Physical Chemistry Laboratory I
Experiment 3
Effect of Ionic Strength on the Solubility of $CaSO_4$
(Revised, 01/25/06)

It is generally assumed that solutions of strong electrolytes are completely dissociated and that the deviations from ideal behavior (in freezing point depression or conductivity) of the electrolyte solutions result from interionic attractions of the ions. However, the early literature is replete with examples of partially dissociated species, or ion pairs for polyvalent electrolytes, even in moderately dilute solutions. There are many recent articles on the dissociation constants of ionic compounds in aqueous solutions. Ion pairs are important for polyvalent electrolytes in water and in media of low dielectric constant (water/organic solvent mixtures or water at high temperatures).

The standard treatment of solubility and solubility product constants in introductory chemistry courses is generally doubly simplified: 1st with the assumption that the activity coefficients are 1, and 2nd with the assumption that the ionic salts are completely dissociated in solution. Both of these assumptions are reasonable for very slightly soluble 1/1 electrolytes (such as AgCl), but neither is correct for more soluble polyvalent electrolytes. Some recent texts for quantitative analysis include significant discussions of activity coefficients and introduce the concept of ion pairs for polyelectrolytes. [1]

The solubility of $CaSO_4$ and the variation of S{$CaSO_4$}with concentration of added electrolyte illustrate the effects of activity coefficients and ion pairs. There have been many articles in Journal of Chemical Education (J. Chem. Ed.) that discuss the solubility and the use of solubility data to calculate $K_{SP}\{CaSO_4\}$. [2 - 7] Ion pairing is not as well known as it should be. Although we will be concerned only with the interactions of Ca^{2+} with SO_4^{2-} in this experiment, non-covalent bonding of Ca^{2+} is frequently observed with other species.

The dissociation reaction that is often used to describe the solubility of $CaSO_4$ assumes that calcium sulfate is completely dissociated in aqueous solution:

$$CaSO_4(S) \rightarrow Ca^{2+}(aq) + SO_4^{2-}(aq). \qquad (1)$$

From this equation, one may write the appropriate equilibrium expression, including activity coefficient effects:

$$K_{SP}^o = a\{Ca^{2+}\}*a\{SO_4^{2-}\} = [Ca^{2+}]\,[SO_4^{2-}]\gamma_\pm^2 \qquad (2a)$$

$$K_{SP}^o = K_{SP}\{Apparent\}\gamma_\pm^2 = S^2\,\gamma_\pm^2 \qquad (2b)$$

In these equations, **a{X}** = activity of X; the concentration of each species, **$[X_i]$**, is given in mol{X_i}/L{sol'n}; $\gamma_\pm$ refers to the mean (geometric average) activity coefficient for the two ions ($\gamma_\pm^2 = \gamma\{Ca^{2+}\}*\gamma\{SO_4^{2-}\}$); **$K_{SP}^o$** is the "true" solubility product constant for $CaSO_4$, *i. e.*, the value at infinite dilution or "zero concentration" of ions; and **K_{SP}\{Apparent\}** is the product of the ionic concentrations, $[Ca^{2+}]*[SO_4^{2-}]$. There is no other source (or sink) of either ion when pure calcium sulfate is dissolved in water; therefore, $[Ca^{2+}] = [SO_4^{2-}] = S(CaSO_4)$.

A. S{$CaSO_4$} in pure water at 25.0 °C.

The determination of the solubility of a dense solid like $CaSO_4(s)$ is not particularly difficult at room temperature. Add some $CaSO_4(s)$ to a 250 mL Erlenmeyer flask {not a volumetric flask}, add ~ 200 mL of distilled H_2O, immerse in the constant temperature bath at 25.0° C for ~ 15 minutes, with stirring: magnetic stirrer and stirring bar. Use the lead weight around the flask to hold it down. Neither the weight of calcium sulfate nor the volume of water is critical as long as solid is present at the end of the experiment. However, record the weight of $CaSO_4{\bullet}2H_2O$ that you use. The solubility of calcium sulfate in water at about room temperature is ~ 0.015 M. Calculate the amount of $CaSO_4{\bullet}2H_2O$ needed to dissolve in 200 mL of water and use ~ 100 % excess.

Let the solution settle for ~ 15 minutes in the constant temperature bath and then use a volumetric pipet to take a 25.00 mL aliquot (sample) of the solution. (Use the automatic pipetter.) Standard quantitative procedures require that you rinse the pipet with the solution being analyzed before taking the sample. Don't touch the pipet to the bottom and remove solid $CaSO_4$. Be careful with the pipet: glass is fragile and broken glass is dangerous, especially when glass breaks in your hands.

Transfer the 25.00 mL aliquot to a beaker, add ~ 50 mL of water to keep the solution from splashing while being stirred (graduated cylinder OK), a pinch of the hydroxynaphthol blue (HNB) indicator, and adjust the pH of the solution to ~ 11 with ~ 5 mL of NH_3/NH_4Cl buffer (graduated cylinder OK). Use pH meter. (See the *Appendix* for general information about the pH meter. Operating instructions are provided.) If necessary, increase the pH by adding a few drops of 1 M NaOH. Titrate the solution with standard EDTA to the appearance of a pure blue. Standardized Na_2H_2EDTA is available. Do the titration in a beaker, so that you can keep the pH electrode in the solution during the titration. Be careful that the stirring bar does not hit the pH electrode. If the pH drops below 10 during the titration, add a few mL of the buffer (or 1 M NaOH) to return the pH to ~ 11.

Analyze duplicate samples. Use both values in your analyses of the data (not the average). $S(CaSO_4, 25\ ^oC) \approx 0.015$ M. If you obtain significantly different values, check calculations and/or repeat the titration. The solubility of $CaSO_4$ does not vary much around room temperature. This analysis gives the total amount of calcium in solution in all forms: $Ca^{2+}(aq)$ and $CaSO_4(aq)$, if it is present. Experiments reported in the literature have sometimes involved very long equilibration times. However, long times do not seem to be necessary for experiments at room temperature.

EDTA titrations are discussed in Harris, *Quantitative Chemical Analysis*, or other recent quantitatative analysis texts. One mole of EDTA reacts with one mole of Ca^{2+}. The end point of the titration is the appearance of a pure blue in a solution that was initially a wine red. This end point is not as easy to see as the phenolphthalein end point for the titration of NaOH with HCl in Exp. 1. However, accurate values for $[Ca^{2+}]$ can be achieved using this standard procedure.

One way to recognize the end point color is to take ~ 50 mL of distilled water, bring to pH ~ 11, add a few drops of EDTA solution to complex any cations that might be present as impurities, and add a pinch of the indicator and observe the color. Keep this solution (or one of the titrated solutions) as a reference for the blue color.

One can use the Debye-Hückel-Guggenheim (DHG) equation to calculate activity coefficients for solutions of known concentration (ionic strength).

$$\log\gamma_j = -\left(\frac{0.509Z_j^{\,2}\sqrt{I}}{1+\sqrt{I}}\right) \quad \text{or} \quad \log\gamma_\pm = -\left(\frac{0.509|Z_+Z_-|\sqrt{I}}{1+\sqrt{I}}\right) \qquad (3)$$

In this equation, the ionic strength, I or μ, is given by the following equation.

$$\mu = I = \frac{\sum_j m_j Z_j^2}{2} \qquad (4)$$

The ionic strength includes all ions in the solution; $\mathbf{Z_i}$ is the charge of an ion of concentration, **m**; and the constant, 0.509, applies to aqueous solutions at 25.0 °C. Oh yes: base 10 logs.This equation gives an activity coefficient of 1 for an ion pair, because $Z = 0$. The DHG equation uses molality, **m**, in calculating the ionic strength, **I** or **μ.** For dilute aqueous solutions, $m \approx M$ and no significant error, < 1 %, is introduced by using molarity in DHG equation.

If one assumes that there are no ion pairs in solution, then $S\{CaSO_4\} = [Ca^{2+}] = [SO_4^{2-}]$ and Eq. (2b) applies. With activity coefficients calculated with the DHG equation, Eq. (3), one can calculate K_{SP}^o from the solubility of $CaSO_4$ in pure water, if there are no ion pairs in solution.

Report your data for the solubility of $CaSO_4$ in pure water in Table 1, appropriately labeled, as V{EDTA}for each titration, $[Ca^{2+}]$ calculated from these volumes, ionic strength, K_{SP}\{Apparent) = $[Ca^{2+}][SO_4^{=}] = S^2$, and K_{SP}^o, calculated from Eq. 2b, using activity coefficients calculated using the DHG model, Eq. 3. The table should also contain footnotes with the concentration of EDTA, the volume of aliquot titrated, and other information essential to the calculations.

Compare these values with literature values for $K_{SP}^o\{CaSO_4\}$ and $S\{CaSO_4\}$. Give references for your values.

B. Effect of ionic strength on S{CaSO$_4$} at 25.0 °C

In separate 250 mL **volumetric flasks**, prepare five solutions of an inert electrolyte, NaCl, of accurately known concentrations. The concentrations should be in the range ~ 0.05 M to ~ 0.25 M. The exact values are not critical but each solution should be known with an accuracy of ~ one part in 1000. A volume of 250 mL of each solution should be sufficient. Use the analytical balance and weigh NaCl to ± 0.0001 g.

Repeat the previous procedure to determine the solubility of $CaSO_4$ in water with each of these salt solutions. That is, add ~ 200 mL of each solution to excess $CaSO_4 \bullet 2H_2O$ (s) in a 250 mL Erlenmeyer flask. Stir the solution (~ 15 minutes) and allow it to settle in the constant temperature bath (~ 15 minutes) as before. These concentrations of added inert electrolyte are such that $S\{CaSO_4\}$ will be significantly larger than the value in pure water. Take an aliquot of the solution and titrate as before. Duplicate titrations should be done for each solution. Use both values in the analysis of your data.

Record your data in Table 2 as M{NaCl}, V{EDTA}, and $S\{CaSO_4, M\}$, with auxiliary data given as footnotes. The values for the concentrations of NaCl should be given to four decimal places and the solubility of $CaSO_4$ should be given to four significant figures (five decimal places). {Yes. This is an overestimation of the reliability of your data.}

Calculate the ionic strength of each solution and list in a column in Table 2. Include all ions in calculating I (or μ): Ca^{2+}, SO_4^{2-}, Na^+, and Cl^-. Use Equation (3) to calculate $\log\{\gamma_\pm\}$ from the ionic strength at each concentration and give these values in Table 2, as well. {You will need these data for a subsequent plot.}

Plot your data as $S\{CaSO_4, M\}$ *vs.* M{NaCl} in Fig. 1, with an appropriate heading.The solubility of $CaSO_4$ should increase monotonically with increasing M{salt}. Include your values for $S\{CaSO_4\}$ with no added inert electrolyte, M{NaCl} = 0. In this figure also plot the literature data from Table A of S{$CaSO_4$} *vs*. M{KNO_3} at the end of this experiment. Should your data and these data be similar? Discuss.

An equation relating the activity coefficients in molal units, **γ**, and in molar units, **y**, is known, $y_\pm = \gamma_\pm(m/M)d_o$. [9] In this equation, d_o is the density of the solvent. From data in the CRC Handbook of Chemistry and Physics, the ratio of molality to Molarity, m/M is less than or equal to 1.01 for M ≤ 0.2 mol/L (mol/dm^3) for several alkali metal salts. Consequently, you may use the DHG equation to calculate activity coefficients using molarities and introduce no significant error in the analysis.

If significant concentrations of ion pairs of $CaSO_4$ exist in aqueous solutions, then $K_{SP}{}^o = [Ca^{2+}][SO_4{}^{2-}]\gamma_\pm{}^2$ is still correct; $[Ca^{2+}] = [SO_4{}^{2-}]$ is still correct; but S{$CaSO_4$} = $[Ca^{2+}]$ is **not** correct. The solubility of $CaSO_4$ is given by a two-term equation,

$$S = [Ca^{2+}] + [CaSO_4, aq]. \tag{5}$$

In Eq. (6), $[Ca^{2+}]$ = the molarity of Ca^{2+} ions in solution and $[CaSO_4,aq]$ = the molarity of the ion pair.

From Eq. (2a) and $[Ca^{2+}] = [SO_4{}^{2-}]$,

$$[Ca^{2+}] = \sqrt{\frac{K_{SP}{}^o}{\gamma_\pm^2}} = \frac{\sqrt{K_{SP}{}^o}}{\gamma_\pm} \tag{6}$$

The additional reaction and equilibrium expression involve the dissociation of the ion pair,

$$CaSO_4(aq) \Leftrightarrow Ca^{2+}(aq) + SO_4{}^{2-}(aq) \tag{7}$$

The dissociation equilibrium constant for this chemical reaction is given in (9)

$$K_D = \frac{[Ca^{2+},aq][SO_4{}^{2-},aq]\gamma_\pm{}^2}{[CaSO_4,aq]} \tag{8}$$

Solving Eq. (9) for $[CaSO_4,aq]$, one obtains the following expression,

$$[CaSO_4,aq] = \frac{[Ca^{2+},aq][SO_4{}^{2-},aq]\gamma_\pm{}^2}{K_D} = \frac{K_{SP}{}^o}{K_D} \tag{9}$$

Substituting this relationship and Eq. (7) into Eq. (6), one obtains (finally)

$$S\{CaSO_4, M\} = \frac{\sqrt{K_{SP}{}^o}}{\gamma_\pm} + \frac{K_{SP}{}^o}{K_D} \tag{10}$$

Plot your data in Fig. 2 as S *vs*. $1/\gamma_\pm$ to get a value for the slope, $\sqrt{K_{SP}{}^o}$, and for the intercept, $K_{SP}{}^o/K_D$. A plot of your data should give a reasonably straight line with a positive intercept. Compare this value for $K_{SP}{}^o$ with the value calculated from the solubility in pure water in part A and with $K_{SP}{}^o$ obtained from the data in Table A, and with values of K_{SP} from the literature (with references).

Plot (Fig 2) and analyze the data for S{$CaSO_4$} vs. M{KNO_3} from Table A in the same fashion.

There is, however, the problem with these values for $K_{SP}{}^o$ and K_D: they are only first approximations to the correct values. The activity coefficients, $\gamma_\pm$, were calculated as if $[Ca^{2+}] = [SO_4{}^{2-}]$ = S. Although $[Ca^{2+}] = [SO_4{}^{2-}]$ is still correct, the analysis should be done again by calculating the activity coefficients, $\gamma_\pm$, using the better estimate for $[Ca^{2+}]$ and $[SO_4{}^{2-}]$ that

$$[Ca^{2=}] = [SO_4{}^{2-}] = S - \frac{K_{SP}{}^o}{K_D} \tag{12}$$

However, you are not required to make this iteration.

The following data were reported in 1918 on the solubility of $CaSO_4$ in solutions of KNO_3 at 25.0 °C.

Table A

M{KNO_3}, M	S{$CaSO_4$},M
0	0.01530
0.02755	0.01805
0.05268	0.02008
0.10307	0.02120

References

1. D. C. Harris, Quantitative Chemical Analysis, 5th Ed., 1999, Chap. 8
2. R. W. Ramette, ***J. Chem. Ed***. 33, 610 (1956).
3. L. Meites, J. S. F Pode, and H. C. Thomas, ***J. Chem. Ed***. 43, 667 (1966).
4. A. K Sawyer, ***J. Chem. Ed***. 60, 416 (1983).
5. R. B. Martin, ***J. Chem. Ed.*** 63, 471 (1986).
6. D. Masterman, ***J. Chem.Ed.*** 64, 409 (1987).
7. S. O Russo and G. I. H. Hanania***, J. Chem. Ed***. 66,148 (1989)
8. J. H. Carpenter, ***J. Chem. Ed***. 66, 184 (1989).
9. R. A. Robinson and R. H. Stokes, Electrolyte Solutions, Butterworths, 1955, p. 30.
10. R. G. Ainsworth, ***J. Chem. Soc. Farad***, 69, 1028 (1973).

Appendix

GENERAL pH METER INSTRUCTIONS

PLEASE TREAT THIS EXPENSIVE EQUIPMENT WITH CARE

- The measuring electrode is fragile: do not stir with it; do not allow a stirring bar to hit it; do not jam it into bottom of any container.

- Unscrew the plastic storage container to remove it from the electrode, leaving the cap on the electrode. Do not pull the container or container cap off of the electrode.

- Always rinse the electrode with distilled water when moving it to a different solution or buffer. Rinse, but do not wipe or blot it.

- The white ring at the top of electrode must remain in its closed position.

- The electrode must **NEVER** dry out: it must always be either in the solution being measured, or in the filled storage container!

- At the end of your experiment session, as part of your clean up, empty the storage container, rinse it out with distilled water, refill it (to about ¾–full) with the KCl storage solution provided, and then return the electrode into the container, standing upright.

- To properly standardize the meter, refer to instructions in the ***Operation Manual*** at the station for the experiment.