Ionic Strength and Activities of Ions Exercise

$$\log \gamma_i = \frac{-0.51 \cdot z^2 \sqrt{\mu}}{1 + (\alpha \sqrt{\mu} / 305)}$$ The extended Debye-Hückel Equation

$$a_i = \gamma_i [i]$$

(1) What happens to the activity coefficient (γ) as the ionic strength increases?

(2) At zero ionic strength what is the value of the activity coefficient (γ)? What is the activity at this same point?

(3) What affect does the charge of the ion in solution have on the activity coefficient? How does this effect change as a function of the ionic strength (μ)?

(4) Does the activity coefficient depend on whether the ion is a cation or an anion?

(5) Does the size of an ion affect the magnitude of the activity for varying ionic strengths?

(6) Let's see how the "spectator" ions present in solution affect the pH of a weak acid

(a) What is the pH of a 0.0200 M benzoic acid (Ka = 6.28×10^{-5}) solution in water?

(b) What is the % dissociation of the benzoic acid in pure water?

Now we'll add some "spectator" ions to the solution. If the benzoic acid is dissolved in 0.10 M $CaCl_2$ instead of pure water:

(c) Calculate the ionic strength of the solution (assume that the contribution from the benzoic acid is negligible).

(d) Find the appropriate hydrated radii (α) and calculate the activity coefficients (γ) for both the H^+ and the benzoate ion.

(e) Now set up the equilibrium expression with the activities of the ions. Calculate the concentration of both the H^+ and the benzoate ion. What is the pH of this solution? What is the % dissociation?

(f) By what % did the benzoic acid dissociation change between the pure water solution and the calcium chloride solution?

(g) How does the presence of the calcium chloride alter the equilibrium? Explain using the skaters analogy.

SUPPORT your answers to questions 3, 4, and 5. By discussing the results of the following graphs (x-y scatter, points only) in Excel:

For all graphs plot the ionic strength (μ) from 0 to 0.1 in steps of 0.0001.

(a) Graph $\boldsymbol{\gamma}$ ***vs.*** $\boldsymbol{\mu}$ for a M^+, M^-, M^{2+}, M^{3+} and an M^{4+} ion each with a hydrated radius (α) of 500 ppm. Place all 5 curves on the same graph (please label each curve)

(b) Graph $\boldsymbol{\gamma}$ ***vs.*** $\boldsymbol{\mu}$ for H^+, Li^+, Na^+, K^+, Cs^+

Ion	Ion size (α, pm)
CHARGE = ±1	
H^+	900
$(C_6H_5)_2CHCO_2^-$, $(C_3H_7)_4N^+$	800
$(O_2N)_3C_6H_2O^-$, $(C_3H_7)_3NH^+$, $CH_3OC_6H_4CO_2^-$	700
Li^+, $C_6H_5CO_2^-$, $HOC_6H_4CO_2^-$, $ClC_6H_4CO_2^-$, $C_6H_5CH_2CO_2^-$, $CH_2{=}CHCH_2CO_2^-$, $(CH_3)_2CHCH_2CO_2^-$, $(CH_3CH_2)_4N^+$, $(C_3H_7)_2NH_2^+$	600
$Cl_2CHCO_2^-$, $Cl_3CCO_2^-$, $(CH_3CH_2)_3NH^+$, $(C_3H_7)NH_3^+$	500
Na^+, $CdCl^+$, ClO_2^-, IO_3^-, HCO_3^-, $H_2PO_4^-$, HSO_3^-, $H_2AsO_4^-$, $Co(NH_3)_4(NO_2)_2^+$, $CH_3CO_2^-$, $ClCH_2CO_2^-$, $(CH_3)_4N^+$, $(CH_3CH_2)_2NH_2^+$, $H_2NCH_2CO_2^-$	450
$^+H_3NCH_2CO_2H$, $(CH_3)_3NH^+$, $CH_3CH_2NH_3^+$	400
OH^-, F^-, SCN^-, OCN^-, HS^-, ClO_3^-, ClO_4^-, BrO_3^-, IO_4^-, MnO_4^-, HCO_2^-, $H_2citrate^-$, $CH_3NH_3^+$, $(CH_3)_2NH_2^+$	350
K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-	300
Rb^+, Cs^+, NH_4^+, Tl^+, Ag^+	250
CHARGE = ±2	
Mg^{2+}, Be^{2+}	800
$CH_2(CH_2CH_2CO_2^-)_2$, $(CH_2CH_2CH_2CO_2^-)_2$	700
Ca^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, $C_6H_4(CO_2^-)_2$, $H_2C(CH_2CO_2^-)_2$, $(CH_2CH_2CO_2^-)_2$	600
Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, S^{2-}, $S_2O_4^{2-}$, WO_4^{2-}, $H_2C(CO_2^-)_2$, $(CH_2CO_2^-)_2$, $(CHOHCO_2^-)_2$	500
Pb^{2+}, CO_3^{2-}, SO_3^{2-}, MoO_4^{2-}, $Co(NH_3)_5Cl^{2+}$, $Fe(CN)_5NO^{2-}$, $C_2O_4^{2-}$, $Hcitrate^{2-}$	450
Hg_2^{2+}, SO_4^{2-}, $S_2O_3^{2-}$, $S_2O_6^{2-}$, $S_2O_8^{2-}$, SeO_4^{2-}, CrO_4^{2-}, HPO_4^{2-}	400
CHARGE = ±3	
Al^{3+}, Fe^{3+}, Cr^{3+}, Sc^{3+}, Y^{3+}, In^{3+}, lanthanides[a]	900
$citrate^{3-}$	500
PO_4^{3-}, $Fe(CN)_6^{3-}$, $Cr(NH_3)_6^{3+}$, $Co(NH_3)_6^{3+}$, $Co(NH_3)_5H_2O^{3+}$	400
CHARGE = ±4	
Th^{4+}, Zr^{4+}, Ce^{4+}, Sn^{4+}	1 100
$Fe(CN)_6^{4-}$	500

a. Lanthanides are elements 57–71 in the periodic table.   SOURCE: J. Kielland, *J. Am. Chem. Soc.* **1937**, .