

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

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Summary: In this study, saturated solutions of Sr(OH)₂ in pure water and in mixed solvent systems (methanol - water, ethanol - water, 1-propanol - water, and 2-propanol - water) at two temperatures were prepared and titrated with standard HCl solution by using pH metry. Using these titration data, the molar solubility (s), solubility product (K_{sp}) and Gibbs free energy (ΔG°), entropy change (ΔS°) and enthalpy change (ΔH°) for dissolution of strontium hydroxide was determined. At room temperature (20°C), the s, K_{sp}, ΔG° were found to be 4.28 x 10⁻² mol L⁻¹, 3.13 x 10⁻⁴ mol³L⁻³ and 19.70 kJ mol⁻¹ respectively. The ΔH° and ΔS° of the reaction is 2.90 kJ mol⁻¹ and - 60.80 J. mol⁻¹ K⁻¹. With increasing percentage content of organic solvent in mixed solvents, the molar solubility and K_{sp} decreased and ΔG°, ΔH° and ΔS° values increased. The results were correlated with the dielectric constant value of the solvents used in the study.

Key words: Dielectric constant; Equivalent point; Thermodynamic parameters; Mixed solvent system.

Introduction

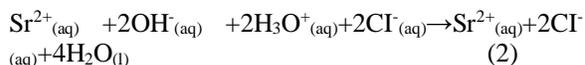
Strontium hydroxide (Sr(OH)₂) is crystalline solid and it is used chiefly in the refining of beet sugar and as a stabilizer in plastic. It may be used in making lubricant soaps, greases, and preparation of other strontium compounds [1, 2].

The solubility of solute is of great practical importance since many industrial process as well as laboratory procedures call for the use of solvent mixtures [3]. The degree of dissolution of sparingly soluble compounds is controlled by different factors such as temperature, pH and dielectric constant etc.

When sparingly soluble compound like strontium hydroxide is added in water, equilibrium is established between the solid and aqueous material that can be shown by the following equation:



The equilibrium concentration OH⁻ is large enough to allow its accurate determination by titrating it with standardized HCl solution using pH meter. The molar solubility “s” of strontium hydroxide is determined from their equivalence points of pH titration curve by using following equation:



$$\text{Moles of OH}^{-} = \text{Moles of HCl} = \text{litres of HCl} \times [\text{HCl}] \quad (3)$$

$$\text{Moles of Sr(OH)}_2 = 1/2 \text{ moles of OH}^{-} \quad (4)$$

$$S = \frac{\text{Mole of Sr(OH)}_2 \text{ in aliquot}}{\text{volume of aliquot in liter}} \quad (5)$$

The solubility product, K_{sp} is evaluated from the molar solubility, using the following equation [4-10]

$$K_{sp} = [\text{Sr}^{+2}] [\text{2OH}^{-}]^2 = 4S^3 \quad (6)$$

The Gibbs free energy (ΔG°) at temperature T, is related to the solubility product constant K_{sp} by following equation [4-10].

$$\Delta G^{\circ} = -R T \ln (K_{sp}) \quad (7)$$

ΔH° and ΔS° are determined from ΔG° values from the dissolution process taken at two different temperatures by using following equations [4-10]

$$\Delta S^{\circ} = (\Delta G^{\circ}_1 - \Delta G^{\circ}_2) / (T_2 - T_1) \quad (8)$$

$$\Delta H^{\circ} = \Delta G^{\circ} - T_2 \Delta S^{\circ} \quad (9)$$

The present work aims to determine the s, K_{sp}, ΔG°, ΔS° and ΔH° from the dissolution of Sr(OH)₂ in water as well as in mixed solvent systems at 20°C and 70°C by pH titration method. Previously, the same method was reported for determination of above parameter of Ca(OH)₂ [4, 9]. Thermodynamics

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study of different salts is important for assessing the physiochemical properties of a chemical system.

Experimental

Analytical grade reagents chemicals were used for present work. All solution was made in deionized water. The equipment used was magnetic stirrer, Thermostat water bath (HAAKE Type T 52 V220, No. 76400, Germany) and pH meter with combined electrode (Mettler Toledo MP220).

Procedure

$\text{Sr}(\text{OH})_2$ saturated solution was made by adding 0.1g of $\text{Sr}(\text{OH})_2$ in volumetric flask (100 ml) having different percentage composition (*i.e.* 0 %, 1 %, 2 %, 3 %, 4 %, 5 %, 6 %, 10 %, 15 %, 20 % and 25 %) of solvents (methanol, ethanol, 1-propanol, 2-propanol) and volume was with deionized water. The solution was stirred for 30 minute and this solution was kept for overnight to get maximum saturation. The saturated solution was filtered using filter paper in a beaker and removed undissolved strontium hydroxide. A 25 ml of filtrate was titrated with standard HCl solution ($0.15 \pm 0.001 \text{ M}$) [9]

Results and Discussion

During titration, the pH of $\text{Sr}(\text{OH})_2$ solution decreased slightly with the addition of every increment (ml) of standard HCl solution by the reaction of hydronium ion from HCl with hydroxyl ion of $\text{Sr}(\text{OH})_2$. However, the pH of solution was sharply decreased at the equivalence point due to elevating concentration hydronium ion in solution (Fig. 1).

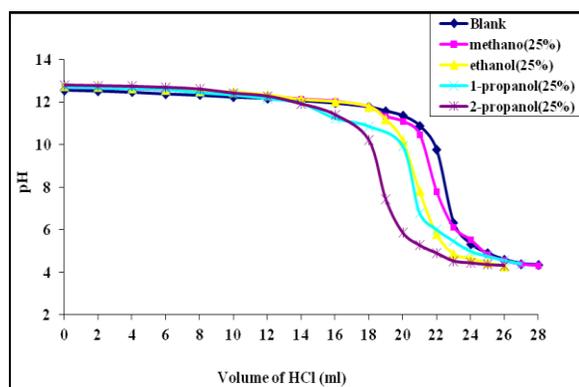


Fig. 1: pH titration curve of Strontium hydroxide in mixed solvent system at 20°C.

In determination of equivalent point, the volume of standard HCl was decreased linearly with increasing percentage content of organic solvent in mixed solvent systems at both temperatures (Fig. 2). The minimum decrease in equivalence point was found in 25% methanol + water system while, maximum decreased in equivalence point was found in 25% 2-propanol- water system (Fig. 2).

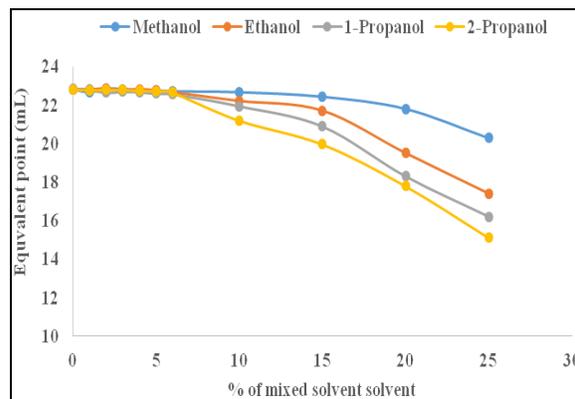
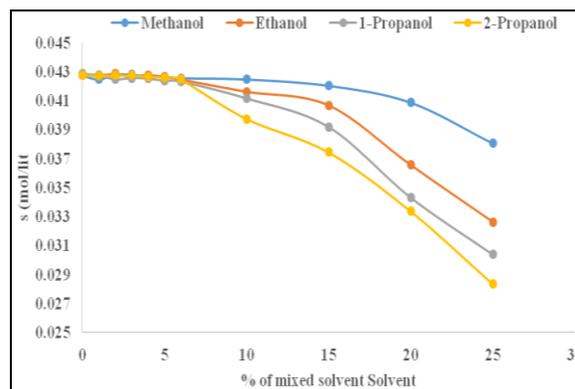


Fig. 2: Effect of mixed solvent system on equivalent point of Strontium hydroxide at 20 °C.

The solubility of $\text{Sr}(\text{OH})_2$ in pure water and mixed solvent systems were evaluated from their equivalent points at two different temperatures. At room temperature (20°C) in pure water, the molar solubility was found to be $4.28 \times 10^{-2} \text{ M}$, whereas $4.45 \times 10^{-2} \text{ M}$ at higher temperature (70°C). These values agree with reported molar solubility of $\text{Sr}(\text{OH})_2$ $3.37 \times 10^{-2} \text{ M}$ at 0 °C [11]. However, the molar solubility values were linearly decreased with increasing percentage composition of organic solvents (Fig. 3). The minimum decrease in molar solubility of $\text{Sr}(\text{OH})_2$ was found in 25 % of methanol-water system, whereas a maximum decreases was found in 25% of 2-propanol - water solvent system.



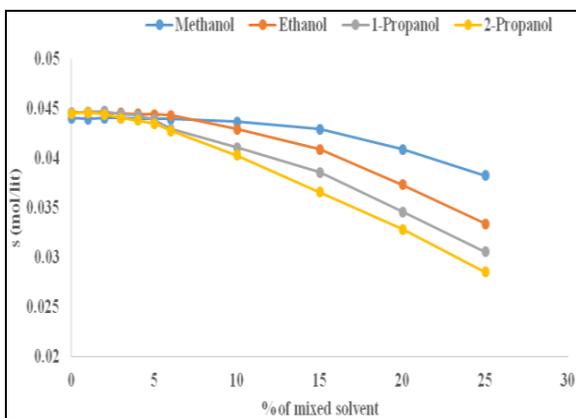


Fig. 3: Effect of added solvents on the molar solubility (s) of Strontium hydroxide at 20°C and 70°C.

The above solubility behavior of $\text{Sr}(\text{OH})_2$ mixed solvent systems is correlated with the dielectric constant values and solvation behaviors [8-10, 12-15]. With increasing percentage compositions of organic solvents in water, the values of dielectric constant decreases as a result solubility decreases. In this study, the molar solubility of $\text{Sr}(\text{OH})_2$ was slightly greater at 70°C. The trend in molar solubility against temperature was due to its lattice energy. For example, with rising temperature, ions-ions interaction is decreased as results in the solvation of ions increases [14-17]. This behavior showed that the dissolution of $\text{Sr}(\text{OH})_2$ is an endothermic reaction.

At room temperature (20 °C), the K_{sp} was found to be 3.13×10^{-4} and its value increased to be 3.55×10^{-4} at higher temperature (70°C). These values agree with standard K_{sp} value 3.20×10^{-4} at 25 °C [18]. However, the K_{sp} values were decreased by increasing % composition of mixed solvent (Fig. 4) and showed similar trends to that of solubility.

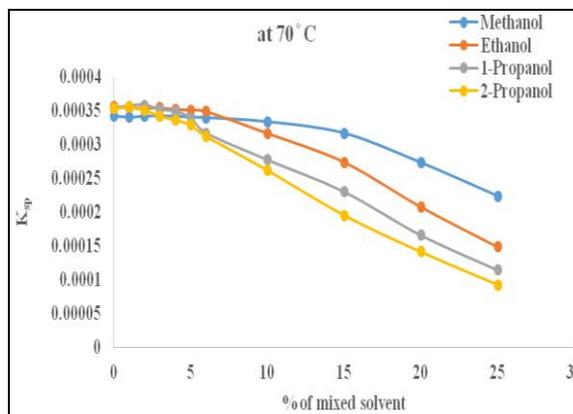
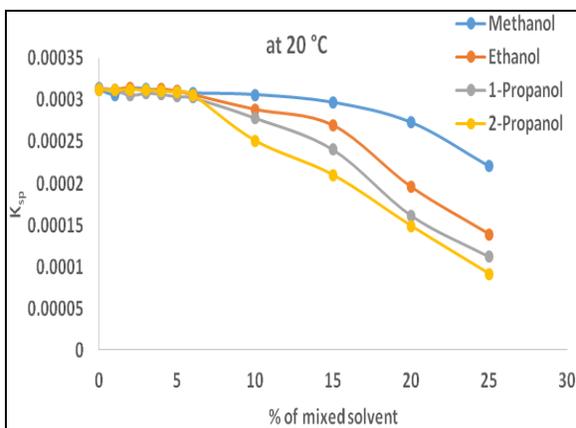


Fig. 4: Effect of added solvents on the K_{sp} of Strontium hydroxide at 20 °C and 70 °C.

The K_{sp} values give ΔG° value of +19.70 $\text{kJ}\cdot\text{mol}^{-1}$ at 20°C and +22.80 $\text{kJ}\cdot\text{mol}^{-1}$ at 70°C. Moreover, ΔG° values increased with increasing percentage composition of organic solvents. The extent of increased in ΔG° values was maximum at 25 % of 2-propanol+ water system and minimum in 25 % of methanol + water system. The change in ΔG° values in mixed solvent system can be correlated with structural change, ϵ , solvation, and ionic radius of the $\text{Sr}(\text{OH})_2$ [17]. The positive ΔG° indicates that the molar solubility of the $\text{Sr}(\text{OH})_2$ is low. In other words, $\text{Sr}(\text{OH})_2$ follows non-spontaneous dissolution process in forward direction in mixed solvent system hence, producing positive values of ΔG° [17, 19, 20].

$\text{Sr}(\text{OH})_2$ has low dissolution in mixed solvent system, the ΔS° and ΔH° of the $\text{Sr}(\text{OH})_2$ could not determine directly. These values have been calculated from the ΔG° values at two temperatures. The ΔH° and ΔS° values of the reaction are +2.90 $\text{kJ}\cdot\text{mol}^{-1}$ and $-60.80 \text{ J mol}^{-1} \text{ K}^{-1}$ respectively were found pure water system. These results are not agreed with reported values of ΔH° and ΔS° evaluated in pure water. Since the ΔG° , ΔS° and ΔH° for the reaction are determined from the temperature dependence. The slightly lowers values ΔS° and ΔH° in the present study comparative to the reported values may be due to the determination of ΔG° at slightly lower temperatures. For example, the present work ΔS° and ΔH° were obtained at 20°C and 70°C (or 55°C in case of methanol+ water system) while in reported work it was inferred at 25°C and 100°C. The reason of chosen of low temperature in the recent work is due to the possibility of evaporation of mixed solvent systems (particularly in case of methanol) which caused a significant decrease in ΔH° and ΔS° values.

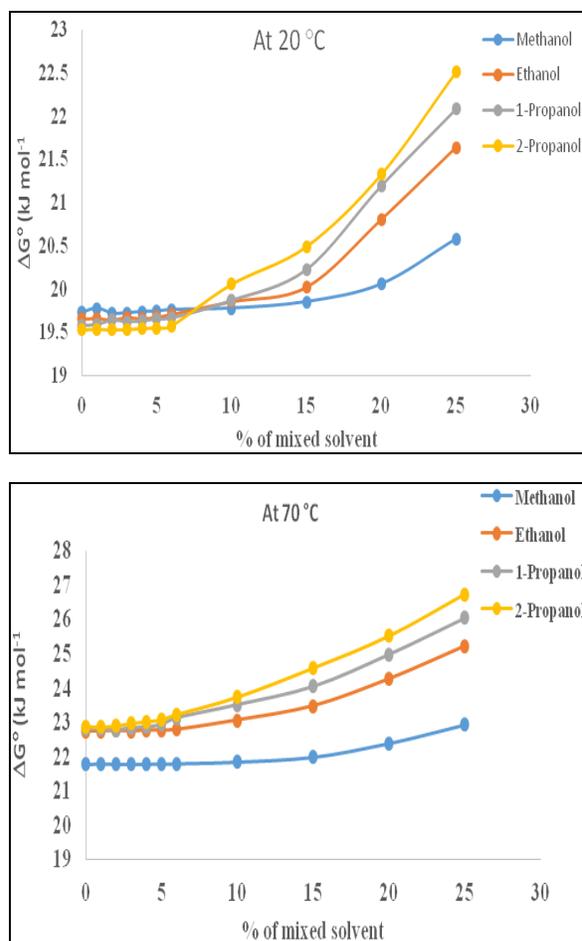


Fig. 5: Effect of mixed solvent systems on the ΔG° of Strontium hydroxide at 20 °C and 70 °C.

A non-linear insignificant variation in entropy values was observed in all mixed solvent systems from 0 - 6% composition and then ΔS° values were decreased up to 25% compositions (Fig. 6). This showed that the presence of higher percentage composition of mixed solvent system significantly decreased ΔS° values or in other word the presence of organic solvents up to 25% decreased disorderness of the systems [21]. Similarly, a closed value of ΔH° having non-linear trend was observed in all mixed solvent systems upto 5% composition then a linear decrease in the ΔH° was found up to 25% compositions. The ΔH° values were almost positive even in the presence of all these mixed solvent systems. This behavior indicates that the dissolution of strontium hydroxide is endothermic in nature.

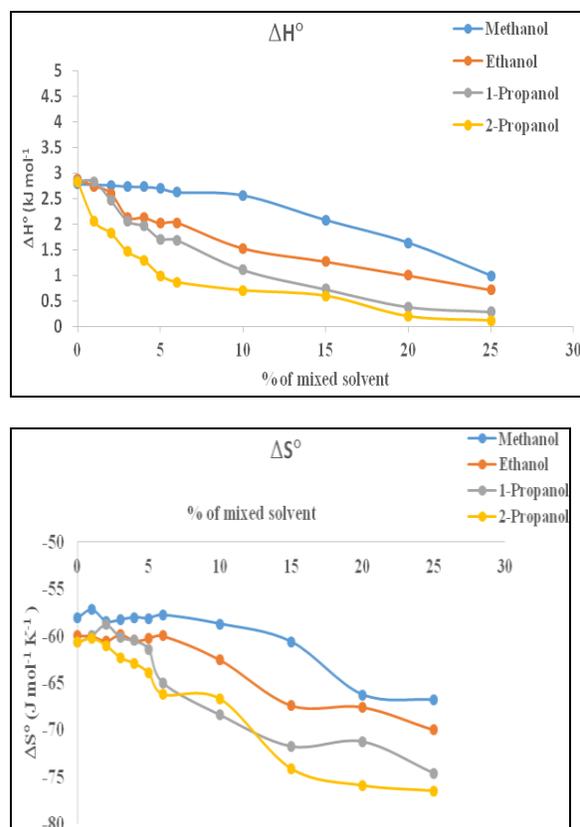


Fig. 6: Effect of mixed solvent systems on the Entropy change (ΔS°) and Enthalpy change (ΔH°) of Strontium hydroxide at 20 °C and 70 °C.

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