Research Article

Estimation of hydration number and its allied parameters of aqueous Diammonium phosphate solution by ultrasonic studies at different temperatures

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ABSTRACT

Ultrasonic velocity of liquids and solutions are a simpler but accurate method of analyzing the interaction between the molecules. The passage of ultrasonic waves through solutions and liquids disturbs the equilibrium between the solute and solvent molecules. The velocity of such a wave is a thermodynamic quantity and it is related to the physico-chemical properties of the medium. Ultrasonic velocity (U), density (ρ) and viscosity (η) of Diammonium phosphate fertilizer in aqueous media have been measured at 303, 308, 313, 318, and 323 ^{0} K to estimate hydration number and its allied parameters like apparent molal volume (φ_v), apparent molal compressibility (φ_k), molar solvated volume (φ_s), limiting apparent molal compressibility (φ_k^0), and limiting apparent molal volume (φ_v^0) and their constants S_k and S_v. The datas have been interpreted in terms of solute - solvent interactions.

Keywords: Adiabatic compressibility, molar hydration number, apparent molal compressibility, limiting apparent molal compressibility, molar solvated volume.
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INTRODUCTION

Ultrasonic investigation in aqueous solutions of electrolytes and non-electrolytes provides useful information in understanding the degree and nature of interaction because intramolecular and intermolecular association related to structural changes affects the ultrasonic velocity[1]. Ultrasonic velocity together with density, viscosity and related parameters of aqueous solutions assist in characterizing the structure and properties of solutions. Various 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. Due to the scarce knowledge about the water structure, the molecular nature of ion-water interaction is not known completely. The interaction of ion with water is described in terms of ion-hydration. Passynski[2] and Barnartt[3] derived the expression for the hydration number, which is the number of water molecules that interact with ions. Literature survey on ultrasound velocity measurements shows that a very few works have been carried out on fertilizer materials[4]. Thus in the present attempt, the technique has been used for the better understanding of molecular interactions in aqueous Diammonium phosphate solution. DAP is one of the important Phosphatic fertilizer which is required by most of the plants and crops. Phosphorus deficiency limits the growth and productivity of plants in many parts of the world. Since many soils are low in P, this nutrient is commonly added to improve crop yield and quality. DAP increases crop yields, improve crop quality, stimulate the maturation of plants, and improve the resistance of plants to lodging and drought. Hence an attempt has been made to understand the physico-chemical behaviour of DAP in water at different temperatures through ultrasonic velocity measurements. Parameters such as adiabatic compressibility (β), molar hydration number (n_h),

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molal hydration number (n_h'), apparent molal volume (φ_v), apparent molal compressibility (φ_k), molar solvated volume (φ_s), limiting apparent molal compressibility (φ_k^0), and limiting apparent molal volume (φ_v^0) and the constants S_k and S_v were calculated to shed more light on various types of intermolecular interactions between the components.

EXPERIMENTAL SECTION

Aqueous solutions of Diammonium phosphate were prepared using AR grade salt at different concentrations ranging from 0.1 to 0.6m. The ultrasonic velocities of the solutions were measured using an ultrasonic interferometer (Mittal F – 81 D) with a single crystal at a frequency of 2 MHz with an accuracy of 0.5%. 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. Ostwald's viscometer was used for viscometric studies.

RESULTS AND DISCUSSION

Adiabatic Compressibility:
Adiabatic Compressibility is a fractional decrease of volume per unit increase of pressure when no heat flows in or out[5]. Increase in compressibility value indicates the weakening of molecular interaction. The increase in velocity and decrease in compressibility was attributed to the formation of hydrogen bonds between solute and solvent molecules [6]. The adiabatic compressibility of DAP solution was calculated using the relation,

$$\beta = 1/(U^2 \rho) \tag{1}$$

where U-Ultrasonic velocity and ρ-density of solution.

The compressibility of DAP solution appears to be decreasing with hydrogen bond strength formed by DAP and water molecules. The adiabatic compressibility values given in table (1) are found to decrease with the increase of concentration and temperature which shows a strong molecular association/interaction is exist between the solute and solvent molecules.

Hydration Number:
When an electrolyte is added to water, some water molecules get arranged around each ion due to their large dipole moment. The interaction between the ion and the surrounding water molecules is referred as hydration [7]. Positive values of hydration number indicate an appreciable solvation of solute. This result provides an added support for the structure promoting nature of the solute as well as the presence of appreciable dipole-dipole interaction between solute and water molecules. It also suggests that compressibility of the solution will be less than that of pure solvent. As a result the solute will gain mobility and have more probability of contacting solvent molecules which may enhance the interaction between solute and solvent molecules[8].

The molar hydration number n_h is obtained from the Passynski's relation given as follows,

$$n_h = [n_1 - \beta N/\beta_0] / n_2 \tag{2}$$

where β and β_0 be the compressibility of solution and solvent respectively, n_1 is the number of moles of the solvent present in 1000 cc of the solution of molar concentration n_2 and N is the number of moles of the solvent in 1000 cc of the solvent. The molar hydration number can also be obtained using Barnatt's equation,

$$n_h = n_1(1 - V\beta / n_1 V_1 \beta_0] / n_2 \tag{3}$$

where V_1 is the molar volume of the solvent and V = 1000 cc.

The values of molar hydration number obtained from equations (2) and (3) are in good agreement. Similarly, the molal hydration number n_h' given by Passynski has been computed using the following two relations,

$$n_h' = [1 - \beta/\beta_0]N' / n_2' \tag{4} \text{ and}$$

$$n_h' = [1 - \beta/\beta_0]n_1 / n_2 \tag{5}$$

where N' is the number of moles of solvent in 1000 gm of solvent and n_2' is the molal concentration of the solution. The values of molal hydration number obtained from equations (4) and (5) are in agreement.

The values of hydration number are found to decrease at higher concentrations at all temperatures which may be due to lack of solvent molecules for ions or occurrence of ion pairing in the solution. The decrease in hydration number at higher concentrations suggests that the strength of interaction gets weakened between the solute and solvent molecules. However, the magnitude of n_h is found to be greater at 313 ^{0} K.

Apparent Molal Volume:
It is defined as change in volume of the solution for the added concentration of solute at a constant temperature and pressure. It is a thermodynamic property helps in elucidating solvation behaviour of electrolyte in the solution. Positive values of φ_v indicate the presence of strong solute-solvent interactions [9]. The apparent molal volume in both molal and molar scales were arrived through the following equations

$$\varphi_v = V_1 ((N\Delta\beta)/(n_2 \beta_0)) - n_h \tag{6}$$

$$\varphi_v = (1000(\rho_0 - \rho))/(n_2 \rho_0) + M_2/ \tag{7}$$

$$\varphi_v = V_1 (N (n_h'/n_1) - n_h) \tag{8}$$

$$\varphi_v = (\beta_0 \ n_h'/\Delta\beta) ((V/ n_1) - V_1)) \tag{9}$$

where, M_2 = molecular weight of solute

The plot of φ_v versus concentration was constructed which satisfies the relation,

$$\varphi_v = \varphi_v^0 + S_v \sqrt{c}$$

The intercept φ_v^0 and slope S_v values were found using least square fitting technique and are given in table (2). φ_v^0 known as limiting apparent molal volume is the measure of solute-solvent interaction whereas the slope S_v measures solute-solute interactions. In the present study, positive non-linear variations were observed for φ_v and the values obtained by the equations (6-9) are all in good agreement. The positive values of φ_v^0 indicate the presence of solute-solvent interactions and the negative values of S_v suggest the presence of weak solute-solute interactions.

Apparent Molal Compressibility:
As apparent molal compressibility φ_k depends on adiabatic compressibility which in turn depends on concentration, it can be said that the apparent molal compressibility φ_k is also related to concentration. It represents the magnitude of ion-solvent interaction [10]. φ_k values were calculated using the relations given below,

$$\varphi_k = - V_1 \beta_0 n_h \tag{10}$$

$$\varphi_k = - n_h'V_1 \beta_0 + \varphi_v \beta \tag{11}$$

and also by the traditional method relations,

$$\varphi_k = (1000(\rho_0 \beta - \rho \beta_0)/n_2 \rho_0) + M_2 \beta_0/\rho_0 \tag{12}$$

$$\varphi_k = (1000/ n_2) (\beta - \beta_0) + \beta_0 \varphi_v \tag{13}$$

and all are found to be identical. From these values, limiting apparent molal compressibility (φ_k^0) and the constant S_k were evaluated and are given in table (2).

The negative values of φ_k indicate ionic and hydrophilic interactions occurring in the system. φ_k^0 provides information regarding solute-solvent interactions and S_k, that of solute-solute/ion-ion interaction in the solution.

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Appreciable negative values of φ_k^0 at all temperatures reinforce existence of ion-solvent interaction in the present system. The negative values of S_k suggest the presence of weak solute-solute interactions.

Molar Solvated Volume: The molar solvated volume φ_s measures the volume of solvated part of the solute present in the solution and φ_s values were calculated using the equations,

$$\varphi_s = (V - n_h') / n_1 \tag{14}$$

$$\varphi_s = V \, \Delta\beta / n_2 \, \beta_0 \tag{15}$$

$$\varphi_s = (n_h' \, V_1 \, \beta_0) / \beta - (n_h V_1 \, \Delta\beta) / \beta \tag{16}$$

$$\varphi_s = (V - (n_1 - n_2 \, n_h) V_1) / n_2 \tag{17}$$

$$\varphi_s = \varphi_v + (n_h V_1) \tag{18}$$

There is a perfect agreement between the values computed by the equations (14-18) and are given in table (1). The φ_s values have the cumulative effect of φ_v and $n_h V_1$ as seen from the equation (18). 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'), and molar solvated volume (φ_s) of aqueous DAP solution

Molality M	β (*10^-10) Kg^-1 ms^-2	Molar hydration number (n_h)		Molal hydration number (n_h')		Molar Solvated Volume (φ_s m^3 mole^-1)				
		Eqn(2)	Eqn(3)	Eqn(4)	Eqn(5)	Eqn(14)	Eqn(15)	Eqn(16)	Eqn(17)	Eqn(18)
303 °K										
0.1	4.3706	9.2571	9.2571	11.569	11.471	208.43	208.42	208.43	208.58	208.42
0.2	4.2186	12.5431	12.5431	15.234	15.024	274.47	274.46	274.47	274.54	274.46
0.3	4.0619	13.6518	13.6518	16.652	16.316	300.01	300.01	300.01	300.06	300.01
0.4	3.9994	11.4469	11.4469	14.431	14.065	260.00	260.00	260.00	260.03	260.00
0.5	3.9637	9.3074	9.3074	12.433	12.035	223.99	223.98	223.99	224.02	223.98
0.6	3.9073	8.3407	8.3407	11.531	11.089	207.74	207.74	207.74	207.76	207.74
308 °K										
0.1	4.3210	8.2867	8.2867	9.992	9.903	180.02	180.06	180.02	180.02	180.06
0.2	4.1719	10.8737	10.8737	14.401	14.137	259.45	259.47	259.45	258.45	259.47
0.3	4.0194	12.8539	12.8539	16.015	15.655	288.53	288.55	288.53	288.53	288.55
0.4	3.9830	9.8692	9.8692	13.156	12.774	237.03	237.04	237.03	237.03	237.04
0.5	3.9163	9.0146	9.0146	12.209	11.793	219.97	219.98	219.97	219.97	219.98
0.6	3.8547	8.2450	8.2450	11.469	11.010	206.63	206.64	206.63	206.63	206.64
313 °K										
0.1	4.2566	9.3855	9.3855	12.695	12.522	228.71	228.71	228.71	228.87	228.71
0.2	4.0666	15.3223	15.3223	18.454	18.112	332.47	332.47	332.47	332.55	332.47
0.3	4.0183	11.3260	11.3260	14.354	14.016	258.61	258.60	258.61	258.66	258.60
0.4	3.9776	8.9062	8.9062	12.090	11.727	217.82	217.82	217.82	217.86	217.82
0.5	3.9203	7.8390	7.8390	11.108	10.703	200.12	200.12	200.12	200.15	200.12
0.6	3.8413	7.7132	7.7132	10.935	10.479	197.01	197.01	197.01	197.04	197.01
318 °K										
0.1	4.20356	10.9785	10.9785	14.199	13.982	255.81	255.81	255.81	255.81	255.81
0.2	4.05006	14.0809	14.0809	16.975	16.642	305.82	305.82	305.82	305.82	305.82
0.3	4.01372	9.6941	9.6941	12.875	12.537	231.96	231.96	231.96	231.96	231.96
0.4	3.96718	7.8471	7.8471	11.153	10.787	200.94	200.94	200.94	200.94	200.94
0.5	3.91508	7.0645	7.0645	10.263	9.876	184.90	184.90	184.90	184.90	184.90
0.6	3.82204	7.2486	7.2486	10.548	10.080	190.03	190.03	190.03	190.03	190.03
323 °K										
0.1	4.21736	6.9557	6.9557	11.492	11.264	207.05	207.05	207.05	207.05	207.05
0.2	4.03714	13.0810	13.0810	17.360	16.898	312.77	312.77	312.77	312.77	312.77
0.3	3.97741	10.8772	10.8772	14.140	13.734	254.74	254.74	254.74	254.74	254.74
0.4	3.9344	8.5112	8.5112	11.990	11.559	216.02	216.02	216.02	216.02	216.02
0.5	3.88519	7.3067	7.3067	10.861	10.396	195.67	195.67	195.67	195.67	195.67
0.6	3.8241	6.9524	6.9524	10.363	9.871	186.70	186.70	186.70	186.70	186.70

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Table 2 - Values of apparent molal volume (φ_v), apparent molal compressibility (φ_k), Limiting apparent molal volume (φ_v^0), Limiting apparent molal compressibility (φ_k^0), constants S_k and S_v of aqueous Diammonium phosphate at 303 ^{0} K, 308 ^{0} K, 313 ^{0} K, 318 ^{0} K, and 323 ^{0} K

Molality M	Apparent molal volume (φ_v) ($m^3 mol^{-1}$)				Apparent molal compressibility ($-\varphi_k$ x 10^{-8} $m^2 N^{-1}$)				(φ_v^0) ($m^3 mol^{-1}$)	S_v	(φ_k^0) (x 10^{-8} $m^2 N^{-1}$)	S_k
	Eqn (6)	Eqn (7)	Eqn (8)	Eqn (9)	Eqn (10)	Eqn (11)	Eqn (12)	Eqn (13)				
303 ^{0} K												
0.1	41.05	40.92	40.93	41.08	-7.48	-7.48	-7.48	-7.48	70.26	33.43	-6.932	-3.066
0.2	47.57	47.50	47.51	47.58	-10.1	-10.1	-10.1	-10.1				
0.3	53.03	52.99	52.99	53.04	-11.02	-11.02	-11.02	-11.02				
0.4	52.90	52.87	52.88	52.91	-9.24	-9.24	-9.24	-9.24				
0.5	55.60	55.57	55.58	55.60	-7.51	-7.51	-7.51	-7.51				
0.6	56.84	56.81	56.82	56.84	-6.73	-6.73	-6.73	-6.73				
308 ^{0} K												
0.1	29.83	29.88	29.83	29.82	-6.61	-6.61	-6.61	-6.61	78.18	-43.47	-7.108	-1.316
0.2	62.38	62.40	62.38	62.37	-8.67	-8.67	-8.67	-8.67				
0.3	55.57	55.59	55.57	55.57	-10.25	-10.25	-10.25	-10.25				
0.4	58.16	58.17	58.16	58.16	-7.87	-7.87	-7.87	-7.87				
0.5	56.59	56.60	56.59	56.59	-7.19	-7.19	-7.19	-7.19				
0.6	57.20	57.21	57.20	57.20	-6.57	-6.57	-6.57	-6.57				
313 ^{0} K												
0.1	58.45	58.29	58.30	58.45	-7.42	-7.42	-7.42	-7.42	56.56	-0.761	-3.740	-7.410
0.2	54.34	54.26	54.26	54.34	-12.1	-12.1	-12.1	-12.1				
0.3	53.01	52.96	52.96	53.01	-8.95	-8.95	-8.95	-8.95				
0.4	56.15	56.11	56.11	56.15	-7.04	-7.04	-7.04	-7.04				
0.5	57.82	57.79	57.79	57.82	-6.20	-6.20	-6.20	-6.20				
0.6	56.99	56.96	56.96	56.99	-6.10	-6.10	-6.10	-6.10				
318 ^{0} K												
0.1	56.08	56.07	56.07	56.07	-8.61	-8.61	-8.61	-8.61	61.19	-9.675	-1.748	-9.978
0.2	49.65	49.64	49.64	49.64	-11.05	-11.05	-11.05	-11.05				
0.3	55.59	55.59	55.59	55.59	-7.60	-7.60	-7.60	-7.60				
0.4	58.17	58.17	58.17	58.17	-6.15	-6.15	-6.15	-6.15				
0.5	56.38	56.38	56.38	56.38	-5.54	-5.54	-5.54	-5.54				
0.6	58.16	58.16	58.16	58.16	-5.68	-5.68	-5.68	-5.68				
323 ^{0} K												
0.1	80.21	80.23	80.23	80.23	-5.46	-5.46	-5.46	-5.46	40.20	44.62	-4.917	-3.617
0.2	74.25	74.25	74.25	74.25	-10.02	-10.02	-10.02	-10.02				
0.3	56.41	56.41	56.41	56.41	-8.54	-8.54	-8.54	-8.54				
0.4	60.83	60.83	60.83	60.83	-6.68	-6.68	-6.68	-6.68				
0.5	62.44	62.44	62.44	62.44	-5.74	-5.74	-5.74	-5.74				
0.6	59.93	59.93	59.93	59.93	-5.46	-5.46	-5.46	-5.46				

CONCLUSION

Various solvation properties of aqueous Diammonium phosphate fertilizer solution were studied at different temperatures. Adiabatic compressibility and apparent molal volume are computed. The values of molar and molal hydration numbers, apparent molal compressibility and molar solvated volume were computed from different theories available in literatures and found to be in good agreement From the investigation it may be presumed that

(i) The existence of ion-solvent or solute-solvent interactions resulting in attractive forces which promote the structure breaking influence of DAP on the solvent.
(ii) The interactions taking place may be due to ion-dipolar/hydrophilic group between the ions (NH_4^+, HPO_4^-) of DAP and (H^+, OH^-) group of water.

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