Biophysical Chemistry for Life Scientists

Biotechnology Research Center, National Taiwan University
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Lecture 9

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Intermolecular interactions: From non-polar and polar molecules to electrolytes

Intermolecular interactions typically lead to extra stabilization of the molecules in a real solution relative to an ideal solution. The extra free energy is given by

$$RT \ln \gamma_B^c \approx (1/2)\, N_A\, c_B\, (1/V_{solution})\, (1/1000) \bullet \int_0^\infty \rho(r)\, U(r)\, 4\pi r^2\, dr$$

where $V_{solution}$ = volume of solution (in liters) containing 1 mole of solute;

$\rho(r)$ = radial distribution function giving the probability of finding another solute molecule at distance r and r + dr;

and $U(r)$ = potential energy of interaction between a pair of solute molecules.

For polar and non-polar molecules, U(r) is negligible beyond the distance of closest approach, σ. Therefore, the integral simplifies to

$$RT \ln \gamma_B^c \approx (1/2)\, N_A\, c_B\, (1/V_{solution})\, (1/1000) \bullet 4\pi\, \rho(\sigma)\, U(\sigma)\, \sigma^2$$

From this result, one can show that even for $c_B \sim 0.05$ M in aqueous solution, $\gamma_B^c \sim 1$. However, this conclusion is not applicable to ionic solutes, because the electrostatic interactions are much longer range. Fortunately, ionic solutions exist as positive and negative ions and the interactions between like charges and unlike charges tend to counterbalance to a large extent. Even then, $\gamma_B^c \sim 1$ only at electrolyte concentrations $< 10^{-4} - 10^{-3}$ M.

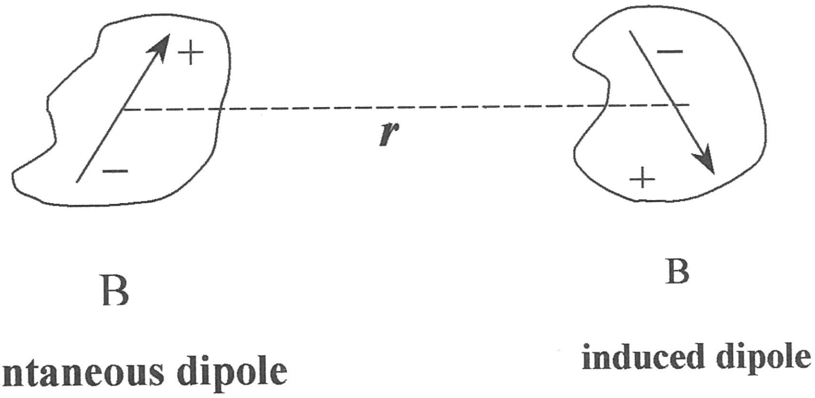
In light of the above results, it is evident that it is quite unnecessary to include activity coefficients for solute molecules in equilibrium calculations, even for polar solutes at cellular concentrations, except for (i) ionic species, which interact at long ranges; and (ii) those solute species that undergo molecular association via "hydrophobic interactions" (see below). We shall deal with activity and activity coefficients of ionic solutes later this morning. In the case of a solute species that undergoes molecular association, we could direct our attention to the activity of the monomer species if we invoke a chemical equilibrium to describe the aggregation, as we have discussed before.

Types of solute-solute interactions

(1) ***London dispersion forces*** –

- principal interaction between non-polar solutes, such as Ar, H_2, molecules with no permanent dipoles:

The electron charge distribution of a molecule can undergo instantaneous fluctuations that give it an instantaneous dipole moment. This instantaneous dipole can induce a dipole moment in another molecule that happens to be close by.



The interaction potential between the molecules, i.e., between the instantaneous and induced dipoles, can be shown to be

$$U_{\text{London}} = -(3/4)\, h\nu_o\, \alpha^2 / r^6 \qquad \text{(attractive)}$$

where α is the polarizability of the molecule ($\mu_{\text{induced}} = \alpha E$), and ν_o is the characteristic frequency of oscillation of the electron cloud.

(2) ***Interactions between two permanent dipoles*** –

- important for polar molecules (molecules with dipole moments

If the solute molecules have permanent dipole moments and they are able to rotate freely in solution, then the potential describing their interaction consists of two terms:

a. The first is associated with the tendency of the molecules to align themselves with one another.

$$U_{\text{dipole-dipole alignment}} = -(2\mu^4/3\,r^6)\,/\,k_BT \qquad \text{(attractive)}$$

μ is the permanent dipole moment associated with each of the molecules and T is the absolute temperature. The temperature-dependence arises from the tendency of the molecules to rotate and "break" the alignment in the solution, which is temperature-dependent. Note that the instantaneous interaction potential between the permanent dipoles is orientation-dependent and is given by

$$U(r) = (\mu_1 . \mu_2 / r^3 \quad - \quad 3 (\mu_1 . r)(r . \mu_2) / r^5 .$$

b. The second term arises from a dipole-induced dipole interaction, namely, an induction effect whereby the permanent dipole of a molecule induces a dipole moment in a second close-by molecule and the resultant potential energy arising from the interaction between the permanent dipole and the induced dipole:

$$U_{\text{dipole-induced dipole interaction}} = -(2 \alpha \mu^2 / r^6) \quad \text{(attractive)}$$

Adding, we obtain

$$U_{\text{polar molecules}} = U_{\text{dipole-alignment}} + U_{\text{dipole-induced dipole}}$$

(3) ***Ionic solutes-***

If the molecules are charged, there would be a coulomb interaction between them. For a pair of charged solutes,

$$z\,|e| \quad \oplus \overset{r}{\rule{4cm}{0.4pt}} \ominus \quad z'\,|e|$$

the potential energy of interaction between the molecules is given by Coulomb's Law:

$$U_{ionic} = (1/\varepsilon)\,(zz'\,e^2/4\pi\varepsilon_o r)$$

where ε = dielectric constant of the medium

ε_o = permittivity of a vaccum

$= 8.854 \times 10^{-12}\ J^{-1}\ c^2\ m^{-1}$ (in SI units)

$1/4\pi\varepsilon_o = 1$ (in cgs units)

and $|e| = 1.62 \times 10^{-19}$ coulomb

(4) *Short-range repulsion-*

The above give the range of interaction potentials between two molecules at long-range. The interaction is typically attractive, except for the coulomb repulsion between two like charges. However, as we bring the molecules closer and closer together so that the electron charge clouds overlap, the molecules will experience a strong repulsion.

This repulsion takes on the mathematical form:

$$U_{repulsion} \quad = \quad +A/\,r^{12} \quad .$$

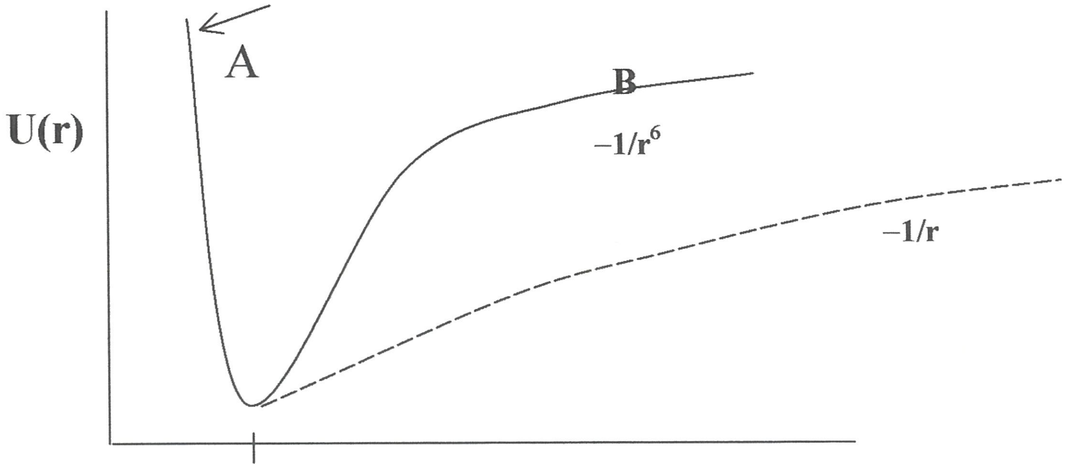
So, for non-polar and polar solutes,

$$U(r) \quad = A/\,r^{12} \quad - \quad B/\,r^{6} \quad ,$$

and for ionic solutes (attractive),

$$U(r) \quad = A/\,r^{12} \quad - \quad B/\,r \quad .$$

The sum of the London dispersion interaction and the dipole-dipole interaction outlined in (1) and (2) above, including the $1/\,r^{12}$ repulsion, is often referred to as the "van der Waal interaction".



σ ≡ distance of closest approach

In dilute solutions, the mean distance between solute molecules is very much greater than σ, the distance of closest approach. Hence, only the attractive part of the potential is important in determining γ_B in dilute solutions.

(5) *The Hydrophobic Interaction or the "Hydrophobic Bond"* –

- important for organic molecules in aqueous solution only!

Many organic molecules are non-polar, and, in fact, they contain groups or molecular surfaces that are either "greasy" or non-polar so that these parts do not interact favorably with the water molecules in direct contact with them. The water molecules are polar, and besides, they interact strongly among themselves to form a well-structured hydrogen-bonded network. Thus, these organic solutes are not well solvated in these regions or domains of the molecule, and often times, they are not even soluble in water unless there are also certain polar or charged functional groups judiciously distributed elsewhere. There are several ways to think about this. According to Otay Sinanoglu, it takes free energy to create a small cavity to accommodate a solute molecule even without grossly disrupting the solvent structure. This free energy is the work required to create the "bubble" or cavity, and is therefore related in part to the surface free energy of the cavity relative to that of the bulk solvent. One could also think about the problem in more molecular terms. In order to accommodate the non-polar surfaces or functional groups, the water molecules need to reorganize themselves differently from the hydrogen-bonded three-dimensional water structure. For example, to accommodate the flat molecular surface of an aromatic purine or pyrimidine base of nucleic acids, the water molecules solvating the aromatic nucleic acid bases must restructure to form a two-dimensional film, pretty much like the film that must obtain at an air-water interface. This process is costly in free energy. At the very least, $\Delta S < 0$, or $-T\Delta S > 0$, because certain hydrogen bonds are broken to form even more stable hydrogen bonds on the molecular surfaces, but more importantly, the water molecules involved have also lost a certain degree of the translational and orientational disorder inherent in the bulk solvent. On the other hand, the solvation of the apolar molecular surface could be neutral, stabilizing or destabilizing in terms of the enthalpy of the solvent, depending on the nature of the molecular surface to be solvated, the roughness of the surface, and the need to bifurcate the hydrogen bonds relative to those in the bulk solvent, in order to create the cavity to accommodate the solute. However, it is clear from these considerations that even under the best scenario, there would only be enthalpy-entropy compensation. Thus, the solvation of a "hydrophobic" surface is not a favorable process. To summarize, we may write

$$\Delta G^{\circ}_{\text{solvation}}(T) \quad = \quad \underbrace{\Delta H^{\circ}_{\text{solvation}}}_{\sim\ \text{neutral}} \quad - \quad \underbrace{T\Delta S^{\circ}_{\text{solvation}}}_{\text{negative}}$$

$$> \quad 0$$

In light of this analysis, it follows that two such molecules would prefer to come together to minimize the molecular surface or non-polar groups exposed to the water solvent; that is, they would associate via direct contact at their apolar molecular surfaces or at the apolar functional groups following displacement of the water of solvation, provided that the solute molecules are not charged, but are otherwise kept in solution by suitable polar groups. The driving force providing this association is called the hydrophobic interaction, and the resultant linkage(s) formed at the points of contact of the opposing molecular surfaces is often times referred to as the "hydrophobic bond". That the hydrophobic interaction has its origin in the incompatibility of apolar molecular surfaces with the highly organized hydrogen-bonded structure of bulk water is unmistaken; however, the driving force for the intermolecular association is often times augmented by the London dispersion and the van der Waal interactions between apolar and polar solute molecules mentioned earlier. The driving force for the overall process may be estimated as follows:

$$\begin{aligned}\Delta G^{\circ}_{\text{association}}(T) &= -\ \text{driving force (per mole of dimer)}\\ &= 2\,(-\,\Delta H^{\circ}_{\text{solvation}} + T\Delta S^{\circ}_{\text{solvation}})\\ &\quad + \Delta H^{\circ}_{\text{van der Waal}} - T\Delta S^{\circ}_{\text{translation}}\end{aligned}$$

where $\Delta H^{\circ}_{\text{van der Waal}}$ denotes the contribution to the enthalpy of formation of the molecular complex, and $T\Delta S^{\circ}_{\text{translation}}$ refers to the loss of configuration entropy, mostly translation, upon complex formation. The dominant terms are 2 $T\Delta S^\circ_{\text{solvation}}$ and $\Delta H^\circ_{\text{van der Waal}}$, which are both negative, so the association proceeds forward.

The hydrophobic interaction, augmented by the van der Waal interaction, is unquestionably responsible for the stacking of the nucleic acid bases observed in aqueous solution, but not in organic solvents; for the presence of secondary structure observed in single-stranded poly-nucleotides, such as poly A, and in single-stranded DNA/RNA in aqueous buffer; for the side-chains of apolar amino acids to come together to form hydrophobic domains called "molten globules" as a "protein-folding" intermediate during the folding of a protein from the random coiled state to the native structure; and for the spontaneous self-assembly of phospholipid molecules to form bilayer membranes. Thus, the hydrophobic interaction, or the hydrophobic effect, plays a prominent role in the physical chemistry of biological molecules, including both molecular structures and interactions.

Electrolytes: Activity and activity coefficient of ions

Assumptions:

- We will consider strong electrolytes that dissociate completely.
- We will use molalities, not molarities, since ions may change solution densities radically.
- We will choose a standard state (hypothetical, to be sure) for individual ionic species such that activity coefficients of individual ions (γ_+, γ_-) approach unity as m approaches infinite dilution.
- RT $\ln \gamma_+$ and RT $\ln \gamma_-$ denote the extra free energy arising from the interaction of the cation (and the anion) with its ionic atmosphere (long range), respectively.

- Any tendency of the solute ions of opposite charge to associate and form ion-pairs will be handled by an ion-pair equilibrium.

Chemical potential for an ideal electrolyte solution

For an ideal solution, solvent (A) satisfies Roault's Law, and we may write for the solvent:

$$\mu_A(T) = \mu^\circ_A(T) + RT \ln x_A$$

If the solution contains a non-dissociating solute B,

then $\mu_A(T) = \mu^\circ_A(T) + RT \ln (1 - x_B)$

But if the solute dissociates into two species,

e.g., $NaCl \rightarrow Na^+ + Cl^-$

then $\mu_A(T) = \mu^\circ_A(T) + RT \ln (1 - 2x_B)$

To obtain the chemical potential for the solute (ideal behavior), we apply the Gibbs-Duhem equation:

$$x_A \, d\mu_A = - x_B \, d\mu_B$$

But $d\mu_A = -2 RT [1/(1-2x_B)] \, d x_B$

Therefore $x_A \, d\mu_A = -(1 - 2x_B)\, 2\, RT\, [1/(1-2x_B)]\, dx_B$

$$= -2\, RT\, dx_B \quad = -x_B\, d\mu_B$$

or $$d\mu_B = (2\, RT/\, x_B)\, dx_B$$

Integrating, we obtain

$$\mu_B(T) = \mu^\circ{}_B(T) + 2RT \ln x_B = \mu^\circ{}_B(T) + RT \ln x_B{}^2$$

Note factor 2 in the exponent of x_B!

We can see this in another way. Take NaCl for example again.

$$\mu_{NaCl} = \mu_{Na+} + \mu_{Cl-}$$

$$\mu_{Na+} = \mu^\circ{}_{Na+} + RT \ln m_{Na+}$$

$$\mu_{Cl-} = \mu^\circ{}_{Cl-} + RT \ln m_{Cl-}$$

$$\mu_{NaCl} = \mu^\circ{}_{Na+} + \mu^\circ{}_{Cl-} + RT \ln (m_{Na+})(m_{Cl-})$$

$$= \mu^\circ{}_{Na+} + \mu^\circ{}_{Cl-} + RT \ln m^2{}_{NaCl}$$

Chemical potential for a non-ideal electrolyte solution

$$\mu_{NaCl} = \mu^\circ{}_{Na+} + \mu^\circ{}_{Cl-} + RT \ln (a_{Na+})(a_{Cl-})$$

$$= \mu^{\circ}_{Na+} + \mu^{\circ}_{Cl-} + RT \ln (\gamma_{Na+} m_{Na+})(\gamma_{Cl-}\, m_{Cl-})$$

$$= \mu^{\circ}_{Na+} + \mu^{\circ}_{Cl-} + RT \ln (a_{+})(a_{-})$$

$$= \mu^{\circ}_{Na+} + \mu^{\circ}_{Cl-} + RT \ln (\gamma_{+} m_{+})(\gamma_{-}\, m_{-})$$

where $a_{+} = (\gamma_{+} m_{+})$ and $a_{-} = (\gamma_{-}\, m_{-})$

or $a_{NaCl} = (a_{+})(a_{-}) \quad = \gamma_{+}\gamma_{-}\, m_{B}^{2}$

since $m_{+} = m_{B}$ and $m_{-} = m_{B}$ for a 1:1 electrolyte.

Mean activity coefficient

It is customary to define mean activity coefficient:

Define $\gamma_{\pm}^{2} \quad = \quad \gamma_{+}\gamma_{-}$

or the geometric mean $\gamma_{\pm} = (\gamma_{+}\gamma_{-})^{1/2}$

Then, $a_{NaCl} \quad = (a_{+})(a_{-}) \quad = \gamma_{\pm}^{2}\, m_{B}^{2}$

General case: Electrolyte $M_{\nu+}N_{\nu-}$

$$M_{\nu+}N_{\nu-} \quad \rightarrow \quad \nu_{+}\, M^{z+} \quad + \; \nu_{-}\, N^{z-}$$

Electrolyte neutral:

$$\therefore \quad \nu_{+}\, |z+| \quad = \nu_{-}\, |z-|$$

or $\nu_{+}\, z+ \quad + \quad \nu_{-}\, z- = 0$

Now,

$$\mu_B = \nu_+\mu_M + \nu_-\mu_N = \nu_+\mu^\circ_M + RT \ln a_M^{\nu+}$$

$$+ \nu_-\mu^\circ_N + RT \ln a_N^{\nu-}$$

$$= \mu^\circ_B + RT \ln a_M^{\nu+} a_N^{\nu-}$$

$$= \mu^\circ_B + RT \ln (\gamma_+^{\nu+}\gamma_-^{\nu-} m_+^{\nu+} m_-^{\nu-})$$

Define $\nu = \nu_+ + \nu_-$ = **total number of ions produced per electrolyte molecule**

and knowing that $m_+ = \nu_+ m_B$ **and** $m_- = \nu_- m_B$,

we can write

$$\mu_B = \mu^\circ_B + RT \ln (\gamma_\pm^{\nu} . \nu_+^{\nu+} . \nu_-^{\nu-} . m_B^{\nu})$$

where

$\gamma_\pm$ = **mean activity coefficient**

$$= (\gamma_+^{\nu+}\gamma_-^{\nu-})^{1/(\nu_+ + \nu_-)}$$

$$= (\gamma_+^{\nu+}\gamma_-^{\nu-})^{1/\nu}$$

Example

$Fe_2(SO_4)_3$: $\nu_+ = 2$; $\nu_- = 3$; **and** $\nu = 5$

$$\mu_{Fe2(SO4)3} = \mu^\circ_{Fe2(SO4)3} + RT \ln (\gamma_\pm^5 . 2^2 . 3^3 . m^5_{Fe2(SO4)3})$$

Debye-Huckel Theory

This is the theory that has been developed to calculate the mean activity coefficients of ionic solutes in solution. While the treatment is quite straightforward, it is beyond the scope of this course. I shall merely sketch the ideas and summarize the results.

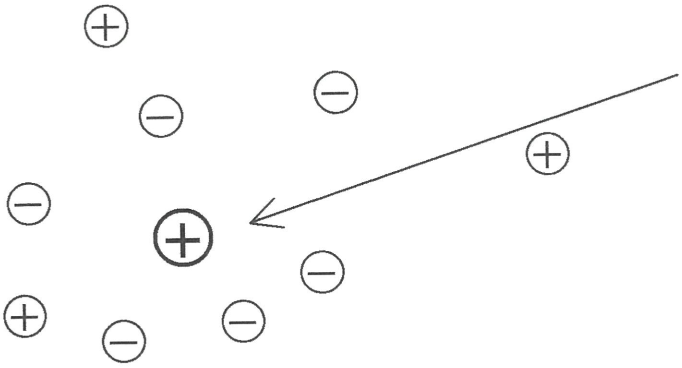
Peter Debye and Huckel made the following assumptions in their treatment:

(1) The ionic solute is a strong electrolyte. It is completely dissociated into ions in the solution.

(2) Observed deviations from ideal behavior (Henry's Law) are due to electrical interactions between the ions.

(3) A continuous dielectric medium is assumed for the solvent with a dielectric constant ε. This condition means that the theory is invalid at concentrations of solute large enough so as to alter the solvent structure for more than a negligible fraction of the solvent.

The objective of the treatment is to calculate the electrostatic potential in the vicinity of a given ion.



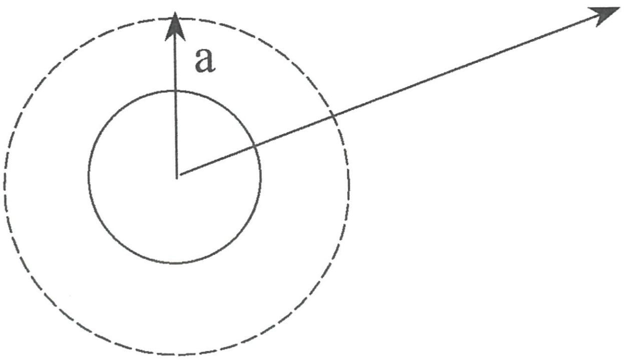
Debye and Huckel showed that the potential near the i^{th} ion is given by

$$\Phi_i(r) = z_i|e|/\varepsilon r - z_i|e|\kappa/\varepsilon(1+\kappa a)$$

where

$$\kappa^2 = (4\pi/\varepsilon)(e^2/k_B T)\Sigma_j z_j^2 n_j$$

a **= distance of closest approach to the i^{th} ion.**



First term: electrical potential due to the ion under consideration, of charge z_i |e | in a medium of dielectric constant ε.

Second term: electrical potential due to all the other ions, which form what is referred to as the ionic atmosphere of the ion under consideration.

Knowing the electrical potential due to the ionic atmosphere, we could now calculate the potential energy of interaction between the i^{th} ion and the ionic atmosphere, or the minimum work that must be expended to place the ion there. This extra free energy is just $k_BT \ln \gamma_i$ per ion, or $RT \ln \gamma_i$ for one mole of the ion.

To compute this work, let's imagine that the i^{th} ion is introduced into the solution in a hypothetical uncharged state, and then calculate the work required to charge this ion to z_i |e| reversibly.

Insertion of the uncharged ion into the solution requires negligible work, at least compared to the charging of the ion, because the electrostatic interaction between the uncharged ion or atom with the ionic atmosphere is very small.

Now the work (reversible) performed to charge up the "ion" from 0 to $z_i\,|e|$ is

$$W = \int_0^{z_i |e|} \Phi_i^{\text{ionic atmosphere}}(q)\; dq$$

Since $\Phi_i^{\text{ionic atmosphere}}(z_i\,|e|) = -\,z_i\,|e|\,\kappa/\varepsilon(1+\kappa a)$

$\Rightarrow \Phi_i^{\text{ionic atmosphere}}(q) = -\,q\,\kappa/\varepsilon(1+\kappa a)$

Therefore,

$$W = \int_0^{z_i |e|} -\,q\,\kappa/\varepsilon(1+\kappa a)\; dq$$

$$= -\,(z_i^2\, e^2\, \kappa) / 2\varepsilon(1+\kappa a) \quad \text{per ion}$$

or for a mole of ion

$$W = -\,N_A\,(z_i^2\, e^2\, \kappa) / 2\varepsilon(1+\kappa a) = RT \ln \gamma_i^{\,m}$$

or

$$\ln \gamma_i^{\,m} = -\,N_A\,(z_i^2\,e^2\,\kappa)\,/\,(2\,RT\varepsilon)(1+\kappa a) \quad < 0$$

$$\text{or} \quad \gamma_i^{\,m} < 1$$

Lewis and Randall defined the quantity ionic strength:

$$I = (1/2)\,\Sigma_j\, m_j\, z_j^2$$

where m_j = molality of ion j

and showed that

$$\log_{10} \gamma_\pm^{m} = (-)\,A_\gamma\,|z+\,z-|\,I^{1/2}\,/\,(1 + Ba\,I^{1/2})$$

where $A_\gamma = (e^2/\varepsilon k_B T)^{3/2}\,(2\pi N_A \rho_{solvent}/1000)^{1/2}\,(1/2.303)$

and $B = [(8\pi/\varepsilon)(e^2/k_B T)(N_A \rho_{solvent}/1000))^{1/2}$

Debye-Huckel Limiting Law

For a solution with sufficiently low ionic strength so that $1 + Ba\,I^{1/2} \approx 1$

we have

$$\log_{10} \gamma_\pm^{m} = (-)\,A_\gamma\,|z+\,z-|\,I^{1/2}$$

A_γ is temperature-dependent as it is proportional to

$$[\rho_{solvent}/\varepsilon^3 T^3]^{1/2}$$

For H_2O, A_γ = 0.511 at 25 °C

0.492 at 0 °C

0.596 at 100 °C

Examples

(a) NaCl $z+ = 1$, $z- = -1$

$$I = (1/2)\,\Sigma_j\, m_j\, z_j^2 = (1/2)\,[(m_+ (1)^2 + m_-(-1)^2)$$

$$= \underline{m}$$

Therefore, at 25 °C, $\log_{10} \gamma_\pm^m = (-)\, 0.511\, (1)\, \underline{m}^{1/2}$

For 0.05 $\underline{m}$ NaCl , $\gamma_\pm^m = 0.76$

(b) 0.01 $\underline{m}$ $MgCl_2$

$$I = (1/2)\,\Sigma_j\, m_j\, z_j^2 = (1/2)\,[0.01 \times 2^2 + .01 \times 2 \times 1^2]$$

$$= (1/2)\,[\,0.04 + 0.02] = 0.03\ \underline{m}$$

and $\gamma_\pm^m = 0.66$

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Problem Set 6
Due Monday, December 4, 2000

(1)Calculate the electric field (E*) and the electrostatic potential (Φ) at a distance r from a charge q_B. What is the direction of the electric field? Recall that $\mathbf{F} = q_A\mathbf{E}^*$ and $U(r) = q_A\Phi(r)$, where q_A is a test charge. **Bold symbols denote vector quantities.**

(2)Calculate the potential energy of interaction between Na^+ and Cl^- separated by a distance of 10 Å (1 nm) (a) in a vacuum; and in (b) in water at 37 °C (dielectric constant $\varepsilon = 74.2$).. Do the calculations in both SI and cgs units.

(3)Calculate the ionic strength of a 0.01 m solution of $Fe_2(SO_4)_3$. Estimate the mean activity coefficient of this solute at 37 °C according to Debye-Huckel theory.

(4)Calculate the ionic strength of a solution containing 0.1 m NaCl and 0.01 m $MgCl_2$.

(5) From Coulomb's Law and the reversible work required to move two oppositely charged ions from infinite separation to a distance r apart, obtain an expression for the free energy of interaction between a pair of ions in solution. Also, obtain an expression for the electrostatic entropy and enthalpy, i.e., the entropy and enthalpy of interaction.

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