The Solubility of $CaSO_4 \cdot 2H_2O$ and Ionic Strength Effect

CHEM 445 - 025L

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ABSTRACT

In this experiment, the solubility of calcium sulfate dihydrate, $CaSO_4 \cdot 2H_2O$, was determined in three different solutions: two distilled water solutions, labeled 1 and 2, and one saline, NaCl, solution. In solutions 1 and 2, the experimental average solubilities, $S_{ave}\{CaSO_4 \cdot 2H_2O\}$, were determined to be 0.0157 ± 0.0007 M and 0.0156 ± 0.0004 M, respectively. Additionally, the average concentration of the calcium ions, $[Ca^{2+}]_{ave}$, was determined, via ion-selective electrode measurements, to be 0.0133 ± 0.0004 M and 0.0135 ± 0.0004 M, in solutions 1 and 2 respectively. Furthermore, the average solubility product constants were determined by calculating the associated activity coefficients via two different methods: K_{sp}° {Debye-Hückel[1]} = $(2.0 \pm 0.1)*10^{-5}$ M and K_{sp}° {Davies[2]} = $(3.6 \pm 0.2)*10^{-5}$ M.

As for the NaCl solution, the experimental average solubility was determined to be 0.0204 ± 0.0007 M. Moreover, through a single iteration of the data collected previously, the calculated average solubility came out to be $S_{ave}\{CaSO_4 \cdot 2H_2O\}$ = 0.043 ± 0.003 M (Debye-Hückel) and $S_{ave}\{CaSO_4 \cdot 2H_2O\}$ = 0.021 ± 0.001 M (Davies). From inspection, it is clear that the Davies model provided better agreement with the experimental data.

INTRODUCTION

Solubility[3] is defined to be the maximum amount of solute that can dissolve in a solvent, at a specific temperature, creating a saturated solution. To determine the solubility of a compound such as gypsum, $CaSO_4 \cdot 2H_2O$, an excess amount of the salt was added to the solvent; in this case, water. To establish equilibrium (rate of dissolving = rate of crystallization), the flask containing the solution was continuously stirred in a constant temperature bath for about an hour. Following that, a measured aliquot of the solution was titrated with standard EDTA, using calcon as the indicator. The result of this analysis gave the total concentration of the calcium in solution (i.e. the solubility). However, since a titrimetric analysis does not provide $[Ca^{2+}]$ alone, a different method had to be utilized: voltage measurements using an ion-selective electrode. With this data, in addition to activity coefficients calculated using both the Debye-Hückel and Davies models, the solubility product and dissociation equilibrium constants were determined. A similar detailed approach was carried out for a second water solution.

Additionally, the solubility of gypsum was determined in an NaCl solution to study the ionic strength effect. As the number of inert ions in a solution increases (or as the ionic strength increases), the ionic atmospheres around the ions (Ca^{2+} and SO_4^{2-}) increases. This, consequently, shields the ions from each other, decreasing their tendency to come together. In other words, the solubility increases. Therefore, one expects the solubility of $CaSO_4 \cdot 2H_2O$ to be relatively high in the NaCl solution compared to the distilled water solutions. Once again, the solubility was determined via a titrimetric analysis using standard EDTA as the titrant and calcon as the indicator.

It is important to note that for each aliquot of titrant, the pH was adjusted to 10 - 11, as EDTA is not very soluble in low pH ranges.

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PROCEDURE

To prepare the first distilled water solution, labeled solution 1, a weighted, excess amount of $CaSO_4 \cdot 2H_2O$ and approximately 200 mL of water were added to a 250 mL Erlenmeyer flask. The flask containing the solution was placed in a constant temperature bath where it was constantly stirred for about an hour until it settled. The same steps were repeated for the second distilled water solution, labeled solution 2; however, this time a larger amount of the salt was added. The NaCl solution was prepared by adding a predetermined weighed amount of the salt to a 250 mL volumetric flask, to ensure that the concentration of the solution fell in the range ~0.1 M to ~0.2 M. A weighed amount of $CaSO_4 \cdot 2H_2O$ was added to a 250 mL Erlenmeyer flask where approximately 200 mL of the saline solution was added. Again, the flask was placed in a constant temperature bath for about an hour such that equilibrium was reached. After all three solutions have settled, each one was titrated three times with standard EDTA.

To prepare the standard EDTA solution, a predetermined weighed amount of $Na_2H_2EDTA \cdot 2H_2O$ was added to a 500 mL volumetric flask, to ensure that the concentration of the solution was ~0.015 M. Five pellets of NaOH were added to the volumetric flask to ensure that the predominant form of EDTA was $EDTA^{4-}$, before the volume was brought up to the mark on the neck.

Before the titrations were carried out, a reference solution was prepared. In a 250 mL Erlenmeyer flask, 75 mL of distilled water, a few drops of EDTA and NaOH, and one tablet of the calcon indicator were added. This solution was blue (the reference color for the endpoint). After each of the three solutions was carefully decanted in three respective beakers, three 25.00 mL aliquots of each solution were pipetted into three respective Erlenmeyer flasks, resulting in 9 total samples. To each sample, one calcon tablet and a few drops of NaOH were added. Consequently, each of the 9 solutions was titrated with the standard EDTA solution, until the initial burgundy color of the sample turned blue.

Next, an ion selective electrode[1], ISE, was used to determine the concentration of the calcium ions in each of the distilled water solutions. The NaCl solution was not used because of the stark difference in ionic strength between the saline solution and that of the calibration solutions. To calibrate the ISE, three standard solutions were used. For each standard solution, two voltage measurements were made to ensure that the results were reproducible. From the data collected a calibration curve was constructed. The same procedure was repeated for the two distilled water solutions. A 50.00 mL aliquot of each solution was stirred with 1.00 mL of the ionic strength adjuster, ISA, before an ISE measurement was made. Two measurements were made for each of the two solutions.

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[1] The ion selective electrode was malfunctioning; therefore, this part of the lab was not conducted. Instead, the lab instructor provided a set of data that was used to construct the calibration curve from which the concentrations of the calcium ions in each distilled water solution were determined.

RESULTS AND DISCUSSION

Table 1[*]: Experimental and ISE Data for Distilled Water Solutions

	Solution 1			Solution 2		
	Experimental Data					
Trial	**1**	**2**	**3**	**1**	**2**	**3**
Initial Volume (mL)	3.1	1.5	12.0	1.4	0.3	1.5
Final Volume (mL)	33.4	32.6	40.5	30.1	30.5	31.5
V{EDTA}[1] (mL)	30.3	31.1	28.5	28.7	30.2	30.0
S{CaSO$_4$•2H$_2$O}[2] (M)	0.0159	0.0163	0.0150	0.0151	0.0159	0.0158
S$_{ave}${CaSO$_4$•2H$_2$O}[3] (M)	0.0157			0.0156		
	ISE Data					
	1	**2**		**1**	**2**	
[Ca^{2+}] (M)	0.0130	0.0135		0.0132	0.0138	
[Ca^{2+}]$_{ave}$ (M)	0.0133			0.0135		
[SO$_4$$^{2-}$] (M)	0.0133			0.0135		
[CaSO$_4$] (M)	0.0025			0.0020		
K$_{sp}$[4]	1.76E-04			1.83E-04		
pK$_{sp}$[5]	3.76			3.74		
I[6] (M)	0.0530			0.0542		
	DHLL[7]	**Davies[8]**		**DHLL**	**Davies**	
γ_+[9]	0.340	0.448		0.336	0.445	
γ_-[10]	0.340	0.448		0.336	0.445	
K$_{sp}$$^{\circ}$[11]	2.03E-05	3.5E-05		2.07E-05	3.6E-05	
pK$_{sp}$$^{\circ}$[12]	4.69	4.45		4.68	4.44	
K$_D$$^{\circ}$[13]	8E-03	1.4E-02		1.0E-02	1.8E-02	
pK$_D$$^{\circ}$[14]	2.1	1.8		2.0	1.7	
K$_D$[15]	0.07			0.09		
pK$_D$[16]	1.2			1.0		

[*][EDTA] = 0.01313 M, V$_{aliquot}$ = 25.0 mL

[1]Volume of EDTA needed to reach the equivalence point
[2]Solubility of CaSO$_4$•2H$_2$O
[3]Average solubility of CaSO$_4$•2H$_2$O
[4]Solubility product constant
[5]pK$_{sp}$ = -log[K$_{sp}$]
[6]Ionic strength
[7]Debye-Hückel Limiting Law
[8]Davies Equation
[9]Activity coefficient of cation, Ca^{2+}

[10]Activity coefficient of anion, SO$_4$$^{2-}$
[11]*True* solubility product constant
[12]pK$_{sp}$$^{\circ}$ = -log[K$_{sp}$$^{\circ}$]
[13]*True* Dissociation equilibrium constant
[14]pK$_D$$^{\circ}$ = -log[K$_D$$^{\circ}$]
[15]Dissociation equilibrium constant
[16]pK$_D$ = -log[K$_D$]

Table 1 shows the collection of data pertaining to the distilled water solutions. The solubility of $CaSO_4 \cdot 2H_2O$ for each of the three samples of solutions, 1 and 2, was determined using the following equation:

$$S = \frac{[EDTA] * V\{EDTA\}}{V_{aliquot}} \quad \text{(Eq. 1)}$$

Consequently, the average solubilities of solutions 1 and 2 were determined to be 0.0157 ± 0.0007 M and 0.0156 ± 0.0004 M , respectively. Both of these values were very close to the known solubility of $CaSO_4 \cdot 2H_2O$ at 25°C, which is approximately 0.015 M[4].

From the average solubility of the compound and the average concentration of the calcium ions, $[Ca^{2+}]_{ave}$, the latter of which was determined using the ion selective electrode, ISE, the concentration of the ion pair, $[CaSO_4]$, for each solution was determined using the equation below:

$$[CaSO_4] = S_{ave}\{CaSO_4.2H_2O\} - [Ca^{2+}]_{ave} \quad \text{(Eq.2)}$$

The value obtained for the concentration of the ion pair for each solution, tabulated in Table 1, was smaller than the corresponding solubility of the compound, as expected.

Since $[Ca^{2+}] = [SO_4^{2-}]$, the solubility product constant, K_{sp}, and the negative logarithm of K_{sp} were easily calculated using the following equations:

$$K_{sp} = [Ca^{2+}][SO_4^{2-}] \quad \text{(Eq. 3)}$$

$$pK_{sp} = -log(K_{sp}) \quad \text{(Eq. 4)}$$

The values obtained for the solubility product constant were not accurate because Eq. 3 assumed ideality (i.e. that the solution is ideal); however, that was not the case because of the strong coulombic attractions between the cations and anions. To rectify this problem, the activity coefficients had to be used to account for the deviation from ideality. Therefore, the "true" solubility product constant, $K_{sp}°$, and the corresponding negative logarithm of $K_{sp}°$ were obtained using the equations below:

$$K_{sp}° = [Ca^{2+}][SO_4^{2-}]\gamma_+\gamma_- \quad \text{(Eq. 5)}$$

$$pK_{sp}° = -log(K_{sp}°) \quad \text{(Eq. 6)}$$

where the activity coefficients, γ_+ and γ_-, were obtained using both the Debye-Hückel Limiting Law and the Davies equations:

$$\text{Debye-Hückel Limiting Law: } log(\gamma_x) = -0.509Z_x^2\sqrt{I} \text{ (Eq. 7)}$$

$$\text{Davies Equation: } log(\gamma_x) = -0.509Z_x^2\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right) \text{ (Eq. 8)}$$

where

$$I = \mu = \frac{1}{2}\sum_j m_j Z_j^2 \text{ (Eq. 9) is the ionic strength}$$

$$Z_x \text{ is the charge of the ion of interest}$$

In Eq. 9, m denotes the molality of each ion. However, since the solutions dealt with in this experiment were relatively dilute, the molality was approximated by the molarity. Furthermore, since the magnitude of the charge was the same for both the cation and anion, the activity coefficients were also the same. From Table 1, it can be seen that the $K_{sp}°$ values for solutions 1 and 2 calculated using the activity coefficients obtained from the Davies equation, were greater than those whose activity coefficients were obtained from the DHLL. Additionally, the former values were closer to the actual value of $K_{sp}°$ which is 3.14E-5[5]. This emphasizes the relatively high degree of accuracy of the Davies equation due to its empirical nature.

Although the ion pair was not factored into the calculation of the ion strength due to its neutrality, its concentration was used to calculate an equilibrium constant known as the dissociation equilibrium constant which measures the likelihood of the $CaSO_4$ to dissociate into its constituent ions, Ca^{2+} and SO_4^{2-}. Once again, there were two "forms" of this equation: One that assumed ideality and the other which took into account the deviations from ideality. Furthermore, the corresponding negative logarithms of both constants could be easily obtained using the following equations:

$$K_D = \frac{[Ca^{2+}][SO_4^{2-}]}{[CaSO_{4,(aq)}]} \quad \text{(Eq. 10)}$$

$$pK_D = -log(K_D) \quad \text{(Eq. 11)}$$

$$K_D° = \frac{[Ca^{2+}][SO_4^{2-}]\gamma^2}{[CaSO_{4,(aq)}]} \quad \text{(Eq. 12)}$$

$$pK_D° = -log(K_D°) \quad \text{(Eq. 13)}$$

The calculated values using the above equations were tabulated in Table 1. Once again, it can be observed that the $K_D°$ values for solutions 1 and 2 calculated using the activity coefficients obtained from the Davies equation, were greater than those whose activity coefficients were obtained from the DHLL. However, there seemed to be an inconsistency among the former and latter values. This might have been due to experimental error (i.e. not being careful or precise when taking measurements).

Table 2[*]: Experimental Data for NaCl Solution

	NaCl Solution		
Trial	**1**	**2**	**3**
Initial Volume (mL)	1.5	2.4	1.5
Final Volume (mL)	41.1	39.7	41.2
V{EDTA}[1] (mL)	39.6	37.3	39.7
S{CaSO$_4$•2H$_2$O}[2] (M)	0.0206	0.0194	0.0206
S$_{ave}${CaSO$_4$•2H$_2$O}[3] (M)	0.0204		
	DHLL[4]	**Davies[5]**	
	NaCl Only		
I$_{NaCl}$[6] (M)	0.1232		
γ_+[7]	0.193	0.352	
γ_-[8]	0.193	0.352	
K$_{sp,ave}$°[9]	2.0E-05	3.6E-05	
[Ca^{2+}] (M)	0.023	0.017	
	All Ions Included		
[Ca^{2+}] (M)	0.023	0.017	
[SO$_4^{2-}$] (M)	0.023	0.017	
I$_{Ions}$[10] (M)	0.217	0.191	
γ_+	0.113	0.314	
γ_-	0.113	0.314	
[Ca^{2+}] (1st Iteration) (M)	0.040	0.019	
S$_{calc}${CaSO$_4$•2H$_2$O} (M)	0.043	0.021	

[*]**[EDTA] = 0.01313 M, V$_{aliquot}$ = 25.0 mL**

[1]Volume of EDTA needed to reach the equivalence point

[2]Solubility of CaSO$_4$•2H$_2$O

[3]Average solubility of CaSO$_4$·2H$_2$O

[4]Debye-Hückel Limiting Law

[5]Davies Equation

[6]Ionic strength determined only by [NaCl] = [Na$^+$] = [Cl$^-$] = 0.123 M

[7]Activity coefficient of cation, Ca^{2+}

[8]Activity coefficient of anion, SO$_4^{2-}$

[9]Average *true* solubility product constant

[10]Ionic strength of all ions in solution

Table 2 shows the collection of data pertaining to the saline, NaCl, solution. The solubility of $CaSO_4 \cdot 2H_2O$ for each of the three samples was determined using Eq. 1. Additionally, the solubility of the compound in the NaCl solution was predicted using the $[CaSO_4]$ and $K_{sp,ave}°$, the latter of which was obtained by taking the average of the $K_{sp}°$ values previously obtained via each method (i.e. DHLL and Davies). This was done by first calculating the ionic strength, using Eq. 9, from only the sodium ions, Na^+, and chloride ions, Cl^-. This value was denoted by I_{NaCl} in Table 2. Consequently, the activity coefficients were calculated via Eq.7 and Eq. 8, where $I = I_{NaCl}$. The next step was to calculate the concentration of the calcium ions, $[Ca^{2+}]$, by rearranging Eq. 5:

$$K_{sp}° = [Ca^{2+}][SO_4^{2-}]\gamma_+\gamma_- \quad (Eq. 5)$$

$$\text{since } [Ca^{2+}] = [SO_4^{2-}]$$

$$K_{sp}° = [Ca^{2+}]^2\gamma_+\gamma_-$$

$$\text{therefore,}$$

$$[Ca^{2+}] = \sqrt{\frac{K_{sp}°}{\gamma_+\gamma_-}} \quad (Eq. 14)$$

After the $[Ca^{2+}]$ was obtained, the ionic strength was recalculated; this time including all the ions in solution: Ca^{2+}, SO_4^{2-}, Na^+, and Cl^-. Using this newly calculated ionic strength, I_{Ions}, the activity coefficients and the new $[Ca^{2+}]$ were recalculated using Eqs. 7, 8 and Eq. 14, respectively. Although another iteration could have been done to obtain a better estimate of $[Ca^{2+}]$, one iteration proved to be sufficient. Using this $[Ca^{2+}]$ and the previously calculated, corresponding $[CaSO_4]$, the solubility of $CaSO_4 \cdot 2H_2O$ was obtained by rearranging Eq. 2. As can be seen from the results obtained, the solubility that was calculated from $[Ca^{2+}]$ which was obtained using activity coefficients determined using the Davies equation, provided better agreement with the experimental data. This is because the Debye-Hückel Limiting Law gives too small of activity coefficients for solutions of high concentrations and therefore, a very high solubility; whereas, the Davies equation, due to its empirical nature, provides a better fit to the data over a wide range of concentrations.

Table 3: Uncertainties Associated with Calculated Values for Solutions 1 and 2

	Uncertainty			
	Solution 1		Solution 2	
$S_{ave}\{CaSO_4 \cdot 2H_2O\}$ (M)	0.0007		0.0004	
$[Ca^{2+}]_{ave}$ (M)	0.0004		0.0004	
$[SO_4^{2-}]$ (M)	0.0004		0.0004	
$[CaSO_4]$ (M)	0.0008		0.0006	
$K_{sp}\{Apparent\}$	8E-06		8E-06	
$pK_{sp}\{Apparent\}$	2E-02		2E-02	
Ionic Strength (M)	0.0004		0.0006	
	DHLL	Davies	DHLL	Davies
K_{sp}°	9E-07	2E-06	9E-07	2E-06
pK_{sp}°	2E-02	2E-02	2E-02	2E-02
K_D°	3E-03	5E-03	3E-03	5E-03
pK_D°	1E-01	1E-01	1E-01	1E-01
K_D	0.02		0.03	
pK_D	0.1		0.1	

The uncertainties in Table 3 were calculated and recorded to one significant figure each, providing a reasonable estimate of the precision associated with each value.

Table 4: Uncertainties Associated with Calculated Values NaCl Solution

	Uncertainty	
$S_{ave}\{CaSO_4 \cdot 2H_2O\}$ (M)	0.0007	
I_{NaCl} (M)	0.0001	
	DHLL	Davies
Average K_{sp}°	1E-06	2E-06
$[Ca^{2+}]$ (M)	1E-03	1E-03
$[SO_4^{2-}]$ (M)	1E-03	1E-03
I_{Ions} (M)	2E-03	1E-03
$[Ca^{2+}]$ (1st Iteration) (M)	0.003	0.001
$S_{calc}\{CaSO_4 \cdot 2H_2O\}$ (M)	0.003	0.001

The uncertainties in Table 4 were calculated and recorded to one significant figure each, providing a reasonable estimate of the precision associated with each value.

CONCLUSION

As can be seen from the experimental data, the solubility of $CaSO_4 \cdot 2H_2O$ was relatively high in the NaCl solution compared to the two distilled water solutions which exhibited similar solubilities. This was expected since as the ionic strength of a solution increases, the solubility of the compound in question increases as well. Furthermore, from the two models that were used to calculate the activity coefficients and consequently the solubility product constants and the average solubility of $CaSO_4 \cdot 2H_2O$ in the NaCl solution, the Davies equation provided better agreement with the experimental data.

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