Study the Density of the Double Salt (Ammonium iron (II) sulfate) Dissolved in Water and Ethylene Glycol at Different Temperatures

Nagham H. Abood
Dept. of Applied Science Chemistry/University of Technology

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Abstract

Densities of double salt $[(NH_4)_2Fe(SO_4)_2.6H_2O]$ dissolved in distilled water and in ethylene glycol at three temperatures (298.15,303.15 and 308.15)k have been utilized to calculate the apparent molar volume($\emptyset v$), limiting apparent molar volume ($\emptyset v°$),experimental slop(Sv). These results provide as information about solute-solvent, solute-solute interaction and structure-forming, structure-breaking tendency from partial molar expansibility($\emptyset_E$).

Key words: double salt, partial molar volume, solute –solvent, solute-solute interactions.

Introduction

Ammonium iron (II)sulfate or Mohr's salt, is the inorganic compound with the formula $[(NH_4)_2Fe\ (SO_4)_2.6H_2O]$ containing two different cations, Fe^{+2} and NH_4^{+1}It is classified as a double salt and ammonium sulfate. It is a common laboratory reagent like the other ferrous sulfate salts , ferrous ammonium sulfate dissolves in water to give the aqueous complex [$Fe(H_2O)_6]^{+2}$, which has octahedral molecular geometry[1].This compound is a member of a group of double sulfates called Schöintes or Tutton's salt , which form monoclinic crystals and have formula $M_2N(SO_4)_2.6H_2O$ [2]from its application in analytical chemistry,this salt is preferredover other salts of ferrous sulfate for titration purposes as it is much less prone to oxidation by air to iron(III).The oxidation of solutions of iron (II) is very pH dependent occurring much more readily at high PH. The ammonium ions make solutions of Mohr's salt slightly acidic, which is slow this oxidation process[3]also there is new application of this salt which has been found in an organic reaction in which the knoevenagel condensation, Michael addition and intermolecular cyclization of 4-hydroxoumarin,malononitrile and aromatic aldehydes led to novel and known pyranocoumarins. Simple operation, the use of readily accessible commercial starting materials, good to excellent yields and short reaction times show efficiency of this method for the synthesis of these biologically interesting products[4].This model compounds in waterand ethylene glycol as solvents helps to understand some thermodynamic properties of solutions[5] ion-water interactions which are very important in chemistry, ions effect on the rates of chemical reaction [6].

Ion –exchange mechanisms used for chemical separations [7] and in this study we will discuss the solute –solute, solute-solvent interactions in the solution of (salt+water) and (salt+ ethylene glycol) at different temperatures as well as the structure- making/breaking tendency of the solute (salt)in the given solutions.

Experimental section

Material

The double salt $[(NH_4)_2Fe\ (SO_4)_2.6H_2O]$ was provided by BDH chemical (England), ethylene glycol (EG), $(HOCH_2CH2OH)$ was provided by Sd Fine-chem-limited (SDFCL). A series of concentration from complex salt was prepared in range (0.025-0.3)M at different temperatures, the molal concentration were calculated from molar concentration (C) mol/L using eq (1) [8]

$$m = \frac{1000C}{1000\,\rho - CM_2}\,(1)$$

Where (M_2)in g/mol is the molecular weight of double salt.

Densities measurements

Densities of solutions were measured by using pycnometer(25)ml which were calibrated with doubly distilled water at three temperatures (298.15,303.15 and 308.15)k the densities of solution were calculated by weights using balance Sartorius BL 2105(Germany) with an accuracy of 10^{-4} gm after reaching thermal equilibrium with a water bath at the studied temperature, divided by the volume of pycnometer.

Results and discussion

The practical data of densities of solution (salt +H2O) and (salt + EG) at (298.15, 303.15 and 308.15) k. were listed in table (1)and the relationship between the density and the molalconcentration were shown in figures (1) and (2).
Table (1) exhibits that the density values of solution in both solvents water and ethylene glycol increased with increasing concentration, in addition these values decrease with increasing temperature at the same concentration. These results agree with general behavior of liquid solutions.

Values of density of solution are plotted versus molar concentration then treated with linear model by the least square approximation by the following equation

$$\rho = a + bc \qquad (2)$$

Where a, b are coefficientThe correlation coefficient (R^2)and standard deviation (σ) are listed in table (2) which are an evident that a good agreement with a linear model.The standard deviation (σ) was estimated from equation (3)

$$\sigma = \left[\sum(\rho_{\mathrm{exp}} - \rho_{\mathrm{cal}})^2/(\mathrm{N} - \mathrm{P})\right] {}^\wedge 0.5 \qquad (3)$$

Where ρ_{exp},ρ_{cal}arethe experimental and calculated density respectively, P is the number of the coefficient in equation (2), N is number of experimental points.

To understand the nature of solute –solvent and solute –solute interactions of this solution we calculated the apparent molar volume ($\emptyset_v$) (cm^3/mole) from equation (4)[9]

$$\emptyset_v = \frac{1}{m}\left(\frac{1000 + m.M_2}{\rho} - \frac{1000}{\rho^\circ}\right) (4)$$

Where ρ,ρ° are the densities of solution and solvent respectively.(m) is the molal concentration of complex salt in (mole/kg). The values of apparent molar volume of the investigated solute are listed in table (3) and shown in figures (3) and (4). These figures clearly show that the values of $\emptyset v$ do not respond in a linear manner at the whole concentration range of the job for both solvents, this case can be attributed to the higher order attractions among solute particles. For this reason the interest was focused on the low concentration region (below 0.1 molal) where these higher order interactions can be neglected, in addition to estimate the partial molar volume at infinite dilution or limiting apparent molar volume($\emptyset v^\circ$) ($cm^3.mol^{-1}$) which considered as a measure of solute –solvent interactions and a measure of molecular volume of solute [10] by using the masons Empirical equation (5)[11]

$$\emptyset v = \emptyset v^\circ + Sv.\sqrt{m} \qquad (5)$$

Where the experimental slope which is a measure of solute-solute interactions[12]. The calculated values of $\emptyset v^\circ$andSv,from the intercept and slope the plottes the values of $\emptyset v$ versus the root concentration $\sqrt{m}$ are listed in table (4),the plots are shown in figures (5) and (6).
In table (4) we can see the values of($\emptyset v^\circ$)were large negative inwater and have an oscillating character with varying temperature which indicates a weak solute –solvent interaction, at the

same time the values of Sv in water are large positive reflecting a strong solute-solute interaction nature which explain the reason behind the non-linear behavior of $\emptyset v$ at concentrations above 0.1 molal, this strong attraction is understood in the light of tendency of Fe^{+2} ions to precipitate as $Fe(OH)_2$ in neutral aqueous solution ($K_{sp}=8\times10^{-16}$) which means the minimum pH to prevent precipitation of iron(ii) ion is 5[12]. In the EG solvent, the values are negative too but at 298.15 k is less negative than in water then the value becomes more and more negative with increasing temperature, this may be due to the formation of some kind of complex between EG molecules and iron ion, but with increasing temperature the stability of this complex decreased as this is clear from the decrease of solute-solvent interaction with increasing temperature. On the other hand the solute –solute interaction increases with increasing temperature reflecting the fact of reducing the capability of dissolution of the salt in EG at higher temperatures.

The relationship between the limited partial molar volume ($\boldsymbol{\emptyset v}°$) and temperature are according by the following equation (6)

$$\emptyset v° = \alpha + \beta T \qquad (6)$$

$$\emptyset_E = [\partial\, \emptyset v°/\, \partial T]p = \beta \qquad (7)$$

The values of first derivative which called partial molar expansibility [13] (Q_E) have been calculated and listed in the table (5)which is a measure to structure –forming, structure –breaking affinity to solute molecules on lengthy range order of solvent molecules,in table (5) the values of (Q_E) are negative in both solvents and this indicate the salt perform as structure breaking behavior, this effect is more strong in EG solvent than on water because the hydrogen bonding network in EG is weaker than that in water so it can be concluded that the salt causes a long range damage to the solvent structure in EG than that it does to the water.

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Table (1) Values of practical densities ρ ($gm.cm^{-3}$) of (salt + water)and(salt +EG) at (298.15, 303.15 and 308.15) k.

C (mole/L)	ρ ($g.cm^{-3}$) in H_2O		
	298 k	303 k	308 k
Solvent (H_2O)	0.99704	0.99565	0.99403
0.025	1.03546	1.03463	1.03275
0.030	1.03654	1.03567	1.03422
0.035	1.03790	1.03661	1.03487
0.040	1.03795	1.03773	1.03613
0.045	1.04054	1.03888	1.03792
0.050	1.04235	1.04100	1.03982
0.100	1.05366	1.05190	1.05053
0.150	1.06528	1.06021	1.06139
0.200	1.07623	1.07423	1.07357
0.250	1.08857	1.08592	1.08583
C (mole/L)	ρ($g.cm^{-3}$) in EG		
	298 k	303 k	308 k
Solvent (EG)	1.1061	1.1042	1.1026
0.025	1.14313	1.14549	1.14486
0.030	1.14618	1.14710	1.14632
0.035	1.14778	1.14829	1.14710
0.040	1.14798	1.14880	1.14671
0.045	1.14901	1.14960	1.14804
0.05	1.15342	1.15208	1.15038
0.100	1.16272	1.16275	1.15962
0.150	1.17073	1.17059	1.16692
0.200	1.17036	1.18144	1.17203
0.250	1.17405	1.1820	1.18965
0.300	1.19085	1.19303	1.19111

Table (2) Values of empirical parameters a ($gm.cm^{-3}$) b ($gm.cm^{-3}.mol^{-1}.L$), R^2 correlation and standard deviation for (salt + water) and (salt +EG).

Density parameters in H_2O				
T/k	a($gm.cm^{-3}$)	b($gm.cm^{-3}.mol^{-1}.L$)	R^2	σ
298	1.0301	0.2285	0.998	0.00461
303	1.029	0.2226	0.998	0.00532
308	1.0274	0.2296	0.999	0.00632
Density parameters in EG				
T/k	a($gm.cm^{-3}$)	b($gm.cm^{-3}.mol^{-1}.L$)	R^2	σ
298	1.143	0.152	0.947	0.00557
303	1.1425	0.1777	0.989	0.00444
308	1.1408	0.175	0.983	0.00699

Table (3a): The values of apparent molar volume of (salt +H_2O) at (298.15, 303.15 and308.15) k.

Root concentration	$\O_v$ ($cm^3.mole^{-1}$) in H_2O		
	298 k	**298 k**	**298 k**
0.158	-1147.90	-1172.24	-1163.53
0.173	-927.14	-945.91	-953.35
0.187	-777.48	-781.60	-779.31
0.200	-632.43	-662.79	-664.38
0.212	-576.32	-571.01	-586.61
0.224	-515.63	-517.19	-526.89
0.316	-174.58	-171.14	-173.88
0.387	-62.95	-38.44	-57.28
0.447	-3.81	-0.75	-5.58
0.500	26.09	31.18	25.08
0.548	60.00	60.76	55.01

Table (3b): The values of apparent molar volume of (salt + EG) at (298.15,303.15 and308.15) k

Root concentration	$\O_v$ ($cm^3.mole^{-1}$) in EG		
	298 k	**298 k**	**298 k**
0.158	-980.96	-1140.54	-1177.31
0.173	-850.35	-939.92	-965.95
0.187	-719.45	-785.76	-797.47
0.200	-589.82	-654.56	-644.44
0.212	-505.55	-558.47	-560.25
0.224	-499.17	-512.03	-511.03
0.316	-156.48	-175.13	-161.45
0.387	-34.39	-45.71	-33.25
0.447	52.31	5.38	40.81
0.500	109.16	58.10	39.84
0.548	99.41	86.97	88.06

Table (4): Limiting apparent molar volume ($\O v°$), experimental slop (Sv) for(salt +H_2O) and (salt + EG) at different temperatures.

(salt+H_2O)		
T/K	$\O v°$	Sv
298	-2614.9	9628.4
303	-2694.0	9975.5
308	-2647.0	9711.1
(salt+ EG)		
T/K	$\O v°$	Sv
298	-2205.4	7873.3
303	-2638.7	9739.6
308	-2771.2	10372.0

Table (5): Apparent molal expansibility for the salt in both solvents

System	Q_E
Salt + H_2O	-3.21
Salt +EG	-56.58

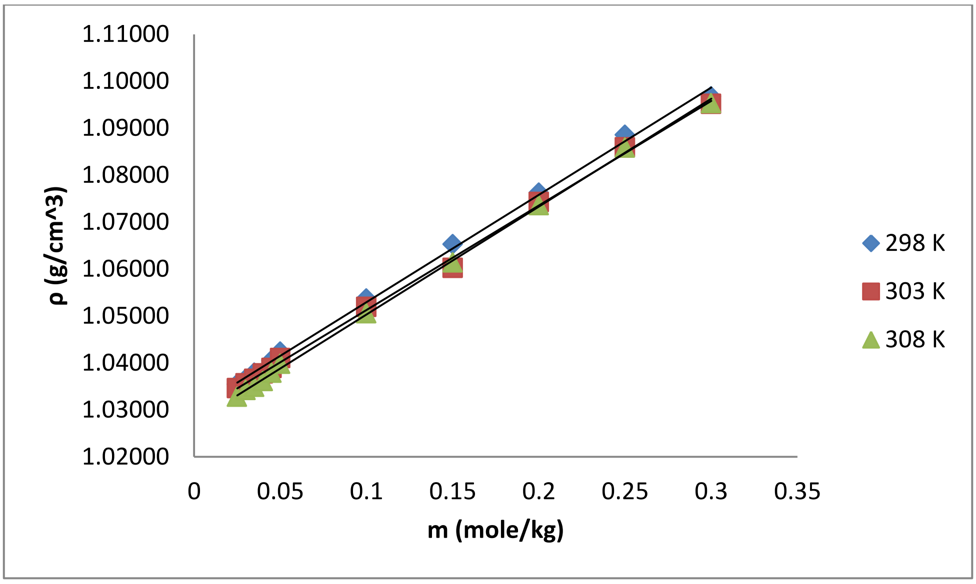

Figure (1): Density data of $[(NH_4)_2Fe\ (SO_4)_2.6H_2O]$ in H_2O

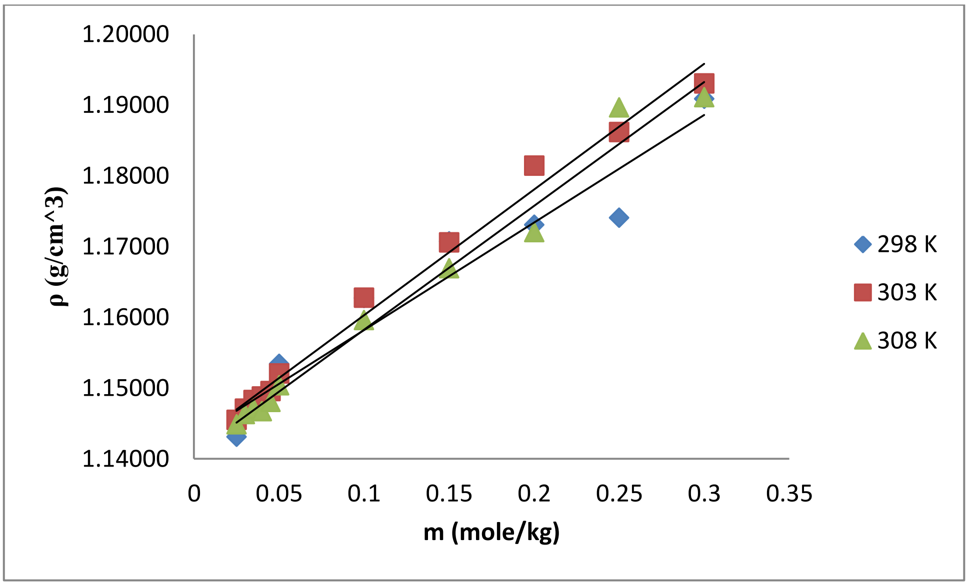

Figure (2): Density data of $[(NH_4)_2Fe\ (SO_4)_2.6H_2O]$ in EG

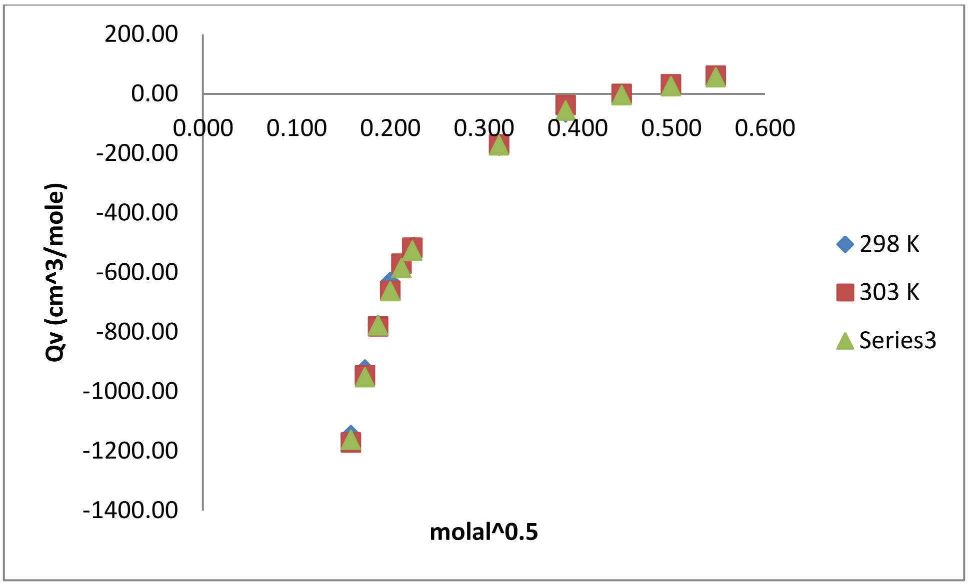

Figure (3): Apparent molal volume of $[(NH_4)_2Fe(SO_4)_2.6H_2O]$ in H_2O

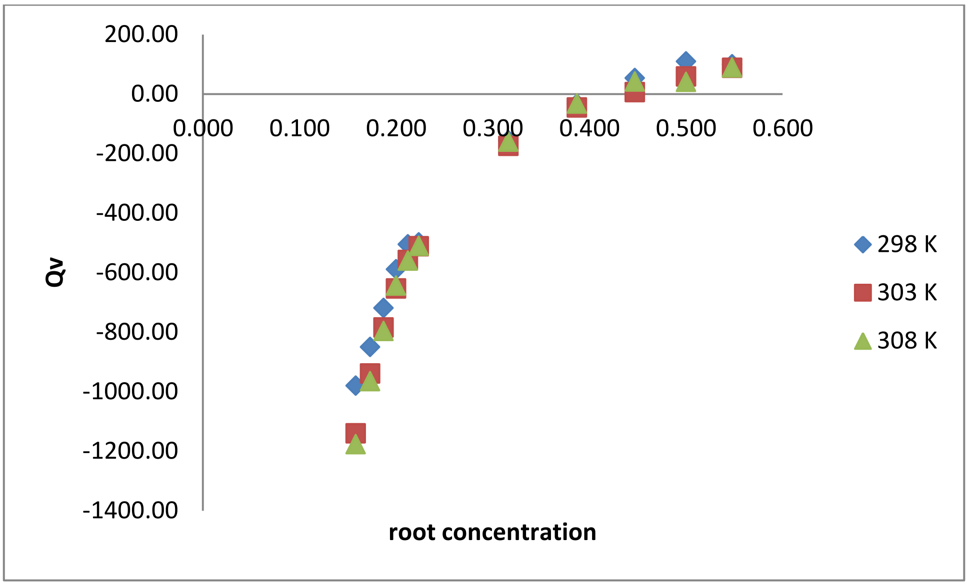

Figure (4) :Apparent molal volume of $[(NH_4)_2Fe(SO_4)_2.6H_2O]$ in EG

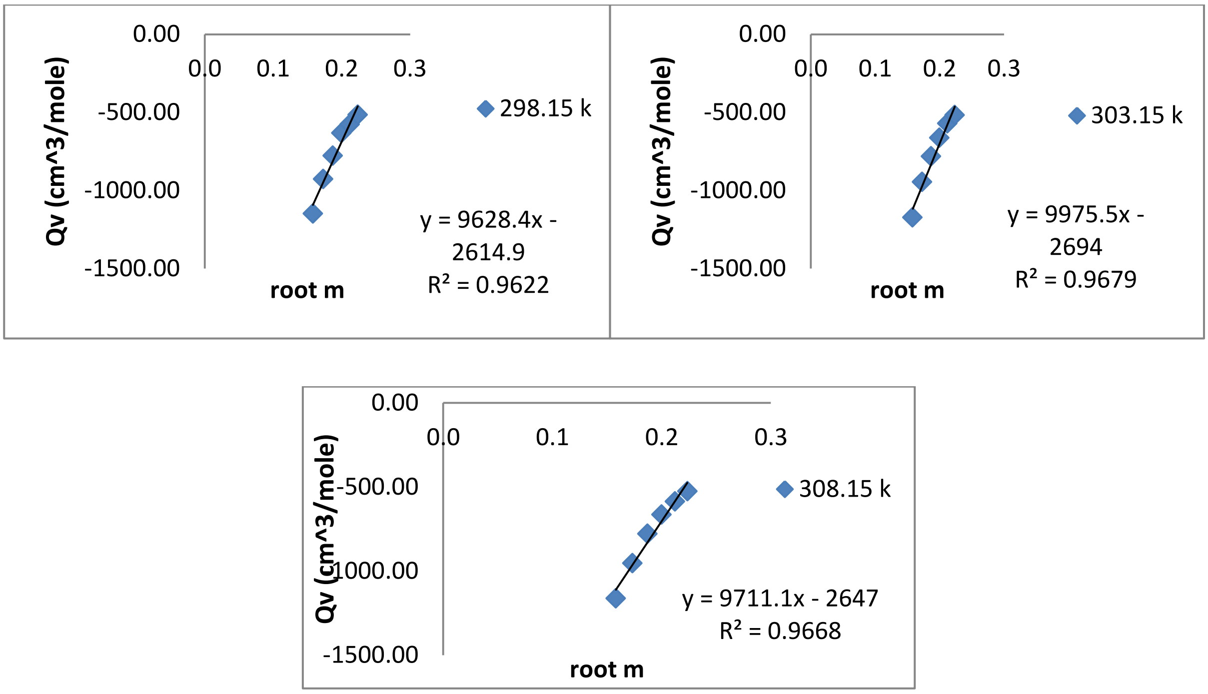

Figure (5): Linearized initial segment of $\emptyset_{\nu}$ vs square root of the molal concentration of $[(NH_4)_2Fe\ (SO_4)_2.6H_2O]$ in H_2O

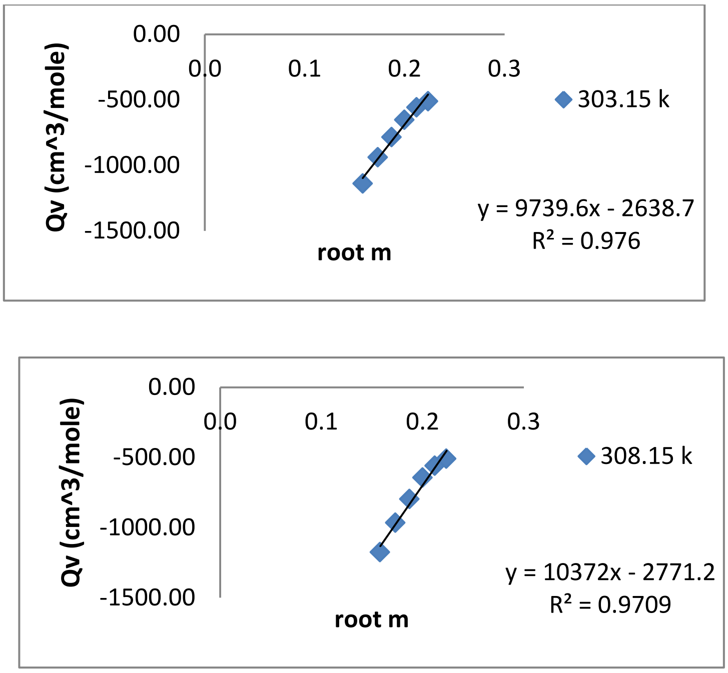

Figure (6): Linearized initial segment of $\emptyset_{\nu}$ vs square root of the molal concentration of $[(NH_4)_2Fe\ (SO_4)_2.6H_2O]$ in EG.