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STUDY OF SOLVATION EFFECT OF AMMONIUM SULPHATE AND AMMONIUM CHLORIDE FERTILIZER SOLUTIONS

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ABSTRACT

The study of the properties of aqueous solutions is very important in many areas of science and researchers are progressing in this direction with a view to know more about the water structure. The ultrasonic velocity measurements are helpful to study the ion-solvent interaction in aqueous and non-aqueous solutions. The ammonical fertilizers of ammonium sulphate and ammonium chloride contain the nutrient nitrogen in the form of ammonium or ammonia. In this present investigation, ultrasonic velocity, density and viscosity of aqueous fertilizer solutions of ammonium sulphate and ammonium chloride were measured at various temperatures from 303˚K to 323˚K. The molal hydration number (n_h), molar hydration number (n_h^1), apparent molal volume (φ_v), apparent molal compressibility (φ_k), limiting apparent molal volume (φ_v^o), limiting apparent molal compressibility (φ_k^o), the constants (S_v & S_k) and molar solvated volume (φ_s) were determined using the measured values. The study of molar hydration number and molal hydration number reveals that there is a significant interaction between solute and solvent molecules due to which the structural arrangement in the neighbourhood of constituent solutes is considerably affected.

KEY WORDS: Molal hydration number, apparent molal volume, apparent molal compressibility, limiting apparent molal volume.

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INTRODUCTION

Ultrasonics is a versatile non-destructive technique and highly useful for investigation of various physicochemical properties of fertilizer solutions. This kind of study is important for both human and plants. Recent developments have found the use of ultrasonic technique in medicine, engineering and agriculture. Ultrasonic study on aqueous solutions of electrolytes and non electrolytes provides useful information in understanding the behavior of liquid systems. Ammonium sulphate contains both nitrogen and sulfur. It is a valuable fertilizer in soils that are deficient in both elements. It may have real advantage over other nitrogen fertilizers in terms of cumulative cost of nitrogen and sulfur. Except rice, all crops absorb nitrogen in nitrate form, these fertilizers are resistant to leaching loss, as the ammonium ions get readily absorbed on the colloidal complex of the soil. In the soil the ammonium ion is released and forms a small amount of acid, lowering the pH balance of the soil[1], while contributing essential nitrogen for plant growth. Ammonium chloride is a combination of two necessary elements for plant growth, and providing the plants with an extra source helps them to reach peak growth and health. The deficiency of ammonium chloride will turn the leaves of the plant yellow and brown. 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. Passyanki and Barnatt pioneers in these studies have derived the expression for the hydration number that is the number of water molecules that interact with the ions. The determination of apparent molal volume, apparent molal compressibility, limiting apparent molal volume and limiting molal compressibility and molar solvated volume using the hydration number has been reported in this investigation.

Experimental details

Ultrasonic Velocity measurement

Ultrasonic velocity was measured using ultrasonic interferometer of fixed frequency 2MHz (Model F-81, Mittal enterprises, New Delhi). The measuring cell of interferometer is a specially designed double walled vessel with provision for maintaining temperature constant. A digital constant temperature bath operating in the temperature range 10˚C to 90˚C with an accuracy of $\pm$ 0.1˚C has been used to circulate water through the outer jacket of double walled measuring cell containing the experimental liquid/ solution.

Density measurement

The density of fertilizer solutions are measured using 10ml of specific gravity bottle. The specific gravity bottle with experimental solution is immersed in a temperature controlled water bath. The density was measured using this formula, $\rho = (w_2-w)/(w_1-w) * \rho_0$. Where, w_1 and w_2 are the density of the distilled water and experimental solution.

Viscosity measurement

The viscosities of the solutions are measured using Ostwald's viscometer with the experimental solution is immersed in a temperature controlled water bath. The time of flow was measured using a stop watch with an accuracy of 0.1sec. The viscosity was determined using the relation, $\eta = \eta_0 (t/t_0)(\rho/\rho_0)$

MATERIALS AND METHODS

Analar grade samples of ammonium sulphate and ammonium chloride fertilizers of molecular weight 132.13 and 53.49g/mole respectively were purchased from Sd fine chemical limited and Moly chemical Mumbai respectively. Double distilled water has been used as a solvent for preparing ammonium sulphate and ammonium chloride fertilizer solutions of different concentrations.

Computation

Using the measured data, the following volumetric, compressibility and transport parameters have been calculated using the standard relations,

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 $\varphi_v = [1000(\rho - \rho_0) / n_2\rho_0] + M / \rho_0$ m^3mole^{-1}

Apparent molal compressibility $\varphi_k = [1000(\rho_0\beta - \beta_0\rho) / n_2\rho_0] + M\beta_0 / \rho_0$ m^2N^{-1}

Molar solvated volume $\varphi s = Vn_h' / n_1$

φ_k is the function of m as obtained by Gucker from Debye Huckel[2&3] 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[4] as

$\varphi_v = \varphi_v^o + S_v m^{1/2}$ m^3mol^{-1}

Where β, ρ and β_0, ρ_0, are the adiabatic compressibility and density of the solution and solvent respectively. M is the molar mass of the solute. n_2 is the moal concentration of the solute. N' is the number of moles of solvent in 1000 gm of solvent and n_2' is the molal concentration of the solution. V is the volume of the solution. φ_k^o and φ_v^o are the limiting apparent molal compressibility and limiting apparent molal volume of solutions respectively. S_k and S_v are the constants.

RESULTS AND DISCUSSION

Adiabatic compressibility

Figures (1&2) show the variation of adiabatic compressibility of ammonium sulphate and ammonium chloride solution in aqueous solution at different temperatures. The values of adiabatic compressibility indicates a decreasing trend in both the systems. The decrease in adiabatic compressibility is attributed to the formation of hydrogen bonds between solute and solvent molecules. The degree of hydrogen bond formation between solute and solvent molecules increases with concentration their by decrease the compressibility of the solutions.

Hydration number

Hydration number n_h is defined as the ratio of the incompressible solvent molecules in the solution n_i to the number of solute molecules. As every solvent has its characteristics 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 solute. The degree of hydration is measured by a quantity known as hydration number assigned to each individual ion. The hydration number is a measure number of water molecules that get attached with each ion at a time during the process of interaction. In this present investigation, both systems show a positive hydration number indicates an appreciable solvation of solutes. This is an added support not only for the structure promoting nature of the solutes 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[5]. The decreasing values of hydration number in ammonium chloride fertilizer solution shows the strength of interaction gets weakened between solute and solvent molecules[6]. The decreasing solvation number with increase in molality may be due to the lack of solvent molecules surrounding the ions or occurrence of ion pairing in this solution. This variation of molal hydration number and molar hydration number with concentration is shown in figures (3, 4, 5, &6).

Table 1

Values of adiabatic compressibility, molal hydration number, molar hydration number, apparent molal volume, apparent molal compressibility, molar solvated volume of aqueous ammonium sulphate solutions at different temperatures.

Conc (mole)	Adiabatic compressibility ($10^{-10}Kg^{-1}ms^{-2}$)	Molal hydration number (n_h)	Molar hydration number (n_h^1)	Apparent molal volume ($m^3\ mol^{-1}$)	Apparent molal compressibility ($10^{-8}m^2N^{-1}$)	Molar solvated volume
			303˚K			
0	4.4637	-	-	-	-	-
0.1	4.3363	15.8389	14.9401	14.9949	-12.075	285.3535
0.2	4.2051	16.0756	13.5391	44.6232	-10.9393	289.6178
0.3	4.1175	14.3498	12.2041	37.6932	-9.8597	258.527
0.4	4.0821	11.8603	8.9012	52.6077	-7.19132	213.6756
0.5	3.9760	12.1280	9.5280	46.0895	-7.6972	218.4982
0.6	3.9298	11.0632	8.0531	53.5954	-6.50567	199.3156
0.7	3.9007	10.0000	6.5626	61.4101	-5.30164	180.1605
			308˚K			
0	4.4003	-	-	-	-	-
0.1	4.3348	8.2612	3.3329	88.4554	-2.6569	148.8356
0.2	4.2014	12.5425	9.2310	58.6785	-7.3612	225.9672
0.3	4.1038	12.4642	8.7903	65.2509	-7.0099	224.5568
0.4	4.0417	11.3091	8.3224	52.9193	-6.6368	203.7468
0.5	3.9928	10.2798	6.7771	62.3805	-5.4045	185.2021
0.6	3.9210	10.0752	6.6808	60.4390	-5.3277	181.5158
0.7	3.8763	9.4416	5.7952	65.0736	-4.6215	170.1019
			313˚K			
0	4.35637	-	-	-	-	-
0.1	4.25066	13.4684	8.7550	83.6793	-6.9252	242.648
0.2	4.19475	10.2964	6.4791	67.8565	-5.1249	185.4999
0.3	4.07573	11.9191	8.4039	62.1455	-6.6474	214.7359
0.4	4.04645	9.8720	5.6876	74.5837	-4.4988	177.8542
0.5	3.96383	10.0030	6.3502	64.9137	-5.0229	180.2149
0.6	3.88366	10.0383	6.7375	58.5174	-5.3293	180.8508
0.7	3.85092	9.2001	5.5984	64.0988	--4.4283	165.7505
			318˚K			
0	4.3139	-	-	-	-	-
0.1	4.2279	11.0562	6.0879	88.3918	-4.7797	199.1899
0.2	4.1693	9.2980	4.8224	79.7576	-3.7856	167.5131
0.3	4.0531	11.1861	7.6241	62.8090	-5.9843	201.5302

0.4	4.0029	10.0025	5.7940	74.7841	-4.5478	180.2067
0.5	3.9270	9.9560	6.2634	65.4077	-4.9161	179.3683
0.6	3.8550	9.8411	6.4452	60.0319	-5.0587	177.2983
0.7	3.8088	9.2835	5.7885	61.9338	-4.5433	167.2519
			323˚K			
0	4.3065	-	-	-	-	-
0.1	4.1505	20.1074	15.7354	75.3286	-12.3565	362.2548
0.2	4.0922	13.8098	8.6366	91.3194	-6.7818	248.7976
0.3	4.0125	12.6320	8.6901	69.1212	-6.8240	227.5783
0.4	3.9682	10.9013	6.4052	79.6046	-5.0297	196.3978
0.5	3.8877	10.7949	6.8754	69.1145	-5.3989	194.4817
0.6	3.8389	10.0453	6.5054	62.3572	-5.1084	180.9772
0.7	3.8064	9.2076	5.5048	65.5115	-4.3226	165.8856

Table 2

Values of adiabatic compressibility, molal hydration number, molar hydration number, apparent molal volume, apparent molal compressibility, molar solvated volume of aqueous ammonium chloride solutions at different temperatures.

Conc (mole)	Adiabatic compressibility ($10^{-10}Kg^{-1}ms^{-2}$)	Molal hydration number (n_h)	Molar hydration number (n_h^1)	Apparent molal volume (m^3 mol^{-1})	Apparent molal compressibility ($10^{-8}m^2N^{-1}$)	Molar solvated volume
			303˚K			
0	4.4637	-	-	-	-	-
0.22	4.3114	8.6059	7.6729	16.1964	-6.2009	155.045
0.44	4.2408	6.2971	4.4358	33.1791	-3.5846	113.4492
0.66	4.1952	5.0579	3.0776	35.4313	-2.487	91.1238
0.88	4.1275	4.7507	2.7304	36.1807	-2.2062	85.5892
1.1	4.0352	4.8436	2.9959	33.0512	-2.4205	87.2637
1.32	3.9385	4.9471	2.9645	35.4845	-2.3949	89.1271
1.46	3.9047	4.7608	2.7227	36.5042	-2.1996	85.7713
			308˚K			
0	4.4003	-	-	-	-	-
0.22	4.2896	6.3482	4.4547	33.6443	-3.5521	114.3695
0.44	4.2409	4.5697	2.2525	41.5092	-1.7961	82.3279
0.66	4.1946	3.9316	1.4415	44.7101	-1.1494	70.8320
0.88	4.0600	4.8768	2.9336	34.6960	-2.3394	87.8624
1.1	3.9741	4.8871	2.8489	36.4154	-2.2719	88.0472
1.32	3.9274	4.5191	2.3954	38.0036	-1.9103	81.4168
1.46	3.9017	4.3072	2.1594	38.4650	-1.7220	77.5998
			313˚K			
0	4.3563	-	-	-	-	-
0.22	4.2384	6.8290	4.4603	42.0435	-3.5281	123.0315
0.44	4.2079	4.2987	1.8790	43.3262	-1.4863	77.4454
0.66	4.1463	4.0538	1.5949	44.0744	-1.2615	73.0336
0.88	4.0450	4.5072	2.5828	34.3048	-2.0430	81.2019
1.1	3.9546	4.6527	2.6909	34.9649	-2.1284	83.8237
1.32	3.9141	4.2682	5.9283	24.2157	-2.2949	76.8966
1.46	3.8949	4.0271	1.9137	37.8059	-1.5137	72.5538
			318˚K			
0	4.3139	-	-	-	-	-
0.22	4.2174	5.6404	3.7129	34.0492	-2.9148	101.618
0.44	4.1487	4.8290	3.0950	41.8755	-1.9465	86.9931
0.66	4.1106	3.9629	2.1346	43.5815	-1.1999	71.3966
0.88	4.0492	3.8696	2.0563	37.7214	-1.3802	69.7158
1.1	3.9422	4.3473	2.4968	34.9856	-1.8694	78.3214
1.32	3.9053	3.9825	2.0195	36.7268	-1.5108	71.7497
1.46	3.8923	3.7154	1.6860	37.8107	-1.2565	66.9377
			323˚K			
0	4.3065	-	-	-	-	-
0.22	4.2194	5.1018	2.3087	49.8115	-1.8132	91.9153
0.44	4.1344	5.0394	2.7405	40.8178	-2.1521	90.7912
0.66	4.0835	4.3549	2.0032	41.9296	-1.5731	78.4583
0.88	4.0368	3.9503	1.8398	37.6206	-1.4447	71.1688
1.1	3.9600	4.0595	1.8407	39.5711	-1.4455	73.1365
1.32	3.9141	3.8316	1.6565	38.8243	-1.3008	69.0305
1.46	3.8981	3.6048	1.4120	39.1973	-1.1088	64.9445

Table.3

The values of limiting apparent molal compressibility (φ_k^o) and limiting apparent molal volume (φ_v^o) their constant S_k and S_v of ammonium sulphate solutions at different temperatures.

Temperature (˚K)	Limiting apparent molal compressibility (φk^0)10^{-8} m^2 N^{-1}	S_k (10^{-8} $m^{-1}N^{-1}$ mol^{-1})	Limiting apparent molal volume (φv^0) m^3 mol^{-1}	S_v ($m^{-1}N^{-1}$ mol^{-1})
303	-16.4976	13.1194	0.6864	71.8480
308	-6.2508	-1.1115	43.5739	34.7684
313	-7.7073	3.7482	88.1783	33.1902
318	-4.5403	-0.4301	101.129	-50.3982
323	-14.4041	12.9067	94.2477	-34.5802

Table.4

The values of limiting apparent molal compressibility (φ_k^o) and limiting apparent molal volume (φ_v^o) their constants S_k and S_v of ammonium chloride solutions at different temperatures.

Temperature (˚K)	Limiting apparent molal compressibility (φk^0)10^{-8} m^2 N^{-1}	S_k (10^{-8} $m^{-1}N^{-1}$ mol^{-1})	Limiting apparent molal volume (φv^0) m^3 mol^{-1}	S_v ($m^{-1}N^{-1}$ mol^{-1})
303	-7.2178	4.6163	13.8920	20.4781
308	3.3579	1.3936	37.6980	0.5737
313	-3.3180	1.2260	53.1710	-17.7241
318	4.8843	-5.9002	39.2123	-1.2300
323	-2.5414	1.1053	52.1065	-12.2397

Figure (1& 2)

Concentration Vs adiabatic compressibility of ammonium sulphate and ammonium chloride solutions

Figure 1

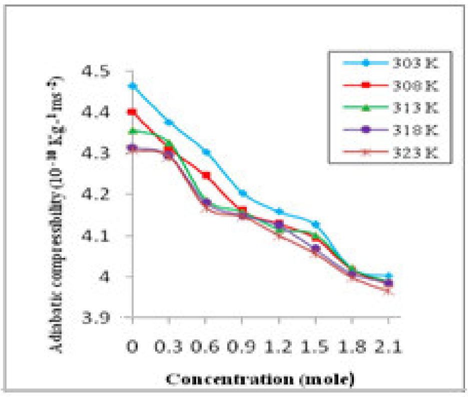


Figure 2

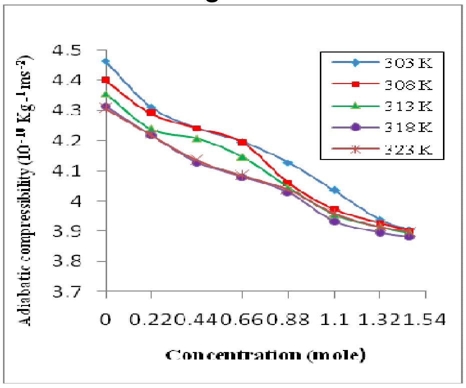


Figure (3&4)
Concentration Vs molal hydration number of ammonium sulphate and ammonium chloride solution

Figure 3

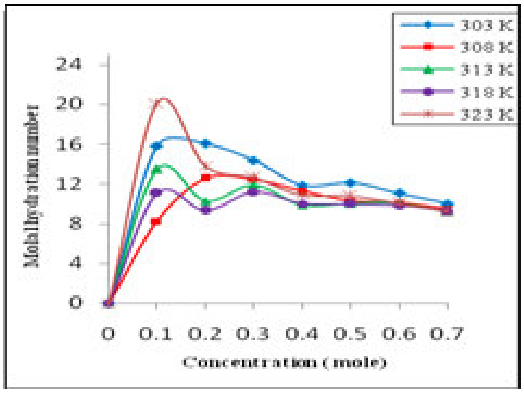


Figure 4

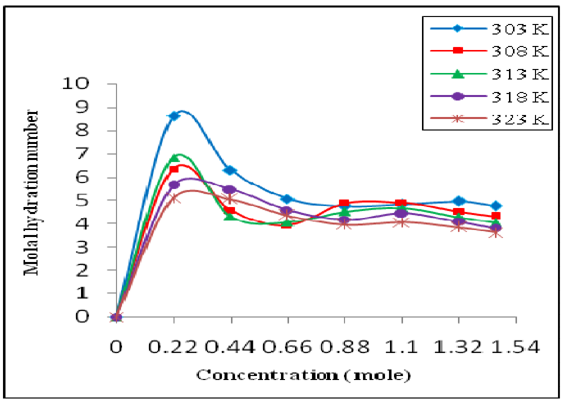


Figure (5&6)
Concentration Vs molar hydration number of ammonium sulphate and ammonium chloride solution

Figure 5

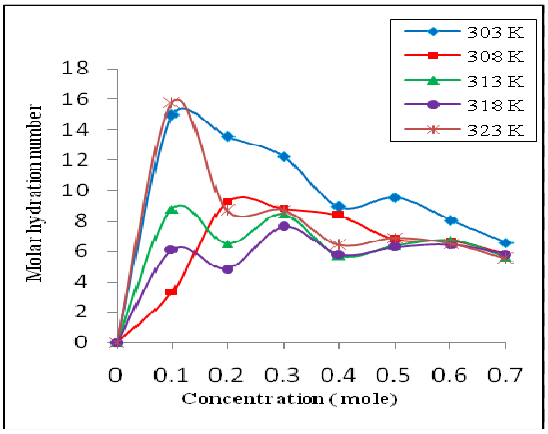


Figure 6

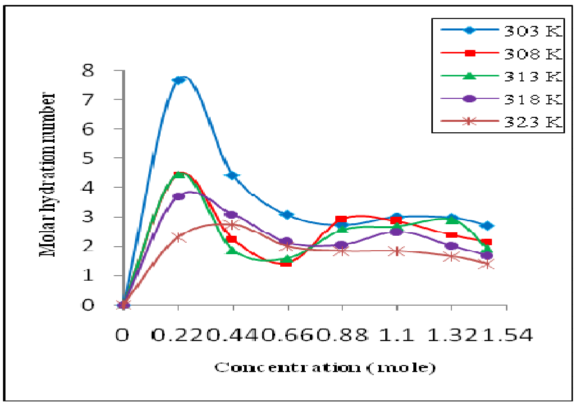


Figure (7&8)
Concentration Vs apparent molal volume of ammonium sulphate and ammonium chloride solution

Figure 7

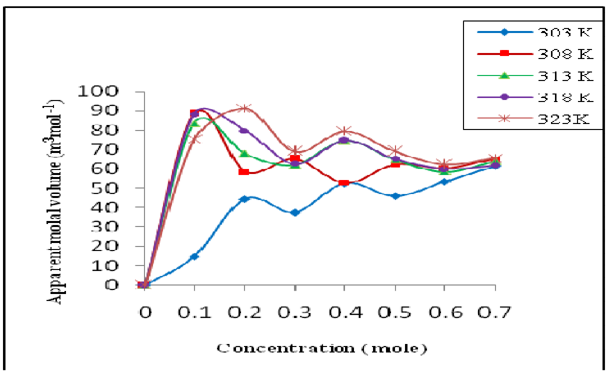


Figure 8

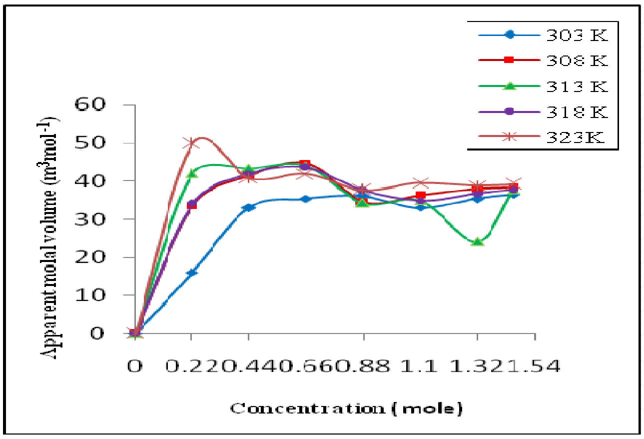


Figure (9&10)
Concentration Vs apparent molal compressibility of ammonium sulphate and ammonium chloride solution

Figure 9

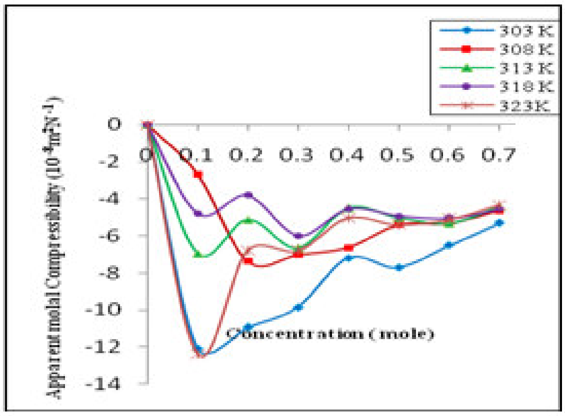


Figure 10

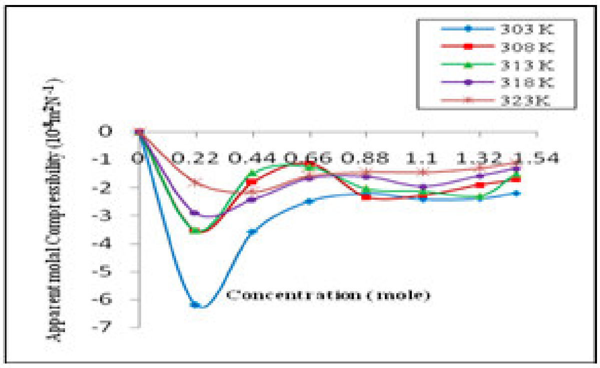


Figure (11&12)
Concentration Vs molar solvated volume of ammonium sulphate and ammonium chloride solution

Figure 11

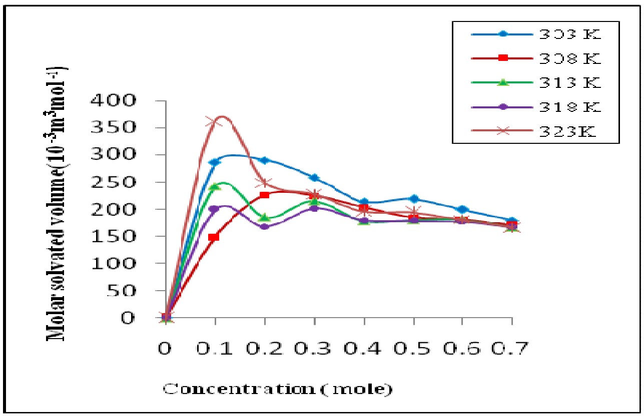


Figure 12

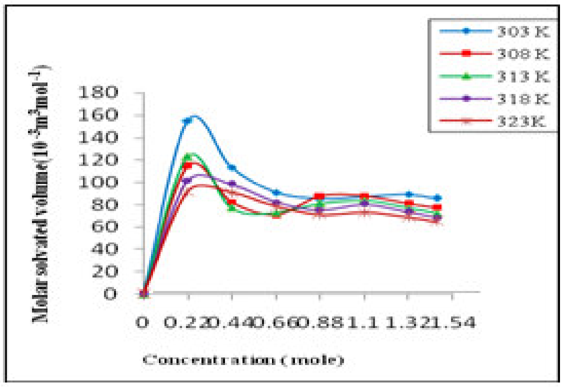


Figure (13&14)
Temperature Vs limiting apparent molal compressibility and their constant of ammonium sulphate and ammonium chloride solution

Figure 13

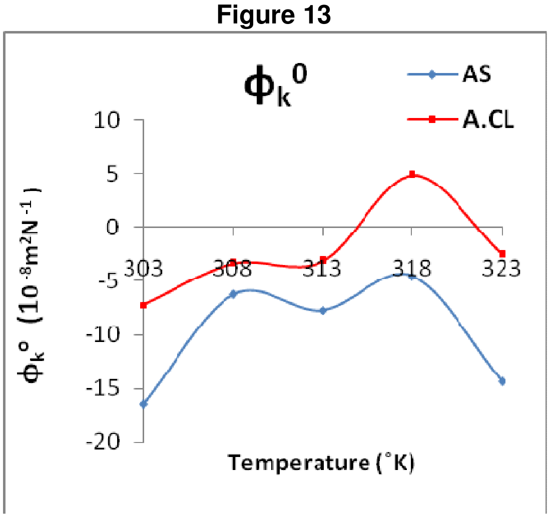


Figure 14

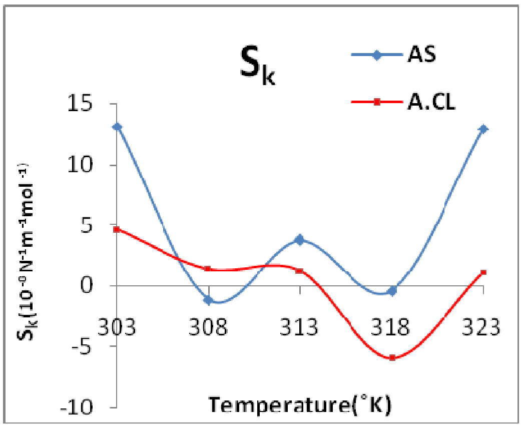


Figure (15&16)
Temperature Vs limiting apparent molal volume and their constant of ammonium sulphate and ammonium chloride solution

Figure 15

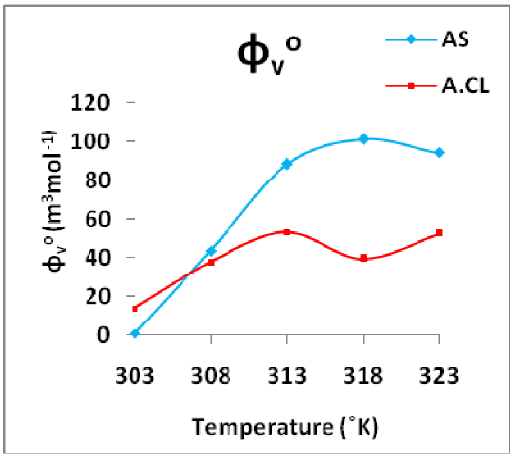
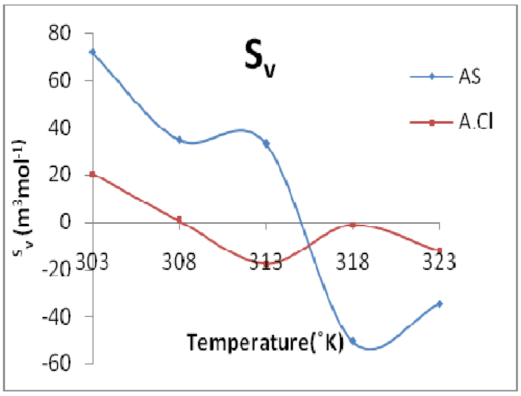


Figure 16



Apparent molal Volume

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 greater than that of ammonium chloride. The higher values of φ_v suggest that the strong solute-solvent interaction occurring in the solution[7]. This variation represents the existence of strong ionic bonding between solute and solvent molecules of ammonium sulphate solutions compared to ammonium chloride solutions. These results suggest that a large portion of water molecules exert electrostatic force which attracts the neighbouring molecules decreasing effective volume of water.

Apparent molal compressibility

The negative values of φ_k for both systems at all temperatures and concentrations which are given in tables (1&2). The variations of φ_k with concentration for both systems are represented graphically in figures (9&10). 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 indicating the ionic interaction occurring in the solution which indicates that the strengthening of ion-solvent interaction in ammonium sulphate solution.

Molar solvated volume

Molar solvated volume has a culmative effect due to φ_v and $n_h v_1$. As the concentration increases φ_s decreases even though φ_v increases, this is because of hydration number rather than by φ_v. Figures 11 & 12 show the molar solvated volume, value is higher in ammonium sulphate solution compared to ammonium chloride solution.

Limiting apparent molal compressibility (φ_k & S_k)

The limiting apparent molal compressibility due to Masson's equation has been computed using least square method. The evaluated parameter limiting apparent molal compressibility (φ_k^o) 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 tables 3&4. It is observed that the values are negative in ammonium sulphate and ammonium chloride fertilizer solutions. Appreciable negative values of φ_k^o for both the systems suggest that the existence of solute – solvent interactions. S_k values are positive in ammonium chloride fertilizer solution. The positive values of S_k indicates the strengthing of ion–ion interactions in the solution[8]. In ammonium sulphate fertilizer solution negative S_k values are observed at 308˚Kand 318˚K. The negative S_k values indicate an weak ion-ion interaction[9].

Limiting apparent molal volume (φ_v & S_V)

The volume behaviour of a solute at infinite dilution is satisfactorily represented by φ_v^o which is independent of the solute–solute interactions and provides information concerning solute–solvent interactions. The values of φ_v^o are positive at all temperatures in both the systems. These values of φ_v^o which are higher in ammonium sulphate solution compared to ammonium chloride fertilizer solution indicating a strong ion–solvent interactions occurring in this system. The S_v values are found to be negative at higher temperatures for both the systems. The negative values of S_v suggest the presence of weak ion-ion interaction.

CONCLUSION

The solvation approach is used to interpret ion-solvent interaction. The solvation number analysis exhibits the effect of solvation is higher in ammonium sulphate than in ammonium chloride fertilizer solutions. The larger values of apparent molal volume (φ_v) are found in ammonium sulphate solution indicating that molecular association is more pronounced in that solution. The present study emphasizes that aqueous ammonium sulphate solution is more solvated than aqueous ammonium chloride solution.

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