

An Acoustical Study to Explore Agriculture Nutrient Management Strategy in View to Enrich Soil Fertility

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ABSTRACT

The present manuscript reports the ultrasonic characterization of Potassium Sulfate (PS): fertilizer at varying concentrations from 0.02-0.2 mol·kg⁻¹ in water and also in 0.5 mol·kg⁻¹ aqueous soil salt solutions at 303.15 °K temperature. Ultrasonic velocity (U) and density (ρ) measurements were carried out by a 2MHz frequency interferometer at a fixed 303.15 °K temperature respectively. Using obtained experimental values, various acoustical and volumetric parameters have been estimated using standard relations. The volumetric and acoustical studies clarify the nature of interaction that exists in binary as well as ternary liquid solutions. The variation in ultrasonic velocity and other parameters plays a significant role in understanding the solute-solute and solute-solvent interactions between the constituent molecules. These studies lead to a better understanding of Potassium Sulfate (PS) and have application in pure and applied research in the field of agriculture in view to increase the fertility of the soil or to counteract the problem of soil salinity. Therefore, the proposed study is worthwhile and interesting in many aspects.

Keywords: Fertilizer, Intermolecular Interaction, Potassium Sulfate, Soil Salinity, Ultrasonic.

I. INTRODUCTION

Soil is the most important component of the environment, but it is the most undervalued, misused and abused one of the earth's resources [1]. Today, soil salinity has become a significant problem affecting

agricultural areas globally. When the concentration of the salts (like: Na^+ , Ca^{++} , Mg^{++} , SO_4^{--} , Cl^- , HCO_3^- , K^+ , CO_3^{--}) in the soil exceeds a particular value, then the detrimental effects of high salinity on plants can be observed at the whole-plant level in terms of plant death and/or decrease in productivity [2]. This excess

concentration of salts in agricultural land not only generates the problem of salinity but adverse effects in plants and possesses risks to human health [3].

Due to this rapid salinization, the scarcity and limited food resources have created burden and pressure for the survival of human needs unless certain measures are taken to overcome this pressure. Accordingly, it is a need to develop a simple and low-cost method for soil salinity management to enhance the productivity of crops to meet the ever-increasing requirement of food and to improve the economy of the nation or globe.

In view to resolving this problem, fertilizers are used in agricultural land worldwide to supply the micro and macronutrients for bulk crop production, to provide better plant nutrition and to increase the fertility of saline soil [4]. Numerous factors are involved in plant response to fertilizers under saline, sodic or waterlogged conditions so that a suitable fertilizer should be used for this purpose. Efficacies of fertilizers applied to salt-affected soils are lower than when applied to non-saline soils. A decrease in the ability of the plants to absorb K or NH_4 usually takes place in saline soils containing excess Na, Mg or Ca. Also, P absorption may be decreased in presence of excess Cl or SO_4 . Application of K, NH_4 or P fertilizers not only corrects their deficiencies but also decreases the adverse effects of Na, Cl or SO_4 on the plants [5].

Ultrasonic is a versatile non-destructive technique and highly useful for investigation of various physicochemical and thermos-acoustical properties of pure liquid as well as liquid solutions [6, 7]. Recent developments have found the use of the ultrasonic technique in medicine, engineering and also in the agriculture field. Thus this kind of study is important for both humans and plants. Because of the above fact, an attempt was made to fulfill the mentioned conditions and carried out such studies on Potassium Sulfate of different concentrations (change by weight fraction) viz. 0.02-0.2 mol/kg in aqueous and 0.5 mol/kg salt solutions namely Sodium Chloride and Magnesium Chloride at a constant temperature of

303.15 °K with the help of Ultrasonic (NDT) technique. Such data is expected to throw light on the intermolecular interaction (solute-solute, solute-solvent and ion-solvent) between molecules of fertilizer-water-saline salts in view to find a way to control soil salinity.

II. MATERIALS AND METHOD

Materials

AR grade chemicals (mass fraction purity 99.9%) as Potassium Sulfate (CAS no.: 7778-80-5), Sodium Chloride (CAS no.: 7647-14-5) and Magnesium Chloride (CAS no.: 7786-30-3) were supplied from Himedia Lab. Pvt. Ltd., Mumbai. Entire chemicals were used without any further purification. The concentrations (0.02-0.2 mol·kg⁻¹) of Ammonium Sulfate in water and 0.5M aqueous saline salt solutions were changed by weight fraction. To maintain the accuracy of experimental data, all the glassware was washed with acetone as well as with double distilled water and well dried before use.

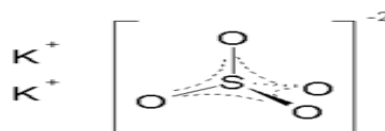


Fig 1: Molecular Structure of Potassium Sulfate

Method

A digital ultrasonic velocity interferometer was used for measuring the speed of sound passing through experimental liquids, operating at frequency 2 MHz supplied from Vi Microsystems Pvt. Ltd., Chennai (Model VCT:71) with an overall accuracy of 0.0001m/s. The source of ultrasonic waves was a quartz crystal excited by a radio frequency oscillator. The cell was filled with the desired experimental solutions and water at constant temperature was circulated in the outer jacket of the cell. The cell was allowed to equilibrate for 30min. before making the measurements.

The densities of the solutions were determined accurately and properly with the help of a 10ml

specific gravity density bottle having an accuracy of $\pm 2 \times 10^{-2}$ kg/m³ and a digital electronic balance (Contech CA-34) having accuracy ± 0.0001 gm was used for the measurement of weight. An average of triple measurements was taken into account for better accuracy. The experimental temperature was maintained constant by circulating water with the help of an automatic thermostatic water bath supplied by Lab-Hosp Company Mumbai having an accuracy of ± 1 °K temperature.

Table 1: Density and Ultrasonic velocity of water at 303.15 °K temperature

| Current Work Data | | Literature Data | |
|-------------------|--------------------|-----------------|--------------------|
| U. Vel. (U) | Density (ρ) | U. Vel. (U) | Density (ρ) |
| m/sec | kg/m ³ | m/sec | kg/m ³ |
| 1507.284 | 995.600 | 1509.100 [8] | 995.642 [9] |

III. DEFINING RELATIONS

For the derivation of several acoustical and thermodynamical parameters the following defining relations reported in the literature are used:

- Adiabatic Compressibility (β) = $1/(U^2\rho)$
- Relative Change in Adiabatic Compressibility

$$\left(\frac{\Delta\beta}{\beta}\right) = \frac{\beta - \beta_0}{\beta}$$

- Intermolecular Free Length (L_f) = $K(\beta)^{1/2}$

Where, K is the Jacobson temperature dependent constant.

- Acoustic Impedance (Z) = $U\rho$
- Pseudo-Gruneisen Parameter (r) = $\left\{\frac{\gamma-1}{\alpha \times T}\right\}$
- Internal Pressure (π_i) = $\left\{\frac{T \times \alpha}{K_T}\right\}$
- Solubility Parameter (δ) = $\sqrt{\pi_i}$

IV. RESULT AND DISCUSSION

In the present work, the ultrasonic velocity of pure water has been measured at 303.15 °K temperature and the observed data are tabulated in **Table 1**. Comparison of observed data with literature data reported for water indicates that our results are in assent with the literature data [10]. The ultrasonic

velocities (U) of fertilizer of varying concentrations (0.02-0.2 mol/kg) in 0.5M solution of both the saline salts solvents (NaCl and MgCl₂) were measured at 303.15 °K temperature. The observed data of ultrasonic velocity increases with an increase in concentration is tabulated in **Table 2** and shown in **Fig 2**. Temperature and concentration of liquid affects the propagation of an ultrasonic wave through the solution. The increase in sound speed is accredited due to the strong interaction between the fertilizer (Potassium Sulfate)-water and fertilizer (Potassium Sulfate)-aqueous saline salt solutions [11].

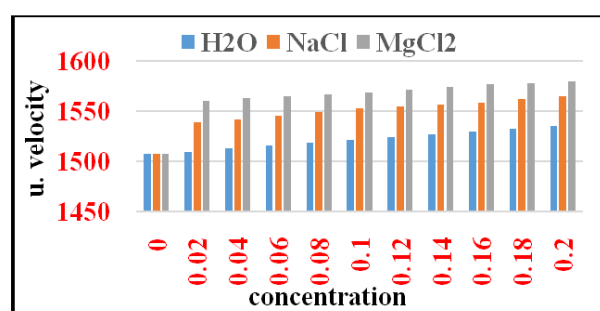


Fig. 2: Ultrasonic velocity versus concentration at 303.15 °K temperature.

The density of pure water has also been measured at 303.15 °K temperature and the observed data is tabulated in **Table 1**. After Comparison of observed data with literature data reported for water indicates that our results show well agreement with the literature data [12, 13]. The density (ρ) of all the systems increases with the rise in concentration as shown in **Fig 3**. It indicates improvement in compactness or structure of solvent by the addition of solute molecules. This shows that a good association occurs between solute and solvent molecules [14]. The increase in density results in increases in the molar volume and ultrasonic velocity, indicating the association in the components of the constituent molecules and confirming the structural rearrangement in the liquid solutions.

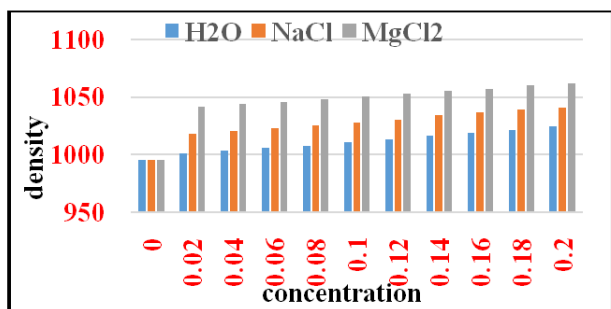


Fig. 3: Density versus concentration at 303.15 °K temperature.

Physicochemical properties of liquid can be understood by adiabatic compressibility (β) as the hydrogen bonding between the unlike components in the solutions decreases with the compressibility. In the present case, it is found that the adiabatic compressibility decreases with an increase in concentration shown in Fig 4. Because, water is a polar solvent and when salts and fertilizer are mixed, the well intermolecular interaction occurred, resulting in close packing of molecules. The decreased values of adiabatic compressibility listed in Table 2 indicate the strong association of fertilizer and saline salts molecules. The compressibility of the solvent is higher than that of the solution and decreases with an increase in the concentration of the solution [15].

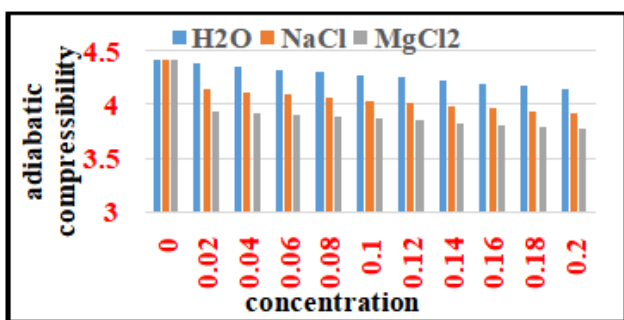


Fig. 4: Adiabatic compressibility versus concentration at 303.15 °K temperature.

The relative change in adiabatic compressibility was calculated with the help of adiabatic compressibility values of solute and solvent. It is listed in Table 3 and shown in Fig 5.

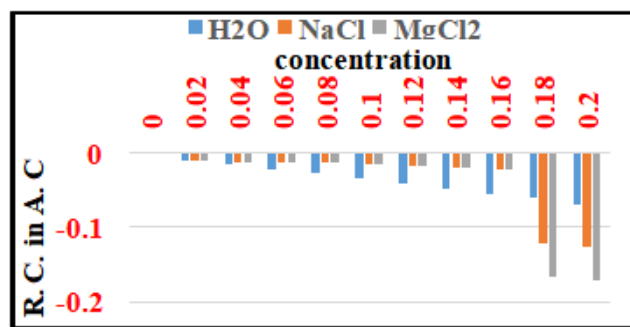


Fig. 5: Relative change in adiabatic compressibility versus concentration at 303.15 °K temperature.

It is found that the negative values of ' $\Delta\beta/\beta$ ' are due to the solute-solvent interaction. Such an increase in ' $\Delta\beta/\beta$ ' with the increase in the concentration of solute (Potassium Sulfate) in water as well as in both the salt solutions may be attributed to an increase in the cohesive forces in solutions [16]. The negative increase in the relative change in adiabatic compressibility values with the rise in concentration confirms the increase of bulk modulus. This increase in bulk modulus indicates that the hydrogen bonding between the unlike components in the solution increases. [17]

Intermolecular free length (L_f) is one of the important parameters that help in determining the mobility, nature as well as strength of interaction between the components of the solution. It is an average distance between the surfaces of two adjacent molecules, which is entitled as the intermolecular free length [18]. Variation of free length is set down in Table 3. It is observed that the values of intermolecular free length decrease with an increase in the concentration of Potassium Sulfate fertilizer in saline salt solutions as well as in water as shown in Fig 6. This indicates that there exists a significant interaction between the fertilizer and water also fertilizer and saline salt solution. Among all the three solutions (H₂O, NaCl, and MgCl₂) intermolecular free length values are found low in MgCl₂ solution, specifying strong intermolecular interaction of fertilizer with aqueous MgCl₂. The observed order of variation of

intermolecular free length (L_f) in water as well as in salt solution is: $MgCl_2 < NaCl < H_2O$ as shown in **Fig 6**.

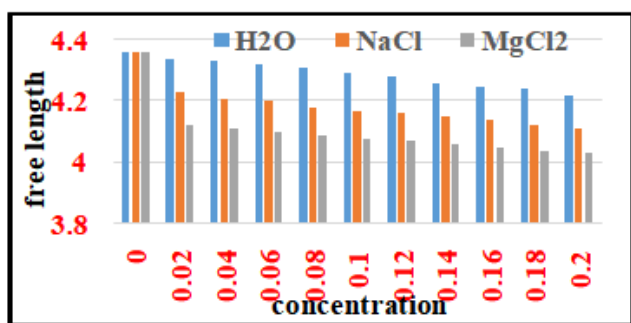


Fig. 6: Intermolecular free length versus concentration at 303.15 °K temperature.

The values of acoustic impedance for fertilizer: Potassium Sulfate of varying concentrations viz. 0.02-0.2mol/kg in water and 0.5M mol/kg aqueous salt solutions of NaCl and MgCl₂ were calculated with the help of speed of sound and density of experimental solutions and after that tabulated in **Table 3** respectively. It is observed from **Fig 7** that the acoustic impedance (Z) of Potassium Sulfate fertilizer increase with an increase in the concentration of fertilizer in water and also in both 0.5M aqueous saline salt solutions and the values-centered around 1 Rayal. The increase in acoustic impedance with the increase in concentration indicates the greater association between solute and solvent through hydrogen bonding [19]. Thus increase in acoustic impedance indicates the associative nature of solute and solvent and enhancement in molecular interaction with less resistance and more viscous force [20]. The order of variation of acoustic impedance (Z) in water as well as in salt solution is $MgCl_2 > NaCl > H_2O$.

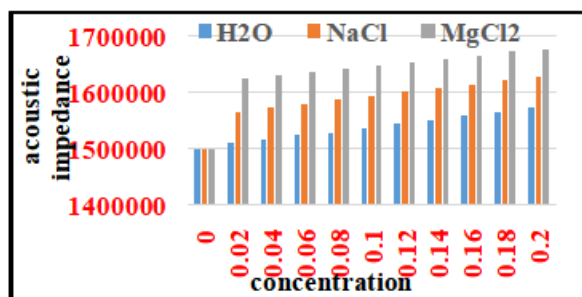


Fig. 7: Acoustic impedance versus concentration at 303.15 °K temperature.

The Pseudo-Grünseien parameter (r) measures the degree of molecular or ionic association. The calculated values of the Pseudo-Grünseien parameter have been listed in **Table 4** and a graph is plotted against the fertilizer concentration at a constant 303.15 °K temperature shown in **Fig. 8**.

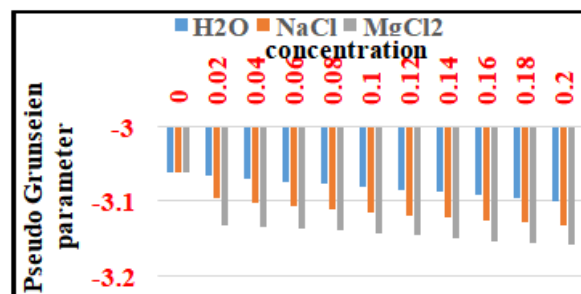


Fig. 8: Psuedo-Gruensien parameter versus concentration at 303.15 °K temperature

It is observed that the Pseudo-Grünseien parameter values are negative and show a decreasing trend of variation with the addition of fertilizer in the solvent. The negative values of the Pseudo-Grünseien parameter suggest the probable formation of an intermolecular complex in the system and strong intermolecular interaction between the solute and solvent [21]. However, it may be noted that such a variation with a change in concentration of fertilizer is trivial. Acoustical parameters tend to illuminate the ilk and strength of the interaction taking place in the corresponding experimental solutions [22]. In the present work, the internal pressure (π_i) increases with an increase in the concentration of fertilizer: Potassium Sulfate in all three solvents is shown in **Fig. 9**. This increasing behavior of the internal pressure in all three solutions indicates the more intermolecular interactions between the fertilizer and soil salt solutions as compared to fertilizer and water [23]. The order of variation found to be: $MgCl_2 > NaCl > H_2O$

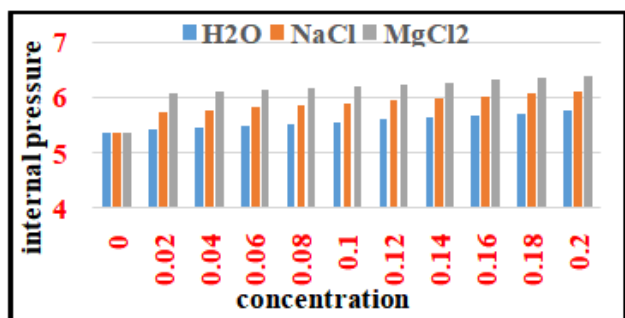


Fig. 9: Internal Pressure versus concentration at 303.15 °K temperature.

The solubility parameter (δ) was calculated by taking the square root of the internal pressure. The calculated values of the solubility parameter for all three solvents were tabulated in *Table 4*. Further, *Fig. 10* shows the variation of the solubility parameter of Potassium Sulfate fertilizer with concentration.

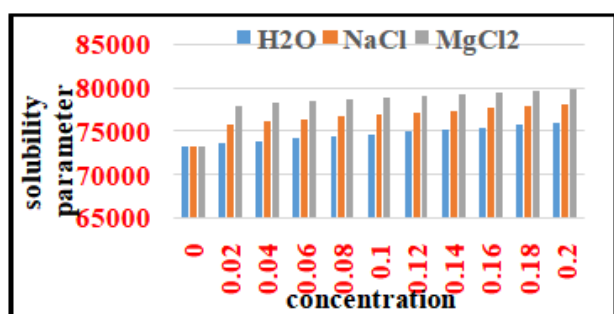


Fig. 10: Solubility parameter versus concentration at 303.15 °K temperature.

The trends of variation of solubility parameters are similar to that of internal pressure. Such an increase in solubility parameter values may be attributed to an increase in the cohesive energy, viscosity and density. It favors the good association among components of

the solution [24]. The increasing trend of the solubility parameter exhibits that the solution is miscible in corresponding solutions and has more tendency to be soluble. The observed trend for solubility parameter was found to be: $MgCl_2 > NaCl > H_2O$

V. CONCLUSION

The various acoustical and physical parameters were determined by using the measured values of density and speed of sound for Potassium Sulfate fertilizer in both water and saline salt solutions (NaCl and MgCl₂) at a constant 303.15 °K temperature. All parameters were used to investigate the intermolecular interactions present between the molecules of Potassium Sulfate fertilizer and saline salts. The impact of concentration on these parameters was observed and explained with the help of physicochemical study. In the light of obtained results and discussions, it was concluded that: the variation in concentration, nature of solute, nature of the solvent and its position plays a major role in determining the kind of interactions occurring in the solution. Also, it is concluded that H-bonding is strong at higher concentrations. Moreover, all the parameters exhibit the maximum values for Potassium Sulfate fertilizer mixed in MgCl₂ solution, because it has a weak interaction with water molecules among the electrolyte solution and therefore can bind with fertilizer molecules more effectively.

Table 2: The values of Ultrasonic Velocity, Density, Adiabatic Compressibility, as a function of the concentration of system (Potassium Sulfate + 0.5M aq. Solution of (NaCl/MgCl₂)) at temperature 303.15 °K respectively

| CONC. (M) (mol/kg) | ULTRASONIC VELOCITY (m/sec) | | | DENSITY (Kg/m ³) | | | A. COMPRESSIBILITY*10 ⁻¹⁰ (m ² N ⁻¹) | | |
|-----------------------|-----------------------------|----------|-------------------|------------------------------|----------|-------------------|--|------|-------------------|
| | H ₂ O | NaCl | MgCl ₂ | H ₂ O | NaCl | MgCl ₂ | H ₂ O | NaCl | MgCl ₂ |
| 0 | 1507.284 | 1507.284 | 1507.284 | 995.6 | 995.6 | 995.6 | 4.42 | 4.42 | 4.42 |
| 0.02 | 1509.607 | 1539.035 | 1560.392 | 1001.452 | 1017.789 | 1041.465 | 4.38 | 4.15 | 3.94 |
| 0.04 | 1512.52 | 1541.905 | 1563.315 | 1003.289 | 1020.389 | 1043.72 | 4.36 | 4.12 | 3.92 |
| 0.06 | 1515.445 | 1545.364 | 1564.991 | 1005.952 | 1023.012 | 1046.06 | 4.33 | 4.09 | 3.9 |
| 0.08 | 1518.38 | 1549.42 | 1566.241 | 1007.395 | 1025.198 | 1048.362 | 4.31 | 4.06 | 3.89 |
| 0.10 | 1521.327 | 1552.331 | 1568.119 | 1010.69 | 1027.692 | 1050.61 | 4.28 | 4.04 | 3.87 |
| 0.12 | 1524.286 | 1554.668 | 1571.259 | 1013.303 | 1030.265 | 1052.72 | 4.25 | 4.02 | 3.85 |
| 0.14 | 1526.661 | 1556.425 | 1573.781 | 1016.186 | 1034.001 | 1055.259 | 4.22 | 3.99 | 3.83 |
| 0.16 | 1529.641 | 1558.775 | 1576.944 | 1019.028 | 1036.467 | 1057.148 | 4.19 | 3.97 | 3.8 |
| 0.18 | 1532.033 | 1562.313 | 1577.579 | 1021.256 | 1038.949 | 1060.504 | 4.17 | 3.94 | 3.79 |
| 0.20 | 1535.636 | 1564.681 | 1579.485 | 1024.39 | 1041.136 | 1062.164 | 4.14 | 3.92 | 3.77 |

Table 3: The values of Relative Change in Adiabatic Compressibility, Intermolecular Free Length and Acoustic Impedance as a function of the concentration of the system (Potassium Sulfate + 0.5M aq. Solution of (NaCl/MgCl₂)) at temperature 303.15 °K respectively

| CONC. (M) (mol/kg) | R. C. IN ADIABATIC COMPRESSIBILITY ---- | | | INTERMOLECULAR FREE LENGTH*10 ⁻¹¹ (m) | | | ACOUSTIC IMPEDANCE (kgm ⁻² s ⁻¹) | | |
|-----------------------|---|----------|-------------------|--|------|-------------------|---|---------|-------------------|
| | H ₂ O | NaCl | MgCl ₂ | H ₂ O | NaCl | MgCl ₂ | H ₂ O | NaCl | MgCl ₂ |
| 0 | 0 | 0 | 0 | 4.36 | 4.36 | 4.36 | 1500652 | 1500652 | 1500652 |
| 0.02 | -0.00898 | -0.00866 | -0.00866 | 4.34 | 4.23 | 4.12 | 1511799 | 1566412 | 1625094 |
| 0.04 | -0.01474 | -0.01085 | -0.01085 | 4.33 | 4.21 | 4.11 | 1517495 | 1573342 | 1631663 |
| 0.06 | -0.02137 | -0.01304 | -0.01304 | 4.32 | 4.2 | 4.1 | 1524465 | 1580926 | 1637074 |
| 0.08 | -0.0268 | -0.01304 | -0.01304 | 4.31 | 4.18 | 4.09 | 1529609 | 1588462 | 1641988 |
| 0.10 | -0.03416 | -0.01525 | -0.01525 | 4.29 | 4.17 | 4.08 | 1537590 | 1595317 | 1647482 |
| 0.12 | -0.04087 | -0.01747 | -0.01747 | 4.28 | 4.16 | 4.07 | 1544564 | 1601719 | 1654096 |
| 0.14 | -0.04709 | -0.01969 | -0.01969 | 4.26 | 4.15 | 4.06 | 1551371 | 1609344 | 1660747 |
| 0.16 | -0.05412 | -0.02193 | -0.02193 | 4.25 | 4.14 | 4.05 | 1558747 | 1615618 | 1667063 |
| 0.18 | -0.05973 | -0.12113 | -0.16686 | 4.24 | 4.12 | 4.04 | 1564598 | 1623163 | 1673028 |
| 0.20 | -0.06799 | -0.1269 | -0.17151 | 4.22 | 4.11 | 4.03 | 1573090 | 1629046 | 1677672 |

Table 4: The values Pseudo-Grunseien Parameter, Internal Pressure and Solubility Parameter of the system (Potassium Sulfate + 0.5M aq. Solution of (NaCl/MgCl₂)) at temperature 303.15 °K respectively

| CONC. (M) (mol/kg) | PSEUDO-GRUNSEIEN PARAMETER ---- | | | INTERNAL PRESSURE*10 ⁹ (Nm ⁻²) | | | SOLUBILITY PARAMETER (Nm ⁻²) ^{1/2} | | |
|-----------------------|---------------------------------|----------|-------------------|---|------|-------------------|---|----------|-------------------|
| | H ₂ O | NaCl | MgCl ₂ | H ₂ O | NaCl | MgCl ₂ | H ₂ O | NaCl | MgCl ₂ |
| 0 | -3.0602 | -3.0602 | -3.0602 | 5.36 | 5.36 | 5.36 | 73195.76 | 73195.76 | 73195.76 |
| 0.02 | -3.06449 | -3.0945 | -3.13024 | 5.42 | 5.73 | 6.07 | 73599.36 | 75716.12 | 77893.21 |
| 0.04 | -3.06815 | -3.10061 | -3.13398 | 5.45 | 5.77 | 6.11 | 73819.38 | 75976.83 | 78140.49 |
| 0.06 | -3.07207 | -3.10442 | -3.13644 | 5.49 | 5.82 | 6.14 | 74083.23 | 76264.53 | 78337.95 |
| 0.08 | -3.07562 | -3.10886 | -3.13845 | 5.52 | 5.86 | 6.16 | 74284.16 | 76555.3 | 78514.86 |
| 0.10 | -3.07975 | -3.11379 | -3.14109 | 5.56 | 5.9 | 6.2 | 74582.61 | 76813.2 | 78716.57 |
| 0.12 | -3.08369 | -3.1176 | -3.145 | 5.6 | 5.94 | 6.24 | 74846.3 | 77050.73 | 78966.62 |
| 0.14 | -3.08708 | -3.12084 | -3.14839 | 5.64 | 5.98 | 6.27 | 75099.28 | 77324.89 | 79212.56 |
| 0.16 | -3.0911 | -3.12382 | -3.15226 | 5.68 | 6.02 | 6.31 | 75376.53 | 77557.83 | 79452.43 |
| 0.18 | -3.09431 | -3.12703 | -3.15393 | 5.71 | 6.06 | 6.35 | 75596.52 | 77843.61 | 79659.04 |
| 0.20 | -3.09906 | -3.13149 | -3.15641 | 5.76 | 6.09 | 6.37 | 75916.64 | 78063.04 | 79831.66 |

IV. FUTURE SCOPE

This kind of information can be useful in improving fertilizer activity according to soil salinity treatment and in other applications by changing the parameters of its molecule. Thermo-acoustical studies could also be used successfully and well supported in this regard. Because of the above interpretation, this kind of study has a bright future scope in the field of agriculture to feed the people and increase the economy of farmers.

V. CONFLICTS OF INTEREST

The authors declare no conflict of interest in the present research work.

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