

A Volumetric and Acoustical Study to Explore Interactions between Saline Salts and Fertilizer in view to Control the Salinity of Soil

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Abstract: 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. Thus the present work is aimed to understand the structural/molecular changes of solute (fertilizer) in solutions (saline salts) which results various solute-solvent, solvent-solvent and ion-solvent interactions in order find any way to control the salinity problem. These interactions depend on the nature of solvent, size and structure of ion. For this purpose Ammonium Sulfate (AS) is being used which contain the 10.6% of nitrogen. The numerous volumetric and acoustical properties depend upon the temperature, concentration and composition were calculated on the basis of measured experimental data of density and sound velocity of Ammonium Sulfate (AS) molecules and different saline salts. The effect of different volumetric and acoustical parameters with change in concentration and temperature were studied and the results were explored in terms of solute-solvent, solvent-solvent interactions and structure making or breaking effects are of great importance in understanding the extent and nature of solutions.

Index Terms: Acoustical properties, Density, Fertilizer, Intermolecular interaction, Sound velocity.

I. INTRODUCTION

Plant faces different environment stresses like high temperature, cold, draught, salinity, UV and other biotic stress. However among these stresses, salinity is considered the most limiting factor for productivity of crops. In agriculture all salts contains some amount of soluble salts. Among these many salts act as a source of essential nutrients for the healthy growth of

plants. However when the quantity/concentration of the salts (like: Na^+ , Ca^{++} , Mg^{++} , SO_4^{--} , Cl^- , HCO_3^- , K^+ , CO_3^{--}) soils exceeds a particular value, then this (Salinity) affects growth rate and it results in plants with smaller leaves, shorter length and sometimes fewer leaves by reducing growth rate. Salinity changes the roots structure by lowering their length and mass, therefore roots may become thinner or thicker. (Shannon et al., 1999)

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. (Gowaliker et al., 2009) During literature survey it has been revealed that, a decrease in the ability of the plant to absorb NH_4 generally take place in saline soils containing excess amount of Na, Mg or Ca. Therefore application of NH_4 fertilizer not only correct the deficiencies but also decrease the adverse effect of Na, Mg and Ca on the plants. As numerous thermodynamic and acoustical properties like acoustic impedance, specific heat ratio, isothermal and isentropic compressibility etc. depend upon the temperature, concentration, composition and therefore are of great importance in understanding the extent and nature of solutions. Therefore the present work aimed to understand the structural (molecular) changes of solute (fertilizer) in solutions (saline salts) which explore various solute-solvent, solvent-solvent and ion-solvent interactions in order find any way to control the salinity problem. These interactions depend on the nature of solvent, size and structure of ion.

II. EXPERIMENTAL PROCEDURE

A. Material

AR grade chemicals (mass fraction purity 99.8%) as Ammonium Sulfate (CAS no.: 7783-20-2), 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 without any further purification. The concentrations (0.02-0.2 mol·kg⁻¹) of Ammonium 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.

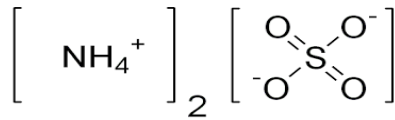


Fig: Structure of Ammonium Sulfate

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 source of ultrasonic waves was a quartz crystal excited by a radio frequency oscillator. The cell was filled with the desired solution and water at constant temperature was circulated in the outer jacket. The cell was allowed to equilibrate for 30min. prior to making the measurements.

The densities of the solutions were determined accurately using 10ml specific gravity bottle having accuracy $\pm 2 \cdot 10^{-2}$ 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 I: Density and Ultrasonic velocity of water at 288.15K 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
1466.032	999.103	1466.25	999.1

Table II: Abbreviations used.

M	Molal Concentration in mol./kg
CAS	Chemical Abstract Service
MHz	Mega Hertz
U_{∞}	Infinite Value of Ultrasonic Velocity

III. DEFINING RELATIONS

A For the derivation of several acoustical and thermo-dynamical parameters the following defining relations reported in the literature are used:

- ❖ Adiabatic Compressibility (β) = $1/(U^2\rho)$
- ❖ Relative Change in Adiabatic Compressibility ($\Delta\beta/\beta$) = $\{\beta - \beta_0\}/\beta$
- ❖ Intermolecular Free Length (L_f) = $K(\beta)^{1/2}$
Where, K be the Jacobson temperature dependent constant.
- ❖ Acoustic Impedance (Z) = $U\rho$
- ❖ Relative Association (R_A) = $(\rho/\rho_0)(U_0/U)^{1/3}$
- ❖ Isothermal Compressibility (k_{T1}) = $1.33 \cdot 10^{-8}/(6.4 \cdot 10^{-4} U^{3/2} \rho)^{3/2}$
- ❖ Isothermal Compressibility (k_{T2}) = $17.1 \cdot 10^{-4}/(T^{4/9} U^2 \rho^{1/3})$
- ❖ Specific Heat Ratio (γ) = $\{ \frac{17.1}{T^{4/9} \rho^{1/3}} \}$
- ❖ Relaxation Strength (r) = $1 - (\frac{U}{U_{\infty}})^2$
- ❖ Non-Linearity Parameter (B/A)-1 = $\{ 2 + [\frac{0.98 \cdot 10^4}{U}] \}$
- ❖ Non-Linearity Parameter (B/A)-2 = $\{ -0.5 + [\frac{1.2 \cdot 10^4}{U}] \}$

Isothermal Compressibility values have been computed using the McGowan's (McGowan's, 1969) Expression, using the arbitrary constant in the denominator of McGowan's expression by a temperature term. Pandey et al. (Pandey et al., 1994) suggested a relation for the evaluation of isothermal compressibility. Furthermore, Non-linearity parameter (B/A) values have been computed using the Hartmann-Balizer (Hartmann, 1979) and Ballou (Ballou et al. 1966) expression.

IV. RESULT AND DISCUSSION

A. Ultrasonic Velocity

In the present work ultrasonic velocity of pure water has been measured at 288.15K temperature and the observed data tabulated in the Table I. Comparison of observed data with literature data reported for water indicated that our results are in assent with the literature data.(Greenspan and Tschiegg, 1957) The ultrasonic velocity (U) of fertilizer: Ammonium Sulfate of varying concentrations (0.02-0.2 mol/kg) in 0.5M solution of both the saline salts solvents: NaCl and MgCl₂ measured at 288.15K temperature. The observed data of ultrasonic velocity increases with increase in concentration is shown in Fig. 1. Temperature and concentration affects 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 salts. During the compression cycle of the ultrasonic wave, hydrogen atom are pushed closed

ensuring in a partially irreversible breaking of hydrogen bonds due to the absorption of energy. The fertilizer molecule form more compact structure with saline salt molecules. This functions as a material medium for sound waves. (Kumar, 2012)

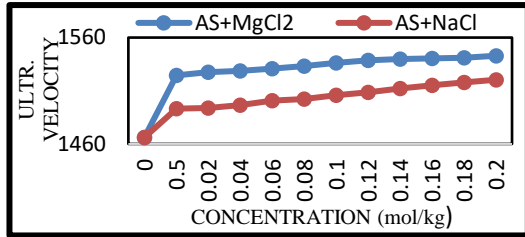


Fig. 1. Ultrasonic versus concentration at 288.15K temperature.

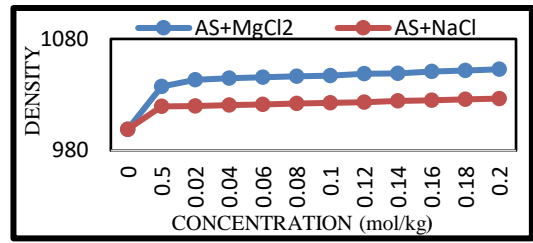


Fig. 2. Density versus concentration at 288.15K temperature.

Table III: The values of Ultrasonic Velocity, Density and Adiabatic Compressibility, as a function of concentration of System (Ammonium Sulfate + 0.5M aq. Solution of (NaCl/MgCl₂) at temperature 288.15K.

Conc. (mol·kg ⁻¹)	T=288.15K					
	U (m/s)		ρ (Kg/m ³)		β*10 ⁻¹⁰ (m ² N ⁻¹)	
	NaCl	MgCl ₂	NaCl	MgCl ₂	NaCl	MgCl ₂
0.00	1466.032	1466.032	0999.100	0999.100	4.66	4.66
0.5M	1493.123	1524.418	1019.700	1037.350	4.40	4.15
0.02	1493.82	1527.372	1020.020	1043.238	4.39	4.11
0.04	1496.658	1528.557	1020.869	1044.752	4.37	4.10
0.06	1500.649	1530.932	1021.234	1045.601	4.35	4.08
0.08	1502.366	1533.112	1022.056	1046.665	4.33	4.06
0.10	1505.812	1536.304	1022.894	1047.105	4.31	4.05
0.12	1508.695	1538.704	1023.444	1048.681	4.29	4.03
0.14	1512.171	1539.907	1024.395	1049.233	4.27	4.02
0.16	1515.079	1540.509	1024.998	1050.962	4.25	4.01
0.18	1517.999	1541.072	1025.894	1051.781	4.23	4.00
0.2	1520.343	1542.922	1026.583	1052.814	4.21	3.99

B. Density

Density of pure water has been measured at 288.15K temperature and the observed data tabulated in the Table I. After Comparison of observed data with literature data reported for water indicated that our results are shows well agreement with the literature data. (Chauhan and Kumar, 2014; Naseem and Jamal, 2013) As density is a measure of compactness in matter within the substance and is closely related to packing of materials in the system and hence different material possess different densities. By increasing pressure on material or substance one can increase the density while increase in temperature results in decrease in density of material or substance. The density (ρ) of both the systems (as shown in Fig. 2), increases with increase in concentration due to improve in compactness or structure of solvent by the addition of solute molecules. This indicates association occurs between solute and solvent molecules. (Malasane, 2013) The increase in density results increase in the molar volume indicating the association in the components of the constituent molecules and confirms the structural rearrangement.

C. Adiabatic Compressibility

Physico-chemical 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 increase in concentration. Because, as water is polar solvent and when salts and fertilizer mixed, the well intermolecular interaction occurred, resulting in close packing of molecules. The decrease values of adiabatic compressibility shown in Fig. 3 Indicate the strong association of fertilize and saline salts molecules. The compressibility of the solvent is higher than that of solution and decreases with increase in concentration of the solution. (Endo, 1973)

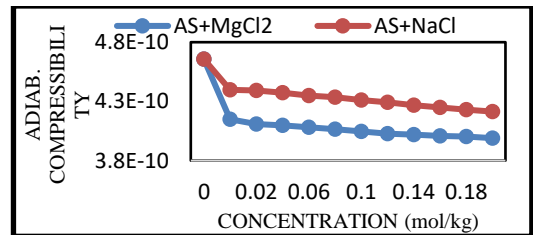


Fig. 3. Adiabatic compressibility versus concentration at 288.15K temperature.

Table IV: The values of and Relative change in Adiabatic Compressibility, Intermolecular Free Length and Acoustic Impedance as a function of concentration of System (Ammonium Sulfate + 0.5M aq. Solution of (NaCl/MgCl₂) at temperature 288.15K.

Conc. (mol·kg ⁻¹)	T=288.15K					
	Δβ/β		L _r *10 ⁻¹¹ (m)		Z	
	NaCl	MgCl ₂	NaCl	MgCl ₂	NaCl	MgCl ₂
0.00	-0.0043	-0.0043	4.36	4.36	1464713	1464713
0.5M	-0.0065	-0.0065	4.24	4.11	1522538	1581355
0.02	-0.0087	-0.0087	4.23	4.09	1523726	1593412
0.04	-0.0109	-0.0109	4.22	4.09	1527891	1596963
0.06	-0.0130	-0.0130	4.21	4.08	1532513	1600744
0.08	-0.0130	-0.0130	4.20	4.07	1535502	1604655
0.10	-0.0153	-0.0153	4.19	4.06	1540286	1608671
0.12	-0.0175	-0.0175	4.18	4.05	1544065	1613609
0.14	-0.0197	-0.0197	4.17	4.05	1549060	1615721
0.16	-0.0219	-0.0219	4.16	4.04	1552953	1619017
0.18	-0.1009	-0.1633	4.15	4.04	1557306	1620869
0.20	-0.1051	-0.1672	4.15	4.03	1560758	1624410

D. Relative Change in Adiabatic Compressibility

After calculating and plotting the graph of relative change in adiabatic compressibility against concentration as shown in Fig. 4 it is found that the negative values of ' $\Delta\beta/\beta$ ' is due to the solute-solvent interaction. Such an increase in ' $\Delta\beta/\beta$ ' with increase in concentration may be attributed to an increase in the cohesive forces in solution. (Sumanthi and Varalakshmi, 2010) The negatively increase in ' $\Delta\beta/\beta$ ' values confirms the negatively increase of bulk modulus values with concentration indicates that the hydrogen bonding between the unlike components in the solution increases. (Iqbal and Venrall, 1989)

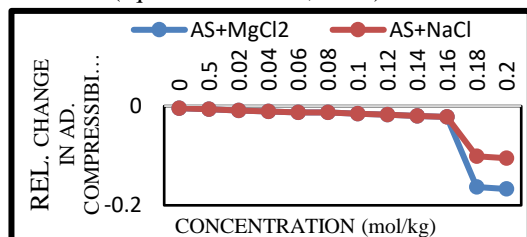


Fig. 4. Relative change in adiabatic compressibility versus concentration at 288.15K temperature.

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. (Thirumaran and Inbum, 2011) intermolecular free length is the major factor in determining the existence of inter or intra molecular interactions among the solute and solvent molecules due to which structural rearrangement is affected. In the current work, using the sound velocity and density data the intermolecular free length calculated with the help of Jacobson's temperature dependent constant. Variation of free length is shown in Fig. 5. It is observed that the free length decreases with increase in concentration of fertilizer in saline solution, shows a significant interaction among the fertilizer and electrolyte solution. Among both the saline salts (NaCl and $MgCl_2$) intermolecular free length values are found low in water, while in the case of electrolyte solutions, it is found low $MgCl_2$ indicating strong intermolecular interaction of fertilizer with $MgCl_2$. The observed order of variation of intermolecular free length (L_f) in water as well as in salt solution is: $NaCl > MgCl_2 > H_2O$

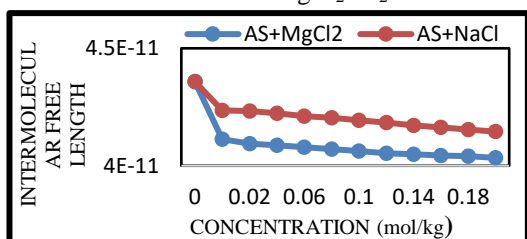


Fig. 5. Intermolecular free length versus concentration at 288.15K temperature.

F. Acoustic Impedance

The values of acoustic impedance for fertilizer: Ammonium Sulfate of different weight fraction viz. 0.02-0.2mol/kg in 0.5M solution of aqueous saline salt solutions of NaCl and $MgCl_2$ were calculated and tabulated in Table IV respectively. It is observed that the acoustic impedance (Z) values of Ammonium Sulfate fertilizer increases with increase in concentration of fertilizer in the both 0.5M aqueous electrolyte solutions and the values centered around 1Rayal as shown in Fig. 6. The increase in impedance values supports to the effective solute-solvent interactions completed through hydrogen bonding. (Nithiyathan and Palanippan, 2012) The increase in the values of acoustic impedance with increase in weight fraction of fertilizer in both electrolyte solutions means the distance between the molecules in the mixture decreases and thereby increasing the potential energy of the interaction between the molecules which leads to observed increase in the value of ultrasonic velocity and decrease in the vales of intermolecular free length. The order of variation of acoustic impedance (Z) in water as well as in salt solution is:

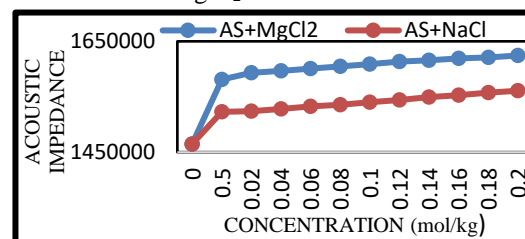
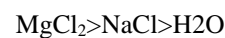


Fig. 6. Acoustic Impedance versus concentration at 288.15K temperature.

G. Relative Association

Relative association (R_A) is depend upon two factors: (1) The breaking of solvent structure on addition of solute to it and (2) the salvation of solutes that are simultaneously present. As shown in Fig. 7, the increase of ' R_A ' with concentration suggests that close association of component of molecules and there exist intermolecular interactions. (Idrees et al., 2003; Mehra and Vats, 2010) Hence, observed order of increasing relative association of Ammonium Sulfate fertilizer in water as well as in both (NaCl and $MgCl_2$) electrolyte solution is: $H_2O < NaCl < MgCl_2$

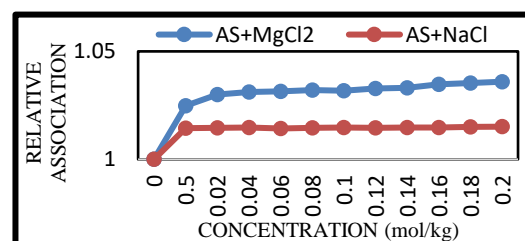


Fig. 7. Relative association versus concentration at 288.15K temperature.

Table V: The values of Relative Association and Isothermal Compressibility (k_{T1}) & (k_{T2}) as a function of concentration of System (Ammonium Sulfate + 0.5M aq. Solution of (NaCl/MgCl₂) at temperature 288.15K.

Conc. (mol·kg ⁻¹)	T=288.15K					
	R _A		(k _{T1} *10 ⁻¹¹) (m ² N ⁻¹)		(k _{T2} *10 ⁻¹¹) (m ² N ⁻¹)	
	NaCl	MgCl ₂	NaCl	MgCl ₂	NaCl	MgCl ₂
0.00	1	1	6.19	6.19	6.42	6.42
0.5M	1.01441	1.02486	5.76	5.35	6.15	5.87
0.02	1.01457	1.03001	5.75	5.29	6.14	5.83
0.04	1.01477	1.03124	5.72	5.27	6.12	5.82
0.06	1.01423	1.03154	5.68	5.24	6.08	5.80
0.08	1.01466	1.03210	5.66	5.22	6.07	5.78
0.10	1.01472	1.03182	5.62	5.19	6.04	5.76
0.12	1.01462	1.03283	5.59	5.16	6.02	5.74
0.14	1.01478	1.03311	5.56	5.15	5.99	5.73
0.16	1.01473	1.03468	5.53	5.13	5.96	5.72
0.18	1.01496	1.03536	5.50	5.12	5.94	5.71
0.20	1.01512	1.03596	5.47	5.1	5.92	5.7

H. Isothermal Compressibility

The overall trends in the isothermal compressibility (k_{T1} and k_{T2}) are as shown in Fig. 8 and Fig. 9. It has been found to be decreasing with increase in concentration of Ammonium Sulfate fertilizer in water as well as in aqueous solution of NaCl and MgCl₂ of 0.5M. The decrease in 'k_T' values with increase in concentration of fertilizer seems to be the result of corresponding decrease in free volume. (Millero, 1969) As the weight fraction of fertilizer increases in the electrolyte solutions, the large proportion of the water molecules are electro-stricted and hence the amount of bulk water decreases causing the compressibility to decrease.

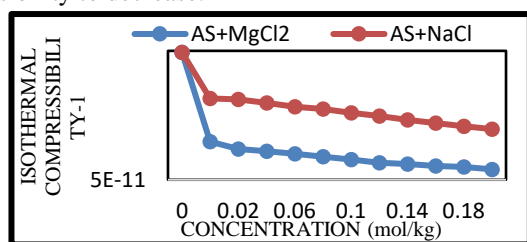


Fig. 8. Isothermal compressibility-1 versus concentration at 288.15K temperature.

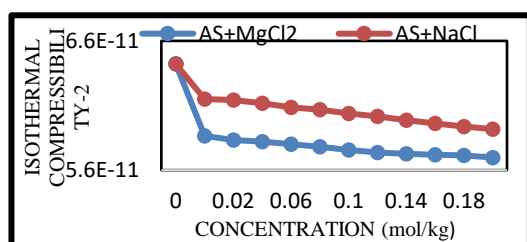


Fig. 9. Isothermal compressibility-2 versus concentration at 288.15K temperature.

I. Heat Capacity Ratio

Fig. 10 shows the variation of specific heat ratio of varying weight fraction (0.02M-0.2M) of fertilizer: AS in water and 0.5M aqueous solution of NaCl and MgCl₂ solution at 288.15K temperature. The heat capacity ratio (γ) is constantly decreasing, which throw light on the fact that specific heat at constant volume is decreasing constantly with increasing concentration.

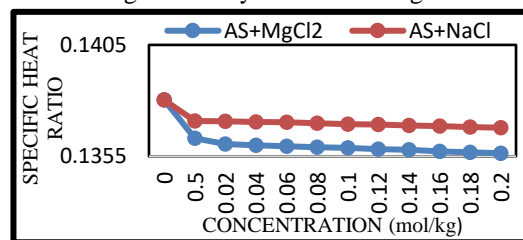


Fig. 10. Specific heat ratio versus concentration at 288.15K temperature.

Table VI: The values of Heat Capacity Ratio and Relaxation Strength as a function of concentration of System (Ammonium Sulfate + 0.5M aq. Solution of (NaCl/MgCl₂) at temperature 288.15K.

Conc. (mol·kg ⁻¹)	T=288.15K			
	γ (K ^{4/9}) ⁻¹ (kg ^{1/3} m ⁻¹) ⁻¹		r	
	NaCl	MgCl ₂	NaCl	MgCl ₂
0.00	0.138027	0.138027	0.160449	0.160449
0.5M	0.137091	0.136309	0.129134	0.092246
0.02	0.137077	0.136052	0.128321	0.088725
0.04	0.137038	0.135986	0.125006	0.087310
0.06	0.137022	0.135949	0.120333	0.084472
0.08	0.136985	0.135903	0.118319	0.081862
0.10	0.136947	0.135884	0.114270	0.078035
0.12	0.136923	0.135816	0.110875	0.075152
0.14	0.136881	0.135792	0.106773	0.073706
0.16	0.136854	0.135718	0.103334	0.072981
0.18	0.136814	0.135683	0.099875	0.072304
0.20	0.1367837	0.135638	0.097093	0.070075

J. Relaxation Strength

Relaxation strength is totally depends on the factor $[1 - \frac{U}{U_{\infty}}]$. Here 'U' be the ultrasonic velocity of solution and 'U_∞' is constant, has value 1600 m/sec. the decrease in values of relaxation strength with increase in concentration indicates solute- solvent interaction in the system (shown in Fig. 11). Which suggest the greater association between fertilizer and saline salts. (Baluja and Karia, 2000)

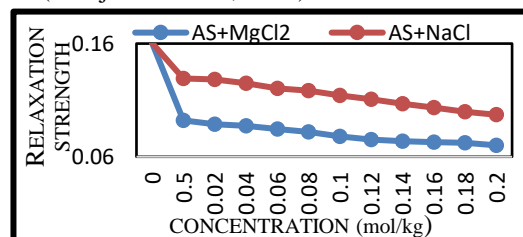


Fig. 11. Relaxation strength versus concentration at 288.15K temperature.

K. Non-linear Parameter

Non-linear parameter (B/A) obtain by Hartmann-Balizer and Ballou is related to the internal pressure, hardness, intermolecular potential, molecular structure and molecular interaction of liquid. Fig. 12 and Fig. 13 shows the non-linearity parameter for both the systems as a function of concentration at 288.15K temperature.(Joshi et al., 2017) The decreasing trends of both these parameters exhibits the interaction between the components of solute and solvent is stronger at higher concentration while mixing. Hence the accuracy of both the methods limits the usefulness of direct application of these methods to fluid mixture investigation. (Pandey et al., 2006; Sharma, 1983)

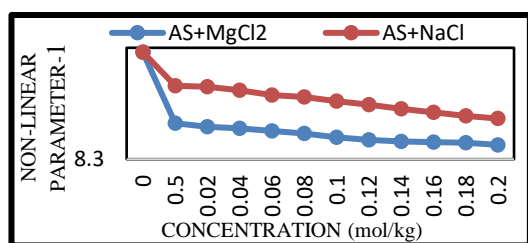


Fig. 12. Non-linearity parameter-1 versus concentration at 288.15K temperature.

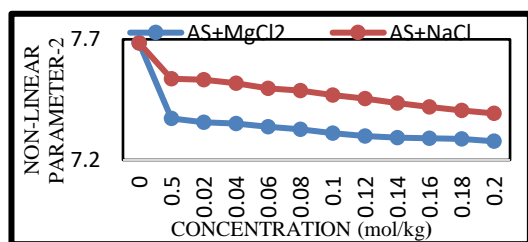


Fig. 13. Non-linearity parameter-2 versus concentration at 288.15K temperature.

Table VII: The values of Non-Linearity Parameter (B/A)₁ and (B/A)₂ as a function of concentration of System (Ammonium Sulfate + 0.5M aq. Solution of (NaCl/MgCl₂) at temperature 288.15K.

Conc. (mol·kg ⁻¹)	T=288.15K			
	(B/A) ₁ (m ⁻¹ s)		(B/A) ₂ (m ⁻¹ s)	
	NaCl	MgCl ₂	NaCl	MgCl ₂
0.00	8.684711	8.684711	7.68536	7.68536
0.5M	8.563424	8.428683	7.536846	7.371857
0.02	8.560362	8.41625	7.533096	7.356632
0.04	8.547922	8.411275	7.517864	7.350541
0.06	8.530508	8.401329	7.49654	7.338363
0.08	8.523044	8.392227	7.487401	7.327217
0.10	8.508117	8.378946	7.469122	7.310954
0.12	8.49568	8.368996	7.453894	7.298771
0.14	8.480749	8.364021	7.43561	7.292678
0.16	8.46831	8.361534	7.420379	7.289633

0.18	8.455867	8.359212	7.405144	7.28679
0.2	8.445914	8.351585	7.392956	7.277451

CONCLUSION

The various volumetric and acoustical parameters determined by using the measured values of density and ultrasonic velocity of Ammonium Sulfate solutions in both electrolyte solution (NaCl and MgCl₂). All parameters used to investigate the intermolecular interactions between the Ammonium Sulfate fertilizer molecules and saline salts. Values of intermolecular free length calculated from adiabatic compressibility data, which is positive and decrease with increasing weight fraction of fertilizer. Furthermore, acoustic impedance of fertilizer in both saline salts becomes positive and centered around unity with increasing weight fraction of fertilizer indicating solute-solute interaction is replaced by solute-solvent interaction. In the light of above observations and discussions, it may be further 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 from the rest acoustical and volumetric parameters it is concluded that H-bonding interaction is strong at higher concentration. Moreover, the values of density, relative association and compressibility for Ammonium 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.

CONFLICTS OF INTEREST

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

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