

Solvent Effect on the Thermodynamic Parameters of $\text{Ca}(\text{OH})_2$ by Conductivity Method

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Abstract

Conductivity method is used for the study of the dissolution of $\text{Ca}(\text{OH})_2$ in water and in mixed solvent systems. The thermodynamic parameters for the dissolution of $\text{Ca}(\text{OH})_2$ such as ΔG° , ΔS° , ΔH° were calculated from solubility values at different temperatures in aqueous medium and in mixed solvent systems (Water+1-propanol, water+2-propanol, water+DMSO and water + THF). It was found that the solubility and solubility product of $\text{Ca}(\text{OH})_2$ significantly decreased linearly by increasing percentage composition of the mixed solvent systems. The Gibbs free energy ΔG° , enthalpy ΔH° and ΔS° were also changed. These results were in agreement with the dielectric constant value of the solvents used in the study.

Keywords: Thermodynamic parameters; Mixed solvent system; Solubility product; Conductivity

Introduction

Calcium Hydroxide has great application in the field of metallurgy, agriculture, paper and glass industry. It is also used in soil amendment to supply calcium to crops [1,2]. It is widely used in manufacturing of steel, chemicals, cement and glass. It is also be used to control air pollution, water and sewage wastewater treatment, diluents and carriers of pesticides such as lime-sulfur, Bordeaux mixture, bleach production, and other chemical substance [2,3]. It is also used in paper industry to dissolve lignin as for the coagulation [2,3].

In the present research work, conductometric titration was used for the study of the influence of mixed solvent system on the solubility of $\text{Ca}(\text{OH})_2$.

The study of equilibrium for many chemical reactions has taken into consideration for the determination of thermodynamic investigation.

The molar solubility "S" solubility product and Gibbs free energy is determined from following equation [1],

$$K_{sp} = [\text{Ca}^{+2}] [\text{2OH}]^2 = 4S^3 \quad (1)$$

$$\Delta G = -R T \ln (K_{sp}) \quad (2)$$

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 [1].

$$\Delta G^\circ = H^\circ - T\Delta S^\circ \quad (3)$$

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

In previously reported only the study of simple conductometric titration of $\text{Ca}(\text{OH})_2$ in aqueous medium at 25 and 100°C. In present work reported the effect of solvent on the dissolution $\text{Ca}(\text{OH})_2$.

Experimental

In the present research work, conductivity method was used for the study of the influence of mixed solvent system on the solubility of $\text{Ca}(\text{OH})_2$.

All reagents are used such as $\text{Ca}(\text{OH})_2$ (E. Merck), 1-Propanol (E. Merck), 2-propanol (E. Merck), Tetrahydrofuran (E. Merck), Dimethyl

sulfoxide (E. Merck), Hydrochloric acid (E. Merck), Oxalic acid (E. Merck), Sodium hydroxide (E. Merck) and Phenolphthalein (E. Merck) each of these analytical grade reagent. These stock solutions were prepared in double distilled water.

Conductivity meter HANNA (HI- 8633) (Romania), IKA-Combimag RCH magnetic stirrer (Germany) Thermostat (Chiller) Haake, (Type T 52, V 220, No 76400, Germany) Electrical Balance (Mettler college 150, Germany) (Table 1).

Preparation of stock solution of $\text{Ca}(\text{OH})_2$

The conductometric titration was performed in order to determine the solubility of $\text{Ca}(\text{OH})_2$, at 5, and 30 \pm 1°C. The following procedure of was followed.

Stock solution of $\text{Ca}(\text{OH})_2$ was prepared by dissolving 0.1 g in 100 ml volumetric flask having different percentage composition (i.e. 5%, 10%, 20%, 30%, 40%, and 50%) of a mixed solvent system (1-propanol, 2-propanol, THF and DMSO). For this purpose solution was stirred for 30 minutes and then this solution was kept overnight to get maximum saturation (Table 2).

The next day the saturated solution of $\text{Ca}(\text{OH})_2$ was filtered using Whatman filter paper 60°A. A 25 ml of filtered solution of $\text{Ca}(\text{OH})_2$ was titrated with standard solution of HCl (0.03 \pm 0.001 M) and the conductivity was recorded using conductivity meter. The reacting mixture flask was placed in water bath during the whole titration and temperature was controlled by thermostat at a fixed temperature.

Results and Discussions

In mixed solvent systems (1-propanol, 2-propanol, DMSO & THF + water) the conductance of $\text{Ca}(\text{OH})_2$ was little by little decreased by

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the addition of each volume (ml) of Standard HCl (0.03 ± 1 N) by the mutual exchange of H^+ and OH ions from acid with analyte after the equivalence point, conductance of mixture is raised sharply in increasing the H^+ ion in solution. This is shown in Figure 1.

The equivalence point of the $Ca(OH)_2$ was also shifted with change of the composition of solvent systems which is shown in Figure 2. In general decreasing phenomenon was observed in each composition of (0%, 10%, 20%, 30%, 40% and 50%) of (1- propanol +water) solvent system at 5 and $30 \pm 1^\circ C$. Similar trend was also observed in 2-propanol, DMSO and THF. However the dissolution of $Ca(OH)_2$ was decreased slightly and by increasing temperatures. The reversed trend in dissolution against temperature, in $Ca(OH)_2$ 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 [4-7]. 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 the various soluble salts in solutions in aqueous medium were calculated at $25^\circ C$, but this paper the solubility of $Ca(OH)_2$ were studied in mixed solvent systems notice able thing is that the solubility of $Ca(OH)_2$ V/S different % composition of mixed solvent systems is showed linear pattern at 5 and $30 \pm 1^\circ C$ which is shown in Figure 3. These decreasing patterns of the solubility of $Ca(OH)_2$ in mixed solvent systems due to decreasing the dielectric constant value of the solvent (Table 3).

The K_{sp} values of $Ca(OH)_2$ were decreased with the increase in percentage composition of mixed solvent systems up to 30%. Beyond this composition they remained unchanged in all mixed solvent systems at all temperatures; however, this trend was comparatively similar to that of solubility which is shown in Figure 4.

The plot of $\Delta^\circ G$ of $Ca(OH)_2$ V/S solvent composition were found to be linear at all temperatures. This linear increasing trend with increasing percentage composition in all these mixed solvent systems is almost similar up to 30% solvent composition, although having a lessers gradient. Above 30% to 50% this response was prominent in $Ca(OH)_2$. The maximum change in $\Delta^\circ G$ was determined in $Ca(OH)_2$.

S #	% of 1-propanol	Parameters in mixed solvent system			
		$K_{sp} \times 10^6 (M^3)$	$\Delta G (Kj/mole)$	$\Delta H (Kj/mole)$	$\Delta S (J/mole)$
1	0	9.19±0.3	26.79±0.06	-20.8±0.21	-171±0.43
2	10	3.88±0.30	28.79±0.227	-12.91±0.03	-150±2.13
3	20	1.53±0.02	30.94±0.077	-5.75±0.06	-132±0.76
4	30	0.55±0.06	33.31±0.478	-5.32±0.21	-139.6±1.21
5	40	0.064±0.01	39.66±0.52	-47.31±0.23	-302±1.42
6	50	0.00864±0.00069	48.23±0.11	-74.83±0.31	-489.6±0.78

Table 1: Effect of mixed solvent system (water+1-propanol) on the K_{sp} and thermodynamic parameters $Ca(OH)_2$ at $5 \pm 1^\circ C$.

S #	% of 2-propanol	Parameters in mixed solvent system			
		$K_{sp} \times 10^6 (M^3)$	$\Delta G (Kj/mole)$	$\Delta H (Kj/mole)$	$\Delta S (J/mole)$
1	0	9.19±0.3	26.79±0.06	-20.8±0.21	-171±0.43
2	10	3.54±0.12	25.00±0.0719	-23.59±0.12	-189.2±2.11
3	20	0.55±0.059	33.29±0.239	-10.05±1.21	-156.8±0.02
4	30	0.146±0.0031	36.37±0.387	-12.54±2.32	-176.4±2.1
5	40	0.0233 ±0.001	42.08±0.350	-28.19±0.21	-244±2.31
6	50	0.000953±0.00017	48.00±0.22	-36.84±21	-305.2±1.1

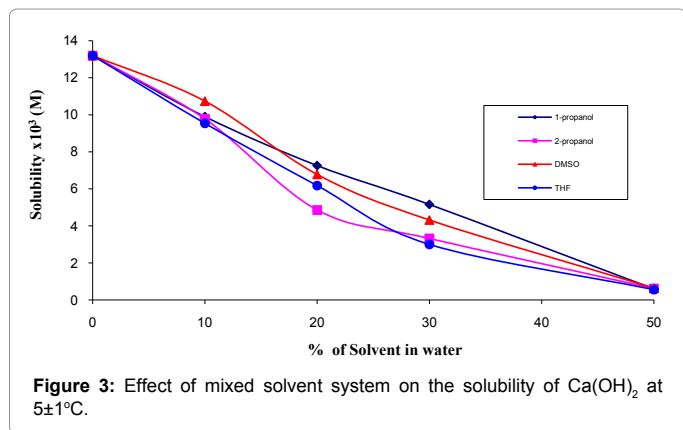
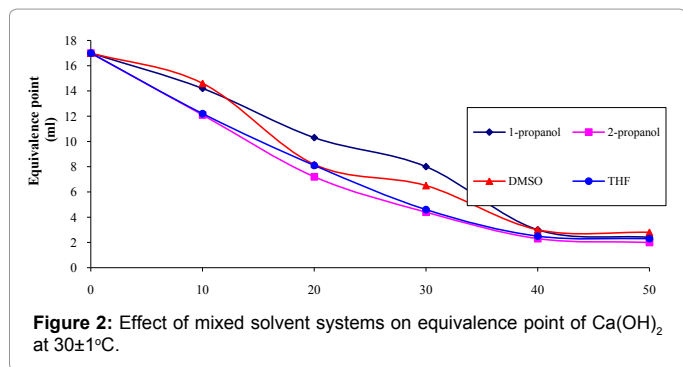
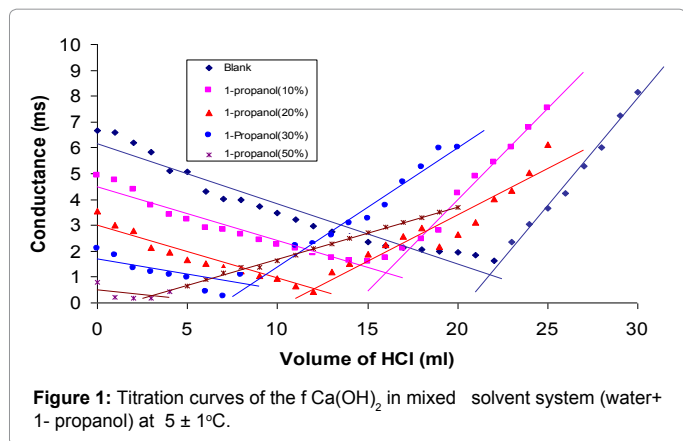
Table 2: Effect of mixed solvent system (water+2-propanol) on the K_{sp} and thermodynamic parameters $Ca(OH)_2$ at $5 \pm 1^\circ C$.

S #	% of DMSO	Parameters in mixed solvent system			
		$K_{sp} \times 10^6 (M^3)$	$\Delta G (Kj/mole)$	$\Delta H (Kj/mole)$	$\Delta S (J/mole)$
1	0	9.19±0.3	26.79±0.06	-20.8±0.21	-171±1.8
2	10	3.47±0.20	39.92±0.21	-22.37±0.12	-185.2±4.3
3	20	0.944±0.18	40.57±0.321	-20.19±1.21	-188±0.21
4	30	0.108±0.039	41.21±0.56	-71.37±0.32	-159±0.65
6	40	0.0396±0.0006	40.80±0.45	-26.38±0.01	-233±3.21
5	50	0.000702±0.00022	52.17±0.621	-15.76±0.21	-232±3.21

Table 3: Effect of mixed solvent system (water+ DMSO) on the K_{sp} and thermodynamic parameters $Ca(OH)_2$ at $5 \pm 1^\circ C$.

S #	% of THF	Parameters in mixed solvent system			
		$K_{sp} \times 10^6 (M^3)$	$\Delta G (Kj/mole)$	$\Delta H (Kj/mole)$	$\Delta S (J/mole)$
1	0	9.19±0.3	26.79±0.06	-20.8±0.21	-171±1.8
2	10	3.47±0.20	29.05±0.077	-14.28±0.03	-185.2±4.3
3	20	0.944±0.18	32.06±0.308	-24.72±0.06	-188±0.21
4	30	0.108±0.039	37.05±0.66	-6.02±0.21	-159±0.65
6	40	0.028±0.0013	41.64±0.210	-38.41±0.01	-278±0.599
5	50	0.000702±0.00022	48.71±1.45	-9.205±0.31	-232±3.21

Table 4: Effect of mixed solvent system (water + THF) on the thermodynamic parameters $Ca(OH)_2$ at $5 \pm 1^\circ C$.

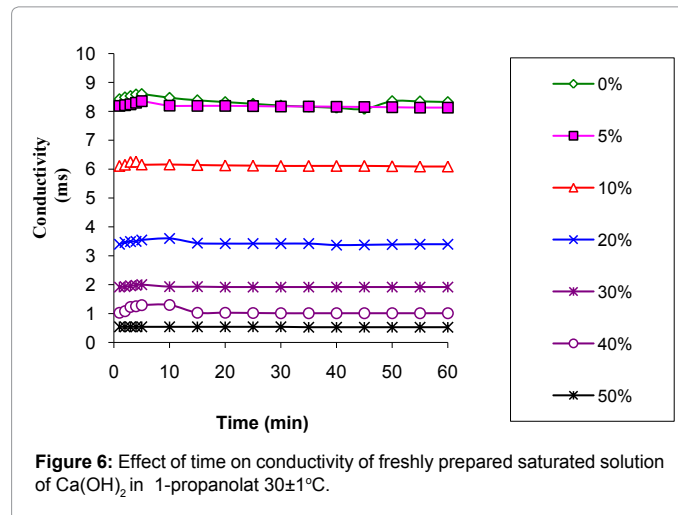
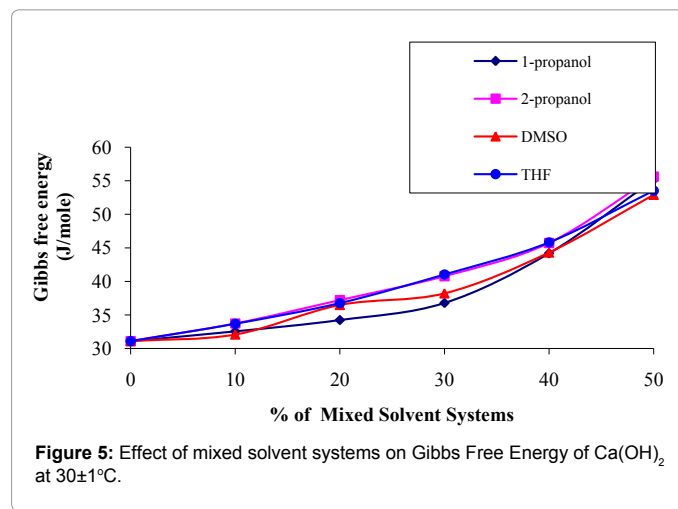
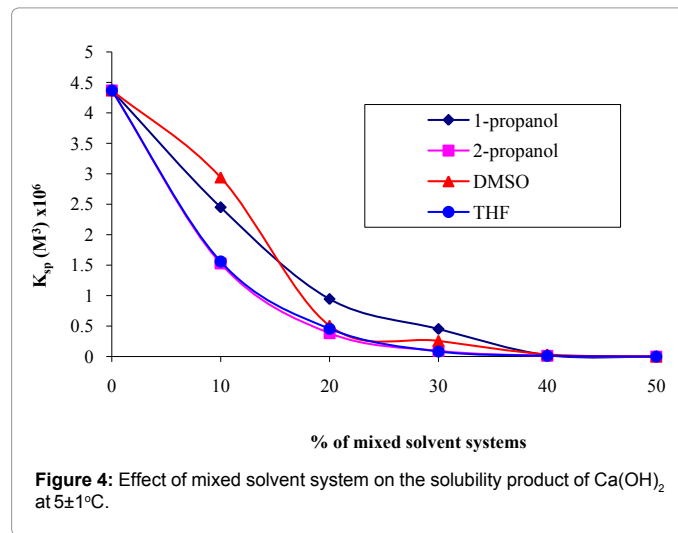


This can be explained on the bases of change in structure change, dielectric constant values, ion solvation, crystal forces and ionic radius of the $\text{Ca}(\text{OH})_2$ positive value of the $\Delta^\circ\text{G}$ explain that the solubility of the $\text{Ca}(\text{OH})_2$ is very low [7]. In other words these $\text{Ca}(\text{OH})_2$ when dissolved in these mixed solvent systems followed non-spontaneous dissolution process in forward direction hence, producing positive values of $\Delta^\circ\text{G}$ [7-10].

However the $\text{Ca}(\text{OH})_2$ are unfortunately less soluble and has low dissolution in water and mixed solvent system., the dissolution enthalpies of the $\text{Ca}(\text{OH})_2$ could not measured directly but have only been evaluate by using formula which explain earlier [11-16] (Table 4).

The enthalpy and entropy values of $\text{Ca}(\text{OH})_2$, in mixed solvent systems showed almost similar and linear trend. The entropy values of the systems having some scattering having positive and negative values,

within percentage composition of mixed solvent system (0–50%). In general it can be concluded that the values of enthalpy followed almost similar behavior with respect to enthalpy changes in these mixed solvent systems and showed both positive as well as negative



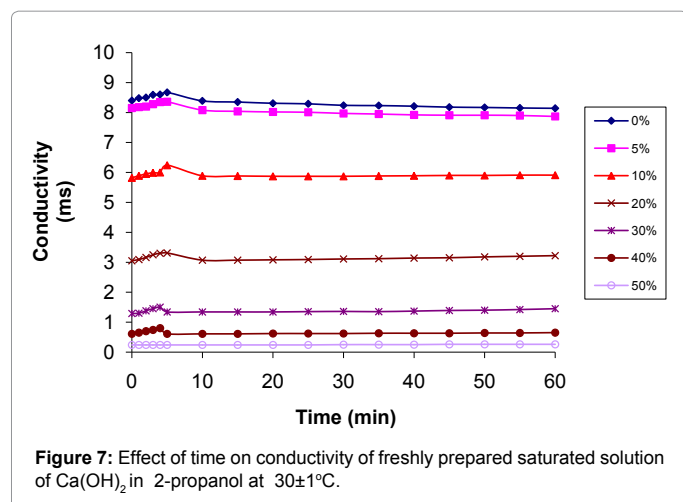


Figure 7: Effect of time on conductivity of freshly prepared saturated solution of $\text{Ca}(\text{OH})_2$ in 2-propanol at $30 \pm 1^\circ\text{C}$.

behavior similar to the trend reported in the literature [8]. The reason of such trend as explained in the reported work is the possibility of destabilization of $\text{Ca}(\text{OH})_2$ in some solvent media decreasing enthalpy range, within a narrow range, which was also appeared in the present research work. Positive and negative enthalpy values confirmed that the destabilization of $\text{Ca}(\text{OH})_2$ in these mixed solvent systems similar to reported work [9]. However, the enthalpies and entropies of $\text{Ca}(\text{OH})_2$ obtained in this way to small changes of the solubility data so that the values calculated from the reported solubility data scatter considerably.

Effect of time on Conductivity at room temperature in mixed solvent systems

Conductivity of $\text{Ca}(\text{OH})_2$ both in the presence and absence of mixed solvent systems was gradually decreased with increasing the percentage composition which is shown in Figures 5-7. The reason of this behavior may be correlated with the possible association of the $\text{Ca}(\text{OH})_2$ resulting decrease in the OH^- conc. confirmed of low conductance values. The other mixed solvent systems were not tried due to instability of the test electrode probe, which was found to be effected in THF and DMSO solvent system, therefore these solvent system were not include this comparative study [17-21].

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