Variation in specific conductance of Ca(OH)₂ solution with temperature, dilution, and addition of Glycerol

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Abstract

Quick and accurate determination of Calcium hydroxide is needed by lime and pharmaceutical industries. It is a slightly soluble salt and its saturated aqueous solution shows anomalous behaviour with respect to temperature and conductance. Ca(OH)₂ is completely soluble in Glycerol but the addition of Glycerol in the saturated aqueous solution of Ca(OH)₂ quenches its conductance. The variation of conductance with dilution and temperature is measured for a wide range. Addition of glycerol in small aliquots is followed with the measurement of conductance. The experimental values put forth in this work would help to understand the properties of a saturated solution of Calcium hydroxide popularly called as "Lime water"

Keywords: *Calcium hydroxide, Lime water, Glycerol*

Introduction:

Calcium hydroxide is a compound of commercial interest. It is utilized in many kinds of industries like agricultural, food, and pharmaceuticals. (PubChem, n.d.) Estimation of Calcium hydroxide with accuracy is of vital importance. It is a slightly soluble salt.(Censi & Martino, 2015) Its solubility product is 9.19×10^{-6} mol dm^{-3} and solubility calculated 1.319×10^{-2} mol dm^{-3} in the water at 25^{0}C(Ali S, 2012). In an experiment(William B Euler & Ruekberg, et. al.) the solubility product was found to be 2.15×10^{-6} mol dm^{-3} at 23^{0}C and thus the solubility calculated is S = 8.13×10^{-3} mol dm$^{-3.}$ Being slightly soluble salt, its limiting conductance is calculated using Kohlrausch's law of independent migration of ions, which is equal to is 257.5 S mol^{-1} (Lingafelter, 1960) 258 S mol^{-1} (Vanysek, n.d.) both considered as theoretical values.

For extremely dilute solutions of strong electrolytes, a graph of conductivity against molar concentration is found linear and its slope is equal to its limiting molar conductance(Martínez & Martínez, 2018). For slightly soluble salt like Calcium hydroxide, a similar experiment is carried out and limiting molar conductance is determined practically.

Calcium hydroxide shows retrograde solubility. Since the solubility of slightly soluble salt is related to conductance, the conductivity may reveal similar behaviour with the change in temperature. This hypothesis is tested in case of Ca(OH)₂ solution at different temperatures.

It is also assumed that the slightly soluble salt dissociates completely in its solution. Calcium hydroxide is completely soluble in glycerol (*Solids Properties*, n.d.). Here the change in conductance of the saturated aqueous solution of Ca(OH)₂ with the addition of glycerol is observed as a function of the composition of glycerol-water system.

supersaturated solution of calcium hydroxide to 8^0C and measuring its conductance with an increase in temperature. For the second parameter conductance was measured starting from $25cm^3$ of saturated solution and adding 25 cm^3 aliquot of distilled water followed by measurement of conductance till the final volume gradually reached to 1700 cm^3 For the third parameter, a calculated aliquot of glycerol (99% AR Fischer Scientific) was added to saturated solution of calcium hydroxide and conductance is measured after mixing each aliquot.

Results and discussion:

If the concentration is kept constant, molar conductivity $\lambda_c = 1000k/C$ becomes directly proportional to the conductivity 'k' in a set of experiment. Like solubility, conductance also rises with a rise in temperature. For a slightly soluble salt, the solubility is related with conductance by the equation $S = \frac{1000k_{corr}}{\lambda_0}$ where k_{corr} = conductivity corrected for the conductance of water. In an experiment (Saeed et al., 2007) dealing with KCl and $CaCl_2$, in both cases, there was a slight increase in molar conductance with temperature. The solubility of AgCl increased with temperature(Dave & Krishnaswami, 2013). Solutions of Copper sulphate and Nickel sulphate(Masood et al., 2013) showed a steep increase in molar conductance with temperature in a range of 25^0C to 50^0C. Calcium and Magnesium sulfates solutions showed a rise in conductance with the rise in temperature(Bester-Rogac, 2008). Both are known to show 'retrograde solubility' which means the solubility decreases with increase in temperature. A detailed study of this paper revealed that the form of calcium sulfate used here is $CaSO_4.2H_2O$ which exhibits an increase in solubility with temperature up to 40^0C and similarly $MnSO_4$ exhibits increase up to 70^0C.
Irrespective of exothermic or endothermic dissolution, commonly, the solubility of a salt in water increases gradually with temperature (Saeed et al, 2007). The slightly soluble salts are no exception to this phenomenon (Dave & Krishnaswami, 2013). As per National lime association, with an increase in temperature, solubility of calcium hydroxide decreases. (National Lime association 2020). A parallel trend is observed in the conductivity of a saturated solution of calcium hydroxide as shown in Table I.

Table I: Variation of specific conductance of a saturated solution of $Ca(OH)_2$ with temperature.

Temperature K	Corrected conductivity mS cm^{-1}
283.15	8.47
288.15	8.1
293.15	7.77
298.15	7.17
303.15	7.01
308.15	6.8
313.15	6.64

Specific Concuctance Vs Temperature
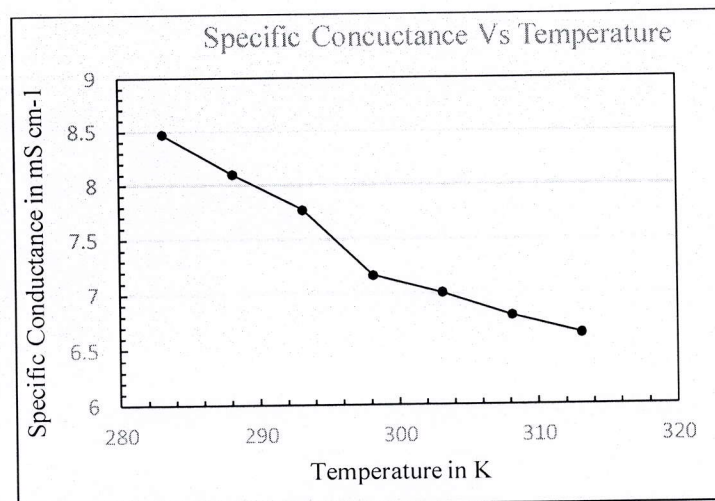
Graph I: Variation of specific conductance of a saturated solution of $Ca(OH)_2$ with temperature

The conductivity of a solution measured is directly proportional to the number of ions within the pair of platinum plates of conductivity cell. With an increase in dilution, this number decreases and proportionately the conductivity decreases. For completely soluble strong electrolytes like KCl (Praharaj et al., 2017) and NaCl (Widodo et al., 2018), conductivity is directly proportional to the concentration. In an experiment, (Martínez & Martínez, 2018) Conductivity for a few salts is determined for very dilute solutions by implementing drop by drop addition of electrolyte into distilled water followed by recording the conductivity in micro- siemens. It showed a linear relationship between conductivity and concentration.A graph is straight line with positive slope equal to limiting molar conductance in case of strong electrolytes. In the present work, specific conductance is observed to be directly proportional to the concentration of the slightly soluble salt solution. (Table II).

Table II : Variation in Specific Conductance of $Ca(OH)_2$ solution on dilution with water

Conc. mmols dm^{-3}	Conductivity $mS\ cm^{-1}$	Conc. mmols dm^{-3}	Conductivity $mS\ cm^{-1}$	Conc. mmols dm^{-3}	Conductivity $mS\ cm^{-1}$	Conc. mmols dm^{-3}	Conductivity $mS\ cm^{-1}$
17.00	7.01	0.94	0.51	0.49	0.24	0.33	0.14
8.50	4.12	0.89	0.48	0.47	0.23	0.32	0.13
5.67	2.93	0.85	0.45	0.46	0.23	0.31	0.13
4.25	2.29	0.81	0.43	0.45	0.22	0.31	0.13

1.70	0.96	0.63	0.32	0.39	0.17	0.28	0.11
1.55	0.87	0.61	0.31	0.38	0.17	0.27	0.11
1.42	0.78	0.59	0.3	0.37	0.16	0.27	0.1
1.31	0.72	0.57	0.29	0.36	0.16	0.27	0.1
1.21	0.68	0.55	0.28	0.35	0.15	0.26	0.1
1.13	0.62	0.53	0.27	0.35	0.15	0.26	0.1
1.06	0.58	0.52	0.26	0.34	0.14	0.25	0.1
1.00	0.54	0.50	0.25	0.33	0.14	0.25	0.09

The graph of specific conductance against a concentration in mmol dm^{-3} is a straight line (Graph I) with slope almost equal to the theoretical value of limiting conductance of Ca(OH)$_2$. From Table II, Slope $= \frac{\sum y}{\sum x} = \frac{40.22}{163.34} = 0.246 \ \frac{\text{miliS cm}^{-1}}{\text{milimoldm}^{-3}} = 246 \ \text{Scm}^2\text{mol}^{-1} =$ limiting molar conductance of (CaOH)$_2$.

Error = 4.46%

In many of the experiments (Flint & Wells, 1933; Miller & Witt, 1929) done before, calcium hydroxide solution was prepared by adding an excess of calcium oxide into the water which resulted into 0.019M Ca(OH)$_2$ estimated volumetrically. Whereas here powder of extra pure 95% precipitated Ca(OH)$_2$ is stirred with distilled water which resulted in 0.017M as the saturated solution.

In this method, a saturated solution is continuously diluted instead of adding electrolyte in distilled water hence as shown in Graph II, close to the origin, the line slightly bends because zero concentration is not achieved by dilution. This work proves that, for a slightly soluble salt too, a 'practical' method is available to determine the limiting molar conductance.


Specific Conductance Vs Concentration
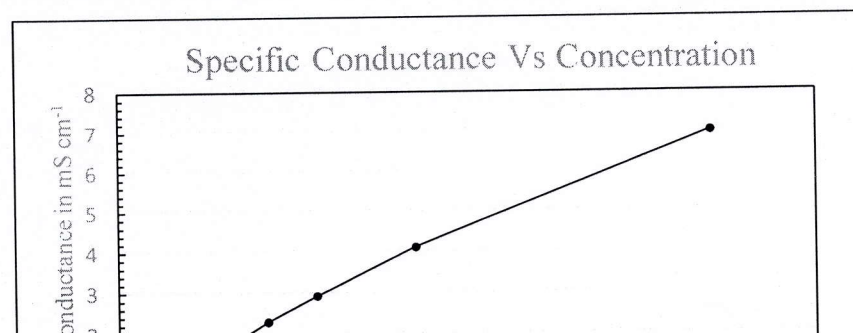
Glycerol is a green solvent with a dielectric constant equal to 42.5(Wolfson et al., 2007) and it is completely miscible in water(Association, 1963). Due to the high dielectric constant equal to 78.5, water it ionizes the dissolved salts. Also, water raises the net dielectric constant of the solvent system when dissolved in another solvent. The dielectric constant of the glycerol-water system varies from 75.7 to 60.0 for 10% to 60% glycerol correspondingly. Salts like $ZnCl_2$ dissolve in this system (Shehata, 1992) and found to show a decrease in conductance with the increase in the percentage of glycerol.

To increase the solubility of calcium hydroxide in water, the addition of glycerol was attempted. Glycerol was added into an aqueous saturated solution of $(CaOH)_2$ in small aliquots. The percentage composition of the solvent system was fairly maintained on a weight basis as shown in Table III and specific conductance was measured at a constant temperature 25^0C.

Table III: Variation of Specific conductance with the percentage of glycerol

Percentage of Glycerin (w/W %)	Sp.Conductance in mS cm^{-1}	Percentage of Glycerin (w/W %)	Sp.Conductance in mS cm^{-1}
0	7.08	45	0.62
5	5.31	50	0.44
10	4.13	55	0.30
15	3.18	60	0.18
20	2.47	65	0.09
25	1.94	70	0.06
30	1.49	75	0.03
35	1.13	80	0.01
40	0.83		-

The graph III shows an exponential decrease in specific conductance indicating that the number of ions between the platinum plates is rapidly decreasing. The specific conductance values became negligibly small above 50% glycerol as if the solution does not contain any of its ions.

Specific Conductance Vs Percentage of Glycerol solution
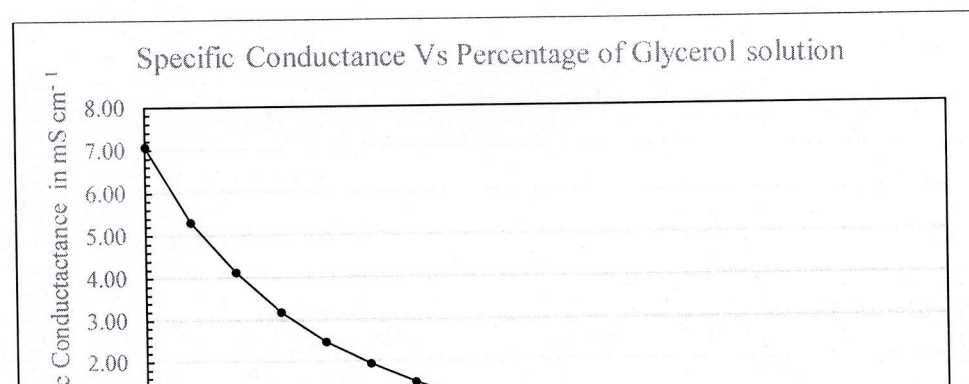
The conductivity of $Ca(OH)_2$ is zero in glycerol (Estrela & Holland, 2003) hence the dilution-like effect is expected. But for the same molality in water solution, the conductivity values in the glycerol -water system are comparatively very low as shown in Table IV.

Table IV: Comparison of specific conductance of solutions having similar concentration in water and water-glycerol system.

Conc. of $Ca(OH)_2$ mmol dm^{-3} in water	Specific conductance mS cm^{-1}	Conc. of $Ca(OH)_2$ in Glycerol-water system		Specific conductance mS cm^{-1}
		mmol dm^{-3}	percentage	
17	7.01	17.00	0%	7.08
8.5	4.12	8.63	55%	0.30
5.6	2.93	5.96	70%	0.06
4.25	2.29	4.07	80%	0.01

Such quenching of conductance is possible when charges disappear from the solution. It means that these ions recombine with each other in glycerol-water system. Practically, the salt behaves like a weak electrolyte in this system.

Conclusion:

Calcium hydroxide commercially called as 'slaked lime' is an important compound in the various industries. It is a slightly soluble salt with practical solubility 1.258 grams per litre by volumetric and 1.018 grams per litre by the conductometric method. The conductivity of $Ca(OH)_2$ solution decreases linearly with dilution. The slope of the graph is 246 S $cm^2 mol^{-1}$ which is equal to its limiting molar conductance. With an increase in temperature, the conductivity of saturated solution of $(CaOH)_2$ decreases. This behaviour is similar to its retrograde solubility in water. In glycerol, Calcium hydroxide dissolves completely but when glycerol is added into the saturated aqueous solution of $Ca(OH)_2$, its conductance decreases with an increase in the percentage of glycerol and becomes negligible above 50% of glycerol-water composition. This indicates that the ions of calcium hydroxide associate in glycerol.

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