



Studying the Molecular Interactions for Potash Alum with Distilled Water Solution of and Aqueous Ethylene Glycol at Different Temperatures

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Abstract

In this study, the density and viscosity of potash-alum salt in distilled water and 20% (v/v) ethylene glycol (EG)+water were measured at different temperatures (298.15, 303.15, and 308.15) K. The (ρ) values were used to calculate the apparent molar volume (ϕ_v), limiting apparent molar volume (θ_v°) and experimental slope (S_v). The values of the partial molar volume at infinite dilution of transfer ($\Delta\theta_v^\circ$) of Potash alum increased with increased temperatures. From the temperature dependence of (θ_v°), the standard apparent molar expansibility (θ_E°) has been obtained. The viscosity coefficients A and B of the Jones–Dole equation were also calculated. The results recommend a strong ion–ion interaction and that potash-alum acts as a structure-breaker in both water and 20(v/v %) EG + water.

Keywords: Potash alum, Apparent Molar Volume, Jones – Dole equation;

1. Introduction

The ion solvation process (the interaction of an organic solvent with ionic and nonionic molecules) can influence the reactivity of dissolved electrolytes and the outcome of a chemical reaction, by rearranging solvent and solute molecules into solvation complexes. [1]. Thus the knowledge of ion–ion, ion–solvent, and solvent–solvent interactions is very important in the technological area and has considerable theoretical and industrial importance [2-4]. Physico-chemical properties of solutions such as viscosity B-coefficient, apparent molar volume at infinite dilution, and the concentration dependence of the apparent molar volume etc. provide significant data for interpretation of various interactions arising between constituents of the investigated solution and to characterize the properties and structure of solutions [5, 6]. Potassium aluminum sulfate or Potash alum is a double salt, in its aqueous solution the ions can be detected side by side. It is commonly used in the chemical treatment of water. This application prompted us to investigate its behavior in ethylene glycol (EG) solvents. EG is one of the versatile contaminated materials and used in many industries like antifreeze, protective coatings, synthetic fibers, films and gas industries. In the literature the main

physicochemical properties of electrolytes and multivalent electrolytes [7-16] has been reported. To the best of our knowledge, no data have been published for potash alum +water, and potash alum +20% ethylene glycol + water at different temperatures in term of viscosity and density. The present work investigates the molecular interaction and some physico-chemical properties of these binary and ternary systems at 298.15, 303.15 and 308.15 K in terms of ion–ion and ion–solvent interactions.

2. Experimental Part

Potash alum [KAL (SO₄)₂.12H₂O] (474g/mole) (Merck) and Ethylene glycol (Merck) were of analytical reagents grade and used without further purification except for placed Potash alum over P₂O₅ to not absorb moisture. The binary solvent mixture of 20% EG +water was prepared by volume. The concentrations within the range (0.015-0.06) M Potash alum in water and in the binary solvent were prepared and kept Sealed. The density of solutions was measured with a single capillary pycnometer (bulb capacity 10cm³). The pycnometer was washed with chromic acid, distilled water, and acetone then dried with warm air and kept in an oven for 1 hour at about

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50°C (its weight must be accurate). The densities of solutions were calculated using this equation.

$$d = \frac{w - w_e}{v} \quad (1)$$

Where w weight of solution, w_e weight of the empty pycnometer and v volume of the pycnometer. The volume of the pycnometer was calculated from the accurate weight w_o (using an electronic balance, Sartorius BL, ∓ 0.0001) and the density d_o of distilled water using this relation at different temperatures.

$$v = \frac{w_o - w_e}{d_o} \quad (2)$$

The viscosities of the solution at different temperatures were calculated using Ostwald's viscometer (10mL) based on the capillary flow method and the flow time was measured using a stopwatch. Density and viscosity measurement was carried out in an electronically controlled thermostatic water bath (JULABO ME-18V Visco Bath, Germany) whose temperature was controlled to $\pm 0.01^\circ\text{C}$.

3. Results and discussion

3.1. Volumetric properties

The experimental (ρ) of Potash alum + water and 20% (EG) as a function of molar concentration at $T = (298.15, 303.15 \text{ and } 308.15) \text{ K}$ are measured and show in Fig. 1. The density of Potash alum in two systems were found varies linearly with molarity of the solution and decrease as the temperature an increase. This behaviour can be interpreted due to the fact that the solution volume increased with increasing temperature while maintaining the weight constant. To understand the molecular interactions in solutions the apparent molar volume ($\phi_V \text{ cm}^3 \text{ mole}^{-1}$) of Potash alum in H_2O and 20% EG+ H_2O were calculated using measured densities using the following equation [17].

$$\phi_V = \frac{1000(\rho_o - \rho)}{C\rho_o} + \frac{M_2}{\rho_o} \quad (3)$$

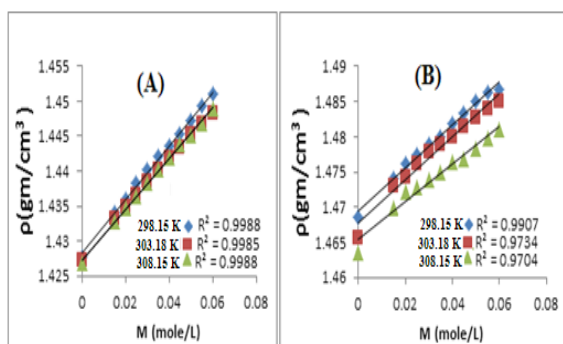


Fig. 1. Densities of Potash alum aqueous solution (A), and (B) 20% EG versus molar concentration at different temperatures.

Where M is the molar mass of Potash alum, ρ and ρ_o represent the densities of solution and solvent respectively. C is the molar concentration of

Potash alum solution. The calculated (ϕ_V) values of the investigated solute are tabulated in Table (1). The values have an increasing trend, becoming more positive as the concentration of Potash alum is increased. Parameters of Masson's Empirical eq.4 [18, 19] were used to found the solute- solute and solute-solvent interaction, (θ_v°) show the nature of the ion-solvent interaction or hydration properties [20, 21] and the volumetric pairwise interaction coefficient (S_v) (experimental slope) provides information regarding ion – ion interactions. These parameters obtained by using a least square fit to the plot of apparent molar volume verses square root of molarity. This type of equation is applicable to the ionic solute where (θ_v°) is limiting apparent molar volume or partial molar volume at infinite dilution that often obtained from the extrapolation of the apparent molal volume (θ_v) to an infinite dilution. The values of (θ_v°) and (S_v) are recorded in Table2.

$$\theta_v = \theta_v^\circ + S_v\sqrt{C} \quad (4)$$

As can be seen from Table (2) the values of limiting apparent molar volume (θ_v°) for Potash alum in water and 20% (v/v)EG+ H_2O are positive but small in magnitude indicating the presence of weak ion-solvent interaction between ions and surrounding solvent molecules due to presence water of hydration which didn't leave ions as single entities.

The values of S_v are also reported in Table (2). The S_v is positive and high for Potash alum in water and 20%EG at different temperatures. The results indicate the presence of strong ion-ion interactions this may be attributed to the absence of appreciable interionic penetration and this the volumetric pairwise interaction coefficient (S_v) gives rise to a positive slope These interactions, however, have lower values at 308.15K, which may be attributed to the increase in solvation of ions with the rise in temperature [2].

To study the influence of the organic solvent in the interaction between the solute and solvent the values of the partial molar volume at infinite dilution of transfer were calculated using the following equation [22, 23].

$$\Delta\theta_v^\circ = \theta_v^\circ(\text{EG} + \text{H}_2\text{O}) - \theta_v^\circ(\text{H}_2\text{O}) \quad (5)$$

The values of $\Delta\theta_v^\circ$ of Potash alum is (14.845, 17.119, and 24.546) at **298.15**, **303.15**, and **308.15K** respectively. The increase in $\Delta\theta_v^\circ$ attributed to the increase in the ionic-hydrophilic interactions between the ethylene glycol functional groups and ions sphere. The variation of partial molar volumes (θ_v°) for Potash alum in water (eq.6) and 20%EG+ H_2O (eq.7) with temperature was described by a polynomial second order in term of absolute T as shown in the following equations.

$$\theta_v^\circ = 0.1372 T^2 - 80.728T + 11882 \quad (6)$$

$$= 0.2402T^2 - 142.24T + 21076 \quad (7)\theta_v^\circ$$

By differentiating the previous equations with respect to temperature ($\frac{\sigma\phi_v^\circ}{\sigma T}$) the standard apparent molar expansibility (θ_E°) can be obtained. (θ_E°) Values give important information related to the solute to solvent interactions [24-26]. The values of (θ_E°) listed in table 2. It evident from table 2 that the values of (θ_E°) are positive and increase with increasing temperature this clearly suggest presence of ion – solvent interaction [27] and some of solvent molecules remain associate with the solute ion even at higher temperature.

3.2 . Viscosity study

The viscosities data η (cp) have been plotted against the molarity of Potash alum+ H₂O and 20%EG+ H₂O at different temperatures and compared in Fig.3. The viscosities found to be increasing with increase in the concentration of Potash alum solutions. This may be attributed to an increasing the frictional resistance of the solution flow. The viscosity values decrease with an increase in temperatures. This may be attributed to decrease the solute–solvent interaction [28].

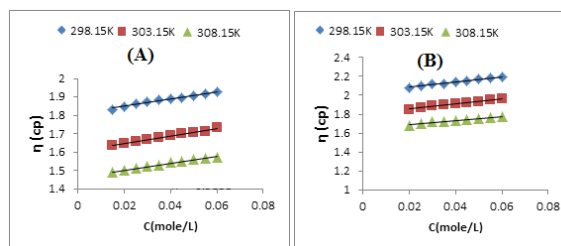


Fig. 2. Viscosities of Potash alum in water (A) and (B) Potash alum in 20 % (v/v) EG+H₂O versus molar concentration at different temperatures.

The relative viscosities of in Potash alum I water and Potash alum in 20%EG+H₂O as function of molar concentration was describe by Jones – Dole equation [29].

$$\frac{\eta}{\eta_0} - 1 = A + B\sqrt{C} \quad (8)$$

Where η and η_0 are the viscosities of the solution and the solvent respectively. η_{rel} Is relative viscosity and C is the molar concentration. Falkenhagen coefficient (A) reflecting the contribution of ion–ion interactions, whereas, B the viscosity coefficient provides information concerning ion–solvent interaction in the solution or in other word effects of solute on the structure of the solvent. The viscosity coefficients B and A were determined by the least-squares method from the slope and intercept of the linear plot of $\frac{\eta_{rel}-1}{\sqrt{C}}$ versus \sqrt{C} and are listed in Table 3.

Table 1 Values of Apparent Molar Volume ($\phi_v \text{ cm}^3 \text{ mole}^{-1}$) as Function of Potash alum (mole/L) in water and 20% EG+ H₂O at Various Temperatures

C mole/L	$\phi_v \text{ cm}^3 \text{ mole}^{-1}$					
	Potash alum (H ₂ O)			Potash alum (20%EG+H ₂ O)		
	298.15 K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K
0.015	59.6060	55.0159	38.5604	83.2921	63.7869	75.1688
0.020	54.2048	62.4192	41.9456	78.9223	79.8717	63.5702
0.025	62.2017	72.6905	37.5332	97.6578	82.2162	79.9215
0.030	61.6924	71.5975	39.9612	115.610	80.1443	87.0787
0.035	61.9294	72.2180	45.6976	121.7228	94.39861	100.6439
0.040	67.7140	74.7854	55.7781	124.3954	106.1798	97.9741
0.045	67.3850	82.0758	58.0154	139.5834	107.3218	102.1107
0.050	75.3920	81.0420	59.8052	135.8934	110.8417	100.0133
0.055	76.9734	83.9413	59.1049	136.2013	115.9323	104.7167
0.060	73.9692	86.3107	61.2060	136.5033	121.7193	119.4057

Table 2 Limiting apparent molar volume (θ_v°) in (**cm³.mol⁻¹**), experimental slop (**S_v**) in (**cm³.mol⁻².L**), and standard apparent molar expansibility (θ_E°) for Potash alum in water and 20 % (v/v) EG+ H₂O at different temperatures.

T/K	Potash alum (H ₂ O)			Potash alum (20%EG+H ₂ O)		
	θ_v°	S _v	(θ_E°)	θ_v°	S _v	(θ_E°)
298.15	7.517	222.6	1.084	22.362	372.77	0.991
303.15	16.311	293.9	2.456	33.43	346.58	3.393
308.15	31.964	182.0	3.828	56.51	340.58	5.795

Table 3. The values of A (L^{3/2}.mole^{-1/2}) and B (L.mole^{-1/2}) coefficients of Potash alum in water and Potash alum in 20% (v/v) EG+H₂O.

T/K	Potash alum (H ₂ O)		Potash alum (20%EG+H ₂ O)	
	A	B	A	B
298.15	0.674	-0.6869	46.201	-120.7
303.15	1.0246	-1.4143	45.586	-118.44
308.15	1.48	-2.6495	46.931	-122.43

The values of A are positive in Potash alum+H₂O and 20% EG+H₂O at all temperature suggesting the presence of strong ion–ion interactions. It also can be observed from Table (3) that the viscosity B coefficient are negative indicating the structure–breaking ability of Potash alum .weakly hydrated ions, have greater tendency to decrease the viscosity of the non-nearest neighboring solvent molecules in ion-solvent system. This conclusion hence supports the behaviours' of (θ_v°) and (S_v).

4. Conclusions

The densities and viscosities of potash alum in water and in aqueous solution of ethylene glycol (EG) have been done. The values of densities and viscosities in two systems are varies linearly with molarity of the solution and decrease with the temperature an increase. Volumetric study of potash alum in two systems indicated the presence of weak ion-solvent interactions and strong ion – ion interactions. The values of standard apparent molar expansibility indicate the presence of ion-solvent interactions because all its values are positive and increase with temperature increasing. From viscosity study the values of Falkenhagen coefficient (A) are positive in two systems at all temperature which indicate presence of strong ion-ion interactions. The viscosity coefficient (B) is negative indicating the structure-breaking ability of potash alum.

5. Conflicts of interest

In accordance with our policy on Conflict of interest please ensure that a conflicts of interest statement is included in your manuscript here. Please note that this statement is required for all submitted manuscripts. If no conflicts exist, please state that “There are no conflicts to declare”.

6. Formatting of funding sources

List funding sources in a standard way to facilitate compliance with the funder's requirements.

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