

Study the Partial Molar Volume of Chrom Alum in Aqueous Poly (ethylene glycol) Solution at Different Temperature

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Abstract

This study present, the density of alum chrom in water and in aqueous solution of poly (ethylene glycol) (1500) at different temperature (288.15, 293.15, 298.15) k. Experimental values of density was used to calculate the apparent molar volume (V_θ), limiting apparent molar volume V_θ° , experimental slope (S_v) and the partial molar volume at infinite dilution of transfer of solute Δv_θ° . These results have been interpreted the molecular interaction in term of ion- solvent, ion- ion interaction. The structure making /breaking capacities have been inferred from the sign of the second derivative of limiting partial molar volume with respect temperature at constant pressure. Alum has been formed to act as structure breaker in water and aqueous PEG solution.

1. Introduction

Great interest has been focused on the measurement, correlation of electrolyte solution. A detailed understanding of such solution requires information on a variety of chemical and physical parameter. The partial molar volume of electrolyte provides valuable information about ion- ion, ion- solvent, and solvent- solvent interaction^[1-5]. This information is fundamental importance for understanding the reaction rates and equilibrium involving dissolved electrolyte. The addition of organic solvent in an aqueous solution of electrolyte bring about a change in solvation of ions that often results in large change in the reactivity of dissolved electrolyte^[6,7].

In the present study, poly (ethylene glycol), HO (CH₂CH₂O)_nOH ($M_w \cong 1500$) is used as solvent^[8] which have wide spread application in many branches of industry such as pharmaceuticals, food, and cosmetics.

In the literature there are many characterizations reported of electrolyte^[9-11], but no data have been reported for alum, this name is given

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to all the double salts, having the composition: $M^{III}M^{III}(SO_4)_2 \cdot 12H_2O$. Chrom alum have the composition $(KCr(SO_4)_2 \cdot 12H_2O)$ which is used (i) as mordent in dyeing (ii) for tanning leather (iii) in photography (during fixing) for hardening of the negatives^[12].

2. Experimental Section

Material. Chrom alum, BDH chemical (England), PEG was provided by Sigma- Aldrich chemicals. bidistilled water was used, for the preparation of solution.

Densities were measured by using 25 mL pyknometer, the volume of the pyknometer were calibrated with deionized and doubly distilled water at (288.15, 293.15, 298.15) K. The densities of alum solution were determined by weights using balance Sartorius BL 210S (Germany) with an accuracy of 10^{-4} after reaching thermal equilibrium with a water bath at the studied temperature, divided by the volume of pyknometer.

3. Results and Discussion

The experimental densities of the binary solution of (alum chrom + water) and ternary solution of (alum + aqueous polyethylene glycol) at different concentration are represented in Table (1).

Table (1) shows that the density values increase with increasing alum concentration in binary and ternary solution over the whole concentration. The density values decrease with the augment of temperature at the same concentration.

Table (1) Experimental densities $\rho(g.cm^{-3})$ for (alum + H_2O) and (alum + PEG) at different temperature

$C_{mol/L}$	(alum + H_2O) Density		
	288.15 K	293.15 K	298.15 K
Water	0.99910	0.99821	0.99704
0.010	1.00242	1.000561	0.99922
0.015	1.00361	1.00203	1.00094
0.020	1.00483	1.00335	1.00287
0.025	1.00638	1.0047	1.00416
0.030	1.00757	1.00602	1.00533
0.035	1.00934	1.00738	1.0069
0.040	1.01053	1.00894	1.00883
$C_{mol/L}$	(alum + EG) Density		
	288.15 K	293.15 K	298.15 K
Solvent (H_2O+EG)	1.00194	1.00086	0.99983
0.010	1.00472	1.00321	1.00122
0.015	1.00594	1.00405	1.00277
0.020	1.00753	1.00579	1.00422
0.025	1.00902	1.00747	1.00542
0.030	1.01038	1.00899	1.00695
0.035	1.01152	1.01132	1.00879
0.040	1.01346	1.01191	1.00998

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The obtained density values are plotted versus molar concentration then treated with linear model by the least square approximation according to the following equation

$$\rho = a + bc \quad (1)$$

The values of a and b coefficient correlation coefficient (r) in addition to standard deviation (σ) are given in Table (2) which show a good agreement with a linear model. The standard deviation (σ) was calculated using equation (2).

$$\sigma = [\sum (\rho_{\text{exp}} - \rho_{\text{cal}}) / N - P]^{0.5} \quad (2)$$

Where ρ_{exp} , ρ_{cal} are the experimental and calculated density respectively, N is the number of experimental points and P is the number of the coefficient in equation (1).

Table (2) Empirical parameters in equation (1), a (gm.cm⁻³), b (g.cm⁻³.mol⁻¹.L) and standard deviation for (alum+H₂O) and (alum + EG)

Alum + H ₂ O				
T/K	a	b	r	σ
288.15	0.999	0.275	0.997	0.000623
293.15	0.997	0.275	0.999	0.000997
298.15	0.996	0.308	0.995	0.000473
Alum+EG				
T/K	a	b	r	σ
288.15	1.001	0.287	0.997	0.000921
293.15	0.999	0.313	0.987	0.001235
298.15	0.998	0.293	0.997	0.000385

The apparent molar volume V_{θ} (cm³.mol⁻¹) for (alum + H₂O) and (alum + PEG) calculated from density using the following standard expression.

$$V_{\theta} = M_2 / \rho^{\circ} - 10^3 / c^* (\rho / \rho^{\circ} - 1) \quad (3)$$

Where ρ , ρ° are the density of solution and solvent respectively:

c is the molar concentration of alum in (mol.L⁻¹): M₂ is its molar mass g.mol⁻¹

The values of the apparent molar volume of the investigated solute are given in Table (3).

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Table (3) Apparent molar volume of (alum + H₂O) and (alum + EG) at different temperature

C _{mol/L}	V _θ (Alum + H ₂ O)		
	288.15 K	293.15 K	298.15 K
0.010	167.560	268.784	278.244
0.015	198.922	244.516	237.455
0.020	213.101	242.346	206.529
0.025	208.397	239.841	213.651
0.030	217.272	239.173	222.410
0.035	207.024	237.551	217.204
0.040	213.852	231.326	204.272
C _{mol/L}	V _θ (alum + PEG)		
	288.15 K	293.15 K	298.15 K
0.010	216.997	258.203	357.471
0.015	229.640	282.517	301.460
0.020	217.496	249.710	278.455
0.025	214.203	232.424	274.654
0.030	216.332	226.229	261.118
0.035	224.127	198.679	242.591
0.040	210.011	221.482	244.949

Apparent molar volume of electrolyte vary with square root of the molar concentration (over wide concentration rang) in accordance with Masson's Empirical relation^[13].

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

This type of equation is applicable to the ionic solute where V_{θ}° is a partial molar volume at infinite dilution or limiting apparent molar volume is regarded as a measure of ion- solvent interaction and S_v is a measure of ion- ion interaction.

The calculated values of V_{θ}° and S_v , from the intercept and slope of the plotted V_{θ} versus $\sqrt{c}$ are given in Table (4).

Table (4) Values of partial molar volume (V_{θ}°) in (cm³.mol⁻¹) experimental slop (S_v) in (cm³.mol⁻².L) for (Alum + H₂O) and (alum + PEG) at different temperature.

T/K	Alum +H ₂ O	
	V_{θ}°	S_v
288.15	180.9	5.687
293.15	259.0	-4.088
298.15	260.9	-8.804
T/K	Alum + PEG	
	V_{θ}°	S_v
288.15	226.2	-2.175
293.15	281.6	-11.27
298.15	307.5	-13.53

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It is evident from Table (4) the values of limiting apparent molar volume for (alum+H₂O) are positive suggesting presence of strong ion-solvent interaction between ions and surrounding water molecule. Large positive V_{θ}° for (alum + PEG) than (alum + H₂O), attributed to entrapped the ions in void formed during uncoiling of polymer in solution and there exists electrostatic attraction between these ions and polymer chain in addition, the interaction between ions and water. The V_{θ}° increase with increasing temperature for (alum + PEG) and (alum+H₂O) may be attributed to the increase in solvation of the ions.

The values of S_v are negative for (alum + PEG) and (alum + H₂O) which reflected that ion-ion interaction are very weak at entire temperature except at 288.15 K.

Further, it is also clear from Table (4) that the values of S_v decrease with the rise in temperature, which may be attributed to the increase in solvation of ions. A quantitative comparison of the magnitude of values of V_{θ}° and S_v shows that V_{θ}° values are much larger in magnitude than those of S_v values, suggesting that ion-solvent interaction dominate over the ion-ion interaction in water and aqueous solution PEG.

The values of the partial molar volume at infinite dilution of transfer of solute from aqueous PEG to water calculated as;

$$\Delta v_{\theta}^{\circ} = V_{\theta}^{\circ}(\text{PEG+WATER}) - V_{\theta}^{\circ}(\text{WATER}) \quad (5)$$

The Values of $\Delta v_{\theta}^{\circ}$ of alum is (45.3, 22.6 and 46.6) at 288.15, 293.15 and 298.15 K. respectively. The increase in $\Delta v_{\theta}^{\circ}$ attributed to the decrease in electrostriction in the presence of PEG. Thus, the electrostriction effect, which bring about the shrinkage in the volume of solvent, decreases in the presence PEG as compared with that in pure water.

The temperature dependence of V_{θ}° for (alum + H₂O) and (alum+PEG) can be represented by the following expression;

$$V_{\theta}^{\circ} = -13305 + 901.5 T - 1.524 T^2 \text{ for (alum+H}_2\text{O)} \quad (6)$$

$$V_{\theta}^{\circ} = -52804 + 354.0 T - 0.59 T^2 \text{ for (alum+PEG)} \quad (7)$$

Where, T is the temperature in Kelvin.

The temperature derivatives of $\theta_v^{\circ} = E_{\theta}^{\circ}$ because $E_{\theta}^{\circ} = \left[\frac{\delta V_{\theta}^{\circ}}{\delta T} \right]_p$ where

E_{θ}° is the partial molar volume expansibilities or limiting apparent molar expansibilities^[14].

The E_{θ}° calculated using the above expressions at 288.15, 293.15 and 298.15 K are listed in Table (5).

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Table (5) Partial molar volume expansibilities (E_θ°) in unit ($\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) and $[\delta^2 \theta_v^\circ / \delta T^2]_p$ in ($\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$) for (alum + water) and (alum + PEG)

T/K	Alum+H ₂ O	
	$\delta \theta_v^\circ / \delta T$	$[\delta^2 \theta_v^\circ / \delta T^2]_p$
288.15	+23	-3.048
293.15	+7	-3.048
298.15	-7	-3.048
T/K	Alum + EG	
	$\delta \theta_v^\circ / \delta T$	$[\delta^2 \theta_v^\circ / \delta T^2]_p$
288.15	13.9	-1.18
293.15	8.08	-1.18
298.15	2.18	-1.18

The values of E_θ° decreases with the increase of temperature, for binary and ternary system indicating that the behavior of alum chrom is just like common electrolyte, in the case of common electrolyte the partial molar volume expansibilities decrease with the rise in temperature this means the structure making tendency of the alum chrom decrease with increasing temperature.

The variation of E_θ° with T, has been found to be linear for (alum+PEG) and (alum + H₂O) as shown in Figure (1).

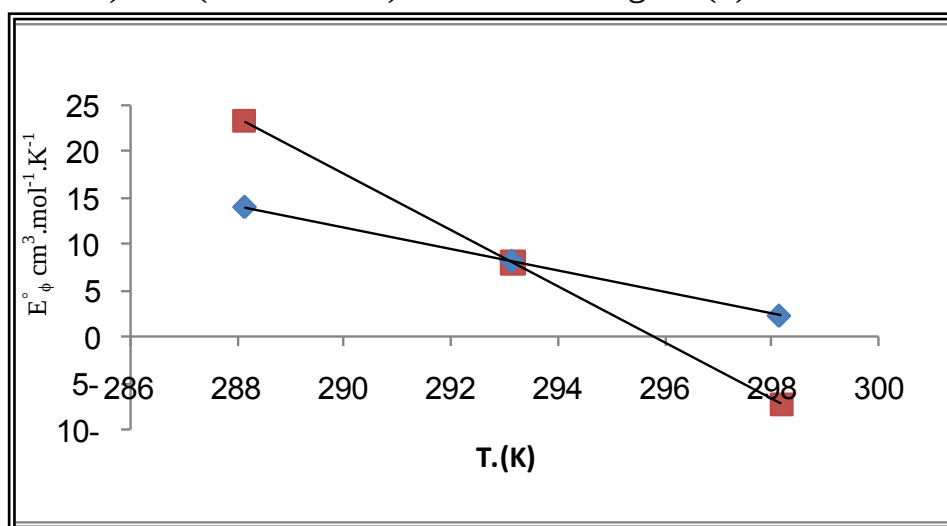


Fig. (1) Variation of E_θ° with T for (alum+PEG) and (alum+H₂O)

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It has been emphasized by number of worker that S_v is not sole criteria for determing the structure making or breaking nature of any solute. Hepler^[15] has developed a technique of examining the sign of $[\delta^2 \theta_v^\circ / \delta T^2]$ for Various electrolytes in term of long rang structure making or breaking capacities of he electrolytes in aqueous solution using the general thermodynamic expression: $[\delta c_p / \delta p]_p = -[\delta^2 \theta_v^\circ / \delta T^2]$ on the bases of this expression, it has been deduced that the structure making electrolytes should have positive value and structure breaking electrolyte negative value.

It is observed that $[\delta^2 \theta_v^\circ / \delta T^2]$ for (alum + PEG) and (alum + H₂O) as shown in Table (5), is negative, thereby showing as structure breakers in water and (water + PEG), on other words, the addition of alum chrome to water and aqueous solution of PEG causes decrease in the structure of water and water + PEG.

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دراسة الحجم المولاري الجزئي لشب الكروم في محلول بولي اثلين كلايكول بدرجات حرارية مختلفة

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الخلاصة

تضمنت هذه الدراسة قياس كثافة شب الكروم في الماء والمحلول المائي للبولي اثلين كلايكول ذو الوزن الجزيئي 1500 وبدرجات حرارة مختلفة (299.15, 293.15, 298.15) مطلقة. استخدمت هذه النتائج لحساب الحجم المولاري الظاهري (V_0)، والحجم الظاهري المحدد (V_0°)، والميل (S_V)، والحجم المولاري الجزئي عند التخفيف الى ما لا نهاية لانتقال المذاب (ΔV_0°)، فسرت هذه النتائج التأثيرات المتبادلة على اساس تأثيرات متبادلة من نوع ايون-مذيب، أيون-أيون. استنتجت قابلية شب الكروم على تكوين أو هدم تركيب المذيب من إشارة المشتقة الثانية للحجم المولاري المحدد مع درجة الحرارة بثبوت الضغط. ووجد ان الشب يسلك كعامل مهدم لتركيب الماء والمحلول المائي للبولي اثلين كلايكول.