Comparative Study On Hydration Properties Of Ammonium Sulphate With Potassium Nitrate And Ammonium Sulphate With Sodium Nitrate Solutions At 303k

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Abstract - Human cultivate plants mainly for food either for themselves or for livestock. The soil fertility status is gradually decreased due to continuous growing of crops. To keep the soil productive, it is essential to apply macro and micronutrients through integrated approach. Plants take up nutrients continuously. It is beneficial to provide them balanced nutrients throughout their growth. Nitrogen increases vegetative growth and produces good quality foliage by promoting the carbohydrate synthesis and encouraging succulence. The comparative study on hydration properties has been made to elucidate the interionic interactions of ammonium sulphate with potassium nitrate solution (AS+PN) and ammonium sulphate with sodium nitrate (AS+SN). The concentration of ammonium sulphate is fixed as 0.3 mole for both the systems. The ultrasonic velocity, density, and viscosity of nitrogenous fertilizer solutions were experimentally measured at different molalities at 303K. From the measured experimental datas, hydration parameters such as molal hydration number (n_h'), apparent molal compressibility (ϕ_k), apparent molal volume (ϕ_v), molar solvated volume (ϕ_s), limiting apparent molal compressibility (ϕ_k^o), limiting apparent molal volume (ϕ_v^o), their constants (S_k and S_v) and viscosity B-coefficient were calculated. From the hydration parameters, it was noticed that more molecular association is takes place in ammonium sulphate with potassium nitrate solution than ammonium sulphate with sodium nitrate solution. While comparing AS+PN and AS+SN mixed fertilizer systems, the results revealed that the strong molecular association takes place in AS+PN fertilizer than AS+SN solution.

Index Terms - Hydration number, apparent molal compressibility, apparent molal volume, molar solvated volume, viscosity B coefficient.

I.INTRODUCTION

Nitrogen increases deep green colour in plants and the size of the cell and makes the cell wall thinner. Nitrogen increases the proportion of water and decreases calcium content in plant tissues. It helps in seed formation and increases the feed value of crops. Nitrogen fertilized crops can utilize more phosphorus, potash and calcium which is known as synergistic effect. It is due to the fact that nitrogen fertilization increases the cation exchange capacity of plant roots and therefore other nutrient ions are absorbed in larger amount[1].

In the recent years, ultrasonic studies are extensively used for characterizing the thermodynamic properties and to predict the solute-solute, solute-solvent and ion-solvent interactions in aqueous as well as non-aqueous and mixed medium. The velocity of sound is used to give information about the bonding between the molecules and formation of complexes at different temperatures through various interactions[2]. The investigation based on the behaviour of propagation of ultrasonic waves in fertilizer system is now well established as an effective means to examine certain physical properties of the materials. From the measured values, solvation parameters are evaluated. Solvation parameters are used to determine the strength of solute-solute, solute-solvent and ionic interaction in fertilizer solutions.

II. MATERIALS AND METHODS

The present study was carried out using AR grade chemicals. Double distilled water was used for the preparation of solutions. A special thermostatic water bath arrangement was used for ultrasonic velocity, density and viscosity measurements. Ultrasonic interferometer (Mittal Enterprises, model F-81D) with an accuracy of 0.5% and the frequency of 2MHz was used in the present work for the measurement of ultrasonic velocity of solutions. Densities and viscosities of the solution were measured by relative method.

III. RESULTS AND DISCUSSIONS

HYDRATION NUMBER

The hydration number is a measure of number of water molecules that get attached with each ion at a time during the process of interaction. Passynski[3] has taken consideration of the adiabatic compressibility of the solute and the solvent for deriving the hydration number and Barnatt[4] has accounted for the solution volume for the same. Assuming the compressibility of the solution to be mainly due to the free solvent molecules, the methodology of computing solvation number has been reported earlier[5-8].

As every solvent has its characteristic structure, its molecules are bound more or less strongly to the solute molecule in the course of hydration. Also the hydration has a marked effect on the structure of the surrounding solvent. A solute molecule in solution surrounded by one or two sheaths of bound solvent molecules very near to the ion. The comparative study on hydration properties has been made to elucidate the interionic interactions of ammonium sulphate with potassium nitrate solution (AS+PN) and ammonium sulphate with sodium nitrate (AS+SN). On comparing these two systems, it is found that ammonium sulphate with potassium nitrate solution show a positive hydration number which indicates an appreciable solvation of solutes. This is an added support not only for the structure promoting nature of potassium nitrate but also for the presence of an appreciable dipole-dipole interaction between solute and water molecules. This also suggests that the compressibility of the solution is less than that of the solvent. As a result solutes will gain mobility and have more probability of contacting solvent molecules[9]. This may enhance the interaction between solute and solvent molecules[10].

The decreasing values of hydration number at higher concentration in the two systems shows the strength of interaction gets weakened between solute and solvent molecules[11]. The decreasing solvation number with increase in concentration may be due to the lack of solvent molecules surrounding the ions or occurrence of ion pairing in this solution, but however it increases the ion-ion interaction in the solutions. There is a regular decrease in solvation number at higher concentrations indicating the decrease in the size of the secondary sheath of solvation with increase in concentration in both the systems.

In ammonium sulphate with sodium nitrate solution, negative hydration number is observed at lower concentration and it becomes positive at higher concentration. Negative solvation number with molality was reported by many researchers[12-13]. The variation of molal hydration number with concentration is shown in figure (1) and tabulated in tables 1 and 2. It may be pointed out that the maximum solvation number is obtained at specific concentration in both system and the ion-solvent interaction is strong at that concentration. From the magnitude of n_h' it can be concluded that there is a stronger molecular association is found in AS+PN mixed fertilizer solution than AS+SN mixed fertilizer solution.

APPARENT MOLAL COMPRESSIBILITY (ϕ_K)

The variations of ϕ_k with concentration for both systems are represented graphically in figure (2). The negative values of apparent molal compressibility indicate the hydrophilic interactions occurring in these systems. Since, more number of water molecules is available at lower concentration of solution, the chances for the penetration of solute molecules into the solvent molecules are highly favoured. The negative values of ϕ_k indicating the ionic interaction occurring in these solutions, which also indicate that the strengthening of ion-solvent interaction in AS+PN solution.

ϕ_k is a function of m and is obtained by Gucker[14] from Debye Huckel theory[15] and is given by

$$\phi_k = \phi_k^o + S_k m^{1/2} \quad \text{.....(1)}$$

where ϕ_k^0 is the limiting apparent molal compressibility at infinite dilution and S_k is a constant. ϕ_k^0 and S_k of equation (1) have been evaluated by the least square method.

The evaluated parameter limiting apparent molal compressibility (ϕ_k^0) which provides information regarding the solute-solvent interactions and its related constant deals with the ion-ion interactions in the solution which are systematically tabulated in table (3). It is observed that the values are positive in both mixed fertilizer solutions. Appreciable positive values of ϕ_k^0 for both the systems suggest that the existence of solute–solvent interactions. From the magnitude, it is concluded that AS+PN stronger in molecular association than AS+SN as it is more compressed. S_k values are negative in both the systems. The negative values of S_k indicates the weakening of ion–ion interactions in the solution[16].

APPARENT MOLAL VOLUME (ϕ_V)

Apparent molal volume and apparent molal compressibility have been proven to be a very useful tool in elucidating the structural interactions occurring in solution. The concentration dependence of apparent molal volume of the solutions can be used to study ion-ion interactions, so the volumes of solutions have been proven to be of scientific interest. The values of ϕ_v of ammonium sulphate with potassium nitrate solution are greater than that of ammonium sulphate with sodium nitrate solution which is graphically represented in figure 3. The higher values of ϕ_v suggest that the strong solute-solvent interaction occurring in the solution[17]. This variation represents the existence of strong ionic bonding between solute and solvent molecules of AS+PN solutions compared to AS+SN mixed fertilizer solutions. These results suggest that a large portion of water molecules exert electrostatic force which attracts the neighbouring molecules decreasing effective volume of water.

The apparent molal volume has been found to differ with concentration according to Masson's empirical relation[18] as,

$$\phi_v = \phi_v^o + S_v m^{1/2} \quad \text{.....(2)}$$

where ϕ_v^0 is the limiting apparent molal volume at infinite dilution and S_v is a constant and these value were determined by least square method.

The volume behaviour of a solute at infinite dilution is satisfactorily represented by ϕ_v^0 which is independent of the solute–solute interactions and provides information concerning solute–solvent interactions. The values of ϕ_v^0 are positive in both the systems (table 3). These values of ϕ_v^0 which are higher in AS+PN solution compared to AS+SN fertilizer solution indicating a strong ion–solvent interactions occurring in this system. The S_v values are found to be negative for both the systems. The negative values of S_v suggest the presence of ion-ion interaction occurring in both the systems.

MOLAR SOLVATED VOLUME (ϕ_S)

$$\phi_s = \phi_v + n_h V_1 \qquad \text{....(3)}$$

Molar solvated volume has a culmative effect due to ϕ_v and $n_h v_1$ as seen from the equation (3). As the concentration increases ϕ_s decreases even though ϕ_v increases, this is because it is mainly detailed by hydration number rather than by ϕ_v. Figure (4) shows the molar solvated volume value is higher in AS+PN solution compared to AS+SN solution. From this it is confirmed that molecular association is greater in AS+PN solution than in AS+SN solution.

VISCOSITY B-COEFFICIENT

The viscosity A and B coefficients of mixed fertilizer solutions were calculated from the Jones-Dole equation[19].

$$\frac{\eta}{\eta_0} = 1 + Am^{1/2} + Bm \qquad \text{..... (4)}$$

where, η and η_0 are the viscosities of the solution and solvent respectively and m is the molal concentration of the solute. A is called the Falkenhagen coefficient which characterises the ionic interaction and B is the Jones-Dole or viscosity B-coefficient which depends on the size of the solute and the nature of solute-solvent interactions.

Viscosity is also an important parameter in understanding the structure and molecular interaction occurring in the solutions and its variation is attributed to the structural changes. Table 3 shows that the value of A is negative and B-coefficient is positive in AS+PN mixed fertilizer solution. A is a measure of ionic interaction and it is evident that there is a weak ion-ion interaction. B-coefficient is also known as measure of order or disorder introduced by the solute into the solvent. It is also a measure of solute-solvent interaction and the relative size of the solute and solvent molecules. The negative value of B-coefficient is found in AS+SN fertilizer solution, which indicates the existence of weak solute-solvent interaction compared to AS+PN solution.

IV. CONCLUSION

A detailed analysis of hydration properties has been carried out for AS+PN and AS+SN mixed fertilizer solutions. The nature and strength of intermolecular interactions were discussed. In AS+PN solution, the positive value of B coefficient supports the behaviour of ϕ_v^0 and S_v shows the dominance of solute-solvent interactions over solute-solute interactions.

Table 1 Molal hydration number (n_h'), apparent molal compressibility (ϕ_k), apparent molal volume (ϕ_v), and molar solvated volume (ϕ_s) of 0.3m of ammonium sulphate + potassium nitrate + water at 303K

Concentration (mole)	Molal hydration number (n_h')	Apparent molal compressibility (ϕ_k) 10^{-8} m ^{2} N^{-1}	Apparent molal volume (ϕ_v) m^3 mole^{-1}	Molar solvated volume (ϕ_s) m^{3}mole^{-1}
0.1	0.7672	4.1311	114.1546	13.8237
0.2	4.4125	-0.3783	70.3090	79.4984
0.3	6.9240	-2.7748	57.3539	124.7459
0.4	6.7149	-2.7225	54.8557	120.9779
0.5	6.5521	-2.8637	48.4937	118.0453
0.6	6.2541	-2.4052	54.2616	112.6771
0.7	5.9883	-2.2319	53.6804	107.8887

Table 2 Molal hydration number (n_h'), apparent molal compressibility (ϕ_k) apparent molal volume (ϕ_v), and molar solvated volume (ϕ_s) of 0.3m of ammonium sulphate + sodium nitrate + water at 303K

Concentration (mole)	Molal hydration number (n_h')	Apparent molal compressibility (ϕ_k) 10^{-8} m ^{2} N^{-1}	Apparent molal volume (ϕ_v) m^3 mole^{-1}	Molar solvated volume (ϕ_s) m^{3}mole^{-1}
0.1	-12.5069	13.2660	96.8605	-225.329
0.2	-0.7570	3.4682	70.5923	-13.6391
0.3	4.5110	-1.1929	52.2989	81.2724
0.4	5.5794	-2.3018	44.6170	100.5207
0.5	5.8920	-2.8135	37.8204	106.1525
0.6	5.4465	-2.3352	41.4107	98.1263
0.7	5.0956	-2.0233	42.6639	91.8042

Table 3 Limiting apparent molal volume (ϕ_v^o), limiting apparent molal compressibility (ϕ_k^o), constants S_v, S_k and viscosity A and B coefficients of Jones-Dole equation for AS+PN and AS+SN solutions at 303K

System	ϕ_v^o m^3 mol^{-1}	S_v m^{-1}N^{-1} mol^{-1}	ϕ_k^o (10^{-8}) m^2 N^{-1}	S_k (10^{-8}) m^{-1}N^{-1} mol^{-1}	Viscosity coefficient	
					A dm$^{3/2}$ mol$^{-1/2}$	B dm^3 mol^{-1}
AS+PN	127.014	-102.336	5.299	-10.881	-0.051	0.047

AS+SN	119.265	-105.256	17.331	-27.042	0.347	-0.213

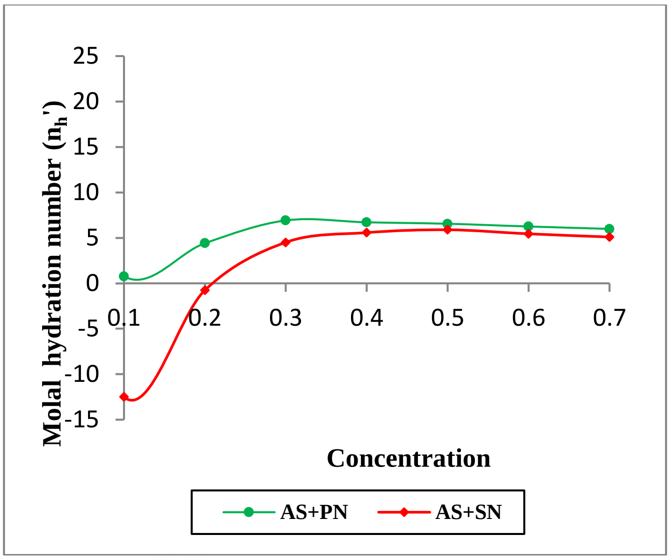

Fig 1 Molal hydration number (n_h') of AS+PN and AS+SN solutions at 303K

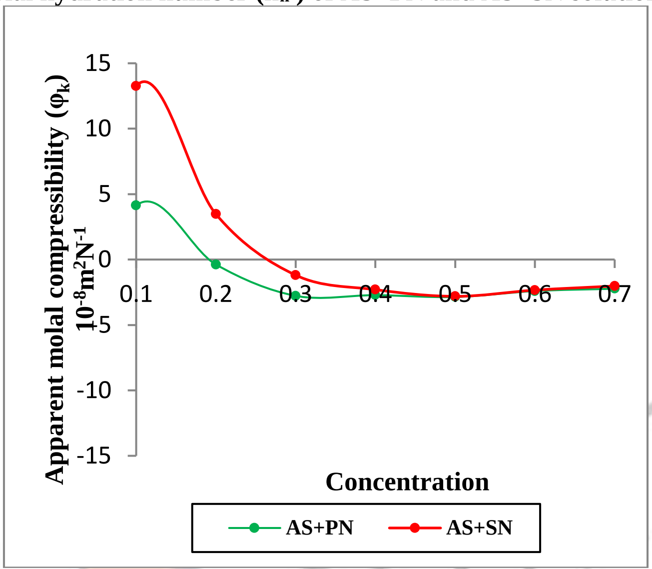

Fig 2 Apparent molal compressibility (ϕ_k) of AS+PN and AS+SN solutions at 303 K

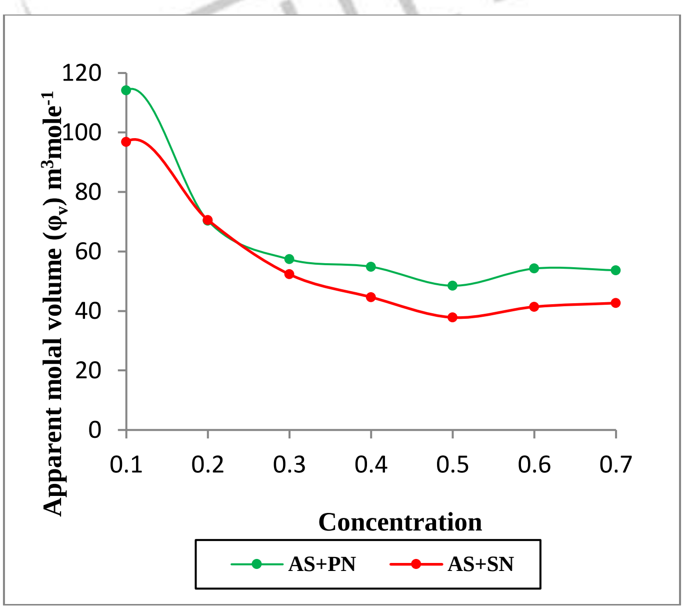

Fig 3 Apparent molal volume (ϕ_v) of AS+PN and AS+SN solutions at 303 K

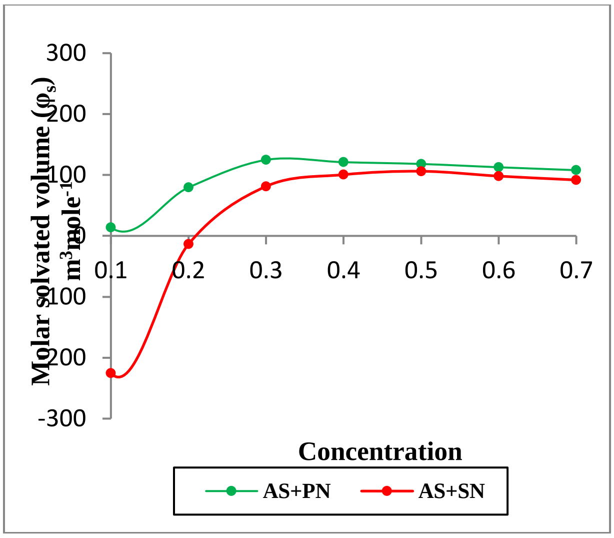

Fig 4 Molar solvated volume (ϕ_s) of AS+PN and AS+SN solutions at 303K

V. REFERENCES

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