obtained from reduction of experimental data for aqueous solutions containing only one of these alkanolamines. (Fig. 9-25)

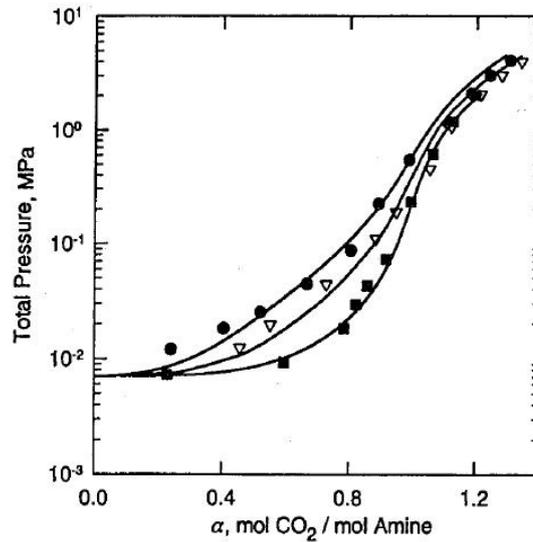


Figure 9-25 Solubility of carbon dioxide at 313.15 K in aqueous alkanolamine solutions. Results for the single-amine and double-amine solutions. Experiment: ● $m_{\text{MDEA}} = 2.63 \text{ mol kg}^{-1}$ (*N*-methyldiethanolamine); ▽ $m_{\text{MDEA}} = 1.28 \text{ mol kg}^{-1} + m_{\text{AMP}} = 1.27 \text{ mol kg}^{-1}$; ■ $m_{\text{AMP}} = 2.43 \text{ mol kg}^{-1}$ (2-amino-2-methylpropanol). — Pitzer's model. (Silkenbäumer *et al.*, 1998).

The work described above shows that it is possible but not easy to describe phase equilibria of aqueous systems containing weak electrolytes and other solutes that react with those electrolytes.

The ion-interaction model of Pitzer is suitable for such calculations; however, the large number of adjustable parameters requires an extensive data base that can be established only by carefully performed experiments.

9.18 Protein Partitioning in Aqueous Two-Phase Systems

Separation of biologically active materials is an important operation in biotechnology.

One useful separation process is provided by liquid-liquid extraction using an aqueous two-phase polymer system formed when two water-soluble polymers are dissolved in excess water.

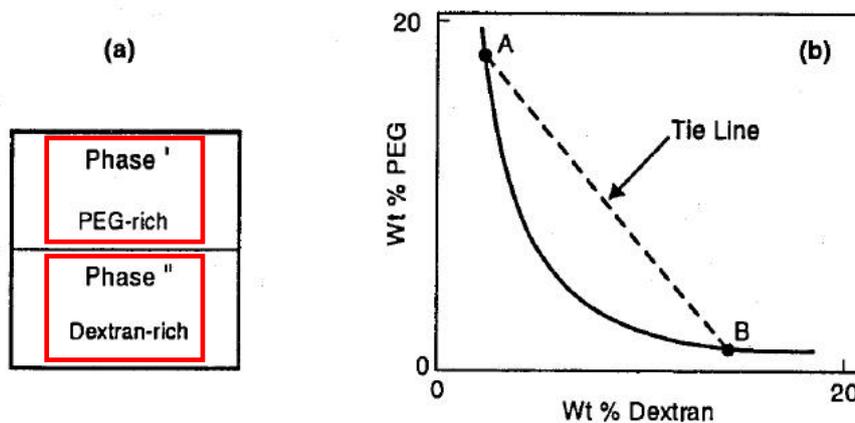


Figure 9-26 Schematics of a two-phase aqueous system $H_2O+PEG+dextran$ for extraction. (a) Phase I: aqueous PEG-rich phase containing only a small amount of dextran; phase II: aqueous dextran-rich phase containing only a small amount of PEG; (b) Calculated phase diagram. Tie-line length is given by \overline{AB} , where A and B represent the equilibrium compositions of phases I and II, respectively.

A mixture of proteins is added to a two-phase aqueous system, each type of protein partitions uniquely between the phases. Therefore, separation can be achieved with an extraction process (Fig.9-27)

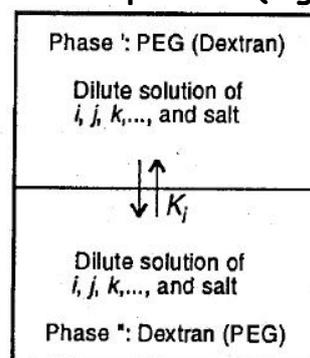


Figure 9-27 Separation of a mixture of proteins i, j, k, \dots by extraction: partition coefficient $K_i = (\text{concentration of protein in phase I})/(\text{concentration of protein in phase II})$.

To prevent denaturation of the biomacromolecules and to maintain pH control, small amounts of salts may be added.

A useful feature of such systems is that the partitioning of biomacromolecules between the two phases can be altered changing the solution pH, ionic strength or the type of salt (electrolyte) added

The difference in salt concentration establishes an electric-potential difference between the two phases;

The difference in salt concentration, pH of the solution and the properties of the phase-forming polymers can result in a change in the partitioning behavior of proteins.

The first task is to calculate the liquid-liquid phase diagram formed by water and the two water-soluble polymers in absence of salt or biomacromolecules. This calculation is achieved by expressing the chemical potential of all three components through an osmotic virial expansion in the polymer concentrations

For equilibrium between phase ' and ''

$$\mu_1' = \mu_1'' \quad \mu_2' = \mu_2'' \quad \mu_3' = \mu_3'' \quad (9-85)$$

Subscript 1 refers to water and subscripts 2 and 3 refer to the water-soluble polymers.

An osmotic virial expansion truncated after the second term gives chemical potentials μ_2 and μ_3

$$\mu_2 - \mu_2^\circ = RT(\ln m_2 + b_{22}m_2 + b_{23}m_3) \quad (9-86)$$

$$\mu_3 - \mu_3^\circ = RT(\ln m_3 + b_{33}m_3 + b_{23}m_2) \quad (9-87)$$

An expression for the chemical potential μ_1 of water is obtained from the Gibbs-Duhem equation,

$$\sum_{i=1}^3 n_i d\mu_i = 0 \quad (9-88)$$

With Eq. (9.86) for μ_2 and Eq.(9-87) for μ_3 , the chemical potentials μ_1 is

$$\mu_1 - \mu_1^0 = \frac{RTM_1}{1000} \left(m_2 + m_3 + \frac{b_{22}}{2} m_2^2 + \frac{b_{33}}{2} m_3^2 + b_{23}m_2m_3 \right) \quad (9-89)$$

Interaction parameter b_{22} , b_{33} , and b_{23} are directly related to osmotic second virial coefficients B_{22}^* , B_{33}^* and B_{23}^* by

$$b_{22} = \frac{2M_2^2 B_{22}^*}{1000^2} \quad (9-90)$$

$$b_{33} = \frac{2M_3^2 B_{33}^*}{1000^2} \quad (9-91)$$

$$b_{23} = \frac{2M_2 M_3 B_{23}^*}{1000^2} \quad (9-92)$$

Consider now a protein component (subscript 4) distributed between the two aqueous phases. The distribution coefficient K is defined by

$$K_4 = \frac{\text{Concentration of protein in phase '}}{\text{Concentration of protein in phase ''}} \quad (9-93)$$

Depending on pH, the protein may be electrically charged and therefore the presence of ions (salts) must be taken into account. When all proteins in the system are dilute, the distribution coefficient for a particular protein is given by (Haynes et al., 1993)

$$\ln K_4 = \ln \frac{\gamma_4''}{\gamma_4'} + \frac{Fz_4(\phi'' - \phi')}{RT} \quad (9-94)$$

F is faraday's constant, ϕ the electric potential, z the electric charge and γ the chemical activity coefficient.

Activity coefficients are found from the osmotic virial expansion with coefficients B_{22}^* , B_{33}^* , B_{23}^* , B_{24}^* and B_{34}^* ; additional terms for protein-salt and polymer-salt interactions are obtained from osmometric data. (Haynes et al., 1989)

The electric-potential difference $\Delta\phi = \phi'' - \phi'$ between the two phases arises as the result of the addition of a salt that fully dissociates into v_+ cations of charge z_+ and v_- anions of charge z_- .

Applying quasi-electrostatic potential theory gives the relation (Haynes et al., 1991)

$$\Delta\phi = (\phi'' - \phi') = \frac{RT}{(z_+ - z_-)F} \ln \left[\frac{(\gamma_-'' / \gamma_-')}{(\gamma_+'' / \gamma_+')^{z_+ / z_-}} \right] \quad (9-95)$$

Two-phase system at equilibrium containing 1:1 electrolyte, i.e., $z_+ / z_- = -1$ and $z_+ - z_- = 2$. In this case, Eq. (9-95) reduces to

$$(\phi'' - \phi') = \frac{RT}{2F} \ln \left(\frac{\gamma_-'' \gamma_+''}{\gamma_-' \gamma_+'} \right) = \frac{RT}{F} \ln \left(\frac{\gamma_{\pm}''}{\gamma_{\pm}'} \right) = \frac{RT}{F} \ln(K_s) \quad (9-95a)$$

Where K_s is the partition coefficient of the salt and, as usual,

$$\gamma_{\pm}^v = \gamma_+^v \gamma_-^v \quad (9-96)$$

The last equality in Eq. (9-95a) holds because, at equilibrium,

$$m_s' \gamma_{\pm}' = m_s'' \gamma_{\pm}'' \quad (9-97)$$

Figure 9-28 compares calculated and experimental partition coefficients for three proteins: albumin, chymotrypsin and lysozyme (Haynes et al., 1991).

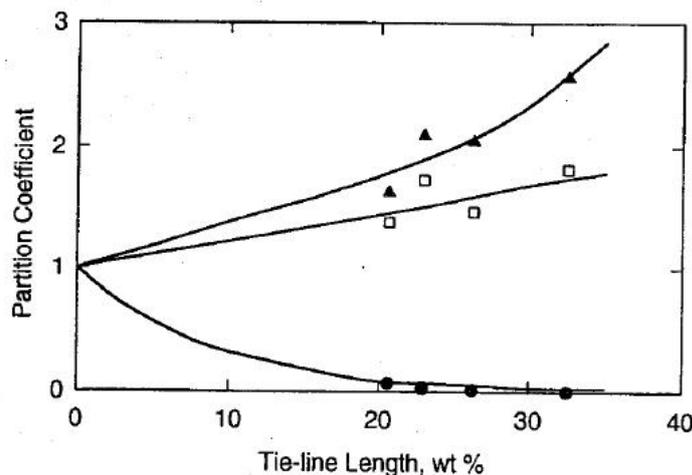


Figure 9-28 Predicted and experimental partition coefficients for a dilute protein mixture in an aqueous two-phase system containing PEG 3350, dextran T-70, and 50 mM KCl (overall) at pH = 7.5 and 25°C. d : diameter (Å); z : electric charge; ●: albumin ($d = 78$; $z = -8$); □: chymotrypsin ($d = 34$; $z = 2$); ▲: lysozyme ($d = 22$; $z = 7$). Lines are calculated using second osmotic virial coefficients obtained from single-phase light-scattering measurements.

Figure 9-29 shows the dramatic effect on the partition coefficient of chymotrypsin when the salt is KI (Haynes et al., 1991). Because the anion (iodide) is bound by α -cyclodextrin and because α -cyclodextrin is predominantly in the aqueous dextran-rich phases, the salt KI partitions toward that phase. The more asymmetric the partitioning of salt, the larger $\Delta\phi$.

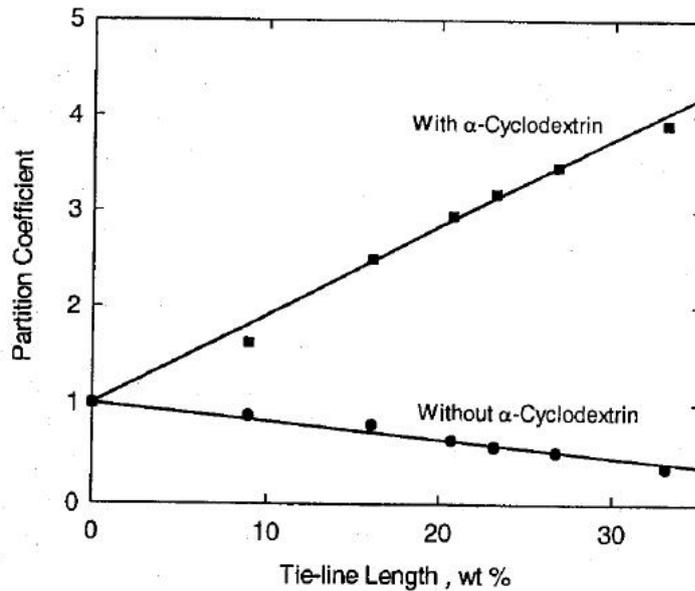


Figure 9-29 Effect of electric-potential difference $\Delta\phi$ on the partition coefficient for chymotrypsin in PEG 3350/dextran T-70/water. $z = 5$; pH = 7.3; 25°C. ● : 1 mM KI; ■ : 1 mM KI + 1 mM α -cyclodextrin. Tie-line length is not affected by α -cyclodextrin.