International Journal of Grid and Distributed Computing
Vol. 13, No. 2, (2020), pp. 28–34

# Solubility of $Ca(OH)_2$ in glycerol-water solutions at various temperatures

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***Abstract***
*Calcium hydroxide is sparingly soluble in water and completely soluble in Glycerol. It dissolves quantitatively in a glycerol-water solution. To estimate its solubility in the glycerol-water system, two independent methods are employed in this work. Conductometric measurements show that conductance of saturated solution of $Ca(OH)_2$ decreases with an increase in the percentage of the glycerol indicating a decrease in solubility. However volumetric determination of the same saturated solution show increase in the amount of dissolved $Ca(OH)_2$. It indicates that the addition of glycerol allows more calcium hydroxide to dissolve but prohibits its dissociation in a glycerol-water mixture. A proper selection of the ratio of water: Glycerol would work as a good solvent for Calcium hydroxide at the desired temperature*
***Keywords:*** *Calcium hydroxide, Glycerol*

## Introduction:

Calcium hydroxide is sparingly soluble salt in water and completely soluble in glycerol. (*Calcium Hydroxide | Ca(OH)2 - PubChem*, n.d.) For sparingly soluble salts, solubility is measured conductometrically by using the formula (Lingafelter, 1960)

$s = 1000\frac{K}{\Lambda_0}$ Where, s = solubility in gram equivalent $dm^{-3}$
K = specific conductance of the saturated solution
$\Lambda_0$ = limiting conductaance

Another method which can be used is the volumetric analysis involving titration of the saturated solution with standard HCl solution using bromothymol blue indicator. (Censi & Martino, 2015).

The true solubility of a salt is represented by solution at equilibrium which results on setting the mixture of an excess of $Ca(OH)_2$ with solvent for more than 38 hrs (Miller & Witt, 1929). Hence for preparation, this method was followed. Even though very viscous, glycerol is chosen in the solvent system because it is a green solvent(Gu & Jérôme, 2010) with high polarity, transparency, less volatility, complete miscibility in water, neutral pH and zero conductivity. The dielectric constant of the water-glycerol system is more than 60 till 90% glycerol, which allows the mixture to remain significantly polar for all compositions. (Association, 1963). Despite such high polarity, solution of $Ca(OH)_2$ in glycerol showed zero conductivity.

In a previous work(Ali S, 2012), solubility product and thermodynamic parameters were measured for four solvent systems involving 1-propanol, 2-propanol, DMSO and THF with water. For $ZnCl_2$, the different solvent systems like ethanol, glycerol and glycol each with water were worked to observe the change in conductance with the change in percentage of organic component(Shehata, 1992). Study of KCl and $CaCl_2$ in aqueous ethanol system was done by conductometry(Saeed et al., 2007). Limiting molar conductance of $CaSO_4$ and $MnSO_4$ at various temperatures are determined(Bester-Rogac, 2008) and also some thermodynamic parameters are calculated from conductance values. In the case of $NiSO_4$ and $CuSO_4$, in aqueous methanol system(Masood et al., 2013) conductance decreases with an increase in the organic component even though they are completely soluble in water and slightly soluble in methanol.

ISSN: 2005-4262 IJGDC

In this work, a variation of conductance with temperature was observed for $Ca(OH)_2$ in glycerol- water system. It provided a conductometric estimation of solubility of $Ca(OH)_2$ in water and also in the glycerol-water mixture. Here, the solute was sparingly soluble in water and completely soluble in the organic solvent. A parallel determination of solubility is done by acid-base titration.

**Materials and Methods:**

Solvent system of Glycerol-Water was prepared by maintaining a weight of system at 50 ± 0.001gm and varying the percentage of Glycerol (99.9%, Fischer Scientific Pvt Ltd) from 0 to 70%. 1.5gm Calcium hydroxide (95% pure, Loba Chemicals Pvt Ltd) was added to each solution and mixed well by shaking the flasks vigorously for 10 minutes. Then the flasks were kept for digestion in an oven at 70$^{o}$C for 2.5 Hrs to obtain a clear supernatant solution. The undissolved calcium hydroxide was then separated by filtering it through Whatmann no. 1 filter paper. These mixtures were allowed to cool down in the refrigerator for 48 Hrs. Conductivity meter "Elico Conductivity Meter CM 180" with a conductivity cell was calibrated, using manufacturer's conductivity standards. The conductivity of the liquids was measured at 283.15K, 288.15K, 293.15K, 298.15K, 303.15K, 308.15K, and 313.15K

After measuring the conductance, 5gm aliquot of each solution was titrated against 0.1N Standard HCl solution using Bromothymol Blue indicator.

**Result and Discussion:**

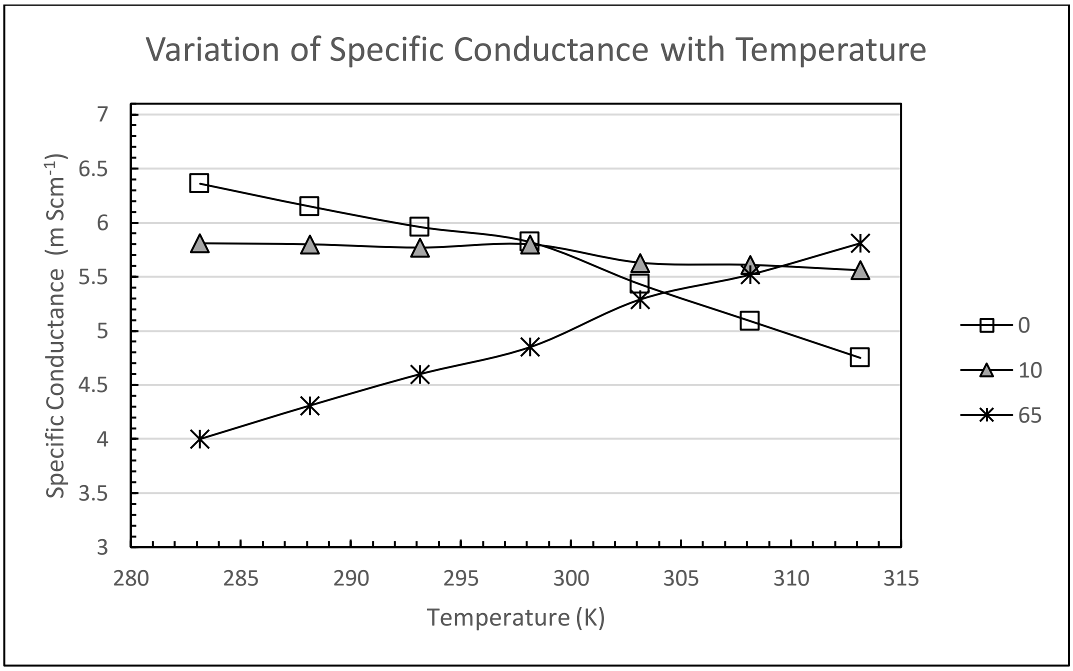
Conductivity of a solution depends on its temperature and concentration of the salts in the solution. Increase in temperature provides kinetic energy to the ions thereby increasing ionic velocity. This results in the increase in conductance with temperature of the solution. Usually, with increase in concentration, ionic strength increases. This raises the number of ions between the platinum plates of the conductivity cell and hence the conductivity raises. Glycerol being a good solvent for calcium hydroxide, its addition is expected to dissolve more solute and hence show increase in conductance with increase in percentage.

**Table I: Variation in Conductivity with Percentage of Glycerol in Water and Temperature (K).**

| Aqueous Glycerol (% w/W) | Conductivity ($10^{-3}$ $Scm^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 283.15K | 288.15K | 293.15K | 298.15K | 303.15K | 308.15K | 313.15K |
| 0 | 6.36 | 6.15 | 5.96 | 5.82 | 5.43 | 5.09 | 4.75 |
| 5 | 6.04 | 5.82 | 5.74 | 5.71 | 5.54 | 5.39 | 5.30 |
| 10 | 5.81 | 5.80 | 5.77 | 5.80 | 5.60 | 5.61 | 5.56 |
| 15 | 5.67 | 5.55 | 5.74 | 5.70 | 5.63 | 5.66 | 5.67 |
| 20 | 5.56 | 5.33 | 5.60 | 5.97 | 5.69 | 5.78 | 5.84 |
| 25 | 5.51 | 5.24 | 5.90 | 5.85 | 6.38 | 5.93 | 5.70 |
| 30 | 5.97 | 5.51 | 6.25 | 6.33 | **7.00** | 6.65 | 6.48 |
| 35 | 6.01 | 5.71 | 5.73 | 6.04 | 6.8 | 6.50 | 6.29 |
| 40 | 5.61 | 5.55 | 5.56 | 5.73 | 6.5 | 6.32 | 6.14 |
| 45 | 5.77 | 5.22 | 5.70 | 6.03 | 6.78 | 6.73 | 6.55 |
| 50 | 5.16 | 4.93 | 5.51 | 5.78 | 6.15 | 6.28 | 6.25 |
| 55 | 4.64 | 4.87 | 5.22 | 5.56 | 5.95 | 6.10 | 6.03 |
| 60 | 4.45 | 4.6 | 4.96 | 5.36 | 5.74 | 5.94 | 5.44 |
| 65 | 4.00 | 4.31 | 4.60 | 4.85 | 5.29 | 5.52 | 5.81 |
| 70 | 3.70 | **3.60** | 4.09 | 4.41 | 4.86 | 5.10 | 5.04 |

ISSN: 2005-4262 IJGDC

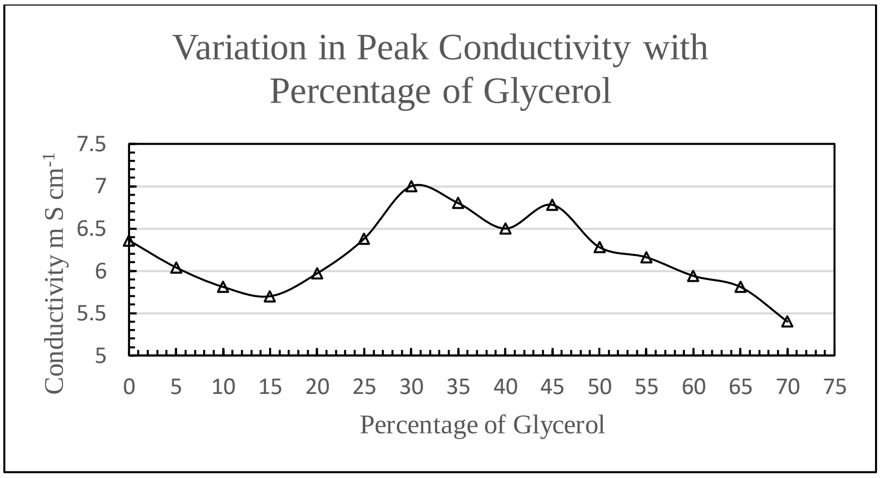
The observation table indicates that there is not much variation in conductance with temperature as well as the composition of solvent system. The range of conductivity is 3.60 to 7.00 mS $cm^{-1}$ with an average of 5.62 mS $cm^{-1}$. To understand the effect of temperature, the graph of temperature with conductivity is plotted for a few composition.




**Graph I(a): Variation in Specific Conductance of $Ca(OH)_2$ with temperature**

With seven different temperatures and fourteen compositions, a plot of all observations becomes too crowdy. Three representative curves indicating the trend are plotted here. For water, the conductance decreases with an increase in temperature which follows the fact that $Ca(OH)_2$ shows retrograde solubility in water. With the addition of glycerol, the concentration of $Ca(OH)_2$ is expected to increase in the solution and thereby rise the conductance but no such increase is observed (Table I). However, the trend of retrograde solubility in water is found to get reversed in Glycerol-Water mixture. As observed from graph I, the curve for the water shows a negative slope. When shifted to glycerol water system, it increases gradually and becomes positive for 65% Glycerol.

Calcium hydroxide shows zero conductivity in glycerol (Safavi & Nakayama, 2000). Hence addition of glycerol has no effect towards rising conductivity. But being a good solvent, it should increase the amount of dissolved calcium hydroxide in glycerol- water system which is expected to add into ionic strength of solution. For all temperatures, the highest value of conductivity is picked up in each composition and plotted against the percentage of Glycerol in Graph I(b).




**Graph I(b): Variation of Peak Conductivity with Percentage of Glycerol**

The highest value of conductivity is 7.00 at $30^0$C for 30% glycerol in water. This is approximately equal to the results in the literature. (Association, 1963)

It was observed that when all the solutions were filtered, the amount of solid $Ca(OH)_2$ left on filter paper was decreasing with an increase in the amount of Glycerol. It indicates that $Ca(OH)_2$ passes into the solution but cannot be estimated using conductance values.

To determine the concentration of $Ca(OH)_2$ in these solutions, a sample of 5gm from each solution was titrated with standard 0.1N HCl (AR 37% Fischer Scientific) using Bromothymol Blue indicator while maintaining the temperature at 293.25K. The concentration of $Ca(OH)_2$ in 5 gm sample is noted in Table II.

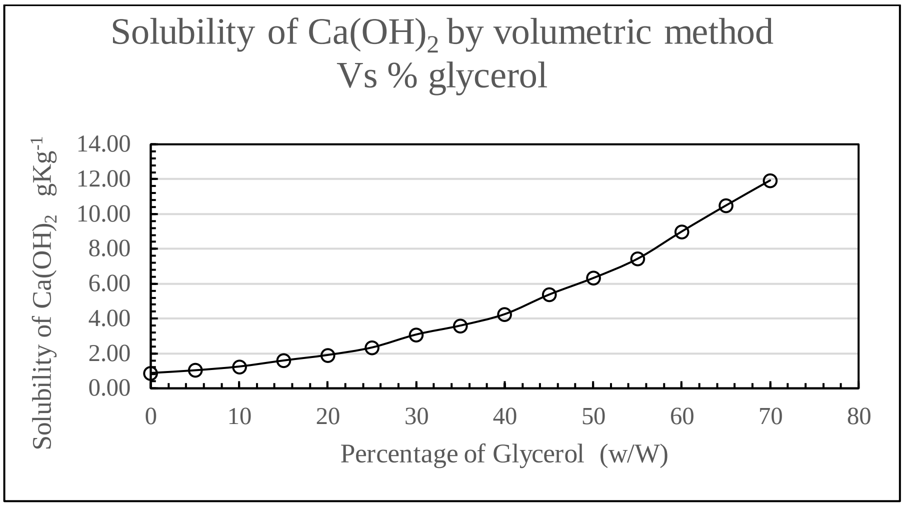
**Table II: Variation in solubility of $Ca(OH)_2$ with percentage of glycerol.**

| No. | Percentage of Glycerol (w/W) | Volume of 0.1N HCl required $cm^3$ | Amount of $Ca(OH)_2$ in gm per 5 gm sample | Solubility of $Ca(OH)_2$ $gKg^{-1}$ in solvent system | Concentration eq.gm $Kg^{-1}$ of Solvent |
|---|---|---|---|---|---|
| 1 | 0 | 1.2 | $4.40 \times 10^{-3}$ | 0.8808 | 0.0238 |
| 2 | 5 | 1.4 | $5.18 \times 10^{-3}$ | 1.0348 | 0.0280 |
| 3 | 10 | 1.7 | $6.29 \times 10^{-3}$ | 1.4718 | 0.0398 |
| 4 | 15 | 2.2 | $8.14 \times 10^{-3}$ | 1.7412 | 0.0471 |
| 5 | 20 | 2.6 | $9.57 \times 10^{-3}$ | 1.9137 | 0.0517 |
| 6 | 25 | 3.2 | $11.72 \times 10^{-3}$ | 2.3432 | 0.0633 |
| 7 | 30 | 4.2 | $15.44 \times 10^{-3}$ | 3.0876 | 0.0834 |
| 8 | 35 | 4.9 | $18.00 \times 10^{-3}$ | 3.6008 | 0.0973 |
| 9 | 40 | 5.8 | $21.28 \times 10^{-3}$ | 4.2554 | 0.1150 |
| 10 | 45 | 7.3 | $26.87 \times 10^{-3}$ | 5.3741 | 0.1452 |
| 11 | 50 | 8.6 | $31.62 \times 10^{-3}$ | 6.3248 | 0.1709 |
| 12 | 55 | 10.1 | $37.14 \times 10^{-3}$ | 7.4279 | 0.2008 |
| 13 | 60 | 12.2 | $44.97 \times 10^{-3}$ | 8.9938 | 0.2431 |
| 14 | 65 | 14.3 | $52.45 \times 10^{-3}$ | 10.4897 | 0.2835 |
| 15 | 70 | 16.2 | $59.65 \times 10^{-3}$ | 11.9307 | 0.3225 |

The increase in solubility of calcium hydroxide with percentage of glycerol in solvnt system is almost linear as shown in the graph II. By method of average, for every gram of glycerol added

ISSN: 2005-4262 IJGDC

0.135 grams of calcium hydroxide dissolves in the solvent system at $30^0$C. Though this is an approximation which can be used to bring calcium hydroxide selectively from a solid matrix into a solution.




**Graph II: Variation in solubility of $Ca(OH)_2$ with percentage of Glycerol**

With increasing percentage of glycerol in the sovent system, more amount of calcium hydroxide dissolves but lesser part of it gets dissociated into solution. The dissociation constant decreases 10 times in 20% of glycerol and 23 times in 40% glycerol with respect to dissociation constant of water. Refer to table III.

**Table III: Variation of the dissociation constant of $Ca(OH)_2$ in glycerol water system with percentage of glycerol.**

| No. | Percentage of Glycerol | Concentration eq.gm $Kg^{-1}$ of Solvent | Equivalent Conductance | Degree of Dissociation α | Dissociation constant $K_D$ at 303.15K |
|---|---|---|---|---|---|
| 1 | 0 | 0.0238 | 228.1053 | 0.8841 | 16.0591 |
| 2 | 5 | 0.0280 | 198.0946 | 0.7678 | 7.1006 |
| 3 | 10 | 0.0398 | 141.5382 | 0.5486 | 2.652 |
| 4 | 15 | 0.0471 | 118.3625 | 0.4588 | 1.83 |
| 5 | 20 | 0.0517 | 110.014 | 0.4264 | 1.6395 |
| 6 | 25 | 0.0633 | 100.7442 | 0.3905 | 1.5842 |
| 7 | 30 | 0.0834 | 83.88333 | 0.3251 | 1.3071 |
| 8 | 35 | 0.0973 | 69.87347 | 0.2708 | 0.9789 |
| 9 | 40 | 0.1150 | 56.51638 | 0.2191 | 0.7067 |
| 10 | 45 | 0.1452 | 46.67984 | 0.1809 | 0.5805 |
| 11 | 50 | 0.1709 | 35.9775 | 0.1394 | 0.3863 |
| 12 | 55 | 0.2008 | 29.63807 | 0.1149 | 0.2993 |
| 13 | 60 | 0.2431 | 23.61398 | 0.0915 | 0.2241 |
| 14 | 65 | 0.2835 | 18.65927 | 0.0723 | 0.1599 |
| 15 | 70 | 0.3225 | 15.072 | 0.0584 | 0.1169 |

The degree of dissociation is calculated from the conductometric method since conductance is a property of ionic strength. Comparing the concentration of calcium hydroxide in all mixtures determined by the volumetric method, it is clear that Glycerol-water system dissolves much greater amount of $Ca(OH)_2$ as compared to water but does not allow dissociation of water to take place.

The dissociation of calcium hydroxide is given as:

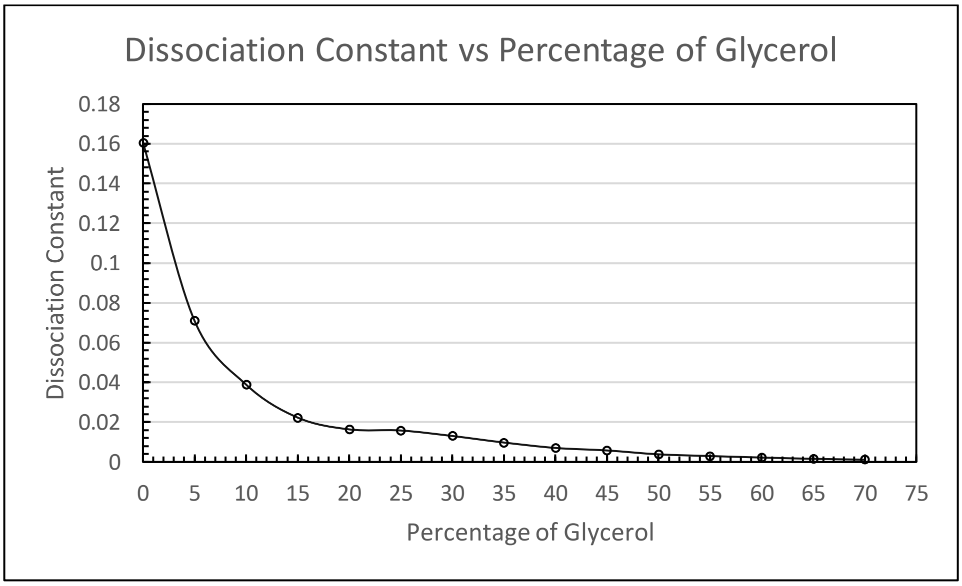
$Ca(OH)_2 \rightleftharpoons Ca^{+2} + 2OH^-$

$K_{dissociation} = \frac{[Ca^{+2}]\,[OH^-]^2}{[Ca(OH)_2]}$

The degree of dissociation $\alpha = \frac{\lambda_c}{\lambda_0}$ where $\lambda_c$= equivalent conductance at concentration 'C'

Dissociation constant $K_D = \frac{\alpha^2 C}{1-\alpha}$

By calculating the degree of dissociation at 293.15°C and equating concentrations of $Ca(OH)_2$ from volumetric analysis, the dissociation constant in various compositions of Glycerol-water system is calculated as given in table III. The graph III shows that with an increase in the percentage of glycerol, dissociation constant decreases. This is in accordance with the change in conductivity with the percentage of glycerol (Safavi & Nakayama, 2000) which is an exponentially decreasing curve. The sharp decrease at 10% glycerol indicates association of calcium and hydroxyl ions and forming a solvent sphere by glycerol water system around undissociated molecule.




**Graph III: Variation in Dissociation constant of $Ca(OH)_2$ with the percentage of glycerol**

**Conclusion:**

Calcium hydroxide is an active salt which is sparingly soluble in water and alcohols but completely soluble in glycerol. In a glycerol-water system, it dissociates feebly showing low conductance values at a wide range of temperature and system composition. Using the volumetric method, the dissolution of $Ca(OH)_2$ is observed to increase with an increase with the percentage of glycerol. By combining the conductometric and volumetric measurements, the dissociation constant of $Ca(OH)_2$ in the glycerol-water system is calculated. It is found that amount of undissociated $Ca(OH)_2$ increases exponentially with an increase in the percentage of Glycerol.

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