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Ultrasonic Analysis of Intermolecular Interaction Through Internal Pressure and Free Volume of Aqueous Fertilizer Solutions

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Abstract: Ultrasonic velocity, density and viscosity were measured for two aqueous fertilizer solutions namely Diammoniumphosphate and Monoammoniumphosphate at different concentrations and temperatures from 303^{0} K to 323^{0} K in steps of 5^{0} K. The observed experimental datas have been used to calculate thermodynamic parameters such as internal pressure, free volume, $\Delta \pi_{i}$, molar cohesive energy, and Gibb's free energy. The results are used to discuss the presence of significant interactions between the component molecules in aqueous fertilizer solutions.

Key words: Adiabatic compressibility, internal pressure, free volume, molar cohesive energy, Gibb's free energy, coefficients of internal pressure and free volume.

Introduction:

Literature survey shows that ultrasonic velocity, density, viscosity and allied thermodynamic parameters plays a key role to study the nature of intermolecular forces in liquid solutions and the physicochemical behaviour of liquid mixture can also be studied with ultrasonic study¹. Proper nutrition is essential for satisfactory crop growth and production. Efficient application of the correct types and amounts of fertilizers for the supply of the nutrients is an important part of achieving profitable yields. The investigation regarding the molecular association in aqueous fertilizer solutions is of particular interest because of their extensive use in agriculture. Diammonium phosphate is an excellent source of P and nitrogen (N) for plant nutrition. It is highly soluble and thus dissolves quickly in soil to release plant-available phosphate and ammonium. The ammonium present in DAP will be gradually converted to nitrate by soil bacteria, resulting in a subsequent drop in pH. MAP has been an important granular fertilizer for many years. It is water soluble and dissolves rapidly in soil if adequate moisture is present. Upon dissolution, the two basic components of the fertilizer separate again to release NH_4^+ and $H_2PO_4^-$. Both of these nutrients are important to sustain healthy plant growth. The pH of the solution surrounding the granule is moderately acidic, making MAP an especially desirable fertilizer in neutral and high pH soils. These applications have greatly stimulated to study the nature of interactions taking place in these systems. In view of the above mentioned importance of the systems, an attempt has been made to elucidate the molecular interactions in the aqueous fertilizer solutions at different temperatures.

Experimental:

The aqueous solutions of fertilizer materials of different concentrations were prepared using AR grade salt. The ultrasonic velocities of the solutions were measured using an ultrasonic interferometer (MittalF - 81

D) with a single crystal at a frequency of 2 MHz with an accuracy of 0.5%. The density of solutions was measured at various temperatures using 10 ml specific gravity bottles by relative method. The temperature was maintained using constant temperature bath with an accuracy of $\pm 0.1^{\circ}$ C. Ostwald's viscometer was used for viscometric studies.

Computation:

Compressibility measurements yield interesting information. They are also highly accurate. It is assumed that the bound water molecules are highly compressed by the intense field of the ion and that further compression affects only the unbound water. The adiabatic compressibility is the fractional decrease of volume per unit increase of pressure, when no heat flows in or out. Adiabatic compressibility can be determined with the measurement of density ρ and ultrasonic velocity U as

$$\beta = 1/(U^2 \rho)$$
 Kg⁻¹ ms⁻²

The internal pressure is obtained from the experimental values of ultrasonic velocity, density and viscosity using the relation,

$$\pi_{i} = bRT^{*} (K\eta/U)^{1/2} * (\rho^{2/3}/M^{7/6})$$
 N/m²

Where, b = 2 cubic packing factor, T- absolute temperature, $K= 4.28*10^9$ dimensionless temperature independent constant, R = Molar gas constant, $\eta -$ viscosity, U – ultrasonic velocity, M – effective molecular weight of the solution, ρ – density.

Free volume is defined as the average volume in which the centre of the molecules can move inside the hypothetical cell due to the repulsion of surrounding molecules. Free volume can be calculated by different methods. Suryanarayana and Kuppusamy² on the basis of dimensional analysis, obtained an expression for free volume in terms of experimentally measurable parameters like ultrasonic velocity and viscosity and is given by

 $V_f = (MU/K\eta)^{3/2}$

Change in internal pressure $\Delta \pi_i = \pi_i - \pi_o$

where π_0 – internal pressure of the solvent.

Cohesive energy is usually given as a product of internal pressure (π_i) and molar volume (V_m) (i.e),

 $MCE = \pi_i * V_m$

The Gibb's free energy is estimated from the following relation

 $\Delta G = -KT \ln (KT\tau/h)$

where K is the Boltzman's constant, T the absolute temperature, 'h' the Planck's constant and τ is the relaxation time.

Results and Discussion:

Adiabatic compressibility:

The compressibility is a macroscopic observable, which is sensitive to solute-solvent interactions. Any modifications induced by the solute on the local structure of the solvent generate changes in adiabatic compressibility of the solutions and therefore compressibility can be used to characterize the solvated properties of solute in dilute solutions³. It is the property of a substance capable of being reduced in volume by application of pressure. The plots of adiabatic compressibility versus mole fraction of both the systems (figure 1) are found to be decreased with increasing concentrations and temperatures. Decrease in adiabatic compressibility may be due to aggregation of solvent molecules around solute molecules. This indicates the existence of solute-solvent interaction⁴. Irrespective of temperatures, at a particular lower concentration, the adiabatic compressibility of MAP is found to be greater than DAP.

$$m^3$$

KJ mol⁻¹

KJ mol⁻¹



Fig1. Molality Vs adiabatic compressibility of DAP and MAP

Internal pressure and free volume:

Internal pressure is the fundamental property of liquid which provides an excellent basis for examining the solution phenomena and studying various properties of liquid state. It is a measure of change in internal energy of liquid solution as it undergoes a very small isothermal change. It is also a measure of cohesive or binding forces between the solute and solvent interactions. The internal pressure of hydrogen bonded liquids (water) is large as compared to non-hydrogen bonded liquid⁵. Free volume is a reverse trend of internal pressure. The free volume of a solute molecule at a particular temperature and pressure depends only on internal pressure of the liquid in which it is immersed. From figure (2, 3), it is observed that there is a non linear variation of internal pressure and free volume for both the systems. The increase in internal pressure is attributed to the association of solute-solvent molecules through hydrogen bonding. The decrease of internal pressure may be due to breaking up of hydrogen bond in the solvent medium and contact ion paring may reduce the association between ion and solvent. This weakening of molecular association leads to a larger free volume available for molecular motion. The decrease of V_f (increase of π_i) indicates the formation of thin or loose solvation layer.



Fig2. Molality Vs internal pressure of DAP and MAP



Fig3. Molality Vs free volume of DAP and MAP

The values of internal pressure decreases as temperature increases which may be due to reduction in cohesive energy between molecules. The internal pressure value is found to be larger for monoammonium phosphate solution and the reverse trend is observed in free volume and hence the solute-solvent interaction is stronger in MAP than DAP.

The difference in the internal pressure $\Delta \pi_i = \pi_i - \pi_o$ predicts the nature of solute. Figure (4) shows the variation of $\Delta \pi_i$ with concentration. Positive $\Delta \pi_i$ is an indication that the solute has the tendency to enhance the internal pressure of the solvent when added to it. Negative $\Delta \pi_i$ denotes that the internal pressure of the solvent is lower than that of the solvent. This may be due to the fact that the cohesive forces may get loosened perhaps by breaking hydrogen bonds in water. In the present work, it is found by observation that the change in internal pressure $\Delta \pi_i$ is found to be negative at higher temperatures in DAP and it reveals that DAP acts as a structure breaker at higher temperatures. $\Delta \pi_i$ is almost positive for all temperatures in MAP and it shows the structure making tendency of MAP and the solute-solvent attraction is predominant in MAP than DAP.



Fig 4. Molality Vs change in internal pressure of DAP and MAP

Suryanarayanan C.V. and Kuppuswamy (1981) have found that at a given temperature a general equation of the form $\pi_i = \pi_0 + Am^2 + Bm$ where π_0 is the internal pressure of the solvent, m is the molality. A and B are temperature dependent coefficients. Thus the effect of repulsive forces or cohesive forces in ion-solvent interaction is very well understood by $\Delta \pi_i$. The coefficient A is found to be positive at 323 ⁰K for MAP, at 313 ⁰ K and 318 ⁰K for DAP, whereas it is negative at all other temperatures for both the systems. The coefficient B determines the sign of $\Delta \pi_i$. It is found to be positive at all temperatures for MAP and negative at higher temperatures for DAP which confirms that MAP acts as a structure maker at all temperatures and DAP

as a structure breaker at higher temperatures. The values of coefficients A and B computed at different temperatures are given in table 3.

A similar relation holds for the free volume, $V_f = V_f(o) + Cm^2 + Dm$. Here $V_f(o)$ is the free volume of the solvent. The arbitrary coefficients C and D are dependent on temperature. The values of coefficients C and D are calculated at all temperatures and are given in table 3. From the perusal of table 3, C and D are found to be a reverse trend of A and B.

Molality	â	$ Đ_{\rm i} (10^8) $	$V_{\rm f} (10^{-8})$	Äði	MCE * 10 ⁴	ÄG * 10 ⁻²¹			
-	Kg ⁻¹ ms ⁻²	N/m^2	m 3		(KJ mol ⁻¹)	(KJ mol ⁻¹) ³			
303 ⁰ K									
0.1	4.3706	26.1868	2.1648	0.2072	4.7497	4.6561			
0.2	4.2186	26.7344	2.0199	0.7547	4.8665	4.8066			
0.3	4.0619	25.7955	2.2286	-0.1841	4.7166	4.486			
0.4	3.9990	26.2091	2.1111	0.2294	4.8077	4.6344			
0.5	3.9630	27.1414	1.8841	1.1618	5.0009	4.9650			
0.6	3.9073	26.4532	2.0188	0.4736	4.8936	4.7729			
308 ⁶ K									
0.1	4.3210	25.9550	2.3331	0.9997	4.7098	4.5670			
0.2	4.1719	24.8217	2.6273	-0.1335	4.5385	4.1960			
0.3	4.0194	25.9274	2.2947	0.9721	4.7516	4.5292			
0.4	3.9830	25.7758	2.3146	0.8205	4.745	4.5183			
0.5	3.9163	26.384	2.1458	1.4287	4.8711	4.7265			
0.6	3.8547	25.5923	2.3339	0.6370	4.7423	4.4849			
313 ⁶ K									
0.1	4.2566	23.875	3.1167	-0.1838	4.3526	3.8542			
0.2	4.0666	23.6344	3.1926	-0.4243	4.3225	3.7176			
0.3	4.0183	24.4173	2.8774	0.3584	4.4794	4.0221			
0.4	3.9767	23.0372	3.3959	-1.0216	4.2451	3.5557			
0.5	3.9203	23.3316	3.2414	-0.7271	4.3175	3.6915			
0.6	3.8413	23.5988	3.1141	-0.4600	4.3799	3.7924			
318 ⁶ K									
0.1	4.2035	23.4320	3.4453	0.1781	4.2794	3.6682			
0.2	4.0500	22.8431	3.7005	-0.4107	4.182	3.4077			
0.3	4.0137	23.0189	3.5823	-0.2349	4.2342	3.5180			
0.4	3.9671	22.9314	3.5913	-0.3224	4.237	3.5189			
0.5	3.9150	23.1944	3.4518	-0.0594	4.2972	3.6357			
0.6	3.8220	23.8449	3.1497	0.5910	4.4367	3.8838			
323 ⁰ K									
0.1	4.2173	23.1992	3.6863	0.6310	4.2563	3.612			
0.2	4.0371	22.9759	3.7580	0.4076	4.2359	3.4935			
0.3	3.9774	23.2118	3.6439	0.6435	4.2798	3.5771			
0.4	3.9344	21.8053	4.3499	-0.7629	4.0415	3.0626			
0.5	3.8851	21.9905	4.2023	-0.5777	4.0945	3.1715			
0.6	3.8241	22.1496	4.0929	-0.4185	4.1339	3.2437			

Table 1. Values of adiabatic compressibility, internal pressure, free volume, $\Delta \pi i$, molar cohesive energy and Gibb's free energy of Diammonium phosphate fertilizer solutions at different temperatures

Molality	â	$ Đ_{\rm i} (10^8) $	$V_{\rm f}$ (10 ⁻⁸)	Äði	MCE *10 ⁴	ÄG *10 ⁻²¹			
_	Kg ⁻¹ ms ⁻²	N/m^2	m ³		(KJ mol ⁻¹)	(KJ mol ⁻¹) ³			
303 ⁰ K									
0.1	4.3549	27.0982	1.9487	1.1186	4.9213	4.9410			
0.2	4.2832	27.0812	1.9385	1.1015	4.9357	4.9485			
0.3	4.199	26.4667	2.0542	0.4870	4.8500	4.7767			
0.4	4.1167	27.6131	1.8133	1.6335	5.0538	5.1002			
0.5	4.0944	27.1199	1.8846	1.1403	5.0022	5.0171			
0.6	4.0454	27.0999	1.8608	1.1202	5.0359	5.0621			
308 ⁰ K									
0.1	4.2982	25.0466	2.5917	0.0914	4.5490	4.2560			
0.2	4.2663	24.9693	2.5773	0.0141	4.5687	4.2922			
0.3	4.1792	25.5182	2.3924	0.5629	4.6906	4.4895			
0.4	4.0703	25.6160	2.3841	0.6608	4.6899	4.4549			
0.5	4.0272	24.9314	2.5466	-0.0237	4.5997	4.2814			
0.6	4.0059	25.0880	2.4547	0.1327	4.6703	4.4129			
313 ⁰ K									
0.1	4.2453	24.3286	3.8723	0.26979	4.4332	4.0035			
0.2	4.2097	24.3989	3.9431	0.3401	4.4745	4.0818			
0.3	4.1191	24.6361	4.0395	0.5773	4.545	4.1862			
0.4	3.9958	24.2994	3.8764	0.2405	4.4750	4.0081			
0.5	3.9512	24.8533	4.0845	0.7944	4.5975	4.2341			
0.6	3.9350	23.9447	3.8631	-0.1141	4.4688	3.9932			
			318	⁰ K					
0.1	4.2048	23.9496	3.2360	0.6958	4.3676	3.8454			
0.2	4.1584	24.3001	3.0591	1.0463	4.4595	4.0205			
0.3	4.0773	23.2780	3.4432	0.0242	4.2947	3.6638			
0.4	3.9651	23.4362	3.3781	0.1824	4.3213	3.6779			
0.5	3.9190	23.5374	3.3086	0.2835	4.3570	3.7420			
0.6	3.8910	23.1931	3.4012	-0.0607	4.3291	3.6839			
			323	⁰ K					
0.1	4.1942	22.4147	4.1145	-0.1534	4.0986	3.2617			
0.2	4.1496	22.8308	3.8618	0.2625	4.1918	3.4569			
0.3	4.0431	22.7382	3.8773	0.1699	4.1919	3.4175			
0.4	3.9501	22.7238	3.8638	0.1556	4.2006	3.4030			
0.5	3.9103	22.4513	3.9824	-0.1169	4.1626	3.3179			
0.6	3.8784	22.3203	3.9846	-0.2479	4.1737	3.3375			

Table 2. Values of adiabatic compressibility, internal pressure, free volume, $\Delta \pi i$, molar cohesive energy and Gibb's free energy of Monoammonium phosphate fertilizer solutions at different temperatures

 Table 3. Values of internal pressure coefficients A & B and free volume coefficients C & D of aqueous

 Diammonium phosphate and Monoammonium phosphate solutions at different temperatures

Temp (°K)	Inter	Free volume V _f (10 ⁻⁸)m ³						
	DAP		MAP		DAP		MAP	
	Α	В	Α	B	С	D	С	D
303	-2.7363	2.4442	-15.3754	9.8061	1.01009	-0.9609	3.6330	-2.4629
308	-12.6699	7.5248	-1.1549	1.1853	2.8818	-2.0552	0.2843	-0.5239
313	1.03156	-1.6177	-4.5993	2.9969	-0.3670	0.4037	1.7461	-1.3714
318	0.5133	-0.3453	-9.6115	4.7138	-0.2415	-0.0817	5.8325	-3.2349
323	-13.9064	5.9894	0.36	-0.1391	7.4704	-3.5185	-0.3369	-0.1560

Molar cohesive energy:

Cohesive energy in a liquid is an indicative of the attractive force existing between the molecules ⁶. The cohesive energy of a material is the energy required to disassemble it into its constituent parts, also known as binding energy⁷. It depends upon the nature of the atoms present in the material⁸. It is usually given as a product of internal pressure (π_i) and molar volume (V_m). A molecule containing strong polar groups exerts corresponding strong attractive forces on its neighbours. If the intermolecular forces are small, the cohesive energy is low and the molecules have relatively flexible chains. The increase in cohesive energy with increase in molar concentration shows the associating tendency of molecules in the solutions. The cohesive energy with concentration. The molar cohesive energy is found to decrease with rise in temperature and the value is found to be greater for the system MAP reinforces the result that strong solute-solvent interactions exist in the system MAP.



Fig 5. Molality Vs cohesive energy of DAP and MAP

Gibb's Free Energy:

An increasing value of ΔG suggests that the closer approach of unlike molecules is due to hydrogen bonding ⁹. Decrease in ΔG suggests longer time for rearrangement of molecules in the solution. The decrease of Gibb's free energy favours the formation of products after reaction¹⁰. The Gibb's free energy shows a similar behaviour as that of a cohesive energy for both the systems and is shown in figure (6).



Fig 6. Molality Vs Gibb's free energy of DAP and MAP

Conclusion:

Internal pressure, free volume and other related parameters were calculated from the measured values of density, viscosity and velocity of aqueous solutions. The variation of thermo dynamical parameters with molality provides useful information about the nature of intermolecular interactions existing in the solutions. $\Delta \pi_i$ has been evaluated which gives an idea about the effect of cohesive forces in ion-solvent interaction. From the results of internal pressure and cohesive energy, it is found that among the systems studied, MAP acts as a structure maker and predominant in solute-solvent interactions.

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