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Ultrasonic studies on inorganic fertilizers

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Abstract:
In the present study, the ultrasonic velocity of aqueous solutions of ammonium sulphate and diammonium phosphate fertilizers has been measured in the concentration range of 0.1m to 0.6m at 303°K. The variation of ultrasonic velocity is not linear and the non-linearity of this is confirmed by adiabatic compressibility study also. The study was also extended to aqueous solution of diammonium phosphate in 0.3m ammonium sulphate to study the influence of ammonium sulphate on the nature of molecular interactions. Using the measured values of ultrasonic velocity, density, viscosity, acoustic parameters like adiabatic compressibility, intermolecular free length, acoustic impedance, relaxation time, free volume, internal pressure and solvation number have been evaluated. These parameters are used to discuss the molecular interactions of these compounds with water molecules

Keywords:

Ultrasonic velocity, viscosity, acoustical parameters, molecular interactions.

Introduction:

Ultrasonic velocity of sound waves in a medium is fundamentally related to the binding forces between the molecules. Ultrasonic velocity measurements have been employed extensively to detect and access weak and strong molecular interactions in binary mixtures. Nitrogen fertilizers promote rapid growth, chlorophyll formation and protein synthesis. Phosphorous fertilizers stimulate early root growth, hasten maturity, stimulate blooming and aids seed formation. Diammonium phosphate is an excellent source of phosphorous and nitrogen for plant nutrition. It is highly soluble and thus dissolves quickly in soil to release phosphate and ammonium. The ammonium present in DAP will be gradually converted into nitrate by soil bacteria, resulting in a subsequent drop in pH. Therefore, the rise in soil pH surrounding DAP granules is a temporary effect. This initial rise in soil pH neighbouring DAP can influence the micro site reactions of phosphate and soil organic matter. The primary use of ammonium sulphate is as a fertilizer for alkaline soils. In the soil the ammonium ion is released and forms a small amount of acid, lowering the pH balance of the soil, while contributing essential nitrogen for plant growth. There it functions to bind iron and calcium cations that are present in both well water and plant cells [1]-[2]. These considerations led as to undertake the study of fertilizers in water. The obtained results are discussed in terms of ion-solvent, solute-solute, solute-solvent interactions and transmission activity.

Experimental Details:

The chemicals used in the present study are AR quality. The solutions were prepared by dissolving known amount of substance in double distilled water, so as to make 0.1m to 0.6m concentration. The 0.3m of ammonium sulphate is mixed with different quantities of DAP. The ultrasonic velocity was measured using a single crystal variable path interferometer working at 2MHz frequency. The accuracy of ultrasonic velocity determination in the solution is $\pm$0.5%. The densities were measured using specific gravity bottles and digital electronic balance with an accuracy of $\pm$0.001Kg/m^3 the viscosity was measured using Ostwald's viscometer with an accuracy of 0.1%. The temperature was maintained constant at 303°K.

Computational methods:

The various physical parameters were calculated from the measured values of ultrasonic velocity (U), viscosity (η) and density (ρ) of aqueous fertilizer solutions using the standard formula,

(i) Adiabatic compressibility

$$\beta = 1/(U^2 * \rho)\ Kg^{-1}ms^2$$

(ii) Inter molecular free length

$$L_f = K*(\beta)^{1/2}\ A^\circ$$

(iii) Free volume

$$V_f = ((U* M_{eff}) / (\eta*K))^{3/2}\ m^3$$

(iv) Internal pressure

$$\pi_i = bRT* (K\eta/U)^{1/2} *((\rho)^{2/3}/(M_{eff})^{7/6})\ 10^{12}\ Pascal$$

(v) Solvation number

$S_n = {ns}/{ni} * (1- (\beta / \beta_0))$

(vi) Acoustic impedance

$Z = (U* \rho)$ Kg $m^{-2}s^{-1}$

(vii) Relaxation time

$\tau = (4/3)* \beta* \eta$ sec

Where, T- absolute temperature, η – viscosity,
U – Ultrasonic velocity,
M_{eff} – effective molecular weight of the solution.
n_s and n_i – number of moles of a solvent and solute in the solution.
β and β_0 – are the adiabatic compressibility of solution and solvent[3].

Results and Discussion

The ultrasonic velocity, density and viscosity of aqueous solutions of ammonium sulphate, diammonium phosphate, ammonium sulphate with DAP at different concentrations are measured at 303°K. Adiabatic compressibility, intermolecular free length, acoustic impedance, internal pressure, free volume and solvation number were calculated and tabulated in table (1).

In ammonium sulphate with DAP solution, the ultrasonic velocity increases with concentration, which suggest that ion-solvent interaction increases with concentration whereas nonlinear variation is noted in ammonium sulphate solution. In diammonium phosphate a solution there is a decrease in ultrasonic velocity is noted at higher concentrations is shown in fig (1). This indicates the structure-breaker nature of the solvent. It may also be true that solvent- solvent interactions bring about a hydrogen bonding between them. Usually the values of ultrasonic velocity of any system vary with increase in concentrations of the solutions. That is the hydrogen bond forming or dissociating properties has thus been correlated with change in velocity.

The figure (2) shows the variation of acoustic impedance with concentration. The acoustical impedance is reciprocal of adiabatic compressibility. The increase of acoustic impedance is an indication of strong interaction between solute and solvent molecules [4]. Certain decrease of acoustic impedance at a particular concentration may be due to the complex formation in the solution and this may be on the basis of the interaction between solute and solvent molecules [5].

The adiabatic compressibility as a function of concentration is shown in fig (3). The compressibility of solvent is higher than that of solution and decreases with increase in concentration of solution. With increase in solute concentration, their electrostatic forces cause the water structure to break and the solute surrounded water molecules are more compactly packed. This hydration affects in turn results in reducing the compressibility with increasing solute concentrations.

The intermolecular free length depends on adiabatic compressibility and shows similar behaviour to that of adiabatic compressibility and inverse to that of velocity [6]. The free length decreases with increase of concentration is observed in AS-DAP solution and is shown in fig (4). This indicates that the structural readjustment in the solution proceeds in the direction of less compressible phase or closer packing of molecules. In ammonium sulphate and DAP solutions there is a sudden increase in free length is observed at 0.5m and 0.6m respectively. This shows a loser packing of molecules or weak interaction.

With the addition of solute it may decrease or enhance the cohesive forces of the solvent and hence internal pressure decreases or increases with the immediate addition of salt in the solvent. Addition of ammonium sulphate in water decreases the cohesive forces of the solvent which is the reason for reduction in lowering of internal pressure and hence it behaves as structure breaker. The decrease of internal pressure may be due to breaking up of hydrogen bond in the solvent medium and contact ion pairing may reduce the association between ion and solvent is shown in fig (5).

The free volume of a solute at a particular temperature and pressure depends only on internal pressure of the liquid in which it is immersed. The weakening of molecular association leads to larger free volume available for molecular motion and reverse effect gives rise to smaller free volume. Thus the effect of concentration on free volume has been studied and it is found to increase with concentration in ammonium sulphate with DAP solutions is shown in fig (6). In ammonium sulphate and DAP solutions abrupt variations is noted. The decrease in free volume is due to the presence of tightly packed solvent molecules around the ions at higher concentrations. This indicates there is a significant interaction between ions and solvent molecules[7].

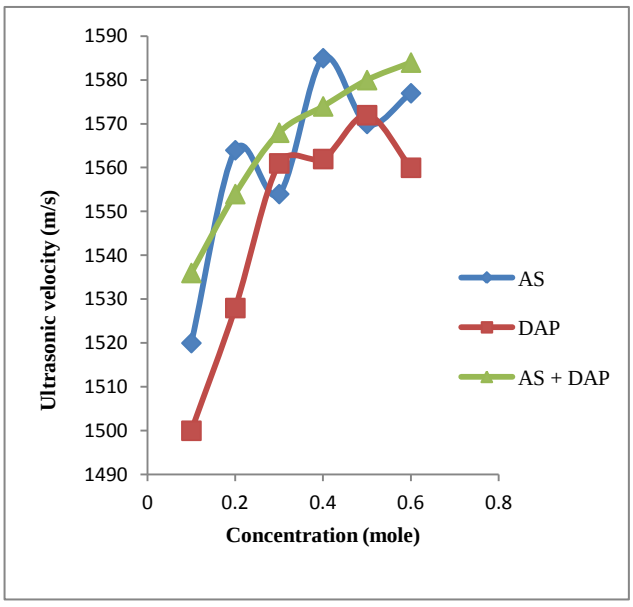
Relaxation time is the time taken for the excitation energy to appear as translational energy and it depends on temperature and impurities. Fig (7) shows variation of acoustic relaxation time with concentration. In ammonium sulphate with DAP solution, relaxation time decreases with increasing concentration. But in other two systems, these changes are not similar to adiabatic compressibility and similar to those found in viscosity. This supports the view that viscous forces play a dominant role in the relaxation processes. It is due to decreasing free space between the molecules. Those strengthen the intermolecular forces [8].

Solvation numbers reflect the dynamic situation of the ion as it moves around in the solution. Solvation number is positive in all the systems. The solvation number is increasing at lower concentrations in the solutions expect for ammonium sulphate with DAP solution. The positive solvation number of the solutions suggests that the compressibility of the solutions

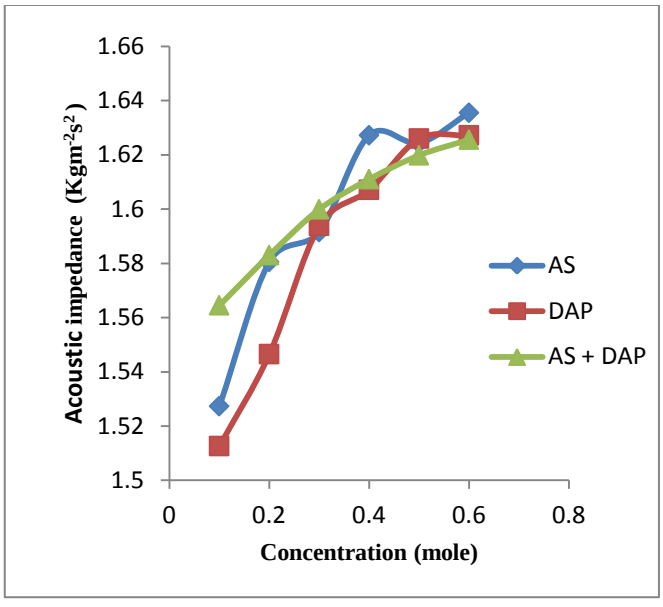
is less than that of the solvent and is shown in fig (8). Ammonium sulphate is more solvated than that of DAP and ammonium sulphate with DAP solutions.

Table 1: Ultrasonic velocity and related acoustical parameters of ammonium sulphate, DAP and ammonium sulphate with DAP

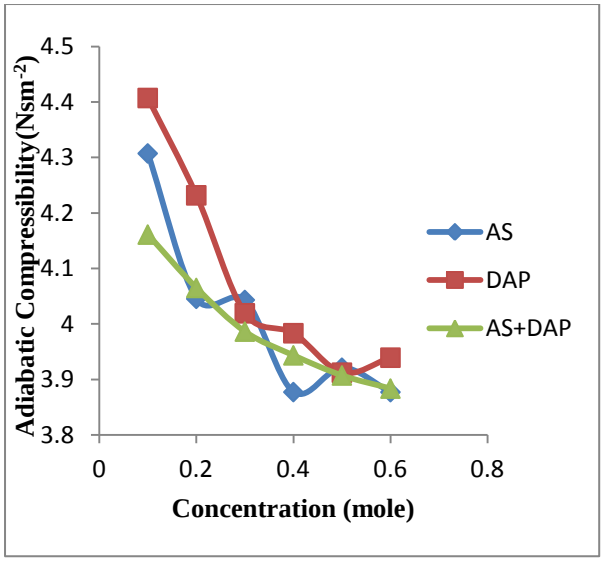
System	Con	U m/s	β (10^{10}) $Kg^{-1}ms^2$	L_f (10^{-10}) M	S_n	$\tau(10^{-10})$s	$\pi_{i(10}{}^{12})$ Pascal	V_f (10^{-3}) m^3	Z (10^6) ($Kgm^{-2}s^{-1}$)
Ammonium Sulphate	0.1	1520	4.3073	0.4150	19.090	4.6402	8.1547	0.7169	1.5273
	0.2	1564	4.0453	0.4022	25.544	4.2955	7.9061	0.7778	1.5805
	0.3	1554	4.0432	0.4021	17.113	4.6142	8.1880	0.7031	1.5915
	0.4	1585	3.8772	0.3938	17.905	4.0805	7.6992	0.8314	1.6272
	0.5	1570	3.9211	0.3960	13.252	4.8284	8.3052	0.6583	1.6243
	0.6	1577	3.8771	0.3938	11.939	4.5344	7.9888	0.7275	1.6355
DAP	0.1	1500	4.4072	0.4198	6.8986	5.1020	8.5300	0.6309	1.5126
	0.2	1528	4.2318	0.4114	14.160	4.9158	8.3747	0.6564	1.5465
	0.3	1561	4.0192	0.4009	18.090	4.6977	8.2517	0.6829	1.5938
	0.4	1562	3.9833	0.3991	14.665	4.8123	8.3221	0.6613	1.6071
	0.5	1572	3.9121	0.3956	13.471	4.9641	8.4243	0.6305	1.6260
	0.6	1560	3.9392	0.3969	10.675	5.0540	8.4457	0.6229	1.6272
Ammonium Sulphate (0.3m) + DAP	0.1	1536	4.1611	0.4079	18.471	4.8664	8.2013	0.6771	1.5645
	0.2	1554	4.0649	0.4032	4.0579	4.7043	8.0166	0.7107	1.5830
	0.3	1568	3.9862	0.3993	14.578	4.6264	7.8945	0.7297	1.5999
	0.4	1574	3.9434	0.3971	12.706	4.4277	7.6612	0.7835	1.6110
	0.5	1580	3.9071	0.3953	11.287	4.3829	7.5690	0.8015	1.6198
	0.6	1584	3.8835	0.3941	10.121	4.3647	7.4821	0.8146	1.6256



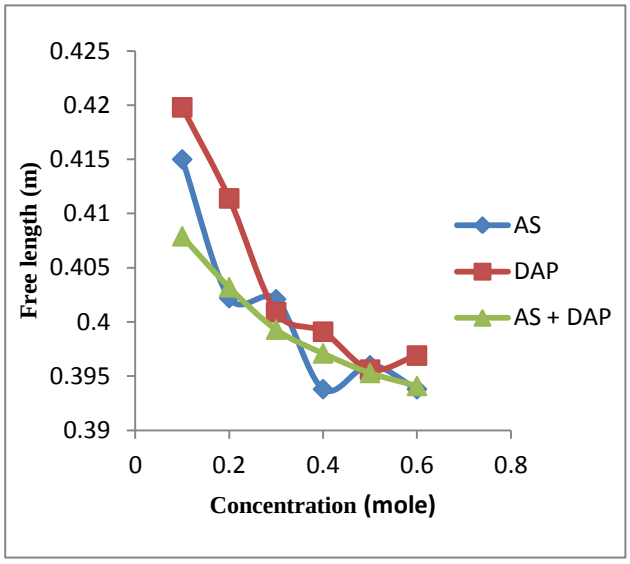
Fig(1) - Concentration (mole) vs Velocity (m/s)



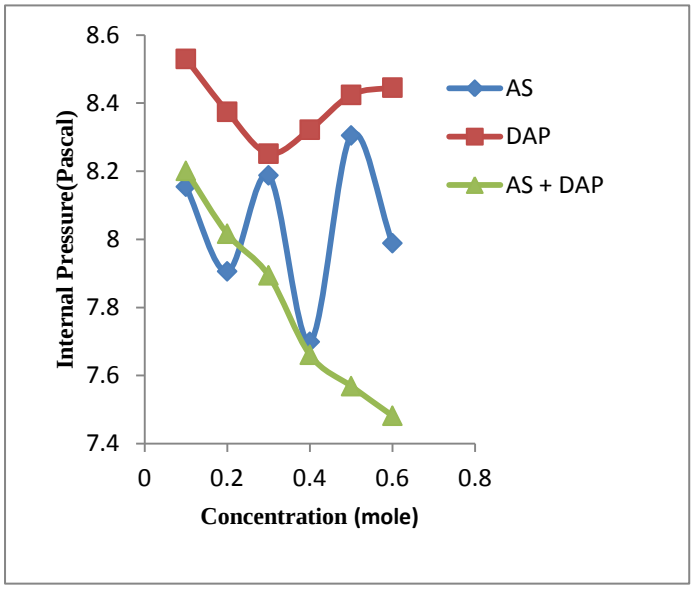
Fig(2) - Concentration (mole) vs Acoustic Impedance ($Kgm^{-2}s^{-1}$)



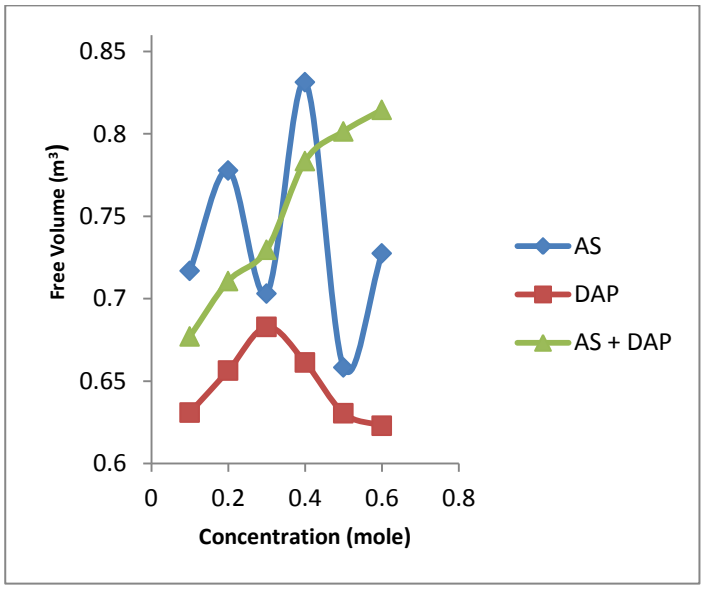
Figure(3) - Concentration (mole) vs Adiabatic Compressibility (Nsm^{-2})



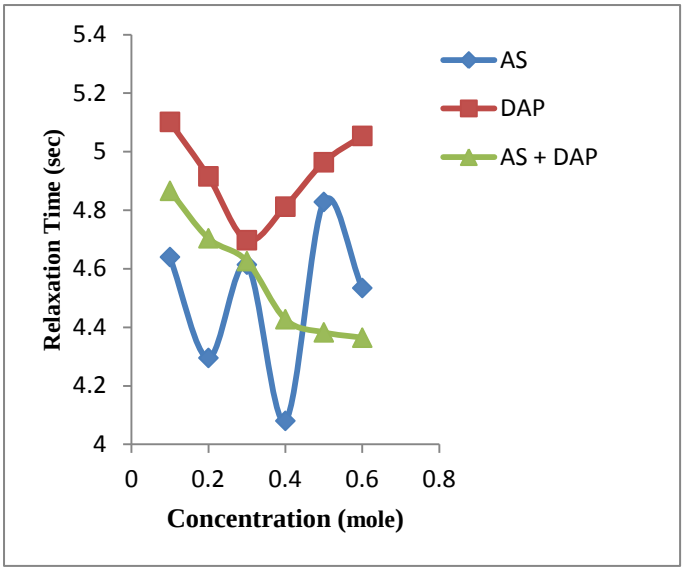
Figure(4) - Concentration (mole) vs Free Length (m)



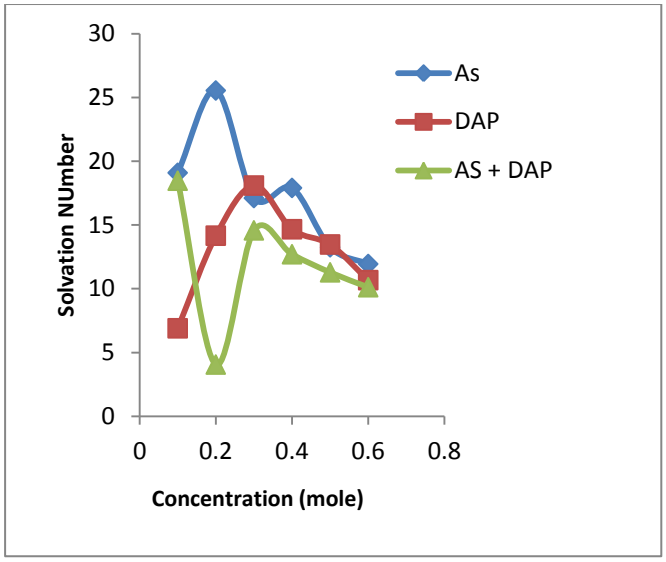
Figure(5) - Concentration (mole) vs Internal Pressure



Figure(6) - Concentration (mole) vs Free Volume (m^3)



Figure(7) - Concentration (mole) vs Relaxation Time (s)



Figure(8) - Concentration (mole) vs Solvation Number

Conclusion:

A systematic study of ammonium sulphate, DAP and ammonium sulphate with water gives information to understand the solute- solvent interactions in aqueous solutions. And eventually, by analyzing all the evaluated parameters which clearly suggest that DAP is a strong structure maker in aqueous ammonium sulphate solution. There is much scope for further studies in these systems by varying pH of the solution and temperature which may reveal more about hydrogen bonding interaction as well as other interaction existing between solute-solvent molecules. Hence it is evident that the ultrasonic velocity measurement in the given medium serves as a powerful tool to study the physico – chemical properties of that medium.

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