

Determination of Thermodynamic Parameters from the Dissolution of Calcium Hydroxide in Mixed Solvent Systems by pH-Metric Method

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Abstract

In the present study the dissolution of calcium hydroxide (Ca(OH)_2) in water as well as in mixed solvents systems such as (methanol + water), (ethanol + water), (1-propanol + water) and (2-propanol + water) in 0-25 percentage compositions range at $293 \pm 1\text{K}$ and $343 \pm 1\text{K}$ or ($328 \pm 1\text{K}$ in case of methanol) was undertaken for the determination of solubility, solubility product constant (K_{sp}), Gibbs free energy change (ΔG°), entropy change (ΔS°) and enthalpy change (ΔH°) by pH-metric method. It was found that the equivalence point was decreased linearly by the increasing of the percentage composition of the mixed solvents systems. This represents that solubility and K_{sp} values are linearly decreased. The solubility of Ca(OH)_2 was decreased at higher temperature compared to room temperature. Furthermore, methanol produced minimum decreased due to its high value of dielectric constant while in 2-propanol showed maximum decreased in solubility and K_{sp} values. On the other hand ΔG° values were linearly increased against percentage composition of mixed solvents systems. Entropy and Enthalpy values were also changed in mixed solvent systems.

Keywords: Thermodynamic parameters; Calcium hydroxide; Mixed solvents; Dielectric constant

Introduction

Calcium hydroxide is used in a broad range of industrial, professional and consumer applications. Calcium hydroxide is used as such or in a mixture for the production of articles to be used in or for vehicles, construction, electronic apparatus, laboratories, fabrics, wood, rubber, plastics, metal, leather, chemicals, pharmaceuticals, pesticides, the treatment of potable water, waste water, municipal sludge cosmetics, personal care products [1-5].

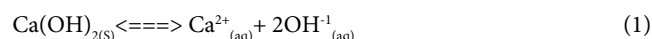
The solubility of solutes in mixed solvents is of great practical importance since many industrial process as well as laboratory procedures call for the use of solvent mixtures. The solubility of solutes in mixed solvents depends primarily on the solvation of solutes or their constituent ions by the components of solvent mixtures [6]. Studying the thermodynamics of different salts, is important for evaluating the single ion thermodynamic parameters which help in explain the preferential solvation of the ions [7].

There are various ways for determination of thermodynamic parameters such as Gibbs free energy change (ΔG°), entropy change (ΔS°) and enthalpy change (ΔH°). These parameters state the physiochemical properties of a chemical system. Previously, many techniques have been applied to find the solubility products of various systems. These techniques include spectral studies, viscosity, refractive index and some electro-analytical method like conductometry, potentiometry, polarography and voltametry etc. Most of the researchers aimed to infer data of very precise solubility product of these systems that are extremely less soluble or nearly insoluble in aqueous systems [8-10]. Method of very precise evaluation of K_{sp} values of various types of reagents having structural dissimilarities are reported [11]. Clark also suggested a method to evaluate solubility product constant for various compounds along with a practical aspect pertaining to the problems associated with the determination of such compounds [12]. A straight forward method was published showing determination of various thermodynamic parameters such as ΔG° , ΔS° and ΔH° for the dissolution of calcium hydroxide in aqueous by simple titration method [13].

Different properties such as solubility, K_{sp} , Gibbs free energy, entropy and enthalpy associated with sparingly soluble salts are influenced with different parameters, such as change in percentage of solvent, amount of salts and temperature etc. [14-16].

In the present research work, pH metric method was used for the study of the influence of mixed solvent system on the solubility K_{sp} , Gibbs free energy, entropy and enthalpy of Ca(OH)_2 .

When a sparingly soluble compound like Ca(OH)_2 is added into water, equilibrium is established between the solid and aqueous material that can be approximately represented by the equation [13].



The molar solubility "S" solubility product and Gibbs free energy is determined from following equations [13].

$$K_{sp} = [\text{Ca}^{+2}] [\text{2OH}^{-}]^2 = 4S^3 \quad (2)$$

$$\Delta G = -RT \ln (K_{sp}) \quad (3)$$

Where "R" is a universal gas constant, T is the absolute temperature and ΔG° is the Gibbs free energy ΔG° is related to ΔH° and ΔS° by the following equation [13].

$$\Delta G^\circ = H^\circ - T\Delta S^\circ \quad (4)$$

The value of ΔG° calculated at two different temperatures T_1 and T_2 provide the values of ΔH° and ΔS° over a small temperature range.

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Received April 30, 2013; Accepted June 17, 2013; Published June 19, 2013

Citation: Ali S, Ali AS (2013) Determination of Thermodynamic Parameters from the Dissolution of Calcium Hydroxide in Mixed Solvent Systems by pH-Metric Method. J Phys Chem Biophys 3: 116. doi:10.4172/2161-0398.1000116

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In previous work conductometric method was used for determination of thermodynamic parameters in mixed solvent systems [17]. But in present work pH metric method has been used.

Experimental

In the present research work, pH –metric method was used for the study of the influence of mixed solvent system on the solubility of $\text{Ca}(\text{OH})_2$. All reagents were used such as $\text{Ca}(\text{OH})_2$ (E. Merck), 1-Propanol (E. Merck), 2-propanol (E. Merck), methanol (E. Merck), ethanol (E. Merck), Hydrochloric acid (E. Merck), Oxalic acid (E. Merck), Sodium hydroxide (E. Merck), Phenolphthalein (E. Merck) and Buffer solutions (E. Merck) each of these analytical grade reagents. These stock solutions were prepared in double distilled water. The equipment used were pH meter (Mettler Toledo MP 220) Japan, IKA Combimag RCH magnetic stirrer (Germany) Thermostat (Chiller) Haake, (Type T 52, V 220, No 76400, Germany). The thermostat environment ($0 - 110 \pm 0.5^\circ\text{C}$) and Electrical Balance (Mettler college 150, Germany).

Preparation of stock solution

The pH metric titration was performed in order to determine the solubility of $\text{Ca}(\text{OH})_2$ at $293 \pm 1\text{K}$, and $343 \pm 1\text{K}$. The following procedure of was followed. Weighed 0.1 g of calcium hydroxide was transferred to a 100 ml volumetric flask and added 0, 1, 2, 3, 4, 5, 6, 10, 15, 20 and 25 percentages of mixed solvents (1-propanol, 2-propanol, methanol and ethanol) and then made up the mark with water. Stirred for 30 minutes and then this solution were kept for 24 hours in thermostat at fixed temperatures to get maximum saturation. This sample was filtered using Whatman filter paper 60A. A 25.00 mL aliquot is transferred to a 100-mL beaker. The sample was titrated with standardized hydrochloric acid $0.03 \pm 0.001\text{ M}$ and pH was recorded during the titration. The reacting mixture flask was placed in water bath during the whole titration and temperature was controlled by thermostat at a fixed temperature. The titration is repeated three times. The neutralized solution was washed down to drain [18]. The equivalence point was obtained by 1st derivative curve. The pH meter was calibrated with buffer solution of pH 4, 7 and 10. The pH meter showed zero error against the buffers.

Results and Discussion

In mixed solvent systems the pH of $\text{Ca}(\text{OH})_2$ was gradually decreased by the addition of each volume (ml) of Standard HCl ($0.03 \pm 0.001\text{ M}$) by the mutual exchange of H^+ and OH^- ions from acid with analyte after the equivalence point, pH of mixture is decreased sharply in increasing the H^+ ion in solution. In all these cases the pH variation started from 12.99 ± 0.01 to 2.62 ± 0.02 . The titration curves were shown in Figure 1.

The decrease in equivalence point while plotting against the varied composition of these mixed solvent systems (0-25 percentages) is represented in Figure 2. The various mixed solvents influenced in equivalent point into different extents depending upon their dielectric constant, solvation behaviors and interaction with water and solute. The methanol+water system showed least variation tendency in equivalence point while 2-propanol+ water showed maximum effect as compared to the equivalence point in pure water at $293 \pm 1\text{K}$ and $343 \pm 1\text{K}$. However the dissolution of $\text{Ca}(\text{OH})_2$ was decreased slightly by increasing temperatures. The reversed trend in dissolution against temperature, in $\text{Ca}(\text{OH})_2$ was found due to its lattice energy. The solvation of ion was possibly influenced by temperature in two ways. For instance it has been reported that ions- ions interaction is usually decreased by increasing temperature that results in the solvation of

ions which enhances by rise in temperature [11,17,19-21]. However, the solvation of ions may inversely be influenced by the rise in temperature, were a possible decrease in solvation occurs with the rise in temperature.

The solubility of calcium hydroxide was slightly decreased by increasing the % composition of mixed solvent systems as compare to pure water shown in the Figure 3 and 4. The decreasing trend in the solubility was minimum up to 5 percentage composition in all the mixed solvent systems whereas, a significant decrease occurred from 6-25 percentage compositions of mixture solvents. The methanol + water system showed minimum decreasing trend while 2-propanol + water system showed maximum at both temperatures. The reason of such behavior is the nature of dielectric constant, extent of solvent-solvent interaction and solvent-solute interaction, which is reported in literature [22-24]. The dielectric constant is the ability of any solvent, which reduces the forces between solute ions. Since the dielectric constant of water is 80, which is greater than that of any solvent so it reduces the force of attraction between solute ions, as a result ions

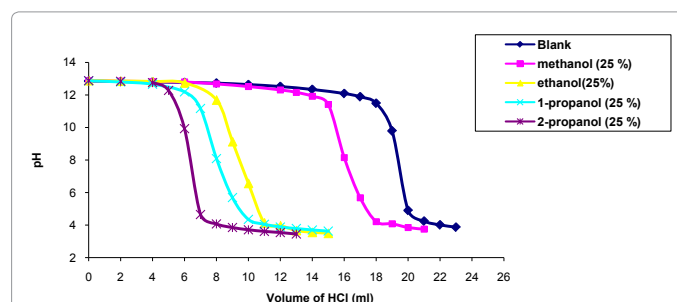


Figure 1: Titration curves of the $\text{Ca}(\text{OH})_2$ in mixed solvent systems at (25 percentage composition) at $293 \pm 1\text{K}$.

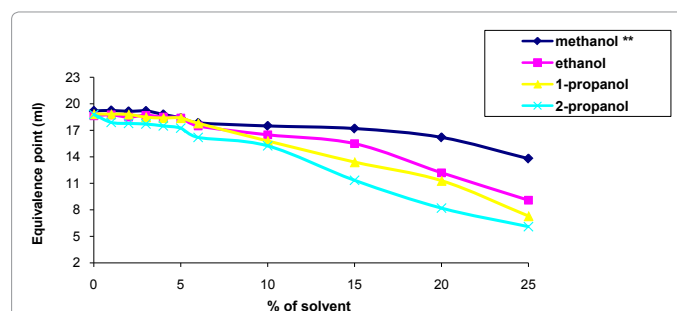


Figure 2: Effect of mixed solvent system on the Equivalence point of Calcium hydroxide at $343 \pm 1\text{K}$.

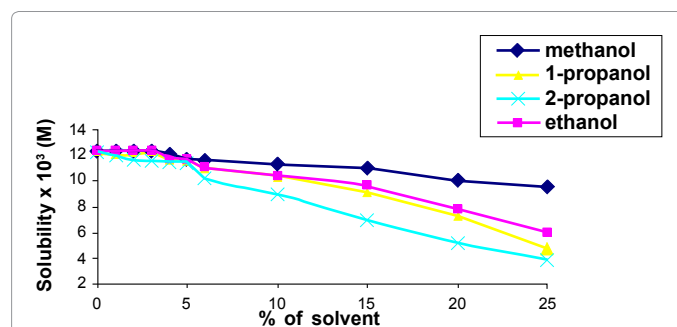
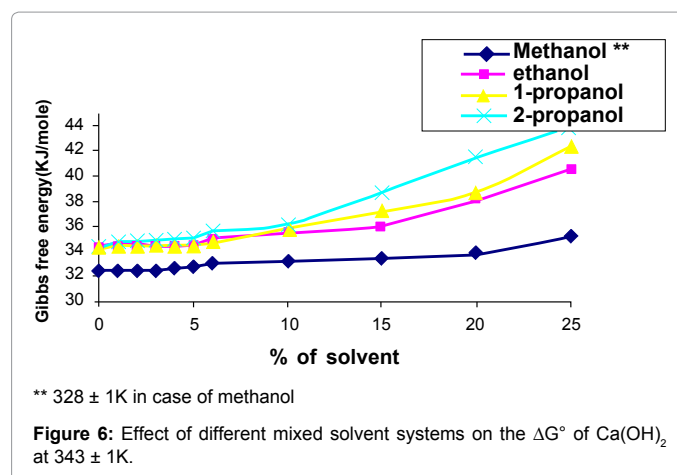


Figure 3: Effect of mixed solvent system on solubility of $\text{Ca}(\text{OH})_2$ at $293 \pm 1\text{K}$.

are separated and solute is dissolved. Therefore, solubility of any salt is greater in water than in the other solvents. The solvents selected in the present research work have the following order of dielectric constant values water>methanol >ethanol >1-propanol >2-propanol [14,25]. As the percentage compositions of these solvents increased in water the values of dielectric constant decreases as a result solubility also decreases.

Solubility product values of Calcium hydroxide, in pure aqueous system as well as in mixed solvent systems like (methanol-water, ethanol-water, 1-propanol-water and 2-propanol water) were calculated from their solubility values from the equation 2 and represented in Table 1 and 2. The Figure 5 showed that a slightly non-linear decreasing trend with least decrease in K_{sp} values was observed in all mixed solvent systems up to their 5% composition against pure water, however from 6%-25% compositions in the presence of mixed solvent systems, a decrease in their K_{sp} values occurred. The reason of non-linearity in the K_{sp} values is due to the term of product of solubility, which altered the behavior in a non-linear fashion (having based $K_{sp} = 4s^3$).

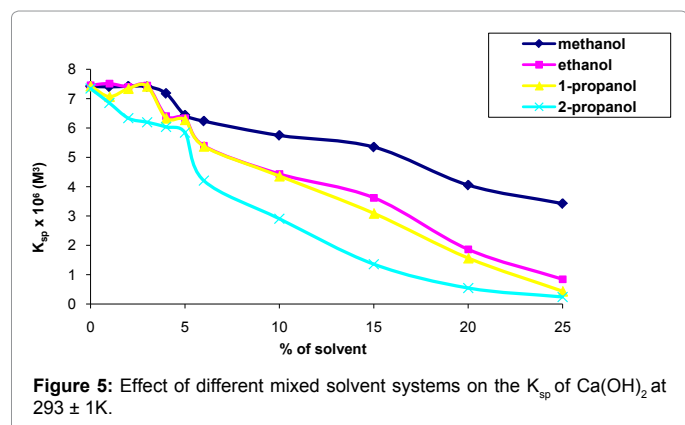
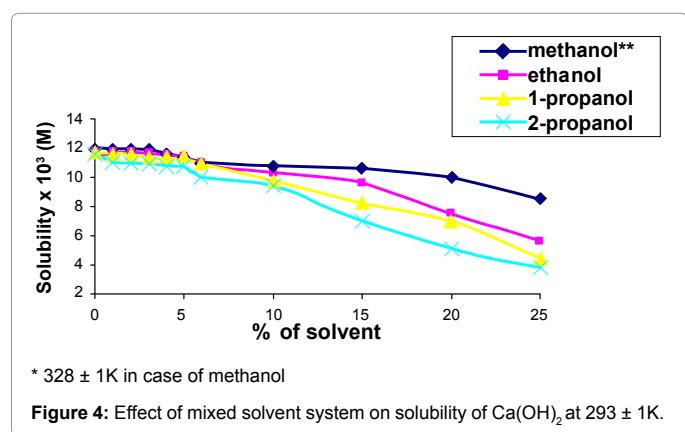
The ΔG° values for the dissolution of Calcium hydroxide in water and mixed solvent system at two different temperatures were evaluated from the K_{sp} values calculated by equation 3 and presented in Table 3 and 4. The Figure 6 showed that the ΔG° values were increased linearly with increase in percentage compositions of mixed solvent systems. This trend was found similar in both temperatures. It was found that the methanol system showed minimum increase in ΔG° values while 2-propanol showed maximum increasing trend against percentage compositions up to 25% composition. This can be explained on the bases of change in structure change, dielectric constant values, ion



solvation, crystal forces and ionic radius of the Ca(OH)_2 . The positive values of the $\Delta^\circ G$ explain that the solubility of the Calcium Hydroxide is very low [9]. In other words these Ca(OH)_2 when dissolved in these mixed solvent systems followed non-spontaneous dissolution process in forward direction hence, producing positive values of $\Delta^\circ G$ [9,26-28]. In the present study the average ΔG° values was obtained in pure water are $28.974 \text{ kJ mol}^{-1}$ and $34.35 \text{ kJ mol}^{-1}$ at 20°C and 70°C are comparable with the reported values 32.3 kJ mol^{-1} and $43.60 \text{ kJ mol}^{-1}$ at 23°C at 100°C respectively by using volumetric titration method and are 26.79 ± 0.06 at $5 \pm 1^\circ\text{C}$ by conductometric method. The slight difference in ΔG° values are due to the selection of temperature because the solubility of calcium hydroxide decreases with the increasing of temperature [26-28].

However the Ca(OH)_2 are unfortunately less soluble and has low dissolution in water and mixed solvent system, the dissolution enthalpies of the Ca(OH)_2 could not measure directly but have only been evaluate by using equation 4 [1-5,29,30].

The ΔS° values were found to be negative and their change with the percentage composition of mixed solvent systems was almost insignificant and non-linear up to 15% mixed solvent compositions, beyond this up to 25% a slightly decrease in ΔS° values was observed having almost similar values. Since the values of ΔS° were taken in Joule/Mole. Kelvin (J/mol.K) rather than Kilo Joule/ Mole. Kelvin (kJ/mol.K), therefore the possibility of scattering is more. In present study the average value of ΔS° was found $-107.53 \text{ Jmol}^{-1}\text{K}^{-1}$ in pure aqueous system while the reported values evaluated in pure water is $-150 \text{ Jmol}^{-1}\text{K}^{-1}$ and -171 ± 0.43 by simple titration method and conductometric method [13,17]. The significant decrease in the ΔS° values comparative to the reported value is due to the determination of ΔG° at slightly lower temperatures compared to the reported temperature (the present work ΔG° were obtained at $293 \pm 1\text{K}$ and $343 \pm 1\text{K}$, while in reported work it was inferred at $298 \pm 1\text{K}$ and $373 \pm 1\text{K}$ and $277 \pm 1\text{K}$ and $303 \pm 1\text{K}$ [13,17]. The reason of selection of low temperature in the present work is due to the possibility of evaporation of mixed solvent systems that caused a significant decrease in ΔS° values. Another significant factor for the influence of mixed solvent systems reveals that the mixed solvent systems linearly decrease the ΔS° values compared to pure aqueous system. This behavior justifies that the presence of mixed solvent systems increased orderness in the molecular state of Calcium hydroxide, moreover with 15%-25% compositions such behavior was found to be opposite collectively where a significant decrease in ΔS° values were occurred, justifying the disorderness appeared



S.No	% of solvent	$K_{sp} \times 10^6 \text{ (M}^3\text{) values}$			
		Methanol- H ₂ O	Ethanol-H ₂ O	1-propanol-H ₂ O	2-propanol-H ₂ O
1	0	7.423 ± 0.12	7.457 ± 0.10	7.434 ± 0.16	7.345 ± 0.11
2	1	7.400 ± 0.17	7.513 ± 0.10	7.069 ± 0.17	6.854 ± 0.10
3	2	7.423 ± 0.11	7.400 ± 0.11	7.345 ± 0.17	6.335 ± 0.08
4	3	7.412 ± 0.12	7.445 ± 0.08	7.423 ± 0.16	6.194 ± 0.09
5	4	7.178 ± 0.16	6.406 ± 0.07	6.335 ± 0.15	6.037 ± 0.09
6	5	6.437 ± 0.08	6.335 ± 0.09	6.285 ± 0.12	5.843 ± 0.09
7	6	6.234 ± 0.13	5.395 ± 0.07	5.377 ± 0.13	4.206 ± 0.06
8	10	5.748 ± 0.14	4.433 ± 0.08	4.361 ± 0.12	2.907 ± 0.04
9	15	5.350 ± 0.05	3.620 ± 0.06	3.091 ± 0.10	1.358 ± 0.04
10	20	4.054 ± 0.10	1.862 ± 0.04	1.567 ± 0.06	0.546 ± 0.02
11	25	3.422 ± 0.09	0.844 ± 0.02	0.436 ± 0.03	0.239 ± 0.01

Table 1: Effect of different mixed solvent systems on the $K_{sp} \times 10^6 \text{ (M}^3\text{)}$ of Ca(OH)_2 at $293 \pm 1\text{K}$.

S.No	% of solvent	$K_{sp} \times 10^6 \text{ (M}^3\text{) values}$			
		Methanol- H ₂ O*	Ethanol-H ₂ O	1-propanol-H ₂ O	2-propanol-H ₂ O
1	0	6.748 ± 0.15	6.185 ± 0.05	6.386 ± 0.12	6.335 ± 0.09
2	1	6.801 ± 0.19	6.285 ± 0.05	6.365 ± 0.14	5.468 ± 0.12
3	2	6.695 ± 0.20	6.037 ± 0.07	6.335 ± 0.15	5.359 ± 0.09
4	3	6.737 ± 0.22	6.234 ± 0.09	6.027 ± 0.16	5.305 ± 0.08
5	4	6.335 ± 0.11	6.037 ± 0.08	5.939 ± 0.14	5.110 ± 0.07
6	5	5.939 ± 0.20	5.939 ± 0.08	5.939 ± 0.13	4.894 ± 0.08
7	6	5.422 ± 0.11	5.110 ± 0.07	5.377 ± 0.14	4.054 ± 0.06
8	10	5.110 ± 0.13	4.283 ± 0.06	3.761 ± 0.10	3.381 ± 0.06
9	15	4.851 ± 0.12	3.551 ± 0.06	2.299 ± 0.08	1.394 ± 0.03
10	20	4.054 ± 0.12	1.732 ± 0.03	1.376 ± 0.06	0.526 ± 0.02
11	25	2.506 ± 0.05	0.719 ± 0.02	0.371 ± 0.03	0.217 ± 0.01

*328 ± 2K in case of methanol

Table 2: Effect of different mixed solvent systems on the $K_{sp} \times 10^6 \text{ (M}^3\text{)}$ of Ca(OH)_2 at $343 \pm 1\text{K}$.

S.No	% of solvent	$\Delta G^\circ \text{ (kJ/mole) values}$			
		Methanol- H ₂ O	Ethanol-H ₂ O	1-propanol-H ₂ O	2-propanol-H ₂ O
1	0	28.970 ± 0.04	28.959 ± 0.02	28.967 ± 0.05	28.996 ± 0.04
2	1	28.978 ± 0.05	28.941 ± 0.04	29.090 ± 0.05	29.166 ± 0.06
3	2	28.970 ± 0.03	28.978 ± 0.03	28.996 ± 0.06	29.359 ± 0.05
4	3	28.974 ± 0.04	28.963 ± 0.03	28.970 ± 0.07	29.414 ± 0.06
5	4	29.052 ± 0.04	29.332 ± 0.03	29.359 ± 0.01	29.477 ± 0.05
6	5	29.320 ± 0.03	29.359 ± 0.04	29.379 ± 0.04	29.557 ± 0.05
7	6	29.398 ± 0.04	29.753 ± 0.04	29.761 ± 0.04	30.364 ± 0.06
8	10	29.598 ± 0.05	30.235 ± 0.05	30.275 ± 0.05	31.270 ± 0.06
9	15	29.774 ± 0.02	30.732 ± 0.03	31.119 ± 0.06	33.137 ± 0.07
10	20	30.454 ± 0.04	32.362 ± 0.05	32.786 ± 0.06	35.375 ± 0.10
11	25	30.870 ± 0.05	34.305 ± 0.06	35.927 ± 0.05	37.404 ± 0.13

Table 3: Effect of different mixed solvent systems on the ΔG° of Calcium hydroxide at $293 \pm 1\text{K}$.

S.No	% solvent	$\Delta G^\circ \text{ (kJ/mole) values}$			
		Methanol- H ₂ O*	Ethanol-H ₂ O	1-propanol-H ₂ O	2-propanol-H ₂ O
1	0	32.471 ± 0.05	34.404 ± 0.03	34.312 ± 0.04	34.335 ± 0.04
2	1	32.450 ± 0.05	34.358 ± 0.02	34.321 ± 0.04	34.757 ± 0.04
3	2	32.492 ± 0.06	34.473 ± 0.03	34.335 ± 0.04	34.815 ± 0.03
4	3	32.475 ± 0.07	34.381 ± 0.04	34.478 ± 0.04	34.844 ± 0.04
5	4	32.643 ± 0.01	34.473 ± 0.04	34.520 ± 0.03	34.952 ± 0.04
6	5	32.819 ± 0.04	34.52 ± 0.04	34.520 ± 0.04	35.076 ± 0.04
7	6	33.067 ± 0.04	34.952 ± 0.03	34.805 ± 0.05	35.616 ± 0.04
8	10	33.229 ± 0.05	35.458 ± 0.04	35.831 ± 0.05	36.136 ± 0.04
9	15	33.371 ± 0.06	35.996 ± 0.05	37.242 ± 0.06	38.678 ± 0.07
10	20	33.861 ± 0.06	38.056 ± 0.05	38.716 ± 0.07	41.475 ± 0.08
11	25	35.173 ± 0.05	40.579 ± 0.08	42.476 ± 0.11	44.021 ± 0.11

*328 ± 2K in case of methanol

Table 4: Effect of different mixed solvent systems on the ΔG° of Calcium hydroxide at $343 \pm 1\text{K}$.

S.No	% of solvent	$\Delta S^\circ (\text{Jmol}^{-1}\text{K}^{-1})$			
		Methanol- H_2O	Ethanol- H_2O	1-propanol- H_2O	2-propanol- H_2O
1	0	-106.082 $\pm$ 0.52	-108.897 $\pm$ 0.08	-106.913 $\pm$ 0.05	-106.775 $\pm$ 0.16
2	1	-105.212 $\pm$ 0.47	-108.347 $\pm$ 0.15	-104.626 $\pm$ 0.29	-111.826 $\pm$ 0.08
3	2	-106.728 $\pm$ 0.66	-109.916 $\pm$ 0.02	-106.775 $\pm$ 0.09	-109.121 $\pm$ 0.07
4	3	-106.099 $\pm$ 0.54	-108.362 $\pm$ 0.16	-110.158 $\pm$ 0.21	-108.603 $\pm$ 0.10
5	4	-108.813 $\pm$ 0.65	-102.836 $\pm$ 0.07	-103.222 $\pm$ 0.12	-109.486 $\pm$ 0.01
6	5	-106.035 $\pm$ 1.88	-103.222 $\pm$ 0.14	-102.830 $\pm$ 0.23	-110.363 $\pm$ 0.07
7	6	-111.187 $\pm$ 0.02	-103.975 $\pm$ 0.01	-100.884 $\pm$ 0.01	-105.039 $\pm$ 0.16
8	10	-110.053 $\pm$ 0.33	-104.460 $\pm$ 0.06	-111.126 $\pm$ 0.11	-97.3188 $\pm$ 0.08
9	15	-109.009 $\pm$ 0.49	-105.281 $\pm$ 0.09	-122.462 $\pm$ 0.01	-110.806 $\pm$ 0.20
10	20	-103.233 $\pm$ 0.02	-113.882 $\pm$ 0.05	-118.590 $\pm$ 0.13	-122.001 $\pm$ 0.01
11	25	-130.386 $\pm$ 0.49	-125.491 $\pm$ 0.13	-130.967 $\pm$ 0.17	-132.344 $\pm$ 0.07

Table 5: Effect of mixed solvent systems on ΔS° of $\text{Ca}(\text{OH})_2$ at 293 $\pm$ 1K and 343 $\pm$ 1K.

S.No	% of solvent	$\Delta H^\circ (\text{kJ/mol.})$			
		Methanol- H_2O	Ethanol- H_2O	1-propanol- H_2O	2-propanol- H_2O
1	0	-2.325 $\pm$ 0.16	-3.167 $\pm$ 0.02	-2.574 $\pm$ 0.02	-2.503 $\pm$ 0.06
2	1	-2.061 $\pm$ 0.13	-3.023 $\pm$ 0.06	-1.776 $\pm$ 0.09	-3.824 $\pm$ 0.03
3	2	-2.516 $\pm$ 0.20	-3.449 $\pm$ 0.03	-2.503 $\pm$ 0.03	-2.833 $\pm$ 0.02
4	3	-2.326 $\pm$ 0.16	-3.005 $\pm$ 0.04	-3.527 $\pm$ 0.07	-2.625 $\pm$ 0.04
5	4	-3.048 $\pm$ 0.18	-1.006 $\pm$ 0.01	-1.092 $\pm$ 0.04	-2.822 $\pm$ 0.01
6	5	-1.961 $\pm$ 0.56	-1.092 $\pm$ 0.03	-0.957 $\pm$ 0.07	-3.001 $\pm$ 0.02
7	6	-3.403 $\pm$ 0.01	-0.921 $\pm$ 0.02	-0.850 $\pm$ 0.01	-0.623 $\pm$ 0.05
8	10	-2.869 $\pm$ 0.09	-0.582 $\pm$ 0.04	-2.508 $\pm$ 0.04	2.561 $\pm$ 0.03
9	15	-2.385 $\pm$ 0.18	-0.327 $\pm$ 0.01	-5.008 $\pm$ 0.01	0.450 $\pm$ 0.07
10	20	-1.861 $\pm$ 0.02	-1.234 $\pm$ 0.01	-2.199 $\pm$ 0.05	-0.616 $\pm$ 0.01
11	25	-7.595 $\pm$ 0.16	-2.716 $\pm$ 0.02	-2.709 $\pm$ 0.06	-1.638 $\pm$ 0.02

^a328 $\pm$ 1K in case of methanol

Table 6: Effect of mixed solvent systems on ΔH° of $\text{Ca}(\text{OH})_2$ at 293 $\pm$ 1K and 343 $\pm$ 1K.

again or in other words the presence of mixed solvent systems up to 15% compositions decreased the process of association of Calcium hydroxide whereas from 15%-25% compositions it enhanced the process of association of Calcium hydroxide. The values of ΔS° shown in Table 5.

The enthalpy values showed in Table 6, having similar behavior with a non-linearity in ΔH° while plotting against % compositions of mixed solvent systems evaluated by measuring ΔG° at temperatures. The extent of scattering in ΔH° values were more closed having non-linear trend due to fact the ΔH° values were evaluated in kilo Joule / Mole (kJ/mol.) compared to ΔS° values (when J/mol. K). The ΔH° values were also in negative even in the presence of all these mixed solvent systems similar to the values reported in the literature [13,17]. Obviously it is due to the exothermic nature of calcium hydroxide. A slightly increase in the ΔH° values compared to the literature related to pure aqueous system is due to the selection of temperature [31-35].

Time effect on pH calcium hydroxide solution showed that an increase in pH was observed in different mixed solvent (at different percentage composition of solvent) as compared to blank. It indicates that less dissociation occurred in blank compared to mixed solvent system within 60 minutes. Maximum pH was observed in 2-propanol to 1-propanol and ethanol while methanol showed an intermediate behavior. It indicates that maximum dissociation of calcium hydroxide occurred in that solvent which has high pH values as compared to other solvent. For approaching limiting value more time was required in various composition of solvent compared to blank. It showed that less time required to maintain the equilibrium state in blank.

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