Chapter 2

EQUILIBRIUM
AND
ACTIVITY

EQUILIBRIUM

- **Certain Temperature and Pressure**
- **Expressed as activity and not Concentration**

Activity and Concentration

$$a_i = C_i\gamma_i$$

$$\boxed{a_i = C_i\gamma_i}$$

$$K_{eq} = \frac{a_C a_D}{a_A a_B}$$

- If activity coeff.=1 a=C
- In diluent solutions
- Mobility, independency of the specie

Keq=activity Coeff. * Kc

$$Keq = \frac{aD.aC}{aA.aB}$$

$$= \frac{\gamma D.\gamma C}{\gamma A.\gamma B} * \frac{[D][C]}{[A][B]} =$$

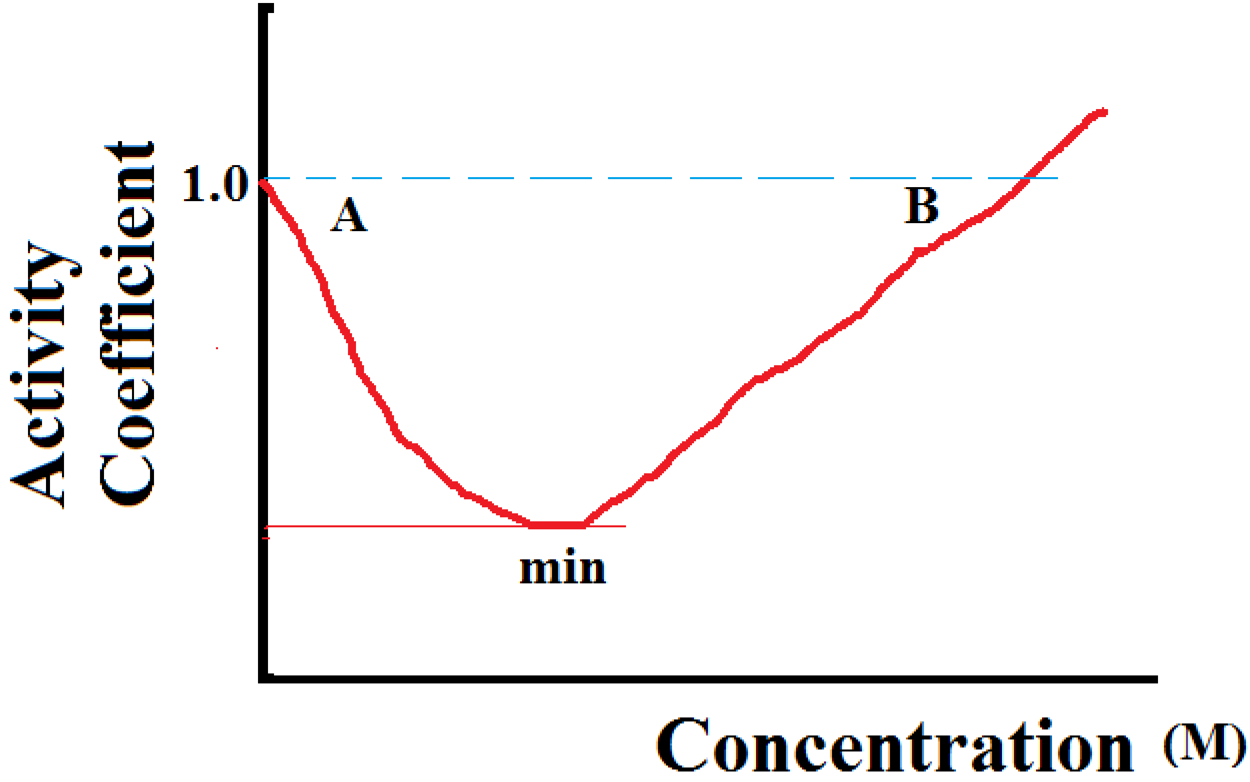
$$= \frac{\gamma D.\gamma C}{\gamma A.\gamma B} * Kc$$

$K_{eq} \neq K_C$

- Ion Interaction
- Ion pairing
- Ion-Association
- Ion-Solvent Interaction

γ & C

- **Ionic Attraction & Solvation**



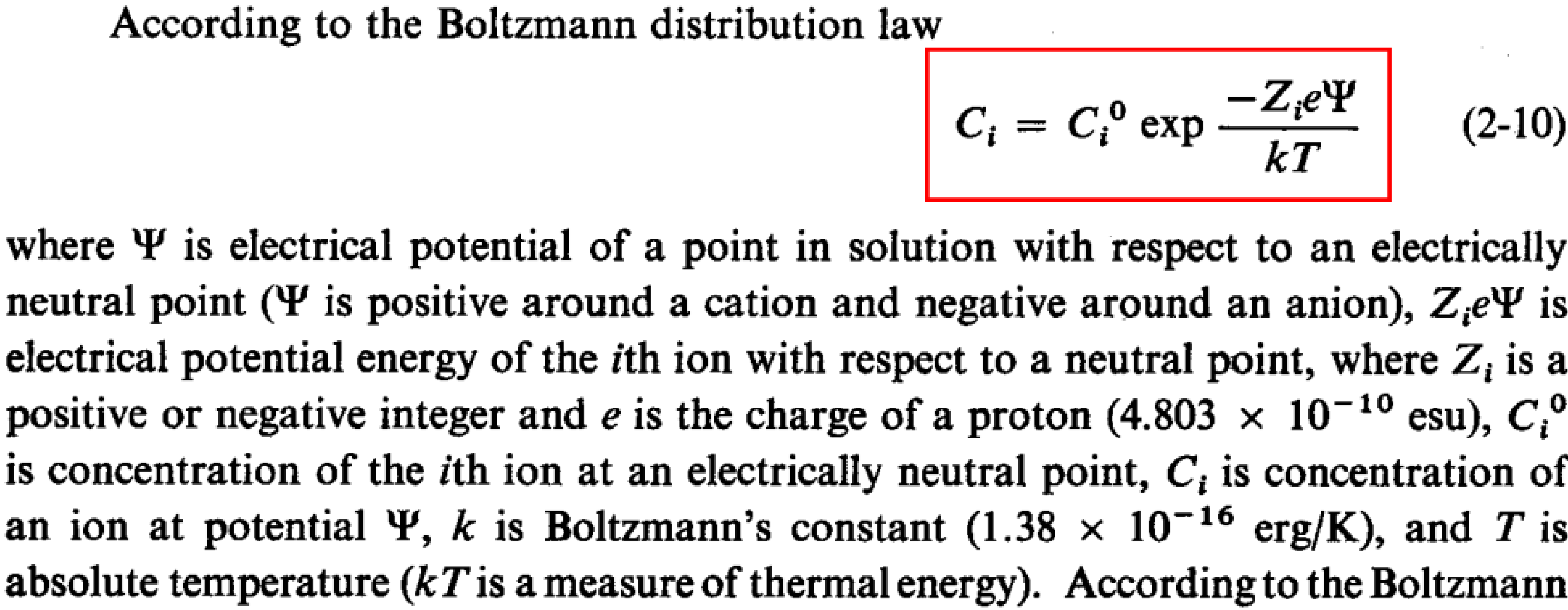
Interaction Types

- Ion-Ion Interaction E@ $1/r^2$
- Ion –dipole Interaction E@ $1/r^4$
- Dipole-Dipole Interaction
- Vander-Valse Interaction E@ $1/r$
- H-bonding

THE DEBYE-H~CKEL THEORY

- To laws that describe interactions among the ions of an electrolyte. These are
- (1) Coulomb's law, the inverse-square law of interaction for particles of unlike charge and of repulsion for particles of like charge,
- $F=q1.q2/r^2$ in the absence of Solvent
- $F=q1.q2/Dr^2$ in the presence of Solvent
- D is the dielectric Constant of the solvent

- (2) the Boltzmann distribution law,



According to the Boltzmann distribution law

$$\boxed{C_i = C_i{}^0 \exp \frac{-Z_i e \Psi}{kT}} \qquad (2\text{-}10)$$

where Ψ is electrical potential of a point in solution with respect to an electrically neutral point (Ψ is positive around a cation and negative around an anion), $Z_i e \Psi$ is electrical potential energy of the ith ion with respect to a neutral point, where Z_i is a positive or negative integer and e is the charge of a proton (4.803×10^{-10} esu), $C_i{}^0$ is concentration of the ith ion at an electrically neutral point, C_i is concentration of an ion at potential Ψ, k is Boltzmann's constant (1.38×10^{-16} erg/K), and T is absolute temperature (kT is a measure of thermal energy). According to the Boltzmann

Assumptions

- 1. Ionic radii $r=0$
- 2. Short range is negligible.
- 3. Viscosity (μ) and Dielectric Constant (D) of the solvent is independent form the solute concentration .
- 4. Thermal agitation> Columbic forces
- 5. 100% dissociation of electrolyte (Ion pairing, Ion association can be omitted.)

$$\boxed{\ln \gamma_i = \frac{-Z_i{}^2 e^2 \kappa}{2DkT}}$$

$$\kappa = \sqrt{\frac{8\pi e^2 N}{1000DkT}}\sqrt{\mu} = 0.33 \times 10^8\sqrt{\mu}$$

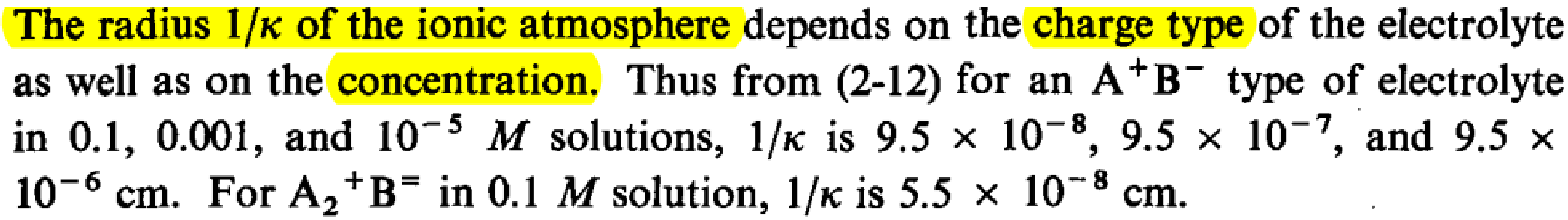
$$\mu = \frac{\sum C_i Z_i^{\,2}}{2}$$

NaCl===>Na+ +Cl- μ=2c/2=c

0.5 M μ =0.5

CaCl2 μ=3C 0.5 M μ=1.5

A^+B^-			$\mu = \frac{C_A Z_A{}^2 + C_B Z_B{}^2}{2} = \frac{C_A + C_B}{2} = C$
$A^{++}B_2{}^-$	$C_A = C$	$C_B = 2C$	$\mu = \frac{4C + 2C}{2} = 3C$
$A^{++}B^=$	$C_A = C_B = C$		$\mu = \frac{4C + 4C}{2} = 4C$
$A^{3+}B_3{}^-$	$C_A = C$	$C_B = 3C$	$\mu = \frac{9C + 3C}{2} = 6C$
$A_m{}^{p+}B_n{}^{q-}$	$C_A = mC$	$C_B = nC$	$\mu = \frac{C(mp^2 + nq^2)}{2}$



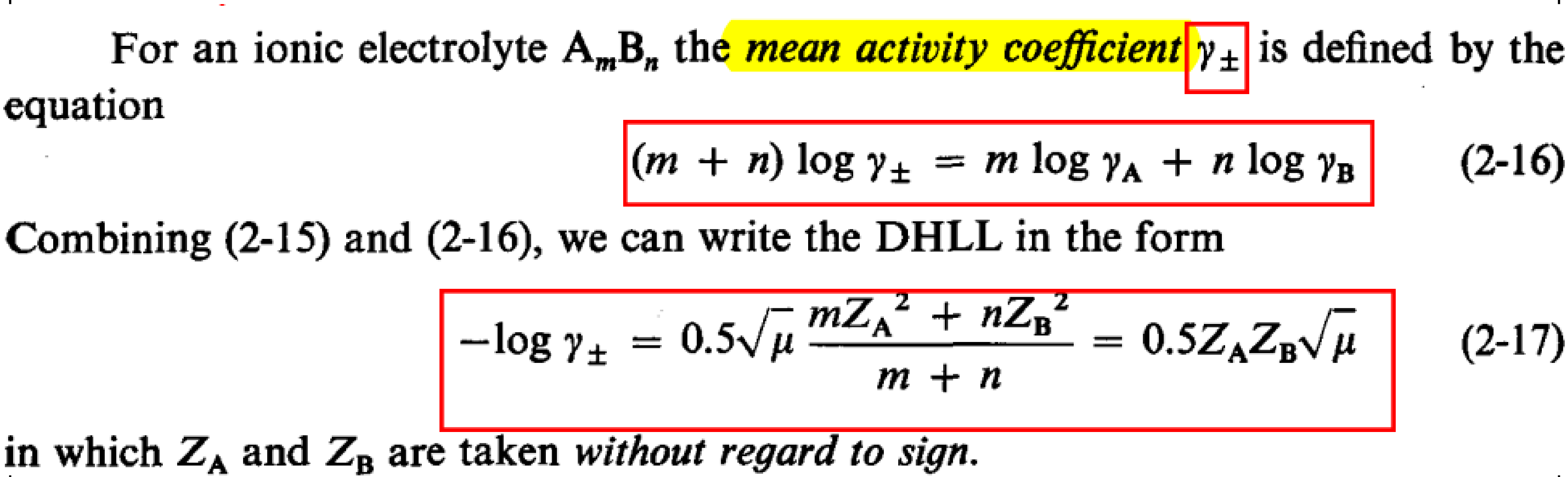
The radius $1/\kappa$ of the ionic atmosphere depends on the charge type of the electrolyte as well as on the concentration. Thus from (2-12) for an A^+B^- type of electrolyte in 0.1, 0.001, and 10^{-5} M solutions, $1/\kappa$ is 9.5×10^{-8}, 9.5×10^{-7}, and 9.5×10^{-6} cm. For $A_2{}^+B^=$ in 0.1 M solution, $1/\kappa$ is 5.5×10^{-8} cm.

$$-\log \gamma_i = AZ_i{}^2\sqrt{\mu}$$

$$-\log \gamma_i = 0.5Z_i{}^2\sqrt{\mu}$$

- The constant A for water at 0°, 25", and 100°C is 0.492, 0.511, and 0.596.

DEBYE-HUCKEL LIMITED LAW (DHLL)



For an ionic electrolyte A_mB_n the *mean activity coefficient* $\boxed{\gamma_\pm}$ is defined by the equation

$$\boxed{(m + n)\log \gamma_\pm = m \log \gamma_A + n \log \gamma_B} \qquad (2\text{-}16)$$

Combining (2-15) and (2-16), we can write the DHLL in the form

$$\boxed{-\log \gamma_\pm = 0.5\sqrt{\mu}\,\frac{mZ_A{}^2 + nZ_B{}^2}{m + n} = 0.5Z_AZ_B\sqrt{\mu}} \qquad (2\text{-}17)$$

in which Z_A and Z_B are taken *without regard to sign.*

EXAMPLE 2-1 Using the DHLL, calculate the activity coefficients of eac ions and the mean activity coefficient of the salt in a 10^{-4} *m* solution of po sulfate.

ANSWER The ionic strength is $3C = 3 \times 10^{-4}$, and $-\log \gamma_{K^+} =$ $10^{-4})^{\frac{1}{2}}$, or $\gamma_{K^+} = 0.98$. Similarly, $-\log \gamma_{SO_4^=} = 0.5 \times 2^2 \times (3 \times 10^{-}$ $\gamma_{SO_4^=} = 0.923$; and $-\log \gamma_{\pm} = 0.5 \times 2 \times (3 \times 10^{-4})^{\frac{1}{2}}$, or $\gamma_{\pm} = 0.961$.

NaCl & KClO4

K+ ClO4-

K+ Cl-

Na+ Cl-

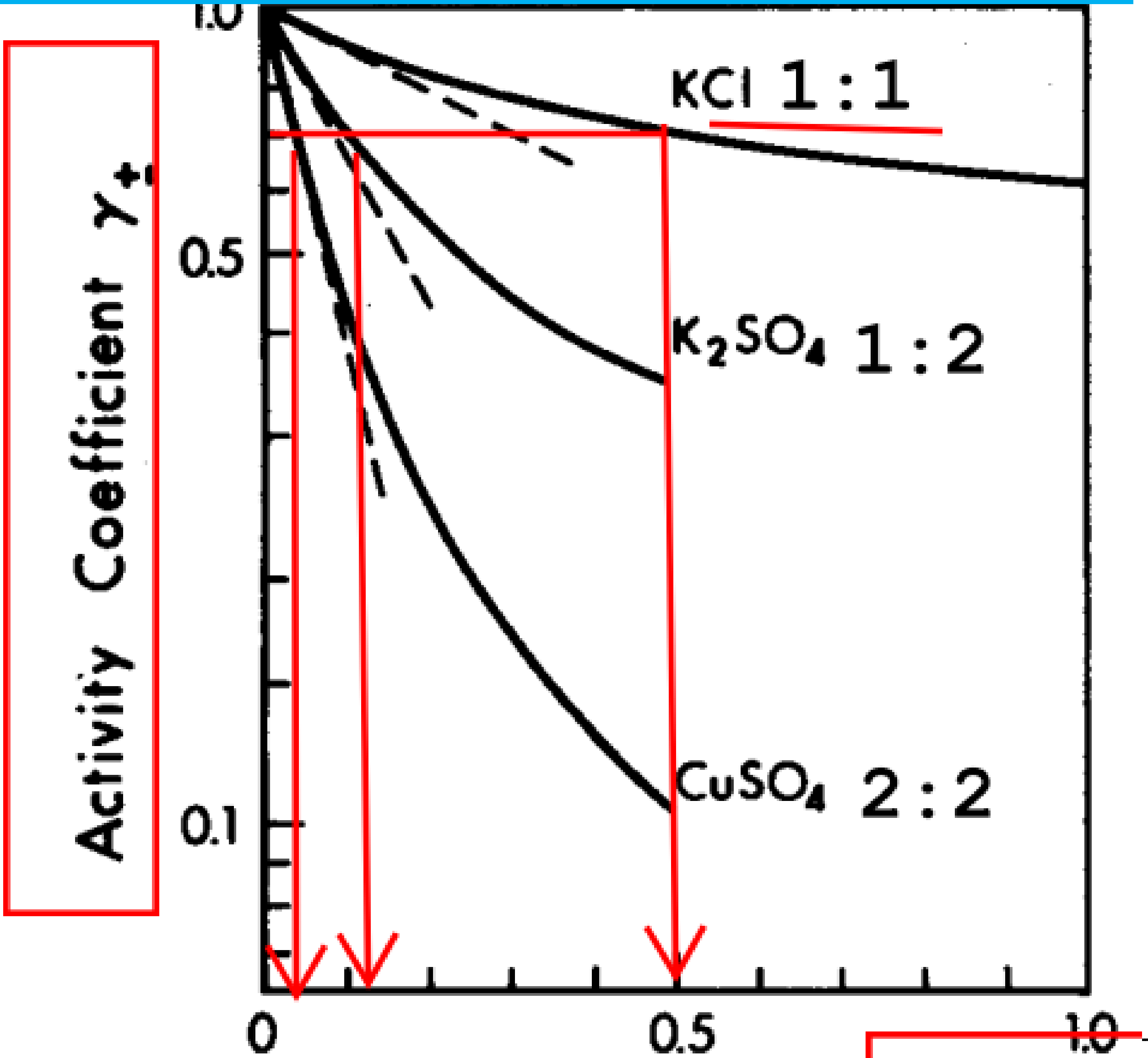
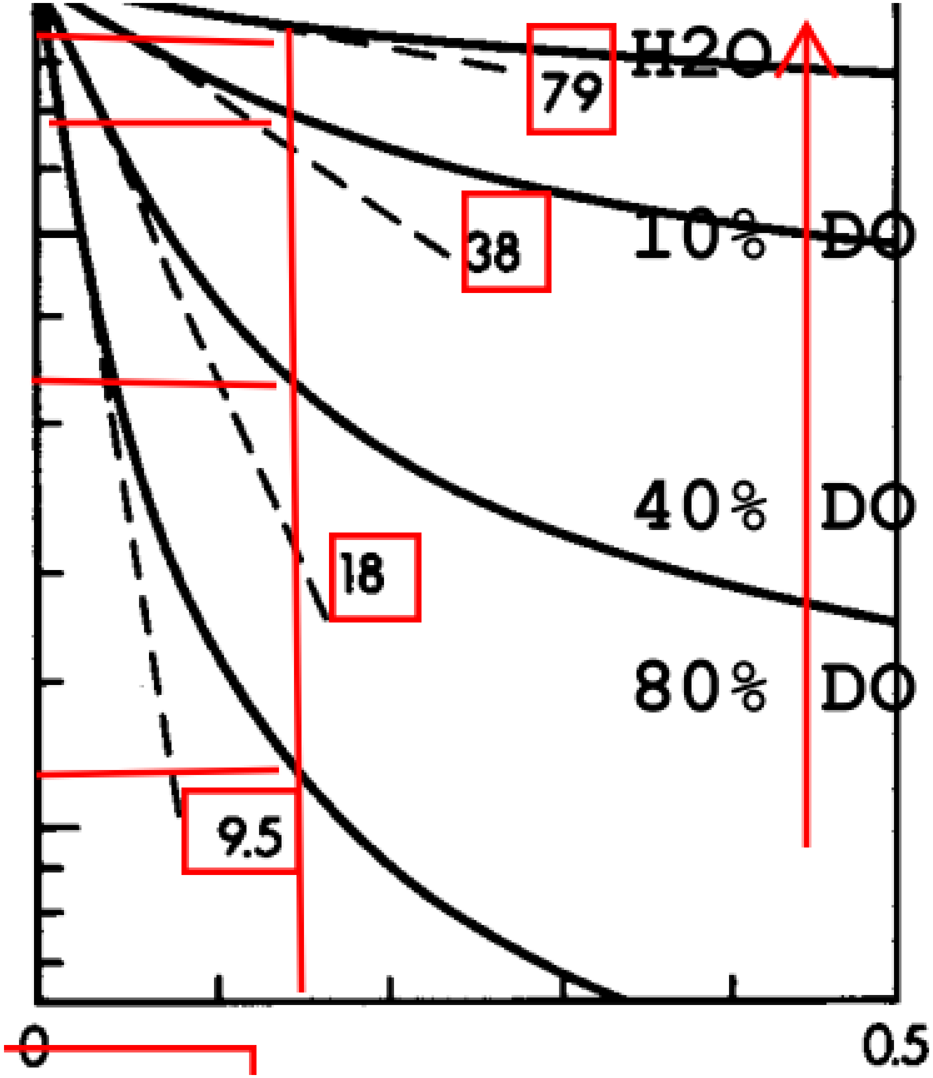


FIGURE 2-3 Activity coefficients calculated by the limiting Debye-Hückel equation (dotted lines) and those observed experimentally. Left, electrolytes of three charge types in water. Right, hydrochloric acid in water-dioxane mixtures with bulk dielectric constants as indicated. (*Adapted from Harned and Owen.*[6])



The right figure

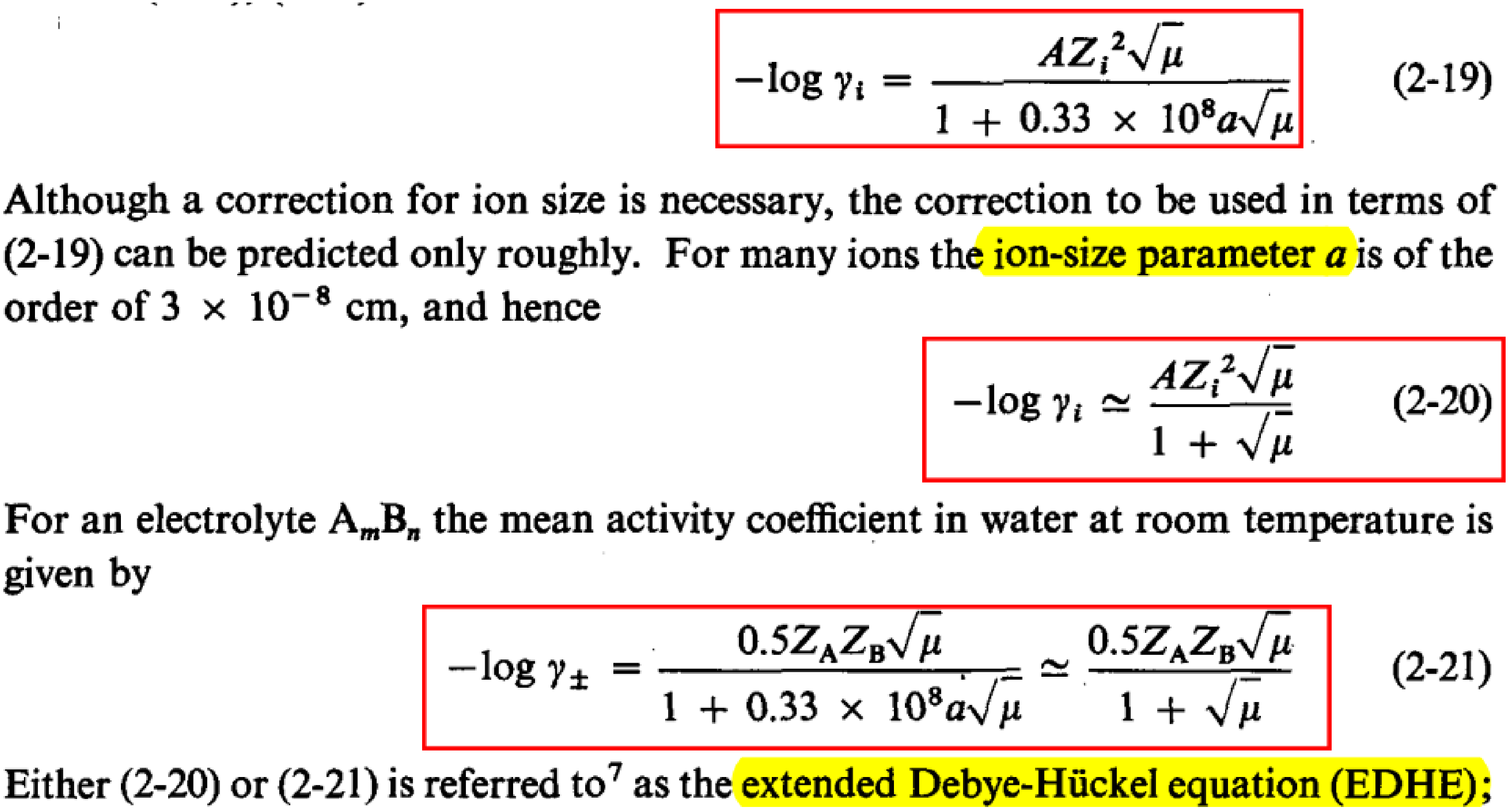
- 1. HCl in H2O (Polar solvent): DO (Non-Polar solvent) mixture
- 2. A significant relationship between γ and ionic strength
- 3.By decrease in D, larger deviation from 1 can be observed.
- 4. At low D, a weak ion solvation may be occurred.
- 5.The formation of ion pair was performed at low concentrations of electrolyte (i.e. HCl)

Extended Deby-Huckel Equation (EDHE)

- **Ionic size**
- **The minor interactions**
- **Ion pairing**
- **Change in D (H2O:DO mixture)**
- **Change in viscosity, fluidity, polarability distribution**
- **Mater Structure (Making or Breaking)**

$$-\log \gamma_i = \frac{A Z_i^2 \sqrt{\mu}}{1 + \kappa a} \tag{2-18}$$

Result: the deviation between experimental and calculated activity coefficient was decreased.
(low ionic strength)



$$-\log \gamma_i = \frac{AZ_i^2\sqrt{\mu}}{1 + 0.33 \times 10^8 a\sqrt{\mu}} \qquad (2\text{-}19)$$

Although a correction for ion size is necessary, the correction to be used in terms of (2-19) can be predicted only roughly. For many ions the ion-size parameter a is of the order of 3×10^{-8} cm, and hence

$$-\log \gamma_i \simeq \frac{AZ_i^2\sqrt{\mu}}{1 + \sqrt{\mu}} \qquad (2\text{-}20)$$

For an electrolyte A_mB_n the mean activity coefficient in water at room temperature is given by

$$-\log \gamma_\pm = \frac{0.5Z_AZ_B\sqrt{\mu}}{1 + 0.33 \times 10^8 a\sqrt{\mu}} \simeq \frac{0.5Z_AZ_B\sqrt{\mu}}{1 + \sqrt{\mu}} \qquad (2\text{-}21)$$

Either (2-20) or (2-21) is referred to[7] as the extended Debye-Hückel equation (EDHE);

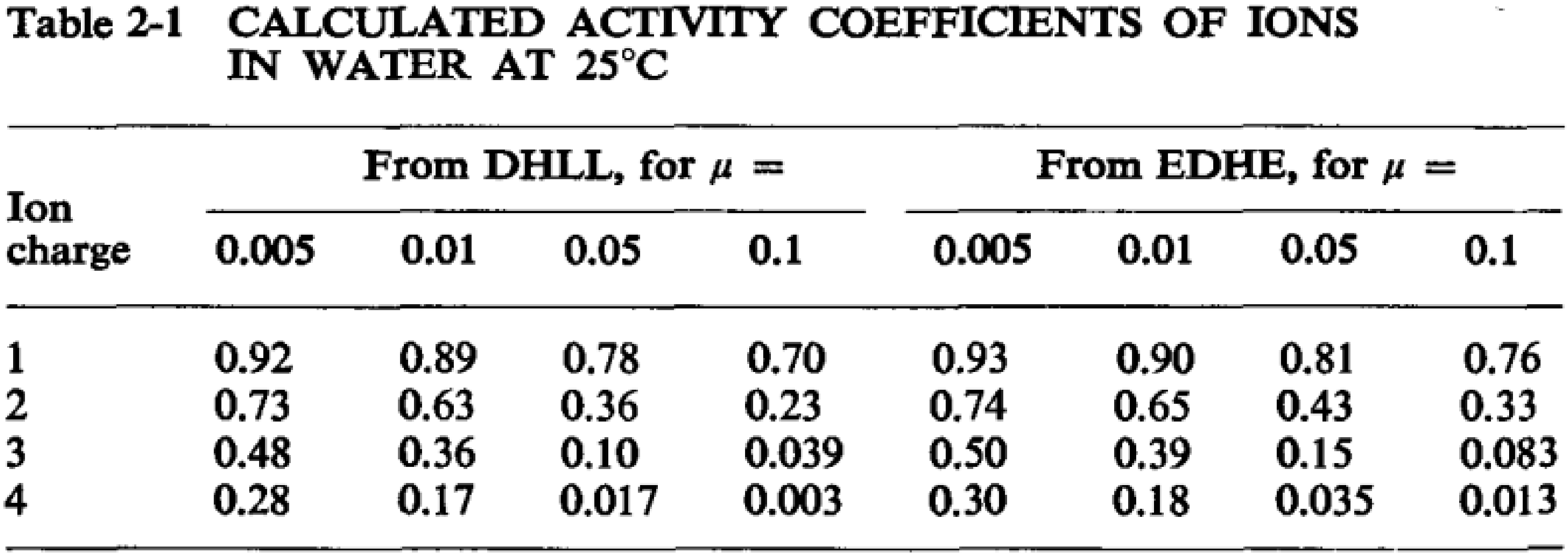


Table 2-1 CALCULATED ACTIVITY COEFFICIENTS OF IONS IN WATER AT 25°C

Ion charge	From DHLL, for $\mu =$				From EDHE, for $\mu =$			
	0.005	0.01	0.05	0.1	0.005	0.01	0.05	0.1
1	0.92	0.89	0.78	0.70	0.93	0.90	0.81	0.76
2	0.73	0.63	0.36	0.23	0.74	0.65	0.43	0.33
3	0.48	0.36	0.10	0.039	0.50	0.39	0.15	0.083
4	0.28	0.17	0.017	0.003	0.30	0.18	0.035	0.013

Kiellands assigned to each ion an empirical value of a parameter a and used (2-19) to calculate its ctivity coefficient.

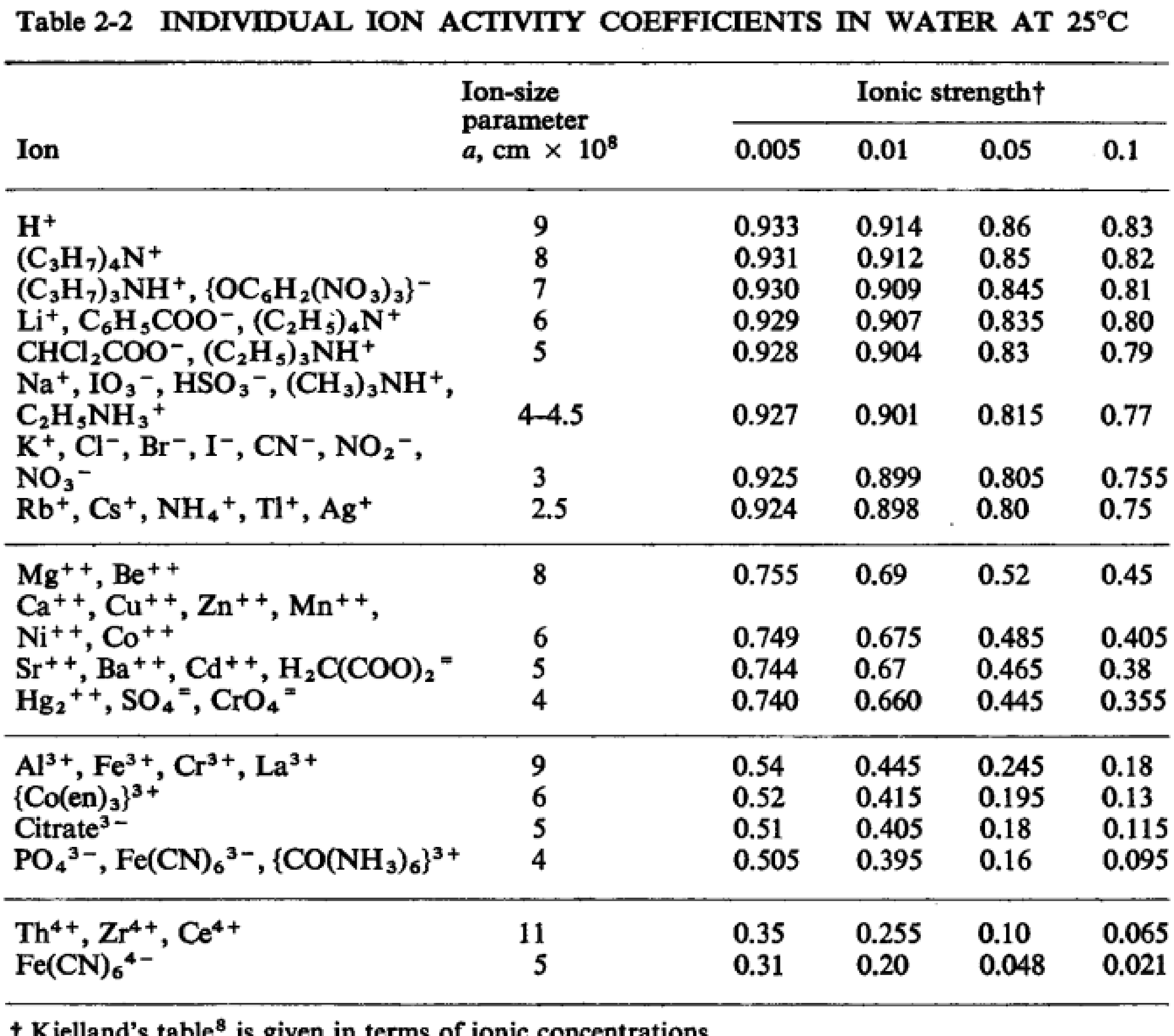
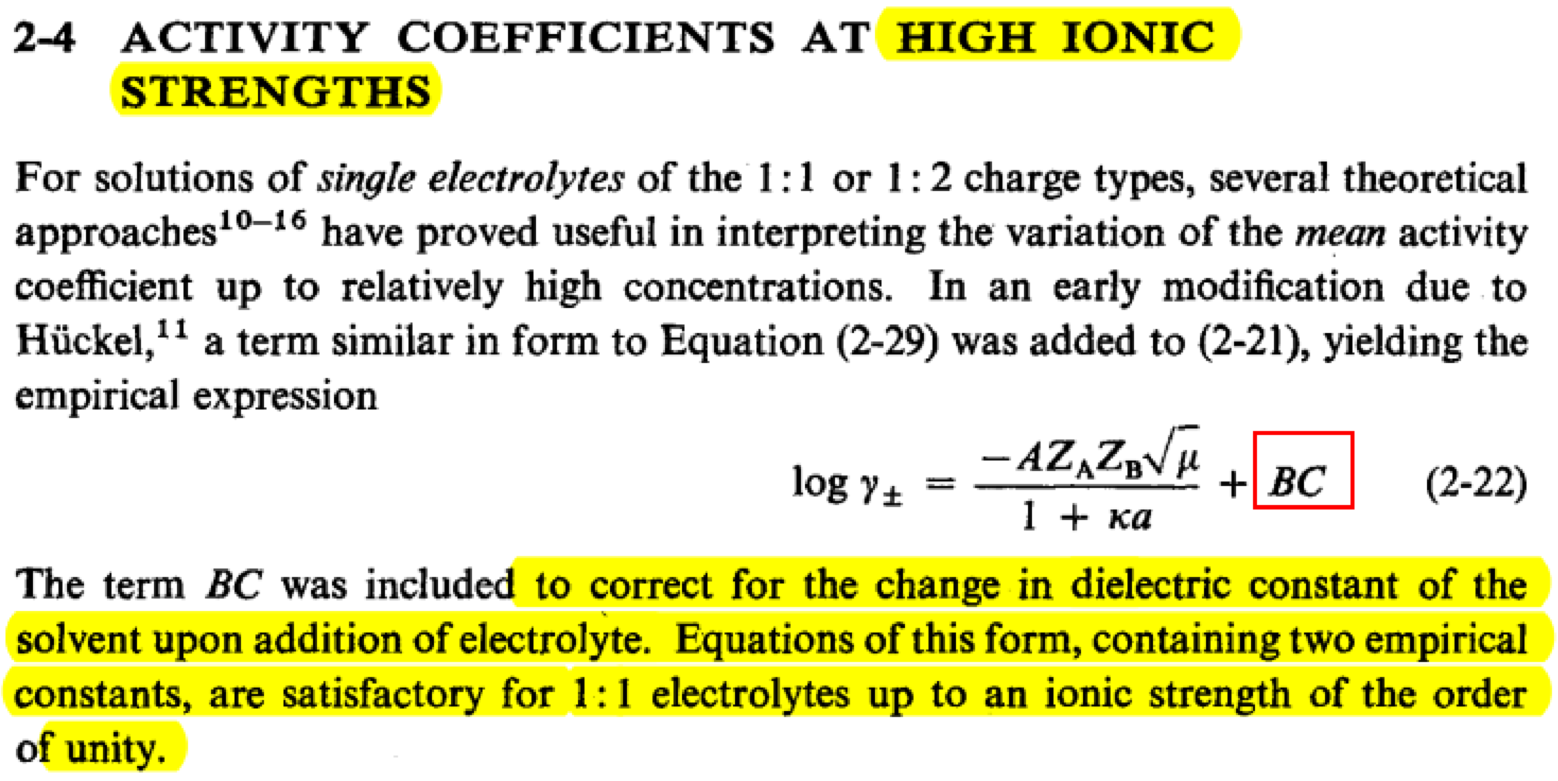


Table 2-2 INDIVIDUAL ION ACTIVITY COEFFICIENTS IN WATER AT 25°C

Ion	Ion-size parameter a, cm × 10^8	Ionic strength†			
		0.005	0.01	0.05	0.1
H^+	9	0.933	0.914	0.86	0.83
$(C_3H_7)_4N^+$	8	0.931	0.912	0.85	0.82
$(C_3H_7)_3NH^+$, $\{OC_6H_2(NO_3)_3\}^-$	7	0.930	0.909	0.845	0.81
Li^+, $C_6H_5COO^-$, $(C_2H_5)_4N^+$	6	0.929	0.907	0.835	0.80
$CHCl_2COO^-$, $(C_2H_5)_3NH^+$	5	0.928	0.904	0.83	0.79
Na^+, IO_3^-, HSO_3^-, $(CH_3)_3NH^+$, $C_2H_5NH_3^+$	4–4.5	0.927	0.901	0.815	0.77
K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-	3	0.925	0.899	0.805	0.755
Rb^+, Cs^+, NH_4^+, Tl^+, Ag^+	2.5	0.924	0.898	0.80	0.75
Mg^{++}, Be^{++}	8	0.755	0.69	0.52	0.45
Ca^{++}, Cu^{++}, Zn^{++}, Mn^{++}, Ni^{++}, Co^{++}	6	0.749	0.675	0.485	0.405
Sr^{++}, Ba^{++}, Cd^{++}, $H_2C(COO)_2^=$	5	0.744	0.67	0.465	0.38
Hg_2^{++}, $SO_4^=$, $CrO_4^=$	4	0.740	0.660	0.445	0.355
Al^{3+}, Fe^{3+}, Cr^{3+}, La^{3+}	9	0.54	0.445	0.245	0.18
$\{Co(en)_3\}^{3+}$	6	0.52	0.415	0.195	0.13
$Citrate^{3-}$	5	0.51	0.405	0.18	0.115
PO_4^{3-}, $Fe(CN)_6^{3-}$, $\{CO(NH_3)_6\}^{3+}$	4	0.505	0.395	0.16	0.095
Th^{4+}, Zr^{4+}, Ce^{4+}	11	0.35	0.255	0.10	0.065
$Fe(CN)_6^{4-}$	5	0.31	0.20	0.048	0.021

† Kielland's table[8] is given in terms of ionic concentrations.



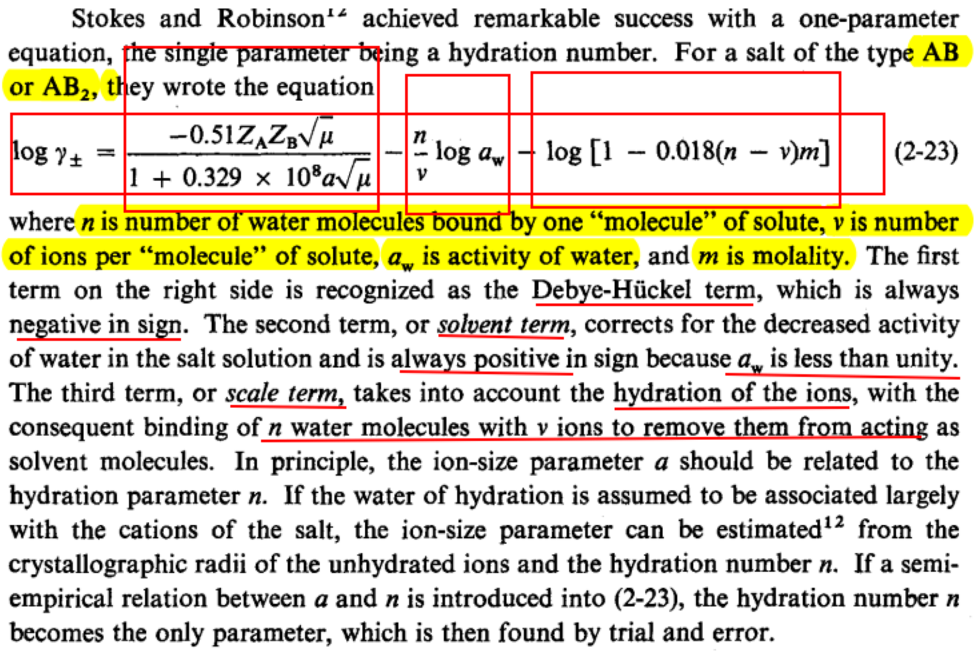
2-4 ACTIVITY COEFFICIENTS AT HIGH IONIC STRENGTHS

For solutions of *single electrolytes* of the 1 : 1 or 1 : 2 charge types, several theoretical approaches[10–16] have proved useful in interpreting the variation of the *mean* activity coefficient up to relatively high concentrations. In an early modification due to Hückel,[11] a term similar in form to Equation (2-29) was added to (2-21), yielding the empirical expression

$$\log \gamma_{\pm} = \frac{-AZ_{\mathrm{A}}Z_{\mathrm{B}}\sqrt{\mu}}{1 + \kappa a} + \boxed{BC} \qquad (2\text{-}22)$$

The term *BC* was included to correct for the change in dielectric constant of the solvent upon addition of electrolyte. Equations of this form, containing two empirical constants, are satisfactory for 1 : 1 electrolytes up to an ionic strength of the order of unity.

parameter equation 'up to an ionic strength of the order of 4



Stokes and Robinson[12] achieved remarkable success with a one-parameter equation, the single parameter being a hydration number. For a salt of the type AB or AB_2, they wrote the equation

$$\boxed{\log \gamma_\pm = \boxed{\frac{-0.51 Z_A Z_B \sqrt{\mu}}{1 + 0.329 \times 10^8 a \sqrt{\mu}}} - \boxed{\frac{n}{\nu} \log a_w} - \boxed{\log [1 - 0.018(n - \nu)m]}} \qquad (2\text{-}23)$$

where n is number of water molecules bound by one "molecule" of solute, ν is number of ions per "molecule" of solute, a_w is activity of water, and m is molality. The first term on the right side is recognized as the Debye-Hückel term, which is always negative in sign. The second term, or *solvent term*, corrects for the decreased activity of water in the salt solution and is always positive in sign because a_w is less than unity. The third term, or *scale term*, takes into account the hydration of the ions, with the consequent binding of n water molecules with ν ions to remove them from acting as solvent molecules. In principle, the ion-size parameter a should be related to the hydration parameter n. If the water of hydration is assumed to be associated largely with the cations of the salt, the ion-size parameter can be estimated[12] from the crystallographic radii of the unhydrated ions and the hydration number n. If a semi-empirical relation between a and n is introduced into (2-23), the hydration number n becomes the only parameter, which is then found by trial and error.

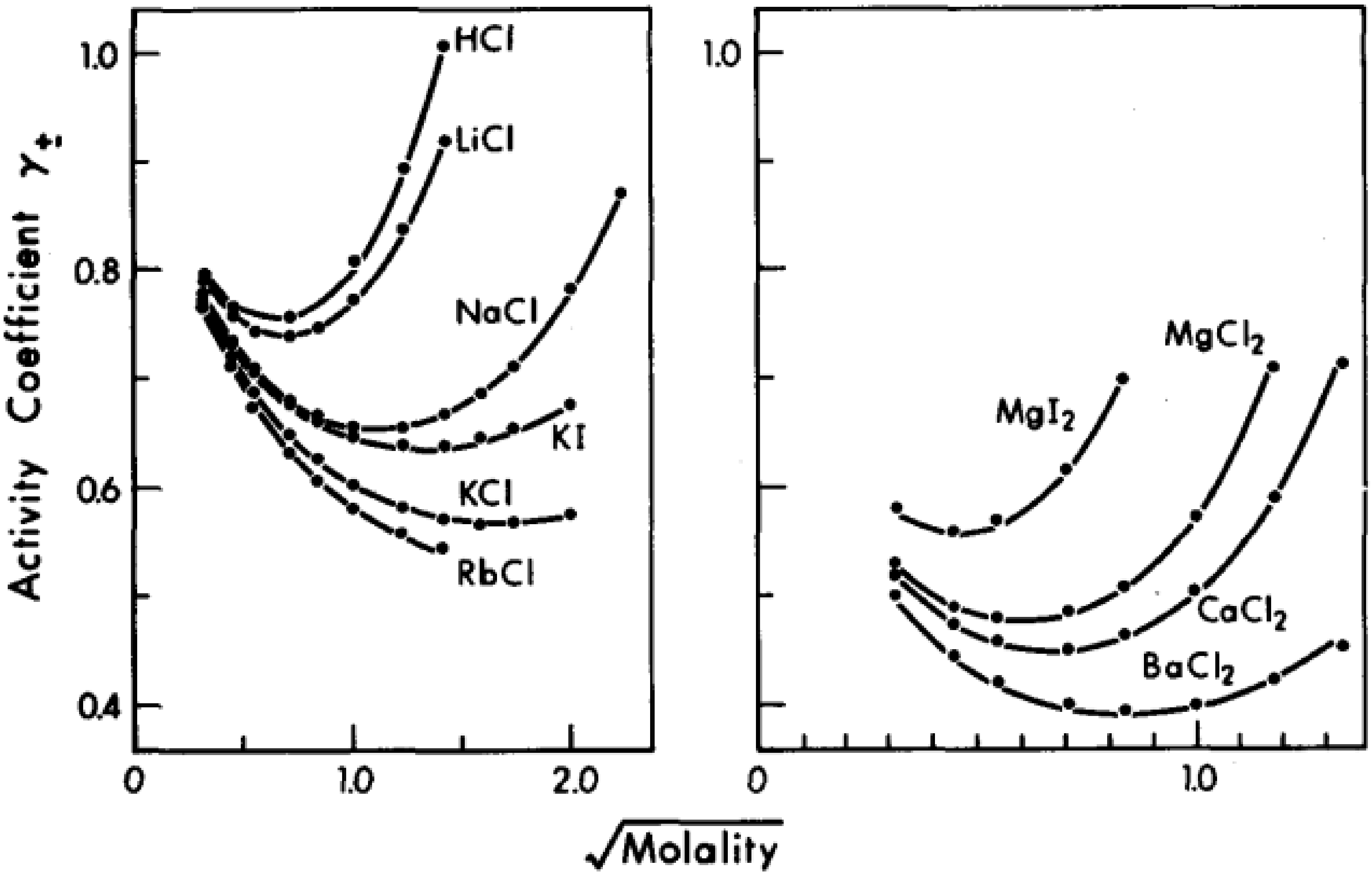
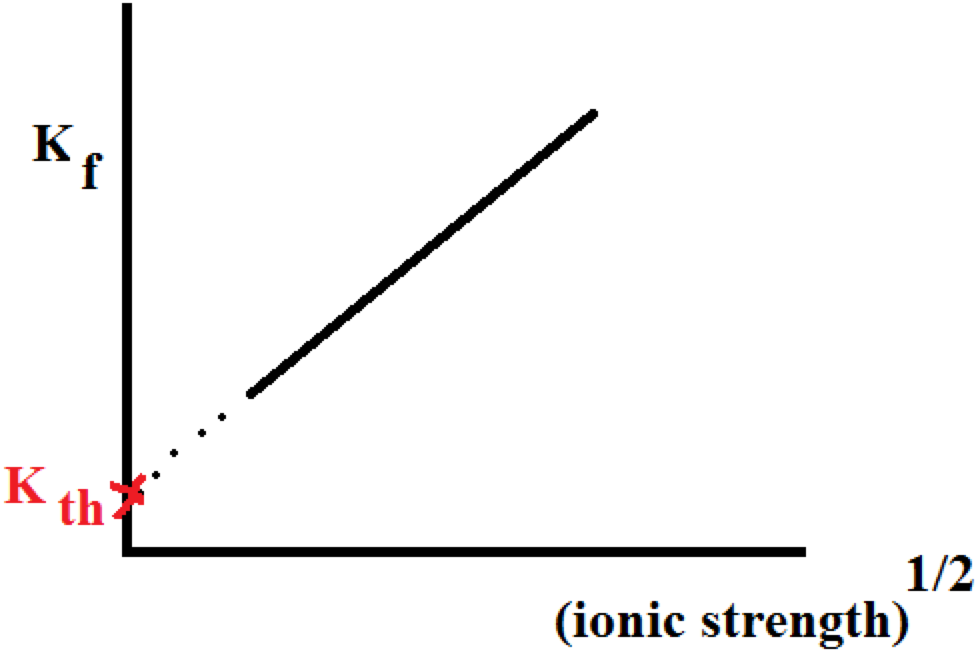


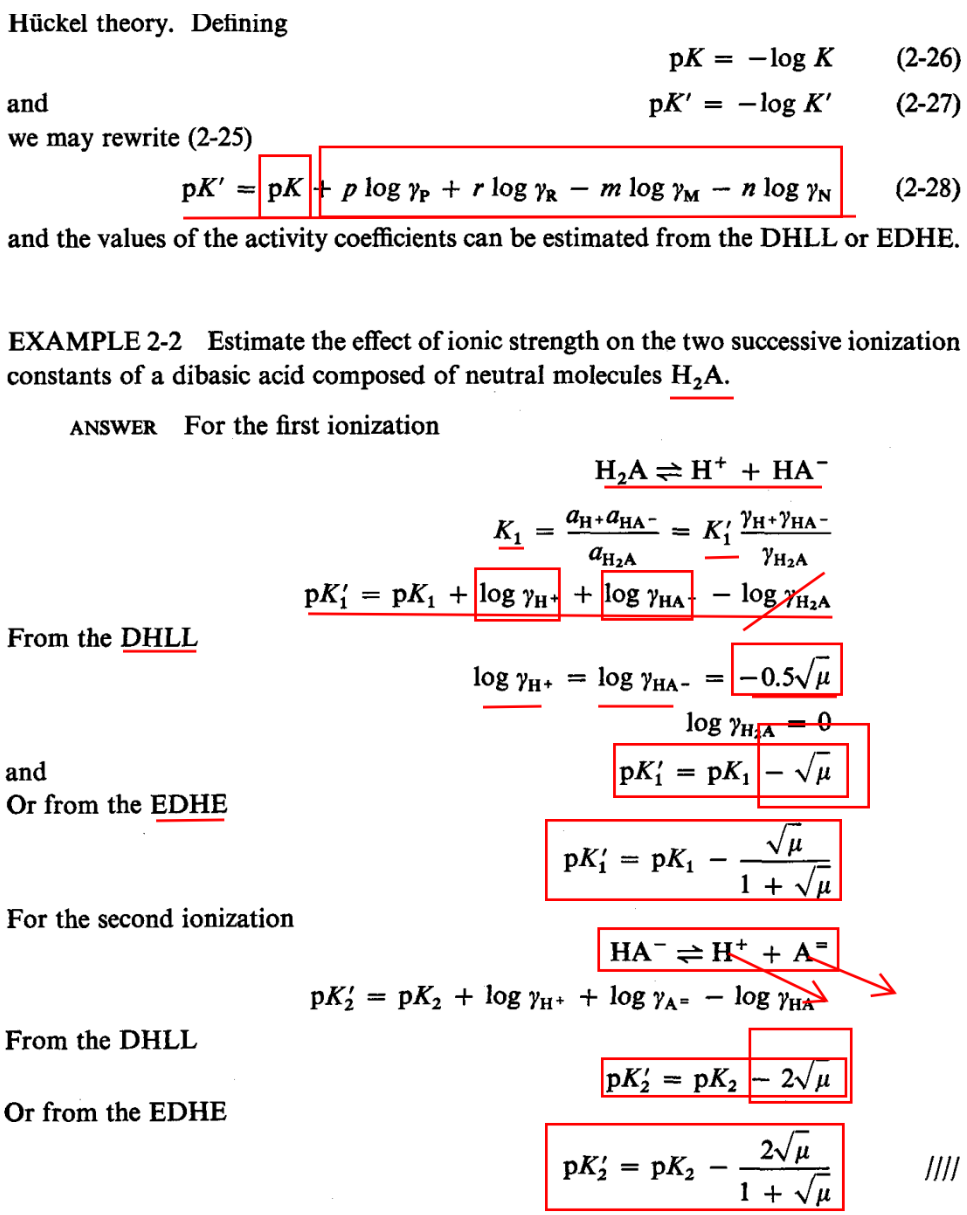
FIGURE 2-4 Comparison of experimental activity coefficients (points) and those predicted (solid lines) by a one-parameter equation. The hydration numbers *n* are HCl, 7.3; LiCl, 6.5; NaCl, 3.5; KI, 2.45; KCl, 1.9; RbCl, 1.25; MgI_2, 20.0; $MgCl_2$, 13.9; $CaCl_2$, 11.9; and $BaCl_2$, 8.4. (*From Stokes and Robinson.*[12])

Mixed electrolyte

- 1. complexation and Kinetic studies
- 2. The elelctrolytes with low complexation ability
- 3. bulky Salts (KClO4, NaClO4, …)
- 4. The change in ionic strength (and activity Coeff.) by addition the metal ion to the ligand solution should be negligible.



SALT EFFECTS ON EQUILIBRIUM CONSTANT



Hückel theory. Defining

$$pK = -\log K \qquad (2\text{-}26)$$

and

$$pK' = -\log K' \qquad (2\text{-}27)$$

we may rewrite (2-25)

$$pK' = \boxed{pK} \boxed{+ p \log \gamma_P + r \log \gamma_R - m \log \gamma_M - n \log \gamma_N} \qquad (2\text{-}28)$$

and the values of the activity coefficients can be estimated from the DHLL or EDHE.

EXAMPLE 2-2 Estimate the effect of ionic strength on the two successive ionization constants of a dibasic acid composed of neutral molecules H_2A.

ANSWER For the first ionization

$$H_2A \rightleftharpoons H^+ + HA^-$$

$$K_1 = \frac{a_{H^+}a_{HA^-}}{a_{H_2A}} = K_1' \frac{\gamma_{H^+}\gamma_{HA^-}}{\gamma_{H_2A}}$$

$$pK_1' = pK_1 + \boxed{\log \gamma_{H^+}} + \boxed{\log \gamma_{HA^-}} - \cancel{\log \gamma_{H_2A}}$$

From the DHLL

$$\log \gamma_{H^+} = \log \gamma_{HA^-} = \boxed{-0.5\sqrt{\mu}}$$

$$\log \gamma_{H_2A} = 0$$

and

$$\boxed{pK_1' = pK_1 \boxed{- \sqrt{\mu}}}$$

Or from the EDHE

$$\boxed{pK_1' = pK_1 - \frac{\sqrt{\mu}}{1 + \sqrt{\mu}}}$$

For the second ionization

$$\boxed{HA^- \rightleftharpoons H^+ + A^=}$$

$$pK_2' = pK_2 + \log \gamma_{H^+} + \log \gamma_{A^=} - \log \gamma_{HA^-}$$

From the DHLL

$$\boxed{pK_2' = pK_2 \boxed{- 2\sqrt{\mu}}}$$

Or from the EDHE

$$\boxed{pK_2' = pK_2 - \frac{2\sqrt{\mu}}{1 + \sqrt{\mu}}} \qquad ////$$

NONELECTROLYTES AND ACTIVITY

- **Nonelectrolytic behavior in solutions containing electrolytes**
- **Salting Out**
- **Salting In**

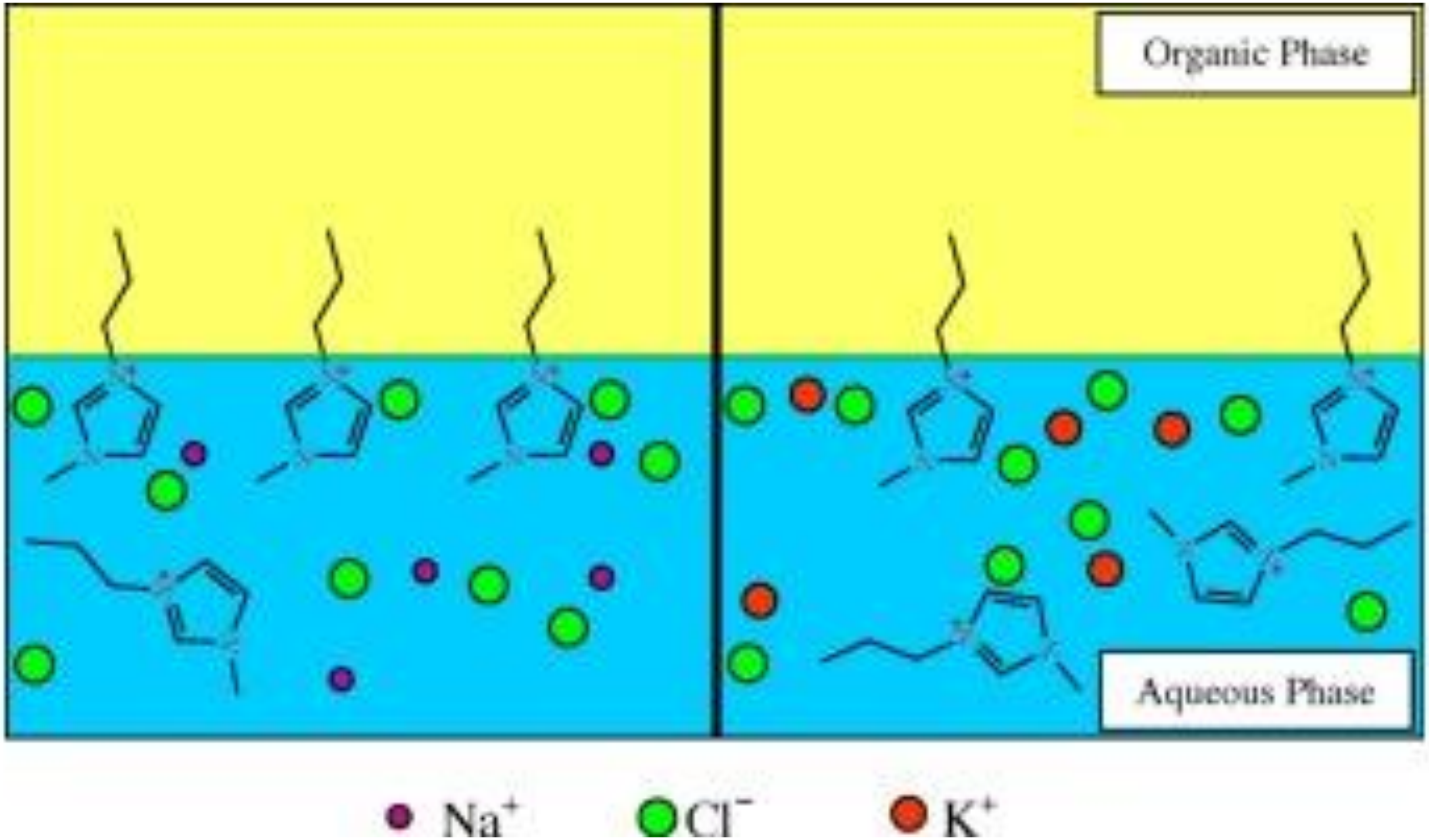
Salting Out

- NaCl+ Juice >>>> CO2
- H2O@CO2 + NaCl>>> H2O@NaCl + CO2 (g)
- Improvement in extraction efficiency (E%) by decrease in solubility of analyte in aqueous phase

Sw >Ss

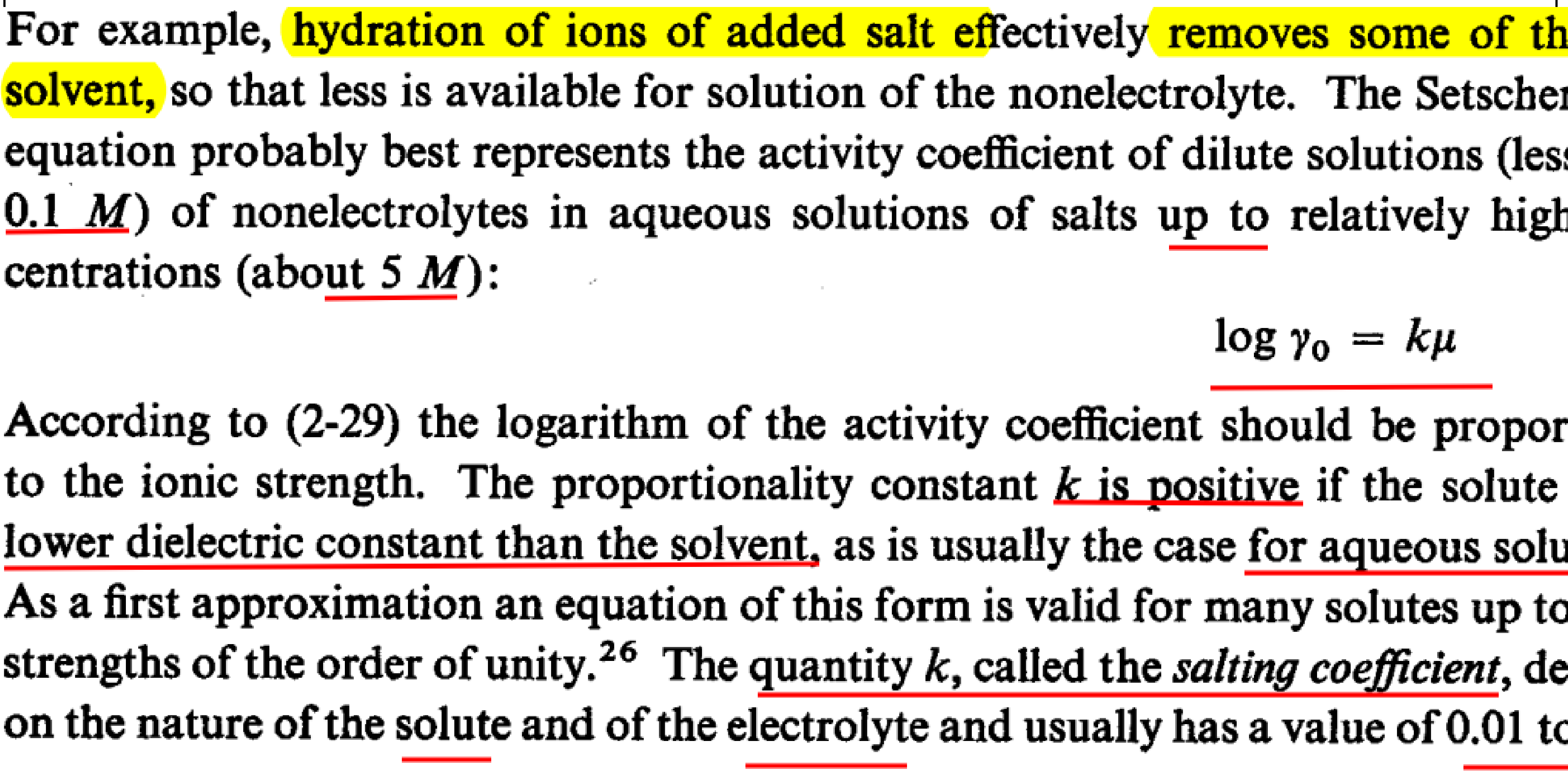
$a_w = \gamma_w S_w = a_s = \gamma_s S_s$, leading to $\gamma_s > \gamma_w$.

- More Free Solvent Molecules>> Effective Solvation >> Decrease in gama


Organic Phase
Aqueous Phase
● Na$^+$
● Cl$^-$
● K$^+$

Salting In

- **By salt addition, a decrease in extraction efficiency may be observed.**
- **In the presence of the ionic salt, solubility of the non-electrolyte component in aqueous phase was improved.**
- **HCN<<<>>>> H+ + CN-**
- **MgSO4>>>>>> Mg2+ + SO42-**
- **SOLUBILITY WATER (15%) < SALT (34 %)**



For example, hydration of ions of added salt effectively removes some of th solvent, so that less is available for solution of the nonelectrolyte. The Setsche equation probably best represents the activity coefficient of dilute solutions (less 0.1 M) of nonelectrolytes in aqueous solutions of salts up to relatively high centrations (about 5 M):

$$\log \gamma_0 = k\mu$$

According to (2-29) the logarithm of the activity coefficient should be propor to the ionic strength. The proportionality constant k is positive if the solute lower dielectric constant than the solvent, as is usually the case for aqueous solu As a first approximation an equation of this form is valid for many solutes up to strengths of the order of unity.[26] The quantity k, called the *salting coefficient*, de on the nature of the solute and of the electrolyte and usually has a value of 0.01 to

Nonelectrolytes in nonaqueous solvents

- Activity coefficients of dilute solutions
- of solutes can be studied **experimentally** by
- **liquid-liquid chromatography**
- **solvent extraction,**
- **light scattering,**
- **vapor pressure,**
- **Freezing point depression.**

- **Making Mater Structure**
- **Improvement in solvent ordering**

- **Breaking Mater Structure**
- **Decrease in solvent ordering**