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Mysterious Effect of Temperature on Conductivity of Calcium Hydroxide

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ABSTRACT

The Solubility of $Ca(OH)_2$ aqueous solution was investigated at certain temperatures that were 30±1ºC, 60±1ºC, 70±1ºC and 80±1ºC. The occult results about solubility were obtained via using conductometry analysis. With the help of specific conductance (***K***) activation energy (*ε*), frequency factor (*A*) of $Ca(OH)_2$ solution calculated. The thermodynamic properties of $Ca(OH)_2$ also examined. Gibbs free energy (***ΔG***), entropy (***ΔS***) and enthalpy (***ΔH***) of $Ca(OH)_2$ determined at different temperatures. Solubility product (K_{sp}) also estimated via equivalence point. Apart this, Ionic strength (μ_i), activity coefficient (f_i) as well as activity (a_i) of $Ca(OH)_2$ evaluated. Entropy as well as ionic strength of $Ca(OH)_2$ ratified that the solubility of calcium hydroxide inversely proportional to temperature.

Key Words: Solubility, Solubility Product, Ionic strength, Activation energy.,

1. INTRODUCTION

Solubility is an important physical property that give broad information about physical and chemical nature of any compound. The dissolution of ionic compounds in respective solvents can predict the electrochemical nature. The Calcium hydroxide is an ionic compound that use in many industries and laboratory practices. Last quarter century the solubility of calcium hydroxide re-determined under controlled conditions (Miller, & Witt, 1929). by different methods. In general, the calcium hydroxide solubility is reversibly proportional to temperature (William, et al 2000). Revolution in knowledge and upsurge in technology make the calcium hydroxide is alpha in among chemicals due to its applications. The $Ca(OH)_2$ is a multipurpose agent in medical science, which is use in treatment of roots resorption, iathrogenic root perforation (Alireza, & Esfahan, 2005). In food industry the importance of $Ca(OH)_2$ is assessed by the comparative study of bagass treatment by calcium hydroxide as well as by the NaOH on composite strength (Anggona, et al 2017). In process metallurgy during the hot metal desulphurization high lime calcium carbide deposit water as calcium hydroxide which has positive impact on desulphurization (Schumann et al 1990). Apart this, this ionic solid sparingly dissolve in water. The equilibrium of $Ca(OH)_2$ in water is represented in equation 1

$$Ca(OH)_2 + H_2O \leftrightarrow Ca^{+2} + 2OH^-_{(aq)} \ldots\ldots\ldots (1)$$

The Solubility product of $Ca(OH)_2$ from equ (1) predict by dissolution of it in water. In professional practices, Solubility of $Ca(OH)_2$ not only predicted in water but in aqueous salt solution, of any concentration, based on it solubility product (Meenendez & Borge **2013**). By The mathematical expression the solubility product of sparingly soluble compound, is the product of concentrations of ions raised to be some exponent equal to co-efficient of balanced equation.

$$K_{sp} = [Ca]^{+2}[OH^-]^2 \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

But the solubility of $Ca(OH)_2$ strongly effected by the presence of other ion in aqueous solution of it. The relation between solution ionic strength and solubility of electrolyte is important (Willey 2004). Ionic strength of electrolytic solution may also be used to predict the Solubility of $Ca(OH)_2$. Because the molar ionic strength is the function of ions concentration present in solution. The ionic strength as well as solubility and solubility product also beholden to temperature.

Lot of work was done on the $Ca(OH)_2$ in different aspects. Literature review revealed that the many research was performed on $Ca(OH)_2$ in chemical, medicinal, dental and industrial level. In field of bioscience, Comparative evaluation of $Ca(OH)_2$plus points and $Ca(OH)_2$ pastes in apexification (Bezgin et al 2012). Effect of Meganese ion on structure of $Ca(OH)_2$ and Mercury adsorption performance of MnX +/$Ca(OH)_2$ composites studied by Yunjun Wang (Wang & Duan, 2011). On industrial level the hypothetical transformation of $Ca(OH)_2$ into $CaCO_3$ in solid state of port land cement (Stepkowska, 2005). Pham trung and et al., worked on the iron free hydroxyapatite powder from synthetic $Ca(OH)_2$ and commercialized $Ca(OH)_2$ (Trung et al 2014). on Fuel industry level the removal of mineral matter from some Australian coals by $Ca(OH)_2$/HCl leaching researched by

Jie Wang and Akira (Jiewang & Akiratomita 2012). At thermodynamic level the reaction of $Ca(OH)_2$ with HCl in the presence of water vapour at low temperature (Bausch et al 2004). Advanced experimental analysis of the reaction of $Ca(OH)_2$ with HCl and SO_2 during spray dry scrubbing process (Liu, 2005). the Raman spectra of $Ca(OH)_2$ and $Ca(OD)_2$ (Dawson 1972).

The main goal of this work to calculate the solubility product (K_{sp}), Thermodynamic parameter of electrolytic solution and Ionic strength of $Ca(OH)_2$ at different temperature by studying the conductometry analysis of it with standard solution of hydrochloric acid (HCl) with the help of this study the physical nature of calcium hydroxide solution will find. Via this study the electrochemical nature of calcium hydroxide also predicted. Conductivity method is important tool to obtain an information regarding ion association and solvation phenomenon.

2. Materials and Methods

Tap Water, De-ionized water, HCl (E-Merck), $Ca(OH)_2$ (E-Merck), For the measurement of Conductance, the conductivity meter (4510 Jenway, Germany) was used.

2.1 Preparation of Stock Solution of $Ca(OH)_2$

0.1gm of $Ca(OH)_2$ was dissolved in water at room temperature, stirred for half an hour and kept overnight. It was filtered in a long stem funnel, 25ml of aliquot was transferred to a 50ml measuring flask and titrated against 0.03N HCl (Std) using the by conductivity bridge. The present work was performed at different temperatures in the 5-30ºC range. Same procedure is repeated at high temperature.

3. Results and Discussion

In present study the several results were obtained which are depicted in following manner.

3.1 Titration curve of $Ca(OH)_2$

The Conductometry titration was performed at certain temperatures that were 30 ± 1ºC, 60 ± 1ºC, 70 ± 1ºC and 80 ± 1ºC. At 30 ± 1ºC, by the addition of HCl (ranging from 0.03 ± 0.001M) the specific conductance of $Ca(OH)_2$ increased. By the addition of HCl the negative ions elevated. With the raising in temperature the conductance of $Ca(OH)_2$ gradually decreased showed in Figure 1. When temperature raise the thermal speed of positive ions also increase in the solution. On other hand the hydration number also raised. The attraction of ions increased the resistivity as a result of this, the conductance decreased.

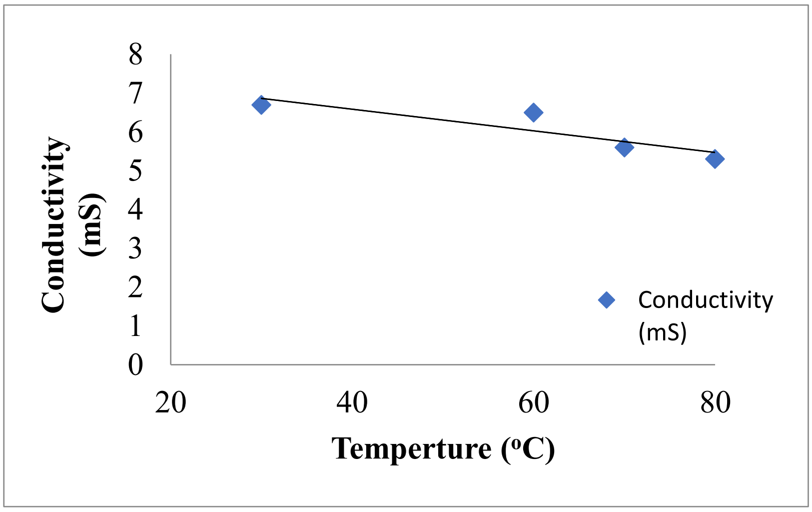

Figure 1: Effect of temperature on the initial conductance of $Ca(OH)_2$ solution absence of the standard HCl (0.03 ± 0.001M)

3.2 Determination of equivalence point in aqueous medium by conductometry:

The main advantage of conductometry analysis, it is applicable to very dilute solution and on coloured compounds. In this method the equivalence point obtained. It is an inflection point which use to determine the end point. According to Gilbert that at any point in titration conductivity is the sum of conductivities of all the ions presents (Pungor, 1965). Conductivity and degree of titration hyperbolically related. By the conductometry analysis of $Ca(OH)_2$ with the HCl it was observed that the conductance of solution decreased at all mentioned temperatures. The decreased in conductance due to association of ions in solution. Viscosity and relative permittivity are the solvent properties help in determining the degree of ion association (Boruń, & Wypych-

Stasiewicz, (2021). After the consumption of all OH^- ions the equivalence point obtained. Further addition of HCl Sharply raise the conductance. It was due to elevation of H^+ in $Ca(OH)_2$ aqueous solution which was depicted in Figure 2 and Table 1.

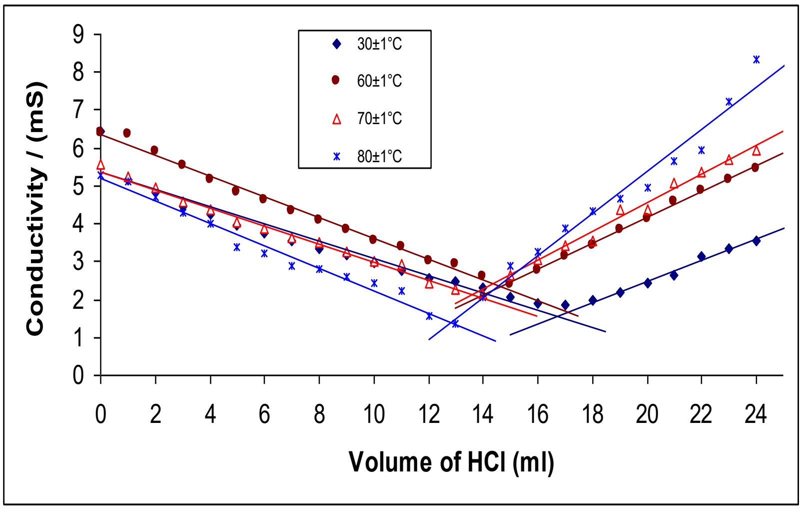

Figure 2: Effect of temperature on the titration curves of $Ca(OH)_2$titrateagainst the standard HCl (0.03 ± 0.001M)

Table 1. Conductivity values of $Ca(OH)_2$ at 30, 60, 70 and 80±1°C

S.No	Volume of HCl	Conductance of Ca(OH)2 at different temperature			
		30±1°C	60±1°C	70±1°C	80±1°C
1	0	6.7±0.1	6.5±0.1	5.6±0.1	5.3±0.1
2	1	5.15±0.1	6.34±0.2	5.24±0.2	5.1±0.1
3	2	4.82±0.2	6.34±0.2	5.92±0.1	4.7±0.1
4	3	4.44±0.2	5.92±0.2	5.55±0.2	4.3±0.2
5	4	4.24±0.1	5.55±0.1	5.15±0.2	4.0±0.2
6	5	3.98±0.0	5.15±0.1	4.83±0.3	3.4±0.2
7	6	3.76±0.1	4.83±0.3	4.62±0.3	3.2±0.2
8	7	3.55±0.1	4.62±0.4	4.33±0.1	2.9±0.1
9	8	3.35±0.3	4.33±0.1	4.08±0.2	2.8±0.1
10	9	3.17±0.2	4.08±0.2	3.83±0.1	2.6±0.1
11	10	2.96±0.2	3.83±0.1	3.55±0.1	2.45±0.2
12	11	2.76±0.1	3.55±0.1	3.4±0.1	2.22±0.2
13	12	2.58±0.1	3.4±0.1	3.01±0.1	1.55±0.1
14	13	2.47±0.1	3.0±0.1	2.95±0.2	1.35±0.1
15	14	2.3±0.2	2.95±0.1	2.61±0.2	2.06±0.2
16	15	2.05±0.3	2.61±0.1	2.39±0.1	2.88±0.1
17	16	1.89±0.3	2.39±0.1	2.76±0.1	3.25±0.2
18	17	1.85±0.2	2.76±0.1	3.14±0.2	3.87±0.1
19	18	1.97±0.1	3.14±0.1	3.44±0.2	4.33±0.1
20	19	2.17±0.1	3.44±0.2	3.82±0.2	4.68±0.1
21	20	2.43±0.2	3.82±0.2	4.14±0.1	4.95±0.2
22	21	2.64±0.2	4.14±0.2	4.58±0.2	5.66±0.3
23	22	3.13±0.2	4.58±0.2	4.86±0.2	5.95±0.3
24	23	3.36±0.2	4.86±0.3	5.15±0.2	7.23±0.2
25	24	3.53±0.2	5.15±0.3	5.45±0.1	8.23±0.1

3.3. Activation energy of $Ca(OH)_2$

Specific conductance is a characteristic property of conducting medium. With the help of conductance, the activation energy of $Ca(OH)_2$ calculated. The experimental measurement of temperature dependence of conductance (Forster, 1964) of most substance examined with the help of equation (3). Mobility of ions depends upon the given temperature to solution. Contribution of each ionic species to conductivity is proportionally to exponential term (Bloom, & Heymann, 1947).

$$\sigma = A\exp(-\varepsilon/RT) \ldots\ldots\ (3)$$

The activation energy via this method was -4.03KJ/mole. While the collision factor was -1.123 from Figure 3.

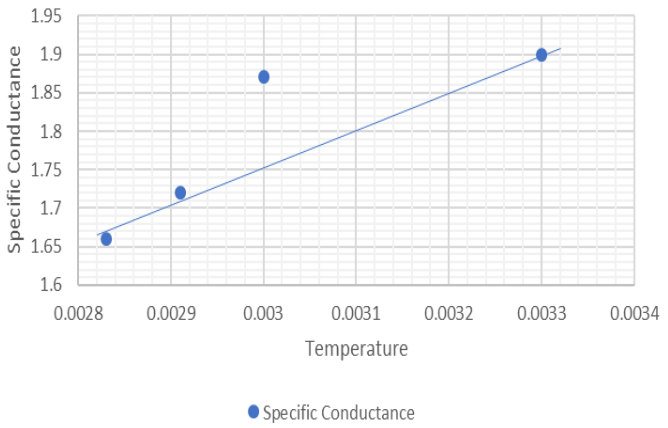

Figure 3: Plot of Specific conductance. Temperature to evaluate the Activation energy of $Ca(OH)_2$

The magnitude of collision between the molecules at high temperature was slow that means the rate of reaction for $Ca(OH)_2$ is also slow. In some cases, at high temperature the effective collision between the molecules was slow due to this ergo the negative value of activation energy was obtained.

3.4. Effect of temperature on the conductivity of $Ca(OH)_2$.

Conductivity of ionic compounds varies with temperature. It was observed that the Conductivity of $Ca(OH)_2$ solution decreased by raising the temperature of System. The decreased in conductance was due to dissociation of $Ca(OH)_2$ in respective solvent. The $Ca(OH)_2$ is a sparingly soluble salt which dissociate at high temperature. The dissociation of $Ca(OH)_2$ elevates the number of ions and resistance increased between the ions. As a result of this the very a smaller number of ions pass the unit area of electrodes. Due to this ergo the specific conductance of solution decreased.

3.5 Ionic strength and Activity of $Ca(OH)_2$:

The ionic strength and activity variation changed the rate as well as also the energy of activation. It is the total electrolytic concentration (Christian, 2013), defined by equation 4. The ionic strength and activity of $Ca(OH)_2$ is measured at 25±1ºC Via equation 4.

$$\mu = 0.5\Sigma C_i Z_i^2 \ldots\ldots\ldots\ (4)$$

In equation 4 the C is concentration of 'i' species and Z is the charge on this species. All cation and anions of solution include in calculation. The ionic strength of $Ca(OH)_2$ was $75e^{-3}$. the low ionic strength suggest that the solubility of $Ca(OH)_2$ is very low in water. At the given ionic strength, the activity coefficient of ion depends upon the ionic valency of ion regardless of the sign of charged ion (Kagawa, & Katruura, 1952). The activity coefficient of $Ca(OH)_2$ finds by using the equation 5.

$$-\log f_i = 0.51 Z_i^2 (\mu)^{0.5} \div 1 + (\mu)^{0.5} \ldots\ldots\ldots\ (5)$$

the equation 5 for the aqueous system and 0.51 is constant for water at 25±1ºC. The activity coefficient of Ca^{+2} ion was 0.37 while the activity coefficient for the OH^- ion was 0.77. The mean activity coefficient of $Ca(OH)_2$given by the expression

$$f_{Ca(OH)_2} = 3\{(f_{Ca^{+2}})(f_{OH^-})\}^{0.5} \ldots\ldots (6)$$

The activity coefficient of $Ca(OH)_2$ was 1.609 at 25±1ºC. This value nearest to Jhonston and Grove calculated activity coefficient of $Ca(OH)_2$ that was 0.72 at 25±1ºC (Flint, & Wells, (1933). Contribution of ions in solution both explained by theoretically as well as experimentally. The activity of Ca ion and OH ion is explained via equation 7.

$$a_i = C_i f_i \ldots\ldots\ (7)$$

f is the activity coefficient and C is the concentration. The activity of Ca^{+2} was 0.01M and for OH^- the activity was 0.02M.

3.6. Determination of the solubility (S) and Solubility Product (Ksp).

There is a equilibrium between the ions and undissociated electrolyte in solution. In saturated solution, at constant temperature and pressure the undissociated species assume to be constant. The product of ionic concentration [A^-] is known as Solubility product (Denbigh, (1941). For the solubility product should be equilibrium for solubility product in solution between the ions and undissociated. Solubility and solubility product of Ca(OH)2 was calculated by using the values of equivalence point of $Ca(OH)_2$, Values of solubility at different temperature were depicted in table 2. The solubility product of $Ca(OH)_2$ was found to be $5.6\pm0.02\text{x}10^{-6}$ M^3. While the experimental value of mean solubility product of $Ca(OH)_2$ in aqueous system observed in literature was $4.78\times10^{-6}M^3$ (Greenberg, & Copeland, 1960). and the Solubility product of $Ca(OH)_2$ at 25ºC was $5\times10^{-6}M^3$ (Clark, Bonicamp, (1998). The very low value of K_{sp} suggested that the ionic strength of $Ca(OH)_2$ in aqueous solution was low.

Table 2: The Solubility of $Ca(OH)_2$ at different temperature

S.NO	Temperature (ºC)	Solubility of $Ca(OH)_2$ (M)
1	30	0.0112±0.01
2	60	0.009±0.03
3	70	0.0096±0.04
4	80	0.0038±0.01

3.7 Determination of Thermodynamics of $Ca(OH)_2$:

During the process of dissolution of electrolyte, the energy of system changed at certain level. This change of energy changes the equilibrium of system as well as entropy (ΔS) and other thermodynamic energies. The Gibbs energy (ΔG), enthalpy (ΔH), entropy (ΔS), equilibrium constant (k_c) of $Ca(OH)_2$ aqueous solution at different temperatures. The enthalpy of $Ca(OH)_2$ was -12.8±1.2Kj/mole. The negative form of enthalpy suggest that the dissolution of $Ca(OH)_2$ was exothermic in nature. Gibbs energy of Solution calculated via equ 9 by using literature (Kinart, Z., (2024).

$$\Delta G = -RTlnk_{sp} \ldots\ldots. \quad (9)$$

The 30.45±0.15 Kj/ mole of gibbs free energy was obtained. The value suggests that the non-spontaneous behaviour of $Ca(OH)_2$ in water. The entropy of system was -143±2.0J/mole K^-. The probability of distribution of Ca(OH)2 in system is decreased due to nonspontaneous nature. The result of entropy ratified that the solubility of $Ca(OH)_2$ inversely proportional to temperature. At high temperature the equilibrium of $Ca(OH)_2$ also disturbed.

Table 3: The Different Physicochemical properties of $Ca(OH)_2$ aqueous solution

S.No	Temp	Physical & Chemical Parameters					
		Eq.Point	ΔS (j/mole)	ΔH (Kj/mole)	ΔG (Kj/mole)	Solubility (M)	K_{sp} (M^3)
1	30	17.5±0.1	-	-	37.86±0.23	0.0112±0.01	±0.01
2	60	15.0±0.5	88±2.3	11.19±0.1	40.5±2.12	0.009±0.03	4.42±0.02
3	70	14.0±0.5	66.5±1.5	17.71±0.23	40.52±2.12	0.0096±0.04	6.27±0.02
4	80	13.1±0.6	65.5±0.5	17.92±0.02	41.15±0.32	0.0038±0.001	8.13±0.1

4. CONCLUSION

The association of ions in electrolytic solution of $Ca(OH)_2$ decreased specific Conductance. It is concluded from this research the $Ca(OH)_2$ was very low solubility at higher temperature. The small value of ionic strength of $Ca(OH)_2$ ratified the result of solubility. Apart this the very low value of entropy in negative also verified the results of solubility. The probability for the arrangement of ions of electrolyte [$Ca(OH)_2$] in solution very low hence the solubility of solution also decreased at higher temperature.

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