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Ultrasonic Studies on Molecular Interaction of Fertilizer in Aqueous Saline Soil Salt Solutions at Different Temperatures

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ABSTRACT

In this paper an attempt is made to understand the structural (molecular) alterations of fertilizer in saline soil salts which results various solute-solvent, solvent-solvent and ion-solvent interactions in order find a way to control the problem of soil salinity. These interactions depend on the nature of solvent, size and structure of ion. For this purpose, Potassium Sulfate (PS) fertilizer is being used which contain the 43% of K concentration. The ultrasonic parameters and characterization help to forecast and understand the behavior of intermolecular interaction, strength as well as the nature of the liquid mixture exist in this system. In view of above facts, the density (ρ) and speed of sound (U) measurements studies on fertilizer: Potassium Sulfate of number of concentrations varying from 0.02-0.2 mol·kg⁻¹ in 0.5M solution of saline soil salt solutions and the results were explored in terms of solute-solvent, solvent-solvent interactions. These are of great importance in understanding the extent and nature of solutions as well as to counteract the problem of soil salinity.

Key words: Acoustical properties, Density, Fertilizer, Intermolecular interaction, Soil salinity

The consistent climate change due to the global warming, excessive application of groundwater and increasing successive use of low-quality water in irrigation with intensive farming and poor drainage generates the soil salinity problem. Now a days this soil salinization becomes a major factor contributing to the loss of productivity of cultivated soils. It was estimated that about 20% (45 million ha) of irrigated land, producing one-third of the world's food, is salt-affected.[1]The salinity of soil has great effects on nutrients availability to plants or crops and on the ability of plant roots to absorb nutrients. Because of low productivity problems in the salt affected soils, fertilizers are applied to counteract the conditions which limit the plant absorption of nutrients [2].

During literature survey it has been revealed that, a decrease in the ability of the plant to absorb potassium generally take place in saline soils containing excess amount of Na, Mg or Ca. Therefor application of potassium fertilizer not only correct the deficiencies but also decrease the adverse effect of Na, Mg and Ca on the plants. Various thermo-acoustic parameters like: adiabatic compressibility,

change in adiabatic compressibility, intermolecular free length, and acoustic impedance were calculated. It was occurred that there is certain degree of variation exist in these parameters with change in concentration and temperature. Therefore, the present work aimed to understand the structural (molecular) changes of Potassium Sulfate fertilizer in saline soil salt solutions like: Sodium Chloride and Magnesium Chloride, which explore various solute-solvent, solvent-solvent and ion-solvent interactions in order find a way to control the salinity problem.

Experimental details

A. Materials

AR grade chemicals (mass fraction purity 99.8%) as Potassium Sulfate (CAS no.: 7778-80-5), Sodium Chloride (CAS no.: 7647-14-5) and Magnesium Chloride (CAS no.: 7786-30-3), were obtained from Himedia Lab. Pvt. Ltd., Mumbai. All chemicals were used as supplied. The concentrations (0.02-0.2 mol·kg⁻¹) of Potassium Sulfate in 0.5M aqueous saline salts were changed by weight. All the glassware's was washed with double distilled water as well as with acetone and dried before use.

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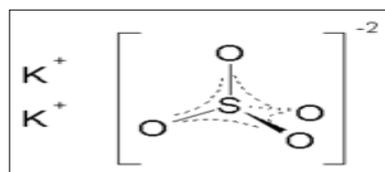


Fig 1 Structure of potassium sulfate

B. Method

A digital ultrasonic velocity interferometer was used for measuring the ultrasonic velocity operating at frequency 2 MHz supplied from Vi Microsystems Pvt. Ltd., Chennai (Model VCT:71) with an overall accuracy 0.0001m/s.

The densities of the solutions were determined using 10ml specific gravity bottle having accuracy $\pm 2 \times 10^{-2}$ kg/m³ and digital electronic balance (Contech CA-34) having accuracy ± 0.0001 gm. 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 ± 1 K temperature.

Table 1 Density and ultrasonic velocity of water at 293.15K and 298.15K temperature

Current work data		Literature data	
U. Vel. (U) m/sec	Density (ρ) kg/m ³	U. Vel. (U) m/sec	Density (ρ) kg/m ³
	293.15K		
1481.496	998.200	1482.63	998.202
	298.15K		
1498.101	997.051	1497.06	997.025

Defining relations

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

$$\text{Specific Heat Ratio } (\gamma) = \left\{ \frac{17.1}{T^{4/9} + p^{1/3}} \right\}$$

$$\text{Isothermal Compressibility } (k_T) = \{ 1.33 \times 10^{-8} / (6.4 \times 10^{-4} U^{3/2} \rho)^{3/2} \}$$

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

Where; K be the Jacobson temperature dependent constant

$$\text{Pseudo-Gruneisen Parameter } (r) = \left\{ \frac{\gamma - 1}{\alpha + T} \right\}$$

$$\text{Internal Pressure } (\pi_i) = \left\{ \frac{T + \alpha}{k_T} \right\}$$

$$\text{Apparent Molar Volume } (V_\phi) = \left\{ \frac{M}{p} - \frac{1000(p - p_0)}{Mpp_0} \right\}$$

$$\text{Solubility Parameter } (\delta) = \sqrt{\pi_i}$$

$$\text{Acoustic Impedance } (Z) = U\rho$$

RESULTS AND DISCUSSION

A. Density

Density of pure water has been measured at 293.15K and 298.15K temperatures and the observed data tabulated in the (Table 2). After Comparison of observed data with literature data reported for water indicated that our results are shows well agreement with the literature data. [3-4] The density (ρ) of both the systems, increases with increase in concentration and temperature due to improve in compactness or structure of solvent by the addition of solute molecules. This indicates association occurs between solute and solvent molecules. [5] The increase in density of fertilizer solutions in both saline salts solutions with rise in concentration results increase in the molar volume indicating the association in the components of the

constituent molecules and confirms the structural rearrangement. Furthermore, density values of system decrease with rise in temperature shows decrease in intermolecular forces due to increasing thermal energy of the system.

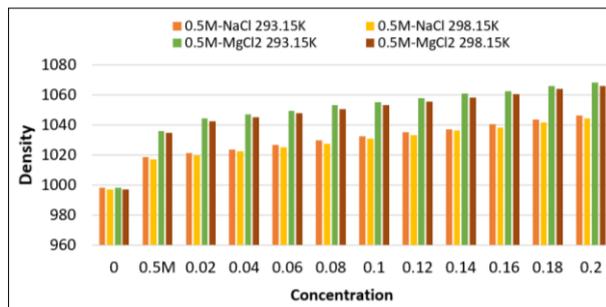


Fig 1 Density versus concentration at 293.15K and 298.15K temperature

Table 2 Density of potassium sulfate + (0.5M) aq. NaCl/MgCl₂ at 293.15K and 298.15K temperatures

Conc. (M) mol·kg ⁻¹	Density			
	0.5M-NaCl		0.5M-MgCl ₂	
	293.15K	298.15K	293.15K	298.15K
0.00	998.20	0997.00	998.20	0997.00
0.5M	1018.54	1017.11	1035.82	1034.51
0.02	1021.13	1019.71	1044.31	1042.39
0.04	1023.70	1022.42	1046.91	1045.01
0.06	1026.67	1025.13	1049.41	1047.62
0.08	1029.64	1027.45	1053.12	1050.25
0.10	1032.22	1030.87	1054.85	1052.93
0.12	1035.00	1033.30	1057.62	1055.49
0.14	1037.12	1036.12	1060.88	1058.00
0.16	1040.52	1038.10	1062.24	1060.43
0.18	1043.50	1041.45	1065.61	1063.71
0.20	1046.08	1044.17	1068.27	1065.93

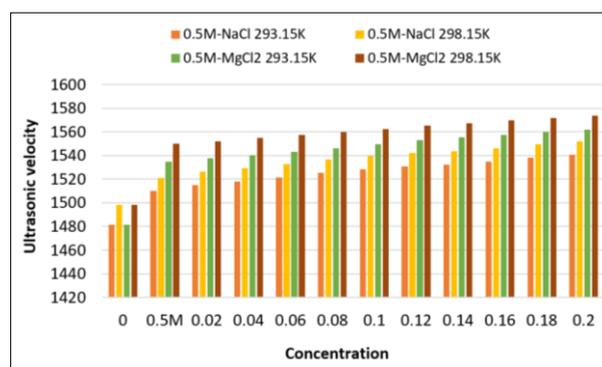


Fig 2 Ultrasonic velocity versus concentration at 293.15K and 298.15K temperature

B. Ultrasonic velocity

In the present work ultrasonic velocity of pure water has been measured at 293.15K and 298.15K temperatures and the observed data tabulated in the (Table 1). Comparison of observed data with literature data reported for water indicated that our results are in assent with the literature data [6]. The ultrasonic velocity (U) of Potassium Sulfate fertilizer of changeable concentrations (0.02-0.2 mol/kg) in 0.5M solution of both the saline salts solvents: Sodium Chloride and Magnesium Chloride measured at 293.15K and 298.15K temperatures. The observed data of

ultrasonic velocity increases with increase in concentration as well as in temperature is tabulated in (Table 3). Temperature and concentration affect the ultrasonic wave passing through solution. The increase in sound speed is accredited to the cohesion brought about by the ionic hydration and the construction of hydrogen bond between the fertilizer-water as well as fertilizer-saline salt solutions [7].

Table 3 Ultrasonic velocity of potassium sulfate + (0.5M) aq. NaCl/MgCl₂ at 293.15K and 298.15K temperatures

Conc. (M) mol·kg ⁻¹	U. Velocity			
	0.5M-NaCl		0.5M-MgCl ₂	
	293.15K	298.15K	293.15K	298.15K
0.00	1481.496	1498.101	1481.496	1498.101
0.5M	1509.908	1521.054	1534.759	1550.048
0.02	1515.046	1526.192	1537.765	1551.883
0.04	1517.916	1529.062	1540.178	1554.952
0.06	1521.375	1532.521	1543.205	1557.415
0.08	1525.431	1536.577	1546.244	1559.887
0.10	1528.342	1539.488	1549.295	1562.366
0.12	1530.679	1541.825	1552.973	1565.476
0.14	1532.436	1543.582	1555.435	1567.349
0.16	1534.786	1545.932	1557.286	1569.852
0.18	1538.324	1549.471	1559.761	1571.735
0.20	1540.692	1551.838	1561.623	1573.621

C. Specific Heat Ratio:

Data inserted in (Fig 3) shows the variation of specific heat ratio at different concentration and at various temperatures viz. 293.15 and 298.15K respectively. The heat capacity ratio (γ) is constantly decreasing with the increment of concentration and temperature, which throw light on the fact that specific heat at constant volume is decreasing constantly with increasing concentration and temperature also.

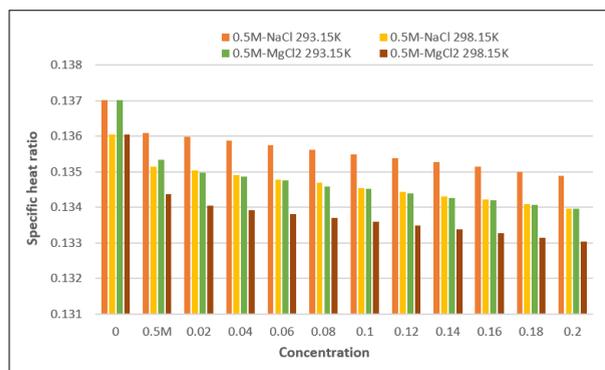


Fig 3 Specific heat ratio versus concentration at 293.15K and 298.15K temperature

Table 4 Specific heat ratio of potassium sulfate + (0.5M) aq. NaCl/MgCl₂ at 293.15K and 298.15K temperatures

Conc. (M) mol·kg ⁻¹	Specific heat ratio			
	0.5M-NaCl		0.5M-MgCl ₂	
	293.15K	298.15K	293.15K	298.15K
0.00	0.136098	0.135142	0.135337	0.134380
0.5M	0.135983	0.135028	0.134969	0.134041
0.02	0.135869	0.134908	0.134858	0.133929
0.04	0.135738	0.134789	0.134751	0.133817
0.06	0.135607	0.134687	0.134592	0.133706
0.08	0.135494	0.134538	0.134518	0.133592
0.10	0.135373	0.134433	0.134401	0.133484

0.12	0.135281	0.134312	0.134263	0.133378
0.14	0.135134	0.134225	0.134206	0.133278
0.16	0.135004	0.134081	0.134064	0.133139
0.18	0.134893	0.133965	0.133953	0.133047
0.20	0.137016	0.136045	0.137016	0.136045

D. Isothermal Compressibility:

Isothermal Compressibility values have been computed using the suggested Mc Gowan's [8] relation. The overall trends in the isothermal compressibility (k_T) are as shown in (Fig 4). It has been found to be decreasing with increase in concentration and temperature. The decrease in ' k_T ' values with increase in concentration seems to be the result of corresponding decrease in free volume [9]. The decrease in free volume with rise in concentration clears the clustering of molecules and hence suggest the increase in interaction.

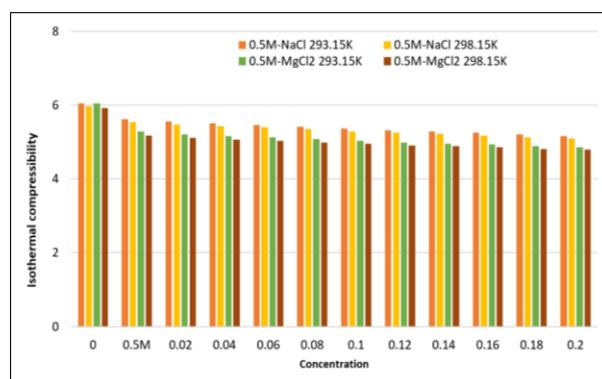


Fig 4 Isothermal Compressibility versus concentration at 293.15K and 298.15K temperature

Table 5 Isothermal compressibility of potassium sulfate + (0.5M) aq. NaCl/MgCl₂ at 293.15K and 298.15K temperatures*10⁻¹¹

Conc. (M) mol·kg ⁻¹	Isothermal compressibility			
	0.5M-NaCl		0.5M-MgCl ₂	
	293.15K	298.15K	293.15K	298.15K
0.00	6.05	5.97	6.05	5.91
0.5M	5.62	5.54	5.29	5.18
0.02	5.56	5.48	5.20	5.11
0.04	5.51	5.43	5.16	5.06
0.06	5.46	5.39	5.12	5.03
0.08	5.41	5.34	5.07	4.99
0.10	5.36	5.29	5.03	4.95
0.12	5.32	5.25	4.99	4.91
0.14	5.29	5.22	4.95	4.88
0.16	5.25	5.18	4.93	4.85
0.18	5.20	5.13	4.88	4.81
0.20	5.16	5.09	4.85	4.79

E. Intermolecular free length

Intermolecular free length (L_f) is one of the important parameter in determining the nature as well as strength of interaction between the components of solution. It is the average distance between the surfaces of two neighboring molecules, which is called intermolecular free length [10]. Variation of free length is set down in (Table 6). It is observed that the free length decreases with increase in concentration of fertilizer in saline salt solutions. This indicates that there exists a significant interaction among the fertilizer and soil salt solution. Among both the saline salts (NaCl and MgCl₂) intermolecular free length values are

found low in water, while in the case of electrolyte solutions, it is found low in $MgCl_2$ indicating strong intermolecular interaction of fertilizer with $MgCl_2$. Increasing trend of Intermolecular free length with rise in temperature is due to the thermal expansion of component molecules of the solution. The observed behavior shows that there is enhanced molecular association. The observed order of variation of intermolecular free length (L_f) in water as well as in salt solution is: $MgCl_2 < NaCl < H_2O$.

Table 6 Intermolecular free length of potassium sulfate + (0.5M) aq. NaCl/ $MgCl_2$. at 293.15K and 298.15K temperatures

Conc. (M) mol·kg ⁻¹	Free length*10 ⁻¹¹			
	0.5M-NaCl		0.5M-MgCl ₂	
	293.15K	298.15K	293.15K	298.15K
0.00	4.37	4.37	4.35	4.35
0.5M	4.23	4.24	4.13	4.13
0.02	4.21	4.22	4.10	4.11
0.04	4.20	4.21	4.09	4.09
0.06	4.18	4.19	4.08	4.08
0.08	4.16	4.18	4.06	4.07
0.10	4.15	4.16	4.05	4.06
0.12	4.14	4.15	4.04	4.04
0.14	4.13	4.14	4.02	4.03
0.16	4.12	4.13	4.02	4.02
0.18	4.10	4.11	4.00	4.01
0.20	4.09	4.10	3.99	4.00

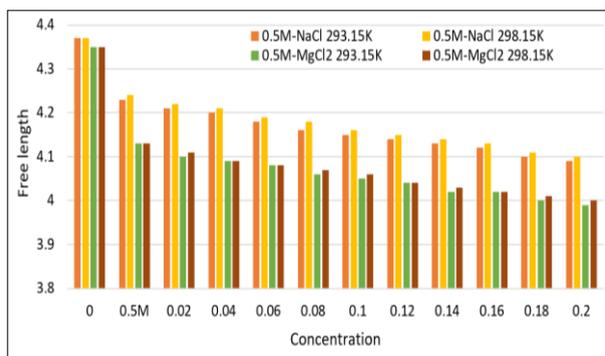


Fig 5 Intermolecular free length versus concentration at 293.15K and 298.15K temperature

F. Pseudo-Grunseien parameter

The Pseudo-Grünseien Parameter (r) measures the degree of molecular or ionic association. The calculated values of ‘ r ’ have been listed in Table-7 and a graph is plotted against the fertilizer concentration at 293.15K and 298.15K temperature shown in (Fig 6). It is observed that the ‘ r ’ values are negative and shows a decreasing (due to negative result) trend of variation with the addition of fertilizer in the solvent. The negative values suggest the probable formation of intermolecular complex in the system and strong intermolecular interaction [11]. However, it may be noted that such a variation with change in concentration of fertilizer is trivial.

G. Internal Pressure:

As we know that the acoustical parameters have tendency to explain the ilk and strength of the interaction taking place in the solutions. In the present system the internal pressure (π_i) increases with increase in concentration of fertilizer at both the temperatures as shown in (Fig 7). This behavior of the solution indicates the

intermolecular space decreases with addition of fertilizer in salt solutions and interaction increases which supports the association among the constituent molecules of the solute and solvent [12].

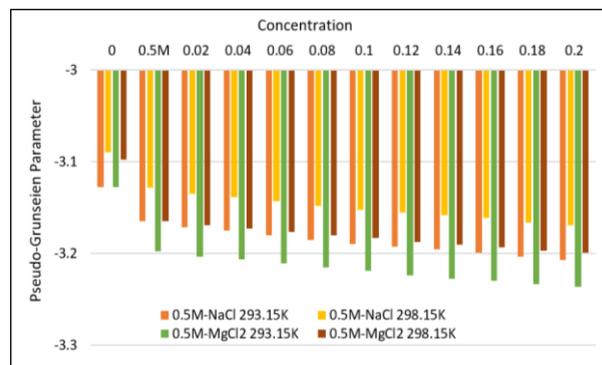


Fig 6 Pseudo-Grünseien Parameter versus concentration at 293.15K and 298.15K temperature

Table 7 Pseudo-Grunseien parameter of potassium sulfate + (0.5M) aq. NaCl/ $MgCl_2$. at 293.15K and 298.15K temperatures

Conc. (M) mol·kg ⁻¹	Pseudo-Grünseien parameter			
	0.5M-NaCl		0.5M-MgCl ₂	
	293.15K	298.15K	293.15K	298.15K
0.00	-3.12742	-3.08961	-3.12742	-3.09734
0.5M	-3.16504	-3.12834	-3.19753	-3.16472
0.02	-3.17147	-3.13466	-3.20343	-3.16910
0.04	-3.17541	-3.13857	-3.20685	-3.17317
0.06	-3.18011	-3.14312	-3.21090	-3.17659
0.08	-3.18546	-3.14817	-3.21534	-3.18002
0.10	-3.18943	-3.15234	-3.21918	-3.18347
0.12	-3.19284	-3.15558	-3.22401	-3.18755
0.14	-3.19541	-3.15832	-3.22767	-3.19030
0.16	-3.19901	-3.16144	-3.23008	-3.19368
0.18	-3.20378	-3.16624	-3.23379	-3.19667
0.20	-3.20715	-3.16960	-3.23661	-3.19934

Table 8 Internal pressure of potassium sulfate + (0.5M) aq. NaCl/ $MgCl_2$. at 293.15K and 298.15K temperatures

Conc. (M) mol·kg ⁻¹	Internal pressure*10 ⁻¹¹			
	0.5M-NaCl		0.5M-MgCl ₂	
	293.15K	298.15K	293.15K	298.15K
0.00	5.06	5.19	5.06	5.23
0.5M	5.39	5.53	5.68	5.85
0.02	5.44	5.58	5.76	5.93
0.04	5.48	5.62	5.80	5.97
0.06	5.52	5.66	5.84	6.01
0.08	5.57	5.71	5.89	6.05
0.10	5.61	5.75	5.92	6.09
0.12	5.64	5.79	5.97	6.13
0.14	5.67	5.82	6.01	6.16
0.16	5.71	5.85	6.04	6.20
0.18	5.76	5.91	6.08	6.24
0.20	5.80	5.94	6.11	6.27

H. Apparent molar volume

The values of the apparent molar volume were calculated with the help of densities of water (solvent) and fertilizer (solute) and listed in (Table 9). It is clear from the trends shown in (Fig 8) that apparent molar volume decreases with increase in fertilizer concentration at both the temperatures. But the obtained values are negative, this

behavior support that there is strong ionic (ion-ion) interaction existing in the fertilizer solution [13]. The same supported by increasing in molar volume with rise in concentration as a result of shrinking in the lacuna in solvent structure due to increased intermolecular hydrogen bonding established with the insertion of fertilizer.

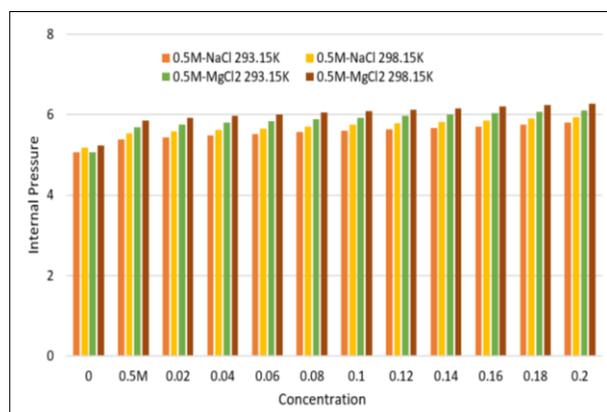


Fig 7 Internal pressure versus concentration at 293.15K and 298.15K temperature

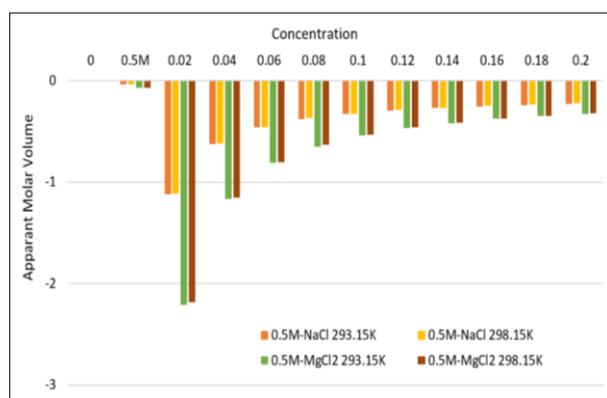


Fig 8 Apparent molar volume versus concentration at 293.15K and 298.15K temperature

Table 9 Apparent molar volume of potassium Sulfate + (0.5M) aq. NaCl/MgCl₂. at 293.15K and 298.15K temperatures

Conc. (M) mol·kg ⁻¹	Apparent molar volume			
	0.5M-NaCl		0.5M-MgCl ₂	
	293.15K	298.15K	293.15K	298.15K
0.00	----	----	----	----
0.5M	-0.03995	-0.03960	-0.07257	-0.07254
0.02	-1.12463	-1.11625	-2.21150	-2.18370
0.04	-0.62369	-0.62326	-1.16512	-1.15177
0.06	-0.46284	-0.45855	-0.81464	-0.80762
0.08	-0.38223	-0.37140	-0.65288	-0.63552
0.10	-0.33001	-0.32938	-0.53786	-0.53262
0.12	-0.29666	-0.29342	-0.46887	-0.46302
0.14	-0.26837	-0.27020	-0.42262	-0.4129
0.16	-0.25438	-0.24802	-0.37731	-0.37464
0.18	-0.24144	-0.23767	-0.35191	-0.34930
0.20	-0.22910	-0.22640	-0.32837	-0.32413

I. Solubility Parameter:

The solubility parameter (δ) is obtained by taking the square root of the internal pressure. The calculated values tabulated in the (Table 10). Further the (Fig 9) shows the variation of solubility parameter of fertilizer with

concentration and temperature. The trends of variation of ' δ ' is similar to that of internal pressure. Such an increase may attributed to an increase in the cohesive energy, viscosity and density and favors the well association among component of solution [14] The increasing trend of the solubility parameter exhibits that the solution has more tendency of soluble.

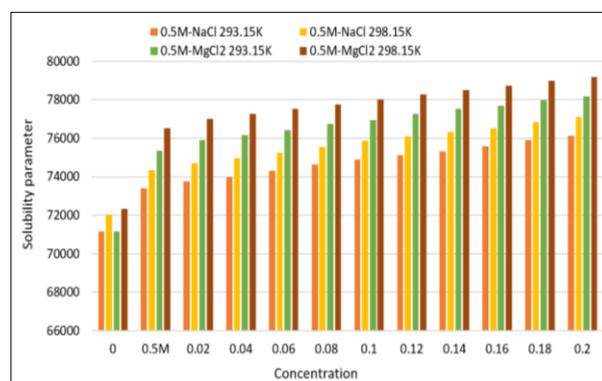


Fig 9 Solubility parameter versus concentration at 293.15K and 298.15K temperature

Table 10 Apparent molar volume of potassium sulfate + (0.5M) aq. NaCl/MgCl₂. at 293.15K and 298.15K temperatures

Conc. (M) mol·kg ⁻¹	Solubility parameter			
	0.5M-NaCl		0.5M-MgCl ₂	
	293.15K	298.15K	293.15K	298.15K
0.00	71163.28	72038.94	71163.28	72341.22
0.5M	73397.28	74354.47	75345.75	76506.92
0.02	73748.34	74708.67	75912.54	76999.05
0.04	74002.21	74972.91	76150.76	77269.26
0.06	74302.06	75262.28	76410.79	77513.50
0.08	74628.01	75557.43	76733.91	77758.96
0.10	74885.13	75861.02	76955.85	78007.78
0.12	75128.31	76088.31	77259.02	78278.16
0.14	75312.84	76310.56	77535.02	78492.05
0.16	75587.89	76516.66	77686.21	78727.97
0.18	75894.95	76845.14	77968.98	78984.77
0.20	76130.17	77090.19	78188.15	79184.46

J. Acoustic Impedance:

The values of acoustic impedance for fertilizer: Potassium Sulfate of different concentration viz. 0.02-0.2mol/kg in 0.5M solution of aqueous electrolyte solution of NaCl and MgCl₂ at 293.15 and 298.15K temperatures were calculated and tabulated in (Table 11) respectively. It is observed that the acoustic impedance (Z) values of Potassium Sulfate fertilizer increase with increase in concentration of fertilizer in the both 0.5M aqueous electrolyte solutions and the values centered around 1 Rayal. The increase in acoustic impedance with the increase in concentration indicates the greater association among solute and solvent through hydrogen bonding. Thus, increase in acoustic impedance indicates associative nature of solute and solvent and enhancement in molecular interaction [15]. The increase in acoustic impedance with rise in temperature is due to ion change in elastic and inertial properties of solution. This indicates the greater association of solute and solvent molecules. The order of variation of acoustic impedance (Z) in water as well as in salt solution is: MgCl₂>NaCl>H₂O.

Table 11 Acoustic impedance of potassium sulfate + (0.5M) aq. NaCl/MgCl₂ at 293.15K and 298.15K temperatures

Conc. (M) mol·kg ⁻¹	Acoustic impedance			
	0.5M-NaCl		0.5M-MgCl ₂	
	293.15K	298.15K	293.15K	298.15K
0.00	1478829	1486476	1478829	1493607
0.5M	1537901	1547079	1589734	1603540
0.02	1547059	1556258	1605904	1617671
0.04	1553891	1563344	1612428	1624936
0.06	1561950	1571033	1619458	1631584
0.08	1570648	1578756	1628380	1638271
0.10	1577585	1587012	1634275	1645062
0.12	1584253	1593160	1642455	1652344
0.14	1589320	1599305	1650130	1658255
0.16	1596945	1604832	1654211	1664671
0.18	1605241	1613699	1662097	1671870
0.20	1611686	1620386	1668228	1677367

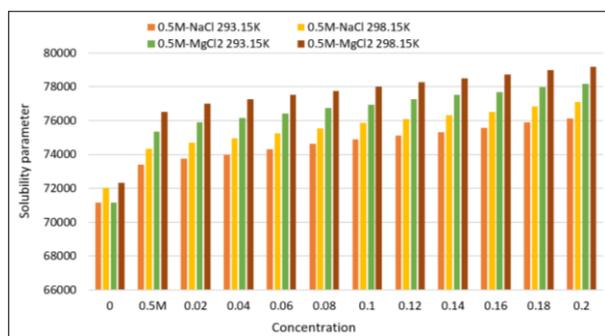


Fig 10 Acoustic impedance versus concentration at 293.15K and 298.15K temperature

CONCLUSION

The various acoustical parameters determined by using the measured values of density and ultrasonic velocity of Potassium Sulfate solutions in both electrolyte solution (NaCl and MgCl₂) at 293.15K and 298.15K temperature. All parameters used to investigate the intermolecular interactions between the Potassium Sulfate fertilizer molecules and saline salts. The impact of variation in concentration and temperature on these parameters were observed and studied. In the light of above observations and discussions, it may be concluded that: the concentration, nature of solute, nature of solvent and its position plays an important role in determining the interactions occurring in the solution. Also, it is concluded that H-bonding interaction is strong at higher concentration. Moreover, the values of density and compressibility for Potassium Sulfate fertilizer are found to be maximum with MgCl₂ coz it has weak interaction with water molecules among the electrolyte solution and ergo can bind with fertilizer molecules more effectively. Rest volumetric and acoustical parameters show that among both saline salts, potassium sulfate fertilizer develops maximum interactions with MgCl₂ salt solution due to superior degree of hydrogen bonding and intermolecular interactions in its aqueous soil salt solutions which indicate the prominent effect of nature of fertilizer molecule on its behavior in solutions. This kind of information can be useful in the manufacturing of more effective fertilizer by increasing their activity according to soil salinity treatment and in other application by changing the ilk of its molecule.

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