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Solvation studies of aqueous Mono ammonium phosphate solution at different temperatures

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ABSTRACT

Phosphorus is essential to all known life forms because it is a key element in many physiological and biochemical process. Phosphorous availability is crucial for the establishment of root system at the beginning of growing season. Phosphorous containing compounds are essential for photosynthesis in plants, for energy transformations and for the activity of some hormones in plants. Mono ammonium phosphate is a fully water soluble fertilizer, a highly efficient source of phosphorous and nitrogen for plants. The ultrasonic velocity measurements are helpful to study the solute-solvent interaction in aqueous and non-aqueous solutions. In this present investigation, ultrasonic velocity, density and viscosity of aqueous fertilizer solution of mono ammonium phosphate were measured at various temperatures from 303˚K to 323˚K. The molal hydration number (n_h), molar hydration number ($n_h^`$), apparent molal volume (φ_v), apparent molal compressibility (φ_k), and molar solvated volume (φ_s) were determined using the measured values. The results have been explained on the basis of molecular interactions occurring in the solutions. These molecular interactions exist between the ions in solutions help in understanding the nature of solute and solvent (i.e.) whether the solute modifies or distorts the structure of the solvent. Apparent molal volume and apparent molal compressibility have been proven to be a very useful tool in elucidating the structural interactions occurring in solution. Appreciable negative values of φ_k at all temperatures suggest the presence of ion-solvent interaction. Positive values of hydration number indicate an appreciable solvation of solute. This result provides an added support for the structure breaking nature of the solute, of which it is evident that the MAP is completely dissolved in water and it can be easily penetrate into the soil. Hence the plants can absorb the nutrients phosphorous supplied by the fertilizer MAP and the growth of the plants may be enhanced.

KEY WORDS: Adiabatic compressibility, molar hydration number, apparent molal compressibility, apparent molal volume, molar solvated volume.

1. INTRODUCTION

Ultrasonic investigation in aqueous solutions of electrolytes provides useful information in understanding the behavior of liquid systems, because intermolecular and intramolecular association, complex formation and related structural changes affect the compressibility of the system which in turn produces corresponding variation in ultrasonic velocity. Studies of densities, viscosities, and ultrasonic speeds of electrolytic solutions are of great use in characterizing the structure and properties of solution. The electrolyte added to the solvent causes a volume contraction due to interaction between the ions and solvent molecules and this may influence other acoustical properties of aqueous solutions. The derived parameters such as apparent molal compressibility, apparent molal volume from the experimental data will provide some significant information regarding the state of affairs in a solution. Literature survey on ultrasound velocity measurements shows that a very few works have been carried out on fertilizer materials. Thus in the present study, the technique has been used for the better understanding of molecular interactions in aqueous Monoammonium phosphate solution. MAP is one of the important Phosphatic fertilizer which is required by most of the plants and crops. Hence an attempt has been made to understand the physico-chemical behaviour of MAP in water at different temperatures through ultrasonic velocity measurements. Parameters such as adiabatic compressibility (β), molar hydration number (n_h), molal hydration number (n_h), apparent molal volume (φ_v), apparent molal compressibility (φ_k), molar solvated volume ($_{\varphi s}$), were calculated to shed more light on various types of intermolecular interactions between the components.

2. EXPERIMENTAL SECTION

The chemicals used in the present work were of AR grade. The required quantity of salt for given molality was dissolved in double distilled water and similar procedure has been adopted for different molalities. The speeds of sound waves were obtained by using ultrasonic interferometer (Mitta lF – 81 D) at a fixed frequency of 2 MHz with an accuracy of 0.5%. An Ostwald's viscometer was used for the viscosity measurement. The density of solutions at various temperatures was measured using 10 ml specific gravity bottles by relative method. The temperature was maintained using constant temperature bath with an accuracy of $\pm$ 0.1^0 C.

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2.1. Theory and calculations: Using the measured data, the following parameters have been calculated:
Adiabatic compressibility $\beta = 1/(U^2\rho)$ $Kg^{-1}ms^2$
Molal hydration number $n_h = [n_1 - \beta N/\beta_0] / n_2$
Molar hydration number $n_h' = [1 - \beta/\beta_0]N' / n_2'$
Apparent molal volume $\varphi_v = (1000(\rho_0 - \rho))/(n_2 \rho_0) + M_2/ \rho_0$ m^3mole^{-1}
Apparent molal compressibility $\varphi_k = (1000(\rho_0 \beta - \rho \beta_0)/n_2 \rho_0) + M_2 \beta_0/\rho_0$ m^2N^{-1}
φ_k is the function of m as obtained by Gucker from Debye Huckel[5&6] theory is
$\varphi_k = \varphi_k^o + S_k m^{1/2}$ $m^2 N^{-1}$
φ_v is the function of m as obtained by Masson's empirical relation as $\varphi_v = \varphi_v^o + S_v m^{1/2}$ m^3mol^{-1}
2.2. Molar solvated volume: $\varphi_s = \varphi_v + (n_h V_1)$: where β_0 and β are the adiabatic compressibilities of solution and solvent, n_1 and n_2 are number of moles of solvent and solute, ρ and ρ_0 are the densities of solution and solvent respectively. M is the molar mass of the solute. N' is the number of moles of solvent in 1000 gm of solvent and n2' is the molal concentration of the solution. φ_k^o and φ_v^o are the limiting apparent molal compressibility and limiting apparent molal volume of their solution respectively. S_k and S_v are the constants.

3. RESULTS AND DISCUSSION

The values of β show a decreasing trend with increasing molal concentration of solutes as well as with temperatures. The adiabatic compressibility value symbolize the increasing electrostrictive compression of solvent around the solute molecules that results in a larger decrease in the compressibility of solutions. The decreasing trend of compressibility may due to the rupture of hydrogen bond strengths formed between the solute and solvent molecules.

The hydration number is a measure of number of water molecules that get attached with each ion at a time during the process of solute-solvent interaction. From the table (1), it is observed that positive values of n_H indicate an appreciable solvation of solutes. This also suggests that the compressibility of the solution will be less than that of the solvent. At high temperatures ions will gain mobility and they are having probability of contacting water molecules. At low molalities ions get enough time to contact the water molecules. These situations increase the interaction between ions and water molecules. The number of water molecules which are aligned in the force field of the ion are high, hence the hydration number is positive and high. The decreasing values of hydration number shows the strength of interaction gets weakened between solute and solvent molecules. The decreasing solvation number with increase in molality may be due to the lack of solvent molecules for ions or occurrence of ion pairing in this solution.

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 following observations have been made on φ_k and φ_v of the aqueous MAP fertilizer solutions at different temperatures.

(i) The values of φ_k are all negative and φ_v are all positive over the entire range of molality and at all temperatures.
(ii) A nonlinear variation has been observed throughout the concentration range for both φ_k and φ_v.
(iii) The variation in n_H values are found to be reflected in the variation of φ_k values with opposite sign.

The negative values of apparent molal compressibility indicate the hydrophilic interaction occurring in the system. This is because at lower concentration of MAP, more number of water molecules are available, hence the chances for the penetration of solute molecules into solvent molecules are highly favoured. Increase in φ_v with respect to concentration supports the existence of solute-solvent interaction. The increasing value of apparent molal compressibility and apparent molal volume with increasing concentration of solute content in aqueous medium reveal the strengthening of the solute-solvent interaction [9]. The limiting apparent molal compressibility φ_k^0 provides information regarding ion-solvent interaction and its associated constant S_k that of ion-ion interactions in the solution. The appreciable negative values of φ_k^0 suggest the existence of ion-solvent interaction. Further, the positive S_k values at all temperatures predicts the presence of weak ion-ion interaction.

The volume behaviour of solute at infinite dilution is satisfactorily represented by the limiting apparent molal volume φ_v^0 values, which are independent of ion-ion interaction. The perusal of table reveals that the values of φ_v^0 are all positive and they are nonlinear with rise in temperature. Meanwhile, the values of S_v which exhibit positive values at all temperatures reflect the existence of weak ion-ion interaction. Though both φ_v^0 and S_v are positive, S_v is lesser in magnitude, hence the chance of occurrence of ion-solvent interactions is greater than ion-ion interaction.

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The molar solvated volume φ_s measure the volume of solvated part of the solute present in the solution. The φ_s values have the cumulative effect of φ_v and n_h V_1 as seen from the equation $\varphi_s = \varphi_v + n_h V_1$. From the result, it is clear that φ_s is mainly detailed by the hydration number rather than by φ_v.

Table.1.Values of adiabatic compressibility (β), molar hydration number (n_h), molal hydration number ($n_{h'}$), apparent molal compressibility (φ_k), apparent molal volume (φ_v), molar solvated volume (φ_s), Limiting apparent molal volume (φ_v^0), Limiting apparent molal compressibility (φ_k^0), constants S_k and S_v of aqueous Monoammonium phosphate at 303 ^{0} K, 308 ^{0} K, 313 ^{0} K, 318 ^{0} K, and 323 ^{0} K

Con (m)	Adiabatic compressibility β ($*10^{-10}$) $Kg^{-1}ms^{-2}$	Hydration number Molar (n_h)	Molal (n_h')	Apparent molal compressibility (φ_k)$*10^{-8}$ $m^2 N^{-1}$	Apparent molal volume (φ_v) ($m^3 mol^{-1}$)	Molar solvated volume (φs) $m^3 mole^{-1}$	(φ_v^0) $m^3 mol^{-1}$	S_v ($m^{-1}N^{-1} mol^{-1}$)	(φ_k^0)$*10^{-8}$ $m^2 N^{-1}$	S_k (10^{-8} $m^{-1}N^{-1} mol^{-1}$)
				303 ^{0} K						
0	4.4637	-	-	-	-	-				
0.1	4.3549	10.472	13.392	-8.45	54.32	243.651				
0.2	4.2835	8.171	11.049	-6.59	54.35	202.126				
0.3	4.1990	7.572	10.724	-6.11	60.69	197.654	48.94	13.04	-10.92	8.44
0.4	4.1166	8.142	10.539	-6.57	47.06	194.358				
0.5	4.0944	5.962	8.881	-4.81	57.60	165.464				
0.6	4.0453	5.078	8.298	-4.10	64.32	156.187				
				308 ^{0} K						
0	4.4003	-	-	-	-	-				
0.1	4.2982	10.650	12.746	-8.49	38.88	231.911				
0.2	4.2663	4.746	8.286	-3.78	66.16	152.202				
0.3	4.1792	5.610	9.059	-4.47	65.81	167.502	40.85	26.08	-8.89	6.28
0.4	4.0703	7.917	10.161	-6.31	43.95	187.452				
0.5	4.0272	6.323	9.097	-5.04	54.94	169.547				
0.6	4.0059	4.668	7.9218	-3.72	64.75	149.376				
				313 ^{0} K						
0	4.3563	-	-	-	-	-				
0.1	4.2453	11.068	13.959	-8.75	53.86	254.833				
0.2	4.2097	5.488	9.141	-4.34	68.64	168.300				
0.3	4.1191	6.025	9.780	-4.76	72.10	181.501				
0.4	3.9958	8.390	11.146	-6.63	54.55	206.909	60.78	3.932	-9.05	5.94
0.5	3.9512	7.111	9.952	-5.62	56.86	185.989				
0.6	3.9350	5.234	8.526	-4.14	66.16	161.206				
				318 ^{0} K						
0	4.3139	-	-	-	-	-				
0.1	4.2048	11.59	13.842	-9.10	41.88	252.903				
0.2	4.1584	6.479	9.778	-5.08	62.26	180.139				
0.3	4.0773	6.428	9.847	-5.04	65.80	182.760	42.35	25.14	-9.99	7.14
0.4	3.9651	8.209	10.873	-6.44	52.73	202.093				
0.5	3.9190	7.073	9.788	-5.55	54.37	183.071				
0.6	3.8910	5.506	8.639	-4.32	63.19	163.379				
				323 ^{0} K						
0	4.3065	-	-	-	-	-				
0.1	4.1942	11.733	14.231	-9.21	46.47	260.703				
0.2	4.1496	7.043	9.880	-5.53	53.54	182.116				
0.3	4.0431	8.110	10.993	-6.36	55.89	203.877	40.10	24.82	-10.66	7.71
0.4	3.9501	8.392	11.101	-6.59	53.78	206.880				
0.5	3.9103	7.164	9.820	-5.62	53.29	183.977				
0.6	3.8784	5.646	8.744	-4.43	62.69	165.690				

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4. CONCLUSION

A detailed analysis of thermochemical properties φ_k and φ_v has been carried out in the present study and intermolecular interactions are discussed. The results have been used to estimate the number of water molecules hydrated to the fertilized material MAP. From the positive values of hydration number and negative values of apparent molal compressibility, it is concluded that appreciable solvation of solute exists**.** The appreciable negative values of $\varphi_k{}^0$ suggest the existence of ion-solvent interaction. From this it is apparent that Map is completely dissolved in water and this solution can be easily penetrate in to the soil so that he plant can absorb the phosphorous from MAP solution that may enhance the growth of the plants.

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