

The Solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and Ionic Strength Effect

CHEM 445 - 025L

Abdul Fayed Abdul Kadir, Matt Varallo

Due Date: April 24th, 2020

Submission Date: April 23th, 2020

TABLE OF CONTENTS

Abstract	2
Introduction	3
Results and Discussion	4
Conclusion	10
References	11

ABSTRACT

Solubility of CaSO_4 was determined from three different solutions: two distilled water and a salt solution, labelled as solution 1, 2, and 3 respectively, where solution 2 was more concentrated than solution 1. The average solubility, $S_{\text{Ave}}\{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\}$, obtained experimentally were 0.01120 ± 0.00014 M, and 0.0129 ± 0.0012 M for solution 1 and 2 respectively. The average concentration for Ca^{2+} ions measured by using ISE for solution 1 and 2 are 0.01095 ± 0.00046 M and 0.01266 ± 0.00099 M respectively. $K_{\text{sp, ave}}$ computed from two different equations; Debye–Hückel limiting law and Davies, were found to be $(1.81 \pm 0.24) \times 10^{-5}$ and $(2.99 \pm 0.40) \times 10^{-5}$ respectively.

Solution 3 was obtained experimentally to have $S_{\text{Ave}}\{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\}$ of 0.00630 ± 0.00052 M. An iteration was done to determine the $S\{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\}$, where it was conducted first by assuming the overall ionic strength was only affected by salt solution, and $S\{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\}$ was found to be 0.0264 ± 0.0035 M and 0.0074 ± 0.0018 M for Debye–Hückel and Davies equation respectively. By taking into account all ions present in the solution in the calculation of ionic strength, $S\{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\}$ was 0.0456 ± 0.0068 M and 0.0174 ± 0.0028 , Debye–Hückel and Davies equation respectively. It was found that Davies has a closer calculated value of $S\{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\}$ to the experimental value than that of Debye–Hückel, although it was not in a good agreement with each other.

INTRODUCTION

Solubility is the ability of a substance (solute) to dissolve in a solvent, where it is measured in the maximum amount of solute dissolved in equilibrium, resulting in a saturated solution ^[1]. The solubility of calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), better known as gypsum, is being investigated as well as the effect of varying the ionic strength of the solution on its solubility. For a slightly soluble polyvalent salts, the assumption of having activity coefficient of 1 in the solution for 1:1 electrolytes would no longer hold, as the interactions of ions (Ca^{2+} and SO_4^{2-}) has some contribution to the overall solubility, due to the consequences of Coulomb's Law. The activity coefficients were determined by two different models, which were Davies and Debye–Hückel limiting law (DHLL) models. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was titrated with the standard ethylenediamine tetraacetic acid (EDTA) in order to find its solubility, where it gave the total amount of calcium in the solution, in both forms of Ca^{2+} ions and CaSO_4 . In order to find the concentration of Ca^{2+} ions alone, a measurement through an ion-selective electrode (ISE) was conducted on the solution.

The variation in ionic strength of the solution is performed by using a distilled water as one of the solvents, and sodium chloride solution (NaCl) as the other. Conceptually, when the concentration of ions in the solution increases, the ionic atmosphere around Ca^{2+} and SO_4^{2-} ions increases too, resulting in a greater shield between the two ions ^[2]. Hence, the solubility of the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ increases.

RESULTS AND DISCUSSION

Table 1: Titration and ISE Data of Distilled Water Solutions*

Titration Data						
Solution #	1			2		
Trial #	1	2	3	1	2	3
V{EDTA} (mL)	4.70	4.70	4.60	4.90	5.30	5.90
S{CaSO ₄ ·2H ₂ O} ¹ (M)	0.0113	0.0113	0.0110	0.0118	0.0127	0.0142
S _{Ave} {CaSO ₄ ·2H ₂ O} ² (M)	0.0112			0.0129		
ISE Data						
Solution #	1			2		
Trial #	1	2		1	2	
[Ca ²⁺] (M)	0.0106	0.0113		0.0134	0.0120	
[Ca ²⁺] _{Ave} (M)	0.0109			0.0127		
[SO ₄ ²⁻] (M)	0.0109			0.0127		
[CaSO ₄] (M)	2.53E-04			2.16E-04		
K _{sp} {apparent} ³	1.20E-04			1.60E-04		
pK _{sp}	3.92			3.80		
Ionic strength (M)	0.0438			0.0507		
Type of Equation	DHLL	Davies		DHLL	Davies	
γ ₊ ⁴	0.375	0.473		0.348	0.454	
γ ₋ ⁴	0.375	0.473		0.348	0.454	
K _{sp} ^{°5}	1.69E-05	2.68E-05		1.94E-05	3.30E-05	
pK _{sp} [°]	4.77	4.57		4.71	4.48	
K _D ^{°6}	0.067	0.106		0.090	0.153	
pK _D [°]	1.18	0.98		1.05	0.82	
K _D ⁷	0.474			0.742		
pK _D	0.32			0.13		

*[EDTA] = 0.06000 M, V{aliquot} = 25.00 mL

^{1,2} Solubility at each volume and average solubility of CaSO₄·2H₂O

^{3,5} Apparent and 'true' solubility product constant

⁴ Activity coefficient of ions of interest

^{6,7} ‘True’ and normal dissociation equilibrium constant

Table 1 shows the experimental data obtained from conducting titration on EDTA and ISE experiment, without the presence of NaCl solution. The volumes of EDTA titrated were used to compute the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $S\{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\}$, by using Eq. 1. The average of $S\{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\}$, $S_{\text{Ave}}\{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\}$ was calculated for each solution, where it was found to be 0.0112 M and 0.0129 M for solution 1 and 2 respectively.

$$S\{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\} = \frac{[EDTA] \times V\{EDTA\}}{V\{aliquot\}} \text{ (Eq. 1)}$$

At 25 °C, in literature, $S\{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\}$ was found to be 0.0139 M ^[3]. It was quite close but still significantly higher than the experimentally obtained value. This might be due to uncertain control in temperature when conducting the experiment, where the reported $S\{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\}$ might not be exactly for the value at 25 °C. ISE was being used to measure the voltage of the remaining solutions from the titration experiment. The ISE was calibrated with known concentrations of Ca^{2+} ions and the calibration curve had a linear trendline with Eq. 2.

$$E = 31.054 \log[\text{Ca}^{2+}] + 109.593 \text{ (Eq. 2)}$$

The measured voltage of each solution was used to find $[\text{Ca}^{2+}]$ in the solution by using Eq. 2. For each solution, the average concentration of Ca^{2+} ions, $[\text{Ca}^{2+}]_{\text{Ave}}$ was computed and was found to be 0.0109 M and 0.0127 M for solution 1 and 2 respectively.

$$S_{\text{Ave}}\{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\} = [\text{Ca}^{2+}]_{\text{Ave}} + [\text{CaSO}_4] \text{ (Eq. 3)}$$

By using the relationship shown in Eq. 3, $[\text{CaSO}_4]$ for each solution could be determined, and it was 2.531E-04 M and 2.161E-04 M for solution 1 and 2 respectively. Different types of equilibrium constants were calculated, including ‘true’ and apparent solubility product constant (K_{sp}° and $K_{\text{sp}}\{\text{apparent}\}$ respectively), and ‘true’ and normal dissociation equilibrium constant (K_{D}° and K_{D}). pK_i for each equilibrium constant is also computed. They were calculated by using Eq. 4 - 8 as listed below:

$$K_{\text{sp}}^\circ = [\text{Ca}^{2+}][\text{SO}_4^{2-}]\gamma_+\gamma_- \text{ (Eq. 4)}$$

$$K_{\text{sp}}\{\text{apparent}\} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] \text{ (Eq. 5)}$$

$$K_{\text{D}}^\circ = \frac{[\text{Ca}^{2+}, \text{aq}][\text{SO}_4^{2-}, \text{aq}]\gamma_+\gamma_-}{[\text{CaSO}_4, \text{aq}]} \text{ (Eq. 6)}$$

$$K_{\text{D}} = \frac{[\text{Ca}^{2+}, \text{aq}][\text{SO}_4^{2-}, \text{aq}]}{[\text{CaSO}_4, \text{aq}]} \text{ (Eq. 7)}$$

$$\text{pK}_i = -\log K_i, i - \text{any } K \text{ of interest (Eq. 8)}$$

Except for $K_{sp}\{\text{apparent}\}$, the rest of the equilibrium constants are functions of ionic strength, I , and activity coefficients of ions present, γ_j . For each solution, γ_j was computed by using two different equations, DHLL and Davies equation. The formula of I and γ_j for each equation are listed in Eq. 9 - 11.

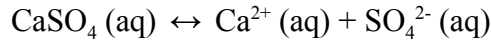
$$I = \frac{1}{2} \times \sum_j^c m_j Z_j^2 \quad (\text{Eq. 9})$$

$$\text{DHLL: } \log \gamma_j = -0.509 Z_j^2 \sqrt{I} \quad (\text{Eq. 10})$$

$$\text{Davies: } \log \gamma_j = -0.509 Z_j^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I \right) \quad (\text{Eq. 11})$$

where Z_j - charge of ion j , m_j - molality concentration of ion j (in dilute solutions, $m \approx M$)

Obtained in literature, $K_{sp}^\circ = 3.14\text{E-}5$ at 25°C [4]. Based on these two solutions, Davies predicted a closer value of K_{sp}° for both solutions, in comparison to DHLL's, although they were significantly different from each other. The K_{sp}° were found to be $2.676\text{E-}05$ and $3.303\text{E-}05$ for Davies, meanwhile $1.685\text{E-}05$ and $1.944\text{E-}05$ for DHLL, solution 1 and 2 respectively. Davies is often used in determining activity coefficients over a wider range of concentrations, unlike DHLL, where it is limited only to very dilute solutions [5].



By referring to the reaction above, the ion pair in this solution is in equilibrium with its constituent ions. Due to Coulomb's law, ion pairing has a more significant effect on the equilibrium constant for polyvalent ions, in comparison to monovalent ions [6]. With the assumption that the activity coefficient of the ions are in unity, K_D° as previously defined could be generated from the reaction above, where $K_D^\circ = 0.106$ and 0.153 by Davies equation, while $K_D^\circ = 0.067$ and 0.090 by DHLL equation, solution 1 and 2 respectively. K_D meanwhile only considers the concentration of ions, not the activity of each ions in the solutions.

Table 2: Experimental and Calculated Data of NaCl Solution *

EXPERIMENTAL DATA				
Trial #	1	2	3	4
V{EDTA} (mL)	2.85	2.42	2.61	2.63
S{CaSO ₄ ·2H ₂ O} ¹ (M)	0.0068	0.0058	0.0063	0.0063
S _{Ave} {CaSO ₄ ·2H ₂ O} ² (M)	0.0063			
CALCULATED DATA				
Type of Equation	DHLL		Davies	
K _{sp,ave} ³	1.81E-05		2.99E-05	
[CaSO ₄] _{Ave} (M)	2.35E-04			
Assume only NaCl affects ionic strength				
Ionic Strength (M)	0.1499			
γ ₊ ⁴	0.163		0.760	
γ ₋ ⁴	0.163		0.760	
[Ca ²⁺] (M)	0.0262		0.0072	
[SO ₄ ²⁻] (M)	0.0262		0.0072	
S{CaSO ₄ ·2H ₂ O} (M)	0.0264		0.0074	
Assume all ions affect ionic strength				
Ionic Strength (M)	0.2545		0.1787	
γ ₊	0.094		0.319	
γ ₋	0.094		0.319	
[Ca ²⁺] (M)	0.0453		0.0171	
[SO ₄ ²⁻] (M)	0.0453		0.0171	
S{CaSO ₄ ·2H ₂ O} (M)	0.0456		0.0174	

*[EDTA] = 0.0600 M, [NaCl] = 0.1499 M, V{aliquot} = 25.00 mL

^{1,2} Solubility at each volume and average solubility of CaSO₄ · 2H₂O

³ Average solubility product constant

⁴ Activity coefficient of ions of interest

Next, the same titration was conducted, but now with the presence of NaCl in the solution, where Table 2 tabulated all the relevant findings. The $S\{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\}$ was obtained in three different ways, where one of them was computed through the titration experiment. The average true solubility product constant, $K_{sp,ave}^\circ$ was determined by using the data in Table 1 for each respective equation (DHLL and Davies). $[\text{CaSO}_4]$ was averaged from the tabulated data in Table 1, denoted as $[\text{CaSO}_4]_{Ave}$.

Two other predictions were conducted by iterations by first assuming the ionic strength of the solution was only affected by the NaCl. Since CaSO_4 is a neutral compound, it is independent of the ionic strength^[6]. Ionic strength calculation was computed with Eq. 9. The activity coefficient of Ca^{2+} and SO_4^{2-} ions were then calculated by using both DHLL and Davies equation (Eq. 10 and 11). Since $[\text{Ca}^{2+}] = [\text{SO}_4^{2-}]$, Eq. 4 could be rearranged as shown in Eq. 12. $[\text{Ca}^{2+}]$ could be computed from Eq. 12 by using the $K_{sp,ave}^\circ$ value determined earlier. $S\{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\}$ was then determined by using Eq. 3.

$$[\text{Ca}^{2+}] = \sqrt{\frac{K_{sp,ave}^\circ}{\gamma_+ \times \gamma_-}} \quad (\text{Eq. 12})$$

The calculation was iterated by changing the value of ionic strength, where now it took into account the concentration of all ions present in the solution. Applying the same formula as before, the value of $[\text{Ca}^{2+}]$ and $[\text{SO}_4^{2-}]$ that were used in the formula were from the previous part of this iteration, where $[\text{Ca}^{2+}] = [\text{SO}_4^{2-}] = 0.0262 \text{ M}$, while $[\text{Na}^+] = [\text{Cl}^-] = 0.1499 \text{ M}$. The activity coefficient was recalculated by using both DHLL and Davies equation, and applying Eq. 12 to find the new $[\text{Ca}^{2+}]$, new $S\{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\}$ could be computed.

It was obtained experimentally that $S\{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\} = 0.0063 \text{ M}$. From the first calculation, $S\{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\} = 0.0264 \text{ M}$ and 0.0074 M from DHLL and Davies equation respectively. After the first iteration, $S\{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\} = 0.0456 \text{ M}$ and 0.0174 M , DHLL and Davies equation respectively. It could be seen that Davies equation had a closer value of $S\{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\}$ to that obtained experimentally than DHLL, although there was a significant difference between these values. As previously discussed, Davies could be widely used for a broader range of concentrations than DHLL. Additionally, it was obtained that $S\{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\}$ at NaCl solution was lower than that at distilled water, which contradicted the fact that as ionic strength increased, the solubility would increase too, as more ions shielded both Ca^{2+} and SO_4^{2-} ions from interacting with each other to form back into its solid salt^[2].

The solutions prepared in the experiment itself are concentrated on the fact that DHLL could not predict the $S\{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\}$ very well^[5]. The significant difference between the experimental and calculated data might be due to error occurring when conducting the experiment. The volume titrated should be more than those when no NaCl is present, since the solution is more concentrated (higher ionic strength). The glassware used might not be properly rinsed with the solutions of interest, or completely dry before use, which contaminate the solution and affect the overall concentration.

Table 3: Uncertainty of values tabulated in Table 1

Solution #	1		2	
$S_{Ave}\{CaSO_4 \cdot 2H_2O\}$ (M)	0.00014		0.0012	
$[Ca^{2+}]_{Ave}$ (M)	0.00046		0.00099	
$[SO_4^{2-}]$ (M)	0.00046		0.00099	
$[CaSO_4]$ (M)	0.00048		0.0016	
$K_{sp}\{\text{apparent}\}$	7.1E-06		1.8E-05	
pK_{sp}	0.026		0.048	
Ionic strength (M)	0.00065		0.0014	
Type of Equation	DHLL	Davies	DHLL	Davies
K_{sp}°	1.0E-06	1.6E-06	2.2E-06	3.7E-06
pK_{sp}°	0.026	0.026	0.048	0.048
K_D°	0.13	0.20	0.65	1.11
pK_D°	0.82	0.82	3.15	3.15
K_D	0.90		5.38	
pK_D	0.82		3.15	

Table 4: Uncertainty of values tabulated in Table 2

Type of Equation	DHLL	Davies
$S_{Ave}\{CaSO_4 \cdot 2H_2O\}$ (M)	0.00052	
$K_{sp,ave}^{\circ}$	2.4E-06	4.0E-06
Assume only NaCl affects ionic strength		
Ionic Strength (M)	0.00014	
$[Ca^{2+}]$ (M)	0.0034	0.00096
$[SO_4^{2-}]$ (M)	0.0034	0.00096
$S_{Ave}\{CaSO_4 \cdot H_2O\}$ (M)	0.0035	0.0018
Assume all ions affects ionic strength		
Ionic Strength (M)	0.0049	0.0014
$[Ca^{2+}]$ (M)	0.0068	0.0023
$S_{Ave}\{CaSO_4 \cdot 2H_2O\}$ (M)	0.0068	0.0028

The uncertainties for each value tabulated in Table 1 and 2 were calculated and as shown in Table 3 and 4 respectively.

CONCLUSION

Davies equation would provide a good estimation in the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in comparison to Debye–Hückel limiting law model, although the computed solubility was not in good agreement with the experimental data, yet, still closer than that of Debye-Hückel. The ionic strength of the solution used does have a significant effect on the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. It was found that at higher ionic strength solutions, the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is lower than that at lower ionic strength solutions. This finding does not correlate with the actual fact that as the ionic strength increases, the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ will increase.

REFERENCES

[¹] Solubility. <https://www.sciencedaily.com/terms/solubility.htm> (accessed Apr 23, 2020).

[²] Harris, D. C. *Quantitative Chemical Analysis*, 9th ed.; Kate Parker.

[³] Calcium sulfate dihydrate.
<https://pubchem.ncbi.nlm.nih.gov/compound/Calcium-sulfate-dihydrate#section=Solubility>
(accessed Apr 21, 2020).

[⁴] Eni Generalic, F. of C. and T. SOLUBILITY PRODUCT CONSTANTS.
https://www.periodni.com/solubility_product_constants.html (accessed Apr 21, 2020).

[⁵] Murray, J. W. Chapter 6 Activity Scales and Activity Corrections.

[⁶] Cruz, Frederico. The Solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and Ionic Strength Effect; Lab Manual, 2018.