

RESEARCH ARTICLE

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# Study of the Thermodynamic Parameters by the Dissolution of Barium Hydroxide in Water through Conductivity Method

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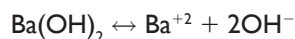
## Abstract

The dissolution of Barium hydroxide ( $\text{Ba}(\text{OH})_2$ ) in pure water was used for finding out its thermodynamic parameters by conductivity method. The effect of ionic salts as well as the influence of some mixed solvent (1,2-propanediol and ethanol) were also studied. It was found that the added ionic salts produced fewer changes in the thermodynamic parameters compared to mixed solvents. Moreover, the combined salts and mixed solvent system collectively changed the thermodynamic parameters more differently as compared to the separate systems. These results were compared with the dielectric constant and ionic strength of the media.

**Keywords:** Barium hydroxide; thermodynamic parameters; conductivity; mixed solvent; dielectric constant.

## 1. Introduction

Barium hydroxide ( $\text{Ba}(\text{OH})_2$ ) is very important due to its industrial applications in different fields. It is used as an additive in thermoplastic, phenolic resins and PVC stabilizers to improve plastic properties. It is also used as general purpose additive for lubricant and grease. It is used in sugar industry, soap manufacturing, fat saponification, fusing of silicates and chemical synthesis of other  $\text{Ba}(\text{OH})_2$  compounds. The significant role of  $\text{Ba}(\text{OH})_2$  is also reported in photographic papers and printing process. It is used in the synthesis of many Chalcones [1, 2]. In synthetic organic chemistry, it is also used for hydrolysis of ester [3, 4] and nitriles [5–7] in preparation of cyclopentanone [8, 9] and in diacetone alcohol [10] etc. Similarly, it is used in the study of endothermic reaction when mixed with ammonium salts. The sparingly soluble salts when dissolved in water dissociate rarely and their degree of dissociation is controlled by various factors like temperature, pH and dielectric constant etc. In case of change in temperature, effect related to the dissociation of  $\text{Ba}(\text{OH})_2$  follows by the following equation:



The concentration of  $\text{OH}^-$  is determined by titrating it with standard HCl solution. The molar solubility "S" of  $\text{Ba}(\text{OH})_2$  is determined from following equations,

$$\begin{aligned} \text{Ba}^{+2}_{(\text{aq})} + 2\text{OH}^-_{(\text{aq})} + 2\text{H}_3\text{O}^+_{(\text{aq})} + 2\text{Cl}^-_{(\text{aq})} &\leftrightarrow \text{Ba}^{+2}_{(\text{aq})} + 2\text{Cl}^-_{(\text{aq})} + 4\text{H}_2\text{O} \\ \text{Moles of hydroxide} &= \text{Moles of HCl} = \text{Liters of HCl} \times [\text{HCl}] \\ \text{Moles of Ba}(\text{OH})_2 &= \frac{1}{2} \text{ moles of OH}^- \text{ where,} \\ S &= \text{Moles of Ba}(\text{OH})_2 \text{ in aliquot/volume of aliquot in liters} \end{aligned} \quad (1)$$

The solubility product ( $K_{sp}$ ) is shown in Equation 2 [11–15]. Since  $K_{sp}$  is used to determine the thermodynamic parameters thus Gibbs free energy for the dissolution of  $Ba(OH)_2$  is shown in Equation 3 [16–20].

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

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

On determination of  $\Delta G^\circ$  value from the dissolution process taken at two different temperatures  $\Delta S^\circ$  and  $\Delta H^\circ$  are also determined by using following equations:

$$\Delta S^\circ = \frac{\Delta G^\circ_1 - \Delta G^\circ_2}{\Delta T_2 - \Delta T_1} \quad (4)$$

$$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ \quad (5)$$

Such information regarding  $\Delta G^\circ$ ,  $\Delta S^\circ$  and  $\Delta H^\circ$  in the present work are studied when the dissolution of  $Ba(OH)_2$  was studied at 10 and  $30 \pm 1^\circ C$ . The same method was followed for  $Ba(OH)_2$  that was reported for  $Ca(OH)_2$  [11, 12].

## 2. Methods

### 2.1. Preparation of saturated solution

The saturated solution of  $Ba(OH)_2$  was prepared by dissolving 0.1 g of analytical grade (E. Merck)  $Ba(OH)_2$  in 100 ml double distilled water. The system was stirred for 30 minutes and placed over night for complete saturation of solution and next day the solubility of  $Ba(OH)_2$  was studied by titrating it with standard solution of HCl ( $0.015 \pm 0.001 N$ ) using conductivity method.

### 2.2. Chemicals

All reagents including  $Ba(OH)_2$ , NaCl, NaOH, HCl and solvents (1,2-propanediol and ethanol) were (E. Merck) of analytical grade. The solutions were prepared in double distilled water without further purification.

### 2.3. Equipments

Conductivity meter Hanna (HI-8033, Portugal), Chiller (Thermostat), Haak (T-25, V-220, No-76400, Germany), Electrical balance (Mettler College 150, Germany) and Magnetic stirrer (IKA Combimag RCH, Germany). All glassware were made of A grade Pyrex quality.

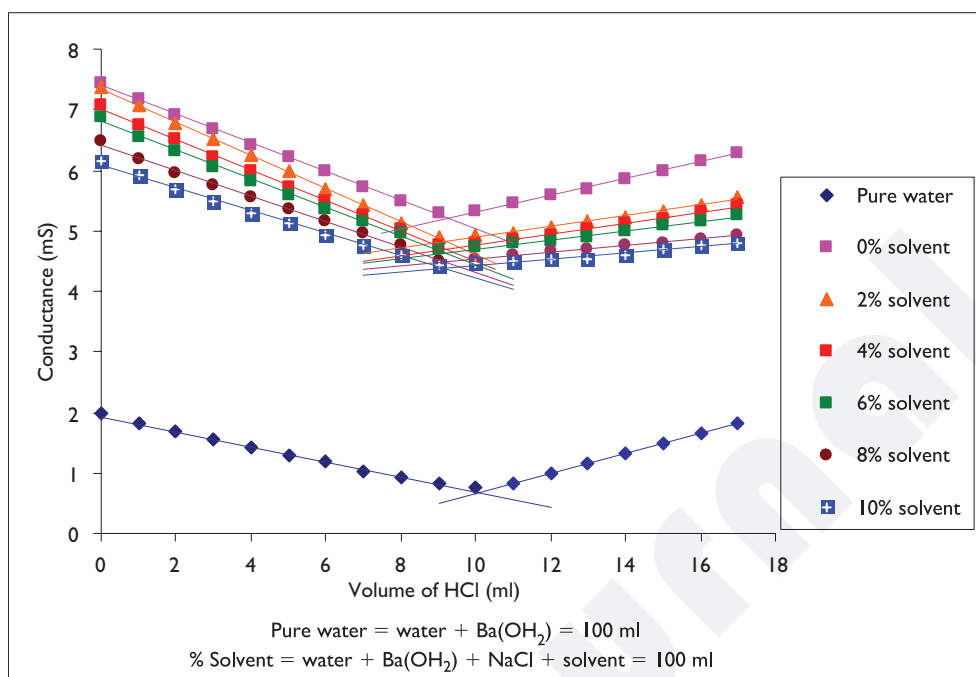
## 3. Results and Discussion

The dissolution of  $Ba(OH)_2$  in pure water, mixed solvent system and in the presence of NaCl was studied using conductivity method. The solubility of  $Ba(OH)_2$  was measured using Equation (1) in which the liberated  $OH^-$  ions were titrated conductometrically against standard HCl solution, and the  $K_{sp}$  of the dissolution of  $Ba(OH)_2$  was evaluated by Equation (2) both at 10 and  $30^\circ C$  (of pure  $Ba(OH)_2$  and of mixed solvent systems). Figures 1 and 2 represent the titration curves obtained from Tables 1 and 2. Figures 1 and 2 as well as Tables 1 and 2 are used for evaluating the solubility (S) and solubility product ( $K_{sp}$ ) values. From  $K_{sp}$  values  $\Delta G^\circ$ ,  $\Delta S^\circ$  and  $\Delta H^\circ$  were determined using Equations (3–5) which are collectively shown in terms of their difference against those taken in pure water system. This difference was shown in Table 3. The general behaviour of  $\Delta G^\circ$ ,  $\Delta S^\circ$  and  $\Delta H^\circ$  were influenced by the presence of % of solvent system as well as amount of NaCl is explained below.

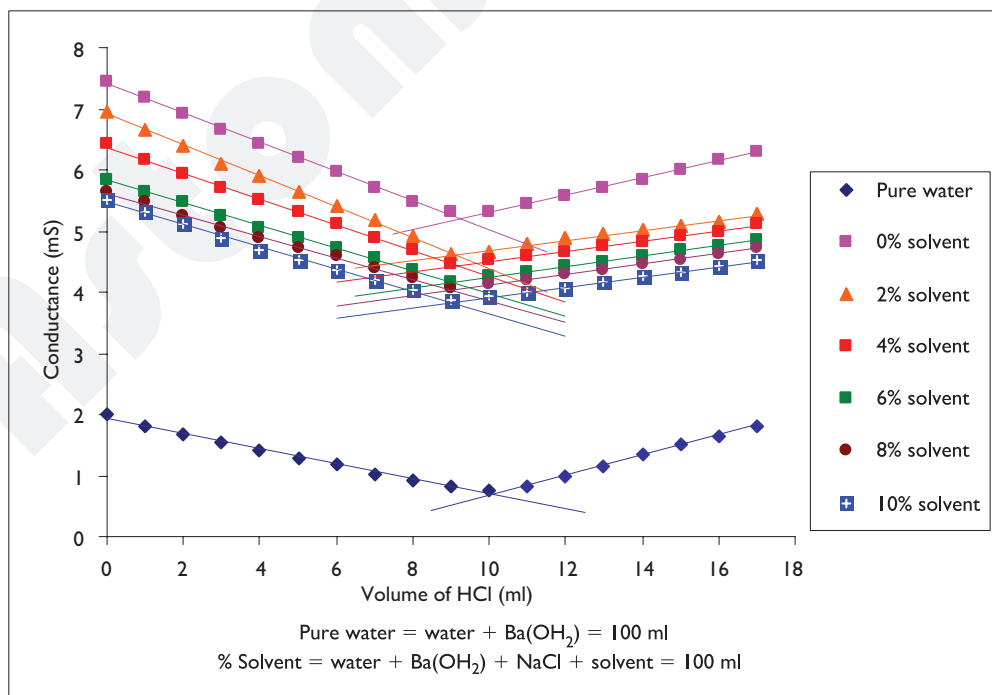
### 3.1. Effect of ionic salt

In the presence of NaCl, the  $\Delta G^\circ$  values were linearly decreased by increasing the amount of NaCl as shown in Table 3. Figures 3 and 4 represent the same property at  $10^\circ C$  for 1,2-propanediol and ethanol, respectively. In a similar way the values of  $\Delta S^\circ$  and  $\Delta H^\circ$  were nonlinearly decreased by increasing the amount of ionic salt.

**Figure 1: Titration curve showing the effect of ionic salt (0.6 g NaCl) on conductance of dissolution of  $\text{Ba}(\text{OH})_2$  in different % composition in mixed solvent system (water + 1,2-propanediol) at  $10 \pm 1^\circ\text{C}$ .**



**Figure 2: Titration curve showing the effect of ionic salt (0.6 g NaCl) on conductance of dissolution of  $\text{Ba}(\text{OH})_2$  in different % composition in mixed solvent system (water + ethanol) at  $10 \pm 1^\circ\text{C}$ .**



**Table 1: Effect of % composition on conductance of dissolution of Ba(OH)<sub>2</sub> in different % composition of water + 1,2-propanediol in presence of 0.6 g NaCl at 10 ± 1°C while titrated with 0.015 N HCl.**

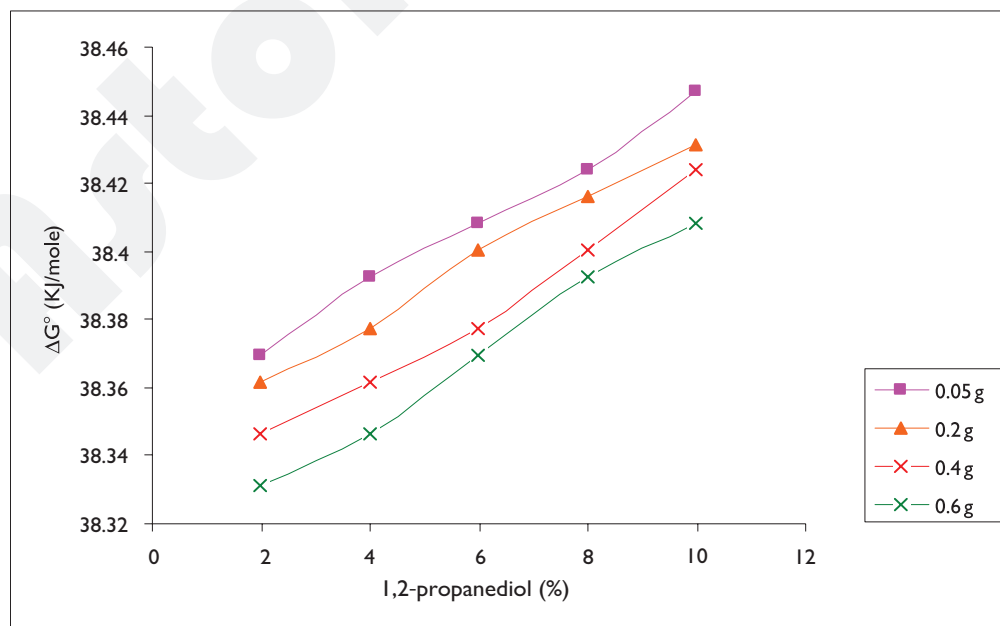
Volume of HCl (ml)	Pure water	Conductance (mS)					
		% Solvent (1,2-propanediol)					
		0%	2%	4%	6%	8%	10%
0	1.99 ± 0.02	7.44 ± 0.02	7.38 ± 0.01	7.06 ± 0.02	6.88 ± 0.01	6.48 ± 0.02	6.14 ± 0.03
1	1.81 ± 0.03	7.18 ± 0.02	7.07 ± 0.03	6.75 ± 0.03	6.55 ± 0.01	6.17 ± 0.01	5.91 ± 0.03
2	1.67 ± 0.02	6.91 ± 0.02	6.78 ± 0.03	6.50 ± 0.02	6.30 ± 0.02	5.96 ± 0.01	5.69 ± 0.02
3	1.54 ± 0.02	6.67 ± 0.01	6.51 ± 0.02	6.23 ± 0.02	6.06 ± 0.03	5.76 ± 0.03	5.50 ± 0.02
4	1.41 ± 0.03	6.42 ± 0.02	6.24 ± 0.03	5.98 ± 0.01	5.83 ± 0.03	5.56 ± 0.02	5.30 ± 0.01
5	1.29 ± 0.02	6.20 ± 0.02	5.98 ± 0.01	5.73 ± 0.01	5.58 ± 0.01	5.35 ± 0.01	5.13 ± 0.01
6	1.18 ± 0.01	5.98 ± 0.03	5.70 ± 0.02	5.50 ± 0.02	5.36 ± 0.02	5.15 ± 0.01	4.94 ± 0.03
7	1.03 ± 0.01	5.72 ± 0.02	5.41 ± 0.02	5.26 ± 0.03	5.16 ± 0.02	4.95 ± 0.02	4.77 ± 0.01
8	0.93 ± 0.01	5.49 ± 0.01	5.14 ± 0.02	5.02 ± 0.02	4.95 ± 0.01	4.75 ± 0.03	4.60 ± 0.02
9	0.82 ± 0.02	5.30 ± 0.01	4.88 ± 0.01	4.77 ± 0.03	4.70 ± 0.03	4.51 ± 0.03	4.43 ± 0.02
10	0.75 ± 0.01	5.32 ± 0.01	4.91 ± 0.02	4.80 ± 0.03	4.73 ± 0.01	4.54 ± 0.01	4.45 ± 0.01
11	0.81 ± 0.02	5.45 ± 0.03	4.97 ± 0.03	4.87 ± 0.01	4.78 ± 0.02	4.60 ± 0.02	4.50 ± 0.03
12	1.00 ± 0.02	5.58 ± 0.02	5.05 ± 0.03	4.93 ± 0.01	4.83 ± 0.01	4.65 ± 0.03	4.53 ± 0.01
13	1.16 ± 0.02	5.70 ± 0.03	5.15 ± 0.01	5.02 ± 0.02	4.90 ± 0.03	4.71 ± 0.02	4.54 ± 0.01
14	1.33 ± 0.03	5.85 ± 0.03	5.23 ± 0.01	5.11 ± 0.03	4.99 ± 0.01	4.76 ± 0.02	4.61 ± 0.03
15	1.50 ± 0.02	6.00 ± 0.02	5.32 ± 0.02	5.19 ± 0.02	5.08 ± 0.03	4.80 ± 0.01	4.70 ± 0.02
16	1.65 ± 0.01	6.10 ± 0.01	5.43 ± 0.03	5.33 ± 0.01	5.17 ± 0.02	4.87 ± 0.01	4.75 ± 0.02
17	1.81 ± 0.01	6.29 ± 0.01	5.54 ± 0.02	5.42 ± 0.01	5.26 ± 0.02	4.93 ± 0.01	4.80 ± 0.02

**Table 2: Effect of % composition on conductance of dissolution of Ba(OH)<sub>2</sub> in different % composition of water + ethanol in presence of 0.6 g NaCl at 10 ± 1°C while titrated with 0.015 N HCl.**

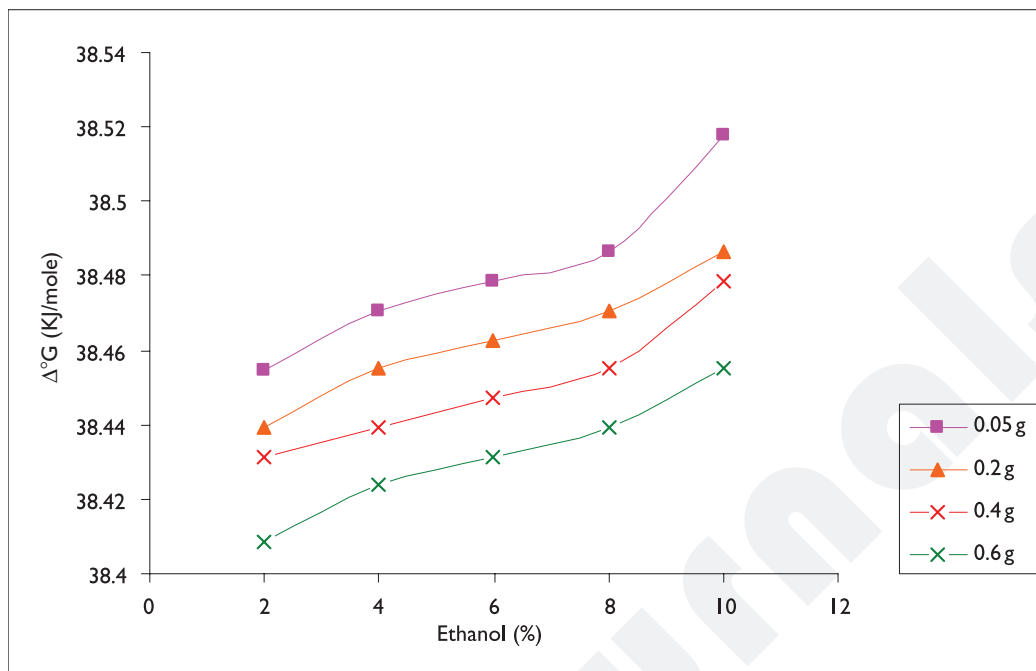
Volume of HCl (ml)	Pure water	Conductance (mS)					
		% Solvent (ethanol)					
		0%	2%	4%	6%	8%	10%
0	1.99 ± 0.02	7.44 ± 0.02	6.95 ± 0.03	6.41 ± 0.02	5.84 ± 0.01	5.64 ± 0.02	5.50 ± 0.02
1	1.81 ± 0.03	7.18 ± 0.02	6.66 ± 0.02	6.15 ± 0.02	5.64 ± 0.01	5.46 ± 0.03	5.30 ± 0.01
2	1.67 ± 0.02	6.91 ± 0.01	6.39 ± 0.02	5.94 ± 0.02	5.47 ± 0.01	5.26 ± 0.03	5.11 ± 0.01
3	1.54 ± 0.02	6.67 ± 0.02	6.11 ± 0.02	5.72 ± 0.03	5.26 ± 0.03	5.05 ± 0.03	4.88 ± 0.01
4	1.41 ± 0.03	6.42 ± 0.02	5.89 ± 0.02	5.51 ± 0.03	5.06 ± 0.01	4.87 ± 0.02	4.70 ± 0.01
5	1.29 ± 0.02	6.20 ± 0.03	5.64 ± 0.03	5.31 ± 0.001	4.88 ± 0.02	4.71 ± 0.02	4.53 ± 0.02
6	1.18 ± 0.01	5.98 ± 0.03	5.41 ± 0.02	5.12 ± 0.01	4.72 ± 0.02	4.58 ± 0.02	4.37 ± 0.02
7	1.03 ± 0.01	5.72 ± 0.03	5.17 ± 0.01	4.89 ± 0.01	4.56 ± 0.02	4.40 ± 0.01	4.19 ± 0.01
8	0.93 ± 0.01	5.49 ± 0.01	4.91 ± 0.01	4.68 ± 0.01	4.37 ± 0.02	4.22 ± 0.01	4.02 ± 0.01
9	0.82 ± 0.02	5.30 ± 0.03	4.62 ± 0.02	4.47 ± 0.01	4.15 ± 0.02	4.07 ± 0.01	3.87 ± 0.03
10	0.75 ± 0.01	5.32 ± 0.01	4.67 ± 0.02	4.52 ± 0.02	4.25 ± 0.01	4.12 ± 0.01	3.92 ± 0.03
11	0.81 ± 0.02	5.45 ± 0.02	4.78 ± 0.02	4.59 ± 0.02	4.32 ± 0.04	4.20 ± 0.01	4.00 ± 0.03
12	1.00 ± 0.02	5.58 ± 0.02	4.87 ± 0.03	4.67 ± 0.02	4.41 ± 0.01	4.28 ± 0.01	4.07 ± 0.03
13	1.16 ± 0.02	5.70 ± 0.02	4.94 ± 0.03	4.75 ± 0.03	4.50 ± 0.03	4.37 ± 0.01	4.16 ± 0.02
14	1.33 ± 0.03	5.85 ± 0.01	5.01 ± 0.01	4.83 ± 0.03	4.59 ± 0.02	4.46 ± 0.01	4.25 ± 0.02
15	1.50 ± 0.02	6.00 ± 0.02	5.08 ± 0.01	4.91 ± 0.02	4.68 ± 0.01	4.53 ± 0.01	4.33 ± 0.02
16	1.65 ± 0.01	6.15 ± 0.01	5.16 ± 0.01	5.00 ± 0.01	4.77 ± 0.01	4.62 ± 0.02	4.42 ± 0.02
17	1.81 ± 0.01	6.29 ± 0.01	5.27 ± 0.02	5.10 ± 0.01	4.85 ± 0.01	4.72 ± 0.04	4.52 ± 0.02

**Table 3: Difference in the value of  $\Delta G^\circ$ ,  $\Delta S^\circ$  &  $\Delta H^\circ$  of solution composition verses pure water.**

Solution composition	Amount of salt (g)	Solvent (%)	$\Delta G^\circ$ at 10°C (KJ/mole)	$\Delta G^\circ$ at 30°C (KJ/mole)	* $\Delta S^\circ$ (J/K/mole)	* $\Delta H^\circ$ (J/K/mole)
$H_2O + Ba(OH)_2 + NaCl$	0.05	0	0.68	0.50	9.27	3303.98
	0.2	0	0.66	0.49	8.85	3187.99
	0.4	0	0.65	0.48	8.56	3072.47
	0.6	0	0.62	0.46	7.85	2842.51
$Ba(OH)_2$ in $(H_2O + 1,2\text{-propanediol})$	0.0	2	0.93	0.81	5.73	2556.14
	0.0	4	0.97	0.83	6.44	2794.81
	0.0	6	1.07	0.93	6.93	3028.67
	0.0	8	1.12	0.94	8.50	3747.08
	0.0	10	1.13	0.95	8.47	3522.64
$Ba(OH)_2$ in $(H_2O + \text{ethanol})$	0.0	2	0.99	0.86	7.58	3158.62
	0.0	4	1.03	0.93	6.11	2783.48
	0.0	6	1.11	0.96	8.44	3524.77
	0.0	8	1.12	0.99	7.52	3272.25
	0.0	10	1.14	1.00	7.07	3144.42
$Ba(OH)_2$ in $(H_2O + 1,2\text{-propanediol}) + 0.6\text{g NaCl}$	0.6	2	0.66	0.50	7.70	2837.47
	0.6	4	0.67	0.51	8.05	2952.58
	0.6	6	0.69	0.53	8.38	3067.80
	0.6	8	0.72	0.54	9.12	3300.59
	0.6	10	0.73	0.55	9.06	3300.34
$Ba(OH)_2$ in $(H_2O + \text{ethanol}) + 0.6\text{g NaCl}$	0.6	2	0.73	0.60	6.55	3589.72
	0.6	4	0.75	0.63	5.72	2368.95
	0.6	6	0.76	0.64	5.61	2346.70
	0.6	8	0.76	0.65	5.58	2345.61
	0.6	10	0.78	0.67	5.51	2342.53

\*Inferred from  $\Delta G^\circ$  taken at 10° and 30°C.**Figure 3: The effect of NaCl on the Gibbs free energy of  $Ba(OH)_2$  in different % composition of 1,2-propanediol at  $10 \pm 1^\circ C$ .**

**Figure 4: The effect of NaCl on the Gibbs Free energy of  $\text{Ba}(\text{OH})_2$  in different % composition of ethanol at  $10 \pm 1^\circ\text{C}$ .**



### 3.2. Effect of mixed solvent system

The values of  $\Delta G^\circ$ ,  $\Delta S^\circ$  and  $\Delta H^\circ$  in presence of mixed solvent system ( $\text{H}_2\text{O} + 1,2\text{-propanediol}$  or  $\text{H}_2\text{O} + \text{ethanol}$ ) both in the presence and in the absence of NaCl are also collectively shown in Table 3. It was found that in case of  $\text{Ba}(\text{OH})_2$  in ( $\text{H}_2\text{O} + 1,2\text{-propanediol}$ , in the absence of NaCl), showed different behaviour compared to that shown in above (water + NaCl) system where the increase in % composition of 1,2-propanediol were generally increased values of  $\Delta G^\circ$  and  $\Delta S^\circ$ . However, the values of  $\Delta H^\circ$  were found to be nonlinear (due to the determination of  $\Delta G^\circ$  in a small difference in temperature taken at 10 and  $30^\circ\text{C}$ ). In case of  $\text{Ba}(\text{OH})_2$  in ( $\text{H}_2\text{O} + \text{ethanol}$ ) only  $\Delta G^\circ$  showed similar trend compared to 1,2-propanediol system. However  $\Delta S^\circ$  and  $\Delta H^\circ$  values were found to be nonlinear (due to the determination of  $\Delta G^\circ$  in small difference in temperature).

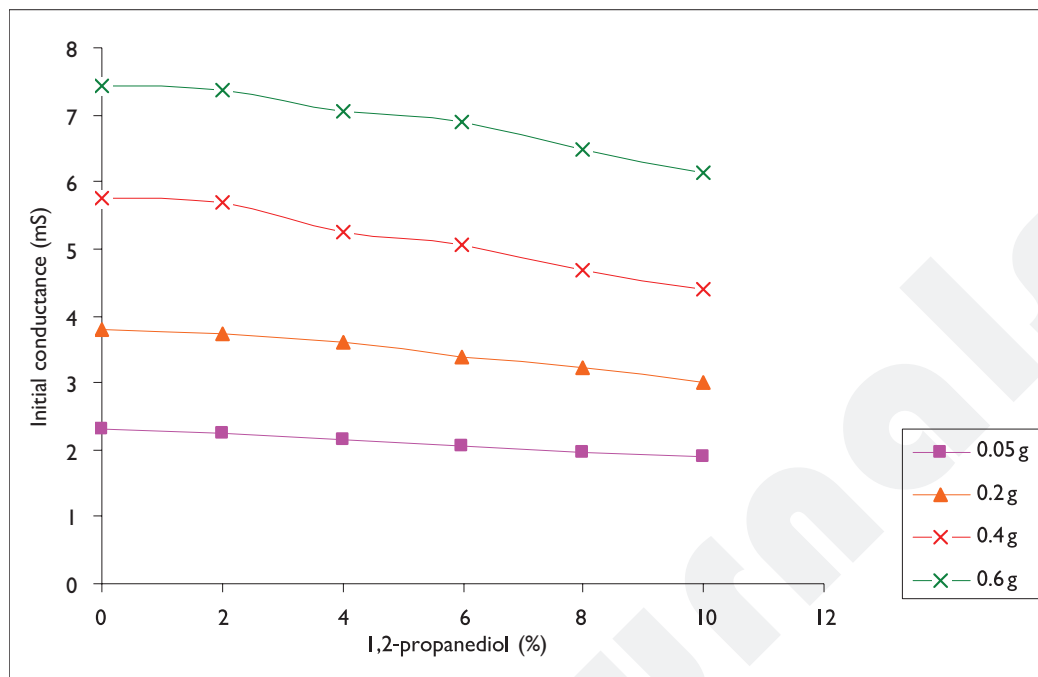
### 3.3. Effect of ionic salt + mixed solvent system

In case of  $\text{Ba}(\text{OH})_2$  in ( $\text{H}_2\text{O} + 1,2\text{-propanediol} + \text{NaCl}$ ) system the same pattern was found i.e., only  $\Delta G^\circ$  values were increased linearly by increasing % composition of 1,2-propanediol. Whereas, both  $\Delta S^\circ$  and  $\Delta H^\circ$  were linearly decreased even at such low difference of temperature. Similarly  $\text{Ba}(\text{OH})_2$  in ( $\text{H}_2\text{O} + \text{ethanol} + \text{NaCl}$ ) system the values of  $\Delta G^\circ$ ,  $\Delta S^\circ$  and  $\Delta H^\circ$  were generally increased by increasing % composition of ethanol.

### 3.4. Qualitative characteristics

In the experiment the initial conductance (in absence of titrant HCl) increased by increasing the amount of NaCl where as the initial conductance decreased by increasing % of solvent (1,2-propanediol or ethanol) at  $10^\circ\text{C}$ , which is shown in Figures 5 and 6. The same result was obtained for  $30^\circ\text{C}$ . This trend is also justified by the dielectric constant values of water, 1,2-propanediol and ethanol which are 80.0, 30.2 and 24.6, respectively which are given in Table 4. These dielectric constant values suggest that the influence of ionic salt (NaCl) enhances the conductance in high dielectric medium compared to solvent having low dielectric medium (hence offering less conductance values).

**Figure 5:** The effect of NaCl on the initial conductance of  $\text{Ba}(\text{OH})_2$  in different % composition of 1,2-propanediol at  $10 \pm 1^\circ\text{C}$ .



**Figure 6:** The effect of NaCl on the initial conductance of  $\text{Ba}(\text{OH})_2$  in different % composition of ethanol at  $10 \pm 1^\circ\text{C}$ .

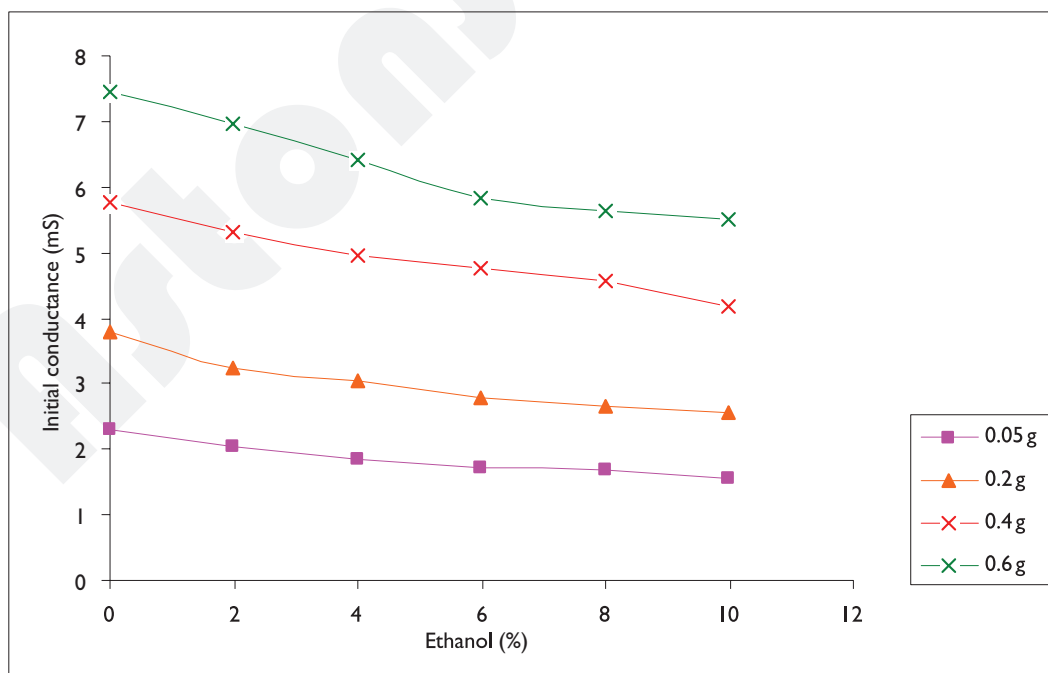




Table 4: Comparison in the value of  $\Delta G^\circ$ ,  $\Delta S^\circ$  &  $\Delta H^\circ$  for different solution composition.

Solution composition	$\Delta G^\circ$ at 10°C (KJ/mole)	$\Delta G^\circ$ at 30°C (KJ/mole)	* $\Delta S^\circ$ (J/K/mole)	* $\Delta H^\circ$ (J/K/mole)	Dielectric constant
H <sub>2</sub> O + Ba(OH) <sub>2</sub> + 0.6 g NaCl	0.62	0.46	7.85	2842.51	80.0 (pure water)
Ba(OH) <sub>2</sub> in (H <sub>2</sub> O + 10% 1,2-propanediol)	1.13	0.95	8.47	3522.64	30.2 (1,2-propanediol)
Ba(OH) <sub>2</sub> in (H <sub>2</sub> O + 10% ethanol)	1.14	1.00	7.07	3144.42	24.6 (ethanol)
Ba(OH) <sub>2</sub> in (H <sub>2</sub> O + 10% 1,2-propanediol) + 0.6 g NaCl	0.73	0.55	9.06	3300.34	
Ba(OH) <sub>2</sub> in (H <sub>2</sub> O + 10% ethanol) + 0.6 g NaCl	0.78	0.67	5.51	2342.53	

\*Inferred from  $\Delta G^\circ$  taken at 10 and 30°C.

#### 4. Conclusion

The thermodynamic parameters of Ba(OH)<sub>2</sub> in mixed solvent systems have been studied. The same Ba(OH)<sub>2</sub> may be used with different solvents to find the conductance and correlate it with dielectric constant values as well as the thermodynamic parameters.

#### Competing Interests

The authors declare that they have no competing interests.

#### Authors' Contributions

SAA proposed the experiment, MZI worked under supervision of SAA and AH helped in discussion and manuscript preparation.

#### Acknowledgement

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