ORIENTAL JOURNAL OF CHEMISTRY
An International Open Access, Peer Reviewed Research Journal

www.orientjchem.org

ISSN: 0970-020 X
CODEN: OJCHEG
2024, Vol. 40, No.(6):
Pg. 1736-1744

Study of the Dissolution of Calcium Carbonate in Different Mixed Solvent at Different Temperatures by Conductometric Method and Data Analysis using Thermodynamic Parameters

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http://dx.doi.org/10.13005/ojc/400626

(Received: July 31, 2024; Accepted: November 07, 2024)

ABSTRACT

Present paper discussed the dissolution behavior of $CaCO_3$ in (water + THF), (water + AN) and (water + DMF) medium at 10^0C to 30^0C by conductometric method. From the molar conductance data, we calculate limiting conductance value at infinite dilution using Karus Bray equation. From these data we calculate thermodynamic parameters like ΔH, ΔG, ΔS, ΔEs & Kc. These data helps us to compare dissolution behavior of $CaCO_3$ in different mixed solvent at different temperatures. From this dissolution study of $CaCO_3$ in different non aqueous systems it was observed that stronger ion interaction occur in case of THF and AN & partial dissociation or ion pairing occur in case of DMF solvent. With increase in temperature, limiting molar conductance increases for all the systems. The present work aims to determine the limiting molar conductance values of Calcium Carbonate in different mixed solvents in different temperatures and also evaluate thermodynamic parameters for supporting the ion-solvation interaction.

Keywords: AN (Acetonitrile), Conductance, $CaCO_3$, DMF(Dimethyl Formamide), Dissolution, THF(Tetrahydro Furan).

INTRODUCTION

Calcium carbonate ($CaCO_3$) is a common inorganic compound found in rocks, shells, and various biological materials. Its solubility and dissolution behavior are of significant interest in various fields such as geology, environmental science, materials science, and industrial processes. The dissolution process of $CaCO_3$ varies greatly depending on the solvent used, with notable differences between aqueous and non-aqueous environments.

The dissolution study of $CaCO_3$ in mixed solvents is essential for a variety of fields, from environmental science to industrial applications. It provides valuable data on how calcium carbonate interacts with different solvent systems, influencing processes like scaling, material degradation, biomineralization, and even carbon sequestration. Understanding these interactions helps in developing strategies to mitigate problems or enhance applications where $CaCO_3$ is a key component.

In aqueous solutions, the dissolution of

$CaCO_3$ is influenced by the solvent's polar nature and its ability to stabilize the ions produced during the dissolution process. Water, being a highly polar solvent, can partially dissolve $CaCO_3$, and this process can be further enhanced by the presence of dissolved carbon dioxide, leading to the formation of carbonic acid. This interaction plays a crucial role in natural processes such as the carbon cycle and the formation of geological features.

Conversely, in non-aqueous solvents, the dissolution behavior of $CaCO_3$ is markedly different. Non-aqueous solvents, typically characterized by their lower polarity and lack of hydrogen bonding capabilities, generally do not support the dissolution of ionic compounds like $CaCO_3$. As a result, $CaCO_3$ remains largely insoluble in these solvents. However, specific conditions, such as the presence of complexing agents or unique solvent properties, can influence the solubility to some extent.

Understanding the dissolution processes of $CaCO_{33}$ in both aqueous and non-aqueous solvents is essential for various practical applications and scientific investigations, including water treatment, biomineralization studies, and industrial processes involving calcium compounds. This introduction sets the stage for a detailed exploration of the mechanisms and factors affecting the dissolution of $CaCO_3$ in different solvent environments.

Dissolution behavior of many salts, weak acids are much interest from many years back[1-4]. The solubility of solvents depends on solutes and constituent ions of the solvent mixtures[5-8]. $CaCO_3$ is a sparyingly soluble salt, its limiting conductance was not measured by directly Onsagar equation. Here we use Karus Bray equation to determine limiting molar conductance of $CaCO_3$ in different mixed solvent medium. Effect of different salts, sparyingly soluble salts, weak acids in different mixed solvent were studied many researchers[9-11]. We already studied the effect of different salts[12-13] and weak acids[14-15] in different mixed solvent systems in our laboratory.

The Karus-Bray equation is significant in electrochemistry because it provides a method for determining the limiting molar conductance (Λ_0) of a weak electrolyte, sprayingly soluble salt etc. Limiting molar conductance refers to the conductance of an electrolyte when its concentration approaches zero. This parameter is important because it reflects the intrinsic conductivity of ions.

Our main objective to study to evaluate limiting molar conductance using Karus-Bray equation and also evaluate thermodynamic parameters for supporting the ion-solvation interaction system with this sprayingly soluble salt.

EXPERIMENTAL

Materials

Calcium Carbonate (Merck), THF (Tetrahydro Furan) (PDFCL, Mumbai), AN (Acetonitrile) (LOBA Chemicals), DMF (Dimethyl Formamide) (LOBA Chemicals) were used as such, without any further purifications.

Solutions preparation

The solution of $CaCO_3$ in water and different compositions (10%, 20%, 40%, 50%, 60%, 80%) were prepared. $CaCO_3$ solution (0.01M) was prepared in water, water + THF, water + AN, water + DMF in volume (v/v) ratio. After that the solution was stirred for 30 min and then this solution was kept overnight to get ultimate saturation. The next day the saturated solution of $CaCO_3$ was filtered using Whatman filter paper.

Conductivity study

Conductivity of $CaCO_3$ mixed solvent solutions were measured with a conductivity bridge (EC-TDS analyser, CM-183, Elico). Cell constant varied from 1.0+10% to 1.0-10% cm inverse. A temperature control bath (made by PDIC, Kolkata) was used to obtain the conductivities at higher temperatures.

RESULT AND DISCUSSION

For this dissolution study we use sprayingly soluble $CaCO_3$. Three solvent systems were taken such as (water+THF), (water+AN) and (water +DMF). Molar conductance of $CaCO_3$ was studied of these three solvent systems by Conductivity Bridge. As $CaCO_3$ is sprayingly soluble salt, so its partial dissociation occurs. So, we can not get limiting molar conductance value from Onsagar equation. To get limiting molar conductance value, we use Karus Bray equation. The equation is $1/\Lambda^0+\Lambda C/(\Lambda_0^2.Kc)$

Where Λ = molar conductance, Λ_0 molar conductance at infinite diluition,

Kc = Dissociation constant, C = conc. in mol/dm^3

If we plot $1/\Lambda$ vs. C, we get the value of Λ_0 from the intercept. Knowing the value of Λ_0 and C, we can easily calculate Kc from the slope of this plot.

Table 1: Physical properties of electrolyte solvents

Sl. No	Solvent	M.W.	Melting Temperature(^{0}C)	Boiling Temperature(^{0}C)	Viscosity (CP)	Dielectric Const	Dipole Moment(D)	Flash Temperature(^{0}C)	Density (g/cc)
1	THF	72.10	-104.8	66	0.48	7.43	1.63	-14	0.887
2	AN	41.05	-45	82	0.346	35.09	3.92	2	0.786
3	DMF	73.09	-61	153	0.79	37.51	3.86	67	0.944

Table 2: Slope value of logΛ vs. logC of $CaCO_3$ with (water+THF), (water+AN) and (water+DMF) medium

Sl. No	Solvent	Slope value in different temperatures		
		10^0C	20^0C	30^0C
1	(water + THF)	-0.267	-0.348	-0.334
2	(water + AN)	-0.627	-0.469	-0.448
3	(water + DMF)	-0.643	-0.643	-0.686

Table 3: Limiting molar conductance value of $CaCO_3$ with (water+THF), (water+AN) and (water+DMF) medium

Sl. No	Temperature(K)	1/T(K^{-1})	(water+THF)	(water+AN)	(water+DMF)
1	283	0.0035	0.0063	0.0173	0.0045
2	293	0.0034	0.0101	0.0182	0.0055
3	303	0.0033	0.0104	0.0196	0.00556

Table 4: Dissociation constant, activation of salvation and different thermodynamic parameters of $CaCO_3$ solvated in (water+THF) medium from 283K to 303K

Sl. No	Temperature(K)	Kc	ΔG(Cal/mole)	ΔS(Cal/mole)	ΔH(Cal/mole)	ΔEs(KCals/mole)
1	283	5376	-5001	-23.04	-1750	4.576
2	293	6578	-5293	-23.24		
3	303	12048	-5284	-24.85		

Table 1 shows the physical properties of our experimental non-aqueous solvents (THF, AN & DMF).

Table 2 shows the logΛ vs. logC values of $CaCO_3$ with these three mixed solvent medium. In case of dissolution of $CaCO_3$ in (water+THF) system, slope of logΛ vs. logC at 10^0C, 20^0C & 30^0C is <-0.5. We assume that there was a stronger ion interaction, aggregation, complex electrolyte behavior occurs.

For the dissolution of $CaCO_3$ in (water+AN) system, at 10^0C, slope value is -0.627 i.e., >-0.5 which indicate ion pairing or partial dissociation occurs, but at 20^0C & 30^0C, slope value is <-0.5. So here stronger ion interaction or aggregation occurs according to Karus Bray equation.

For the dissolution of $CaCO_3$ in (water+DMF) system, slope of logΛ vs. logC at 10^0C, 20^0C & 30^0C we observed that slope value is >-0.5, it can be stated that ion pairing or partial dissociation occurs.

Limiting molar conductances are tabulated in the Table 3 of $CaCO_3$ with these three mixed solvent medium. Limiting molar conductance value increases with increase in temperature for these three mixed solvent medium.

With the help of Karus-Bray equation Kc value can be easily calculated. We know that ΔG -RTlnKc, knowing the value of Kc at different mixed solvent medium at different temp, we can easily calculate the value of ΔG. Negative value of ΔG tells us about the spontaneity condition of this dissolution process.

Plot of logKc vs. 1/T, from the slope we can calculate ΔH (change in enthalpy). Using the value of ΔH, we can easily calculate the value of ΔS (change in entropy).

From thermodynamics, we also know that

$$\Delta S = (\Delta G - \Delta H)/T$$

If we plot $\log\Lambda_0$ vs. 1/T, from the slope we can easily calculate activation energy for this dissolution process.

From the Table 4, Kc value increases from 10^0C to 30^0C of $CaCO_3$ in (water+THF) medium. Negative value of ΔG tells us about the spontaneity condition of this dissolution process. ΔS value also decreases and also tells us the decrease of disorderness. Change in enthalpy value is negative means that the dissolution process is exothermic in nature. ΔEs value is 4.576 K Cals/Mole of $CaCO_3$ in (water+THF) medium.

Table 5: Dissociation constant, activation of salvation and different thermodynamic parameters of $CaCO_3$ solvated in (water+AN) medium from 283K to 303K

Sl. No	Temperature(K)	Kc	ΔG(Cal/mole)	ΔS(Cal/mole)	ΔH(Cal/mole)	ΔEs(Kcal/mole)
1	283	1136	-4096	-18.75	-1400	0.686
2	293	1785	-4508	-19.49		
3	303	3448	-4581	-21.13		

Table 6: Dissociation constant, activation of salvation and different thermodynamic parameters of $CaCO_3$ solvated in (water+DMF) medium from 283K to 303K

Sl No.	Temperature(K)	Kc	ΔG(Cal/mole)	ΔS(Cal/mole)	ΔH(Cal/mole)	ΔEs(Kcal/mole)
1	283	4366	-4714	-22.13	-1550	2.059
2	293	5000	-4959	-22.21		
3	303	9090	-5488	-23.22		

From the Table 5, Kc value increases from low temperature to high temperature. Negative value of ΔH corresponds to the exothermic process of this dissolution of $CaCO_3$ in (water+AN) medium. ΔG value is negative, so spontaneity arises. ΔS value is also negative, dissolution process is not disordered. ΔEs value is 0.686 K Cals/Mole of $CaCO_3$ in (water+AN) medium. ΔEs value is less than the other two medium.

From Table 6, Kc value increase from 10^0C to 30^0C for the $CaCO_3$ in (water+DMF) medium. Negative value of ΔG also increases from lower temperature to higher temperature. This means that spontaneity increases at higher temperature. Negative ΔS value also increases from 10^0C to 30^0C. This indicates the dissolution of $CaCO_3$ in (water+DMF) medium disorderness increases. Change in enthalpy value is negative means that the dissolution process of $CaCO_3$ in (water+DMF) medium is exothermic in nature. ΔEs value is 2.059 K Cals/Mole of $CaCO_3$ in (water+DMF) medium.

From these three mixed solvent medium, according to ΔEs value $CaCO_3$ in (water+AN) medium is more favourable than the other two medium.

But from other data e.g., Kc, ΔG, ΔS value suggests that $CaCO_3$ in (water+DMF) medium is more favourable than the other two medium.

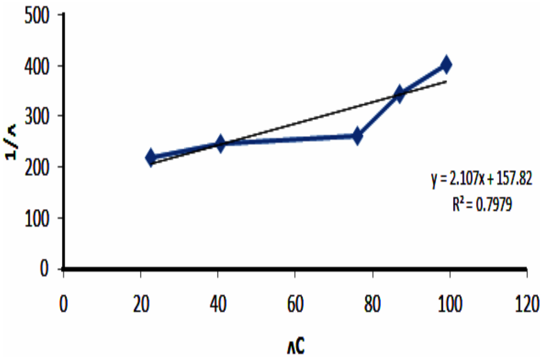

Fig. 1. Plot of 1/Λ Vs ΛC of $CaCO_3$ in (water+THF) mixed solvent medium at 10^0C

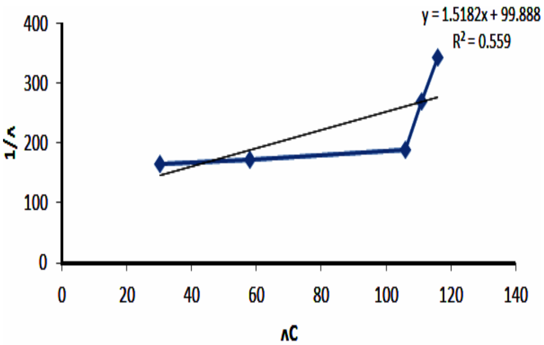

Fig. 2. Plot of 1/Λ Vs ΛC of $CaCO_3$ in (water+THF) mixed solvent medium at 20^{0}C

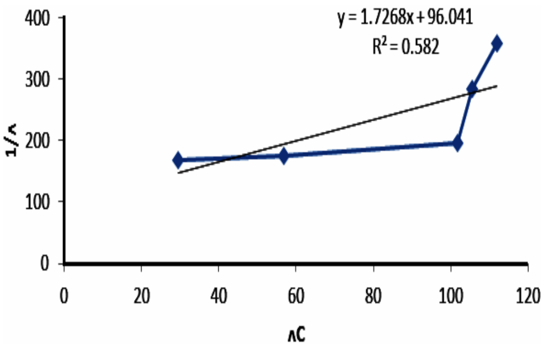

Fig. 3. Plot of 1/Λ Vs ΛC of $CaCO_3$ in (water+THF) mixed solvent medium at 30^{0}C

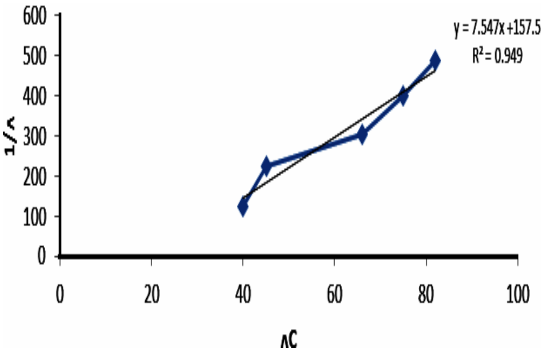

Fig. 4. Plot of 1/Λ Vs ΛC of $CaCO_3$ in (water+AN) mixed solvent medium at 10^{0}C

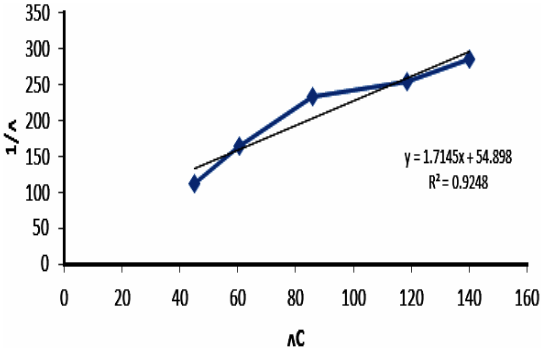

Fig. 5. Plot of 1/Λ Vs ΛC of $CaCO_3$ in (water+AN) mixed solvent medium at 20^{0}C

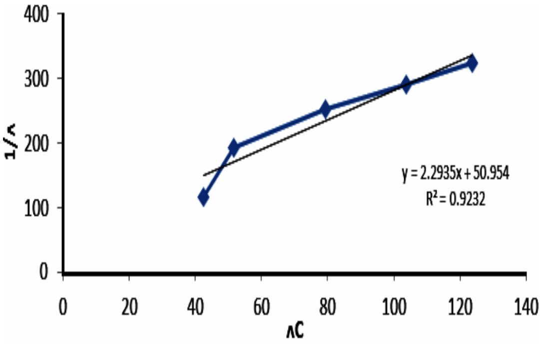

Fig. 6. Plot of 1/Λ Vs ΛC of $CaCO_3$ in (water+AN) mixed solvent medium at 30^{0}C

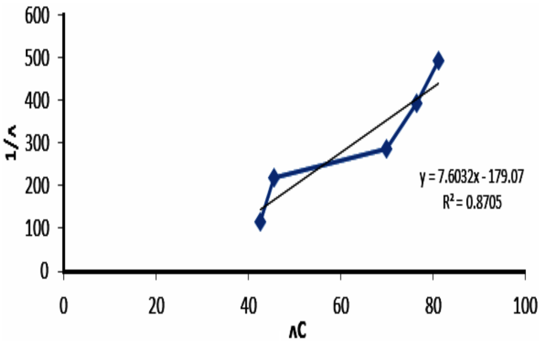

Fig. 7. Plot of 1/Λ Vs ΛC of $CaCO_3$ in (water+DMF) mixed solvent medium at 10^{0}C

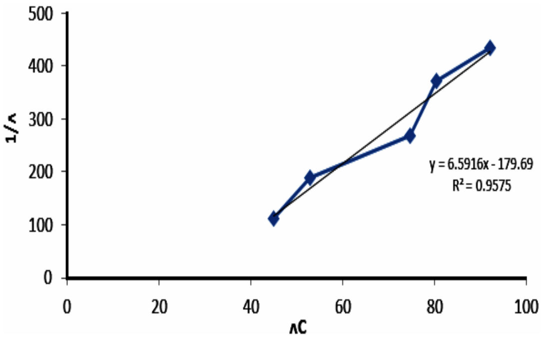

Fig. 8. Plot of 1/Λ Vs ΛC of $CaCO_3$ in (water+DMF) mixed solvent medium at 20^{0}C

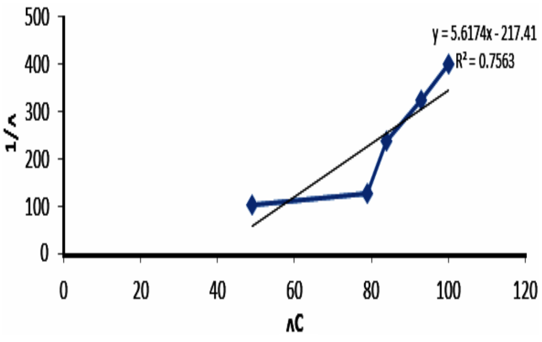

Fig. 9. Plot of 1/Λ Vs ΛC of $CaCO_3$ in (water+DMF) mixed solvent medium at 30^{0}C

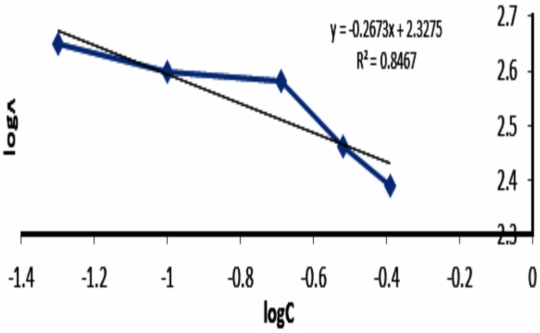

Fig. 10. Plot of logΛ Vs logC of $CaCO_3$ in (water+THF) mixed solvent medium at 10°C

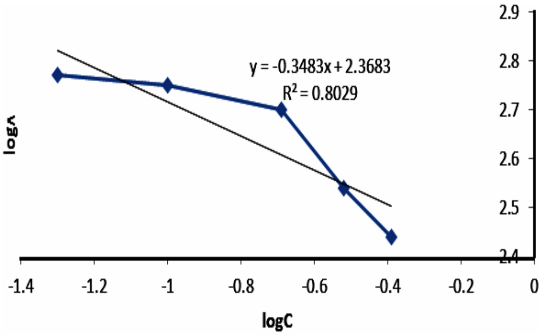

Fig. 11. Plot of logΛ Vs logC of $CaCO_3$ in (water+THF) mixed solvent medium at 20°C

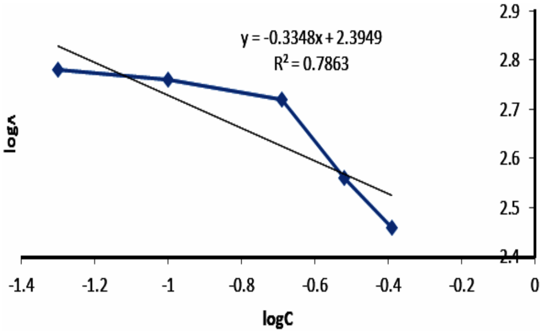

Fig. 12. Plot of logΛ Vs logC of $CaCO_3$ in (water+THF) mixed solvent medium at 30°C

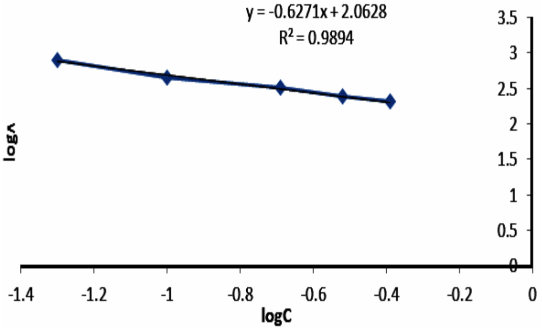

Fig. 13. Plot of logΛ Vs logC of $CaCO_3$ in (water+AN) mixed solvent medium at 10°C

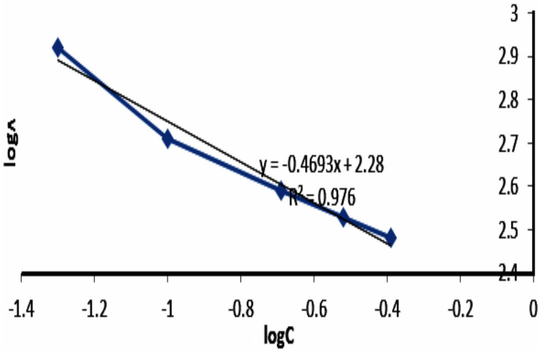

Fig. 14. Plot of logΛ Vs logC of $CaCO_3$ in (water+AN) mixed solvent medium at 20°C

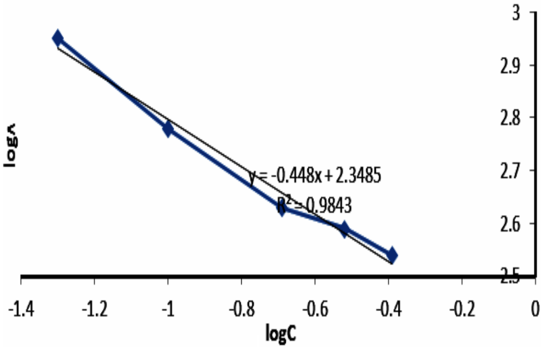

Fig. 15. Plot of logΛ Vs logC of $CaCO_3$ in (water+AN) mixed solvent medium at 30°C

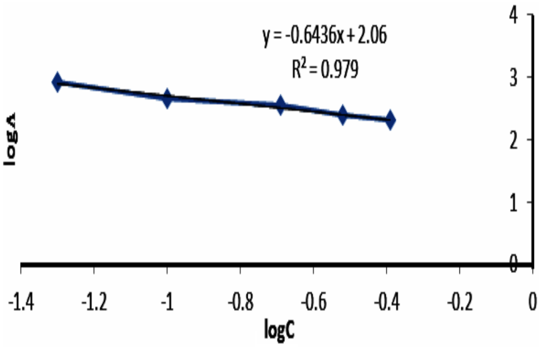

Fig. 16. Plot of logΛ Vs logC of $CaCO_3$ in (water+DMF) mixed solvent medium at 10°C

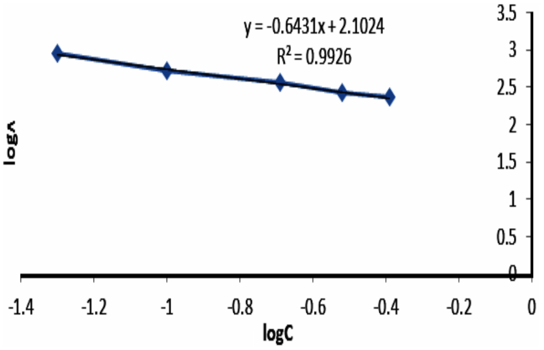

Fig. 17. Plot of logΛ Vs logC of $CaCO_3$ in (water+DMF) mixed solvent medium at 20°C

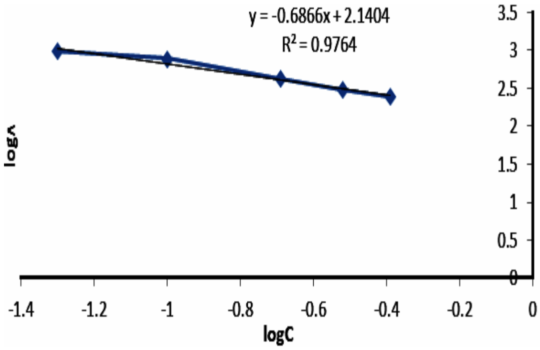

Fig. 18. Plot of logΛ Vs logC of $CaCO_3$ in (water+DMF) mixed solvent medium at 30_0C

Figure 1 to Fig. 3 shows the plot of 1/Λ Vs. ΛC of $CaCO_3$ in (water+THF) in different temperatures. From this plot we can calculate the limiting molar conductance with the help of intercept value.

Figure 4 to Fig. 6 shows the plot of 1/Λ Vs. ΛC of $CaCO_3$ in (water+AN) in different temperatures.

Figure 7 to Fig. 9 shows the plot of 1/Λ Vs. ΛC of $CaCO_3$ in (water+DMF) in different temperatures.

From these plots we can calculate limiting molar conductance value from the intercept and Kc (dissociation constant) from the slope values. Limiting molar conductance value increases from lower temperature to higher temperatures for these three mixed solvent with $CaCO_3$. Kc values are more increases for $CaCO_3$ with (water+THF) system than $CaCO_3$ with (water+DMF) system. But for the $CaCO_3$ with (water+AN) system Kc values are less increases from lower to higher temperatures.

Figure 10 to Fig.12 shows the Plot of logΛ Vs logC of $CaCO_3$ in (water+THF) mixed solvent medium at 10^0C to 30^0C. In case of dissolution of (water+THF) system, slope of logΛ vs. logC at 10^0C, 20^0C & 30^0C is <-0.5. We assume that there was a stronger ion interaction, aggregation, complex electrolyte behavior occurs.

Figure 13 to Fig. 15 shows the Plot of logΛ Vs logC of $CaCO_3$ in (water+AN) mixed solvent medium at 10^0C to 30^0C. For the dissolution of $CaCO_3$ in (water+AN) system, at 10^0C, slope value is -0.627 i.e., >-0.5 which indicate ion pairing or partial dissociation occurs, but at 20^0C & 30^0C, slope value is <-0.5 . So here stronger ion interaction or aggregation occurs according to Karus Bray equation.

Figure 16 to Fig.18 shows the Plot of logΛ Vs logC of $CaCO_3$ in (water+DMF) mixed solvent medium at 10^0C to 30^0C. For the dissolution of $CaCO_3$ in (water+DMF) system, slope of logΛ vs. logC at 10^0C, 20^0C & 30^0C we observed that slope value is >-0.5, it can be stated that ion pairing or partial dissociation occurs.

Plot of logKc vs. 1/T, from the slope we can calculate ΔH (change in enthalpy). Using the value of ΔH, we can easily calculate the value of ΔS (change in entropy).

All the values of ΔG, ΔH and ΔS values are tabulated in Table.

The dissolution data will be analyzed to derive thermodynamic parameters. The Gibbs free energy change (ΔG) will be calculated using the relationship between the equilibrium constant and temperature. Enthalpy ($_3$H) and entropy (ΔS) changes will be determined using the van't Hoff equation, which relates the change in the equilibrium constant with temperature.

Understanding the dissolution of $CaCO_3$ in mixed non-aqueous solvents has significant implications for various industrial and scientific applications. For instance, in pharmaceuticals, the solubility and stability of active ingredients can be influenced by the solvent environment. In materials science, the interaction of $CaCO_3$ with organic solvents can impact the fabrication and properties of composite materials. Moreover, this study will contribute to the fundamental knowledge of solubility and thermodynamics in mixed solvent systems, which is critical for designing processes and products in chemical engineering and related fields.

This study aims to bridge the knowledge gap regarding the dissolution of $CaCO_3$ in non-aqueous solvent systems, providing insights into the thermodynamic parameters governing this process. Through conductometric analysis and temperature variation, this research will offer a comprehensive understanding of how mixed non-aqueous solvents influence the dissolution behavior of $CaCO_3$, paving the way for future applications and theoretical advancements.

THF is a versatile solvent that dissolves both polar and non-polar compounds relatively well. It is particularly good for dissolving polymers and organic compounds.

AN is highly effective for dissolving polar compounds and salts due to its high polarity. It's commonly used in high-performance liquid chromatography (HPLC).

DMF is excellent for dissolving a wide range of polar and non-polar substances, including high molecular weight polymers and inorganic salts. It's often used in organic synthesis and for dissolving difficult-to-dissolve compounds.

Dissolution Power of THF, AN & DMF are different. THF shows good balance between polarity and non-polarity, making it a versatile solvent for many organic compounds and polymers. Not as good as DMF or AN for highly polar compounds or salts. AN (Acetonitrile) was best for highly polar compounds and salts due to its high polarity and less effective for non-polar substances. DMF was the best overall solvent for a wide range of substances, including both polar and non-polar compounds. Its ability to act as both a hydrogen bond donor and acceptor enhances its dissolution power.

This study emphasizes how changes in solvent composition can significantly impact the dissolution behavior of $CaCO_3$, which is important for optimizing processes in fields such as material science, environmental chemistry, and industrial applications.

CONCLUSION

For the dissolution of $CaCO_3$ in (water+THF) system, slope of $\log\Lambda$ vs. $\log C$ at 10^0C, 20^0C & 30^0C is <-0.5. We assume that there was a stronger ion interaction, aggregation, complex electrolyte behavior occurs.

For the dissolution of $CaCO_3$ in (water+AN) system, at 10^0C, slope value is -0.627 i.e., >-0.5 which indicate ion pairing or partial dissociation occurs, but at 20^0C & 30^0C, slope value is <-0.5 . So here stronger ion interaction or aggregation occurs according to Karus Bray equation.

For the dissolution of $CaCO_3$ in (water+DMF) system, slope of $\log\Lambda$ vs. $\log C$ at 10^0C, 20^0C & 30^0C we observed that slope value is >-0.5, it can be stated that ion pairing or partial dissociation occurs. Kc value increases from 10^0C to 30^0C of $CaCO_3$ in (water+THF) medium. Negative value of ΔG tells us about the spontaneity condition of this dissolution process. ΔS value also decreases. Dissolution process is exothermic in nature (ΔH=-ve). ΔEs value is 4.576 K Cals/Mole of $CaCO_3$ in (water+THF) medium.

Kc value increases from low temperature to high temperature. Negative value of ΔH corresponds to the exothermic process of this dissolution of $CaCO_3$ in (water+AN) medium. ΔG value is negative, so spontaneity arises. ΔS value is also negative, dissolution process is not disordered. ΔEs value is 0.686 K Cals/Mole of $CaCO_3$ in (water+AN) medium. ΔEs value is less than the other two medium.

Kc value increases from 10^0C to 30^0C for the $CaCO_3$ in (water+DMF) medium. Negative value of ΔG also increases from lower temperature to higher temperature. This means that spontaneity increases at higher temperature. Negative ΔS value also increases from 10^0C to 30^0C. Change in enthalpy value is negative means that the dissolution process of $CaCO_3$ in (water+DMF) medium is exothermic in nature. ΔEs value is 2.059 K Cals/Mole of $CaCO_3$ in (water+DMF) medium.

From this dissolution study of $CaCO_3$ in different non aqueous systems it was observed that stronger ion interaction occur in case of THF and AN & partial dissociation or ion pairing occur in case of DMF solvent. With increase in temperature, limiting molar conductance increases for all the systems.

ACKNOWLEDGEMENT

Author is grateful to the Department of Chemistry, A.K.P.C. Mahavidyalaya for all necessary supports and also thankful to Arnab Hazra , 2nd Year Mechanical Engineering student of NIT Durgapur, West Bengal for drawing necessary plots. Also thankful to Dr. Paramartha Ghosh, Principal for encourage the all types of research work.

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