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Viscosity and Density of Chrom Alum in Aqueous Poly (Ethylene Glycol) Solution at Different Temperature

S. H. Merza

Department of Chemistry, College of Education, Ibn-Al-Haitham, University of Baghdad

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Abstract

Density data of alum chrom in water and in aqueous solution of poly (ethylene glycol) (1500) at different temperatures (288.15, 293.15, 298.15) k have been used to estimate the apparent molar volume (V_θ), limiting apparent molar volume (V_θ°) experimental slope (S_v) and the second derivative of limiting partial molar volume $[\delta^2 \theta_v^{\circ} / \delta T^2]_p$ .The viscosity data have been analyzed by means of Jones –Dole equation to obtain coefficient A, and Jones – Dole coefficient B, Free activation energy of activation per mole of solvent, $\Delta\mu_1^{0*}$ solute, $\Delta\mu_2^{0*}$ the activation enthalpy ΔH^*,and entropy, ΔS^* of activation of viscous flow. These results have been discussed in terms of solute –solvent interaction and making/breaking ability of solute in the given solution.

Key word :chrom alum,apparent molar volume ,Solute – solvent interaction

Introduction

Measurements of some bulk properties like density (ρ) and viscosity (η) provides insight into the intermolecular an arrangement of the components in solution and helps to understand the thermodynamic properties of solution [1]. Ion-water interactions are important throughout biology and chemistry. In chemistry, ions affect the rates of chemical reactions[2-3],ion-exchange mechanisms, widely used for chemical separations[4]. Ions have long been classified as being either Kosmotropes (structure makers) or chaotropes (structure breakers) according to their relative abilities to induce the structuring of water. The degree of water structuring determined the increase or decrease in viscosity in water due to added salt. The viscosity (η) of an aqueous salt solution typically has the following dependence on ion concentration (c)[5]:

$$\eta / \eta_0 = 1 + A \sqrt{c} + B c \qquad (1)$$

Where η_0 are the viscosity of solvent, A is a constant independent of concentration (c) , which characterize the ionic solute interaction [6] , the constant B, which is called the Jones- Dole[7] B coefficient , is the quantity that defines the degree of water structuring around the ions and has been measured for wide electrolyte in aqueous and non aqueous solution . The viscosity B coefficient is positive for all Kosmotropic ions and negative for chaotrpic ion. Different physical parameters ,such as partial molar volume, V_θ°, second derivative of infinite dilution of the partial molar volume with temperature $[\delta^2 \theta_v^\circ / \delta T^2]_p$ and the viscosity B coefficient were calculated ,the free energy of activation of viscous flow per mole of solvent ($\Delta\mu_1^{0*}$) and solute ($\Delta\mu_2^{0*}$) are calculated too .

All these parameter are used to discuss the solute –solute and solute –solvent interaction in the binary solution of (alum chrom + water) and ternary solution of (alum + aqueous polyethylene glycol) at different concentrations and at different temperatures as well as the structure making /breaking tendency of the solute(Alum) in the given solution. Alum name is given to all the double salts having composition: $M^IM^{III}(SO_4)_2.12H_2O$. Chrom alum have the composition ($KCr(SO_4)_2.12H_2O$) which is used in dyeing, for tanning leather and in photography (during fixing) for hardening of the negatives[8].

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 Measurement

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}gm after reaching thermal equilibrium with a water bath at the studied temperature, divided by the volume of pyKnometer.

Viscosities Measurement

The viscosity of aqueous solution of chrom alum were determined using an ubbelhode type[9] viscometer. The temperature of the solution was maintained within ± 0.01K .The Viscosity (η) of solvent and aqueous solution of alum chrom were calculated from the relation[10]

$$\eta = c\rho\, t \qquad (2)$$

where(ρ)is the density in $gm.cm^{-3}$,(t) is the flow time in second ,(c $cm^2\ s^{-2}$) is the viscometer constant.

Results and Discussion

The measured densities and viscosities of the binary solution of (alum chrom + water) and ternary solution of (alum+aqeous PEG) at different concentrations are represented in Table(1).Table(1)shows an increasing in density and viscosity with the increase alum chrom concentration in the solution over the whole concentration , and these values decrease with the increase of alum at the same concentration.

The apparent molar volume V_θ ($cm^3.mol^{-1}$) for (alum + H_2O) and (alum + PEG) calculated from density using the following standard expression.[11]

$$V_\theta = M_2/\ \rho_0 - 10^3/c^*\ (\rho/\rho_0 - 1) \qquad (3)$$

Where ρ, ρ_0 are the density of solution and solvent respectively, c is the molar concentration of alum in ($mol.L^{-1}$) M_2 is its molar mass $g.mol^{-1}$. The values of the apparent molar volume of the investigated solute are given in Table (3).

Apparent molar volume of electrolyte varies with square root of the molar concentration (over wide concentration rang) in accordance with Masson's Empirical relation[12].

$$V_\theta = V_\theta^\circ + S_V\sqrt{C} \qquad (4)$$

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 ameasure 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 plotes V_θ versus $\sqrt{c}$ are given in Table (4).

It is evident from Table (4) the values of limiting apparent molar volume for (alum+H_2O) are positive suggesting presence of strong ion– solvent interaction between ions and surrounding water molecule. Large positive V_θ° for (alum + PEG) than (alum + H_2O), attributed to entrapped the ions in void formed during coiling 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+H_2O) may be attributed to the increase in solvation of the ions. The values of S_v are negative for (alum + PEG) and (alum + H_2O) which reflected that ion–ion interaction are very weak at entire temperature except at 288.15 K.

The experimental values of V_{θ}° were related to temperature using the quadratic equation[13]

$$V_{\theta}^{\circ} = a+ b\, T+c\, T2 \qquad (5)$$

The coefficient a, b, c were determined and equ (5) has the following forms for alum chrom in water and aqueous solution PEG

$$V_{\theta}^{\circ} = -13305+ 901.5\, T-1.524\, T2 \text{ for (alum+H2O)} \qquad (6)$$

$$V_{\theta}^{\circ} = -52804+ 354.0\, T-0.59\, T2 \text{ for (alum+PEG)} \qquad (7)$$

Thus, from equations (6and7), it can be observed that the values of $[\delta 2\ \theta\ v^{\circ} /\delta\ T2]$ p are negative for (alum + PEG) and (alum + H2O) , indicating the structure breaking ability of alum in water and aqueous PEG.

The viscosity data were analyzed by means of Jones – Dole equation [14]

$$\eta_{rel} = \eta / \eta_0 =1+AC^{1/2}+BC \qquad (8)$$

Where η_{rel} is the relative viscosity, C is the molar concentration. The viscosity coefficients A and B were obtained from the intercept and slope of the plots (η_{rel} -1)/ $C^{1/2}$virsus $C^{1/2}$ .The values of A and B are listed in Table (5).

Perusal of Table(5)shows that the values of A are positive in(alum+H_2O)and(alum + EG)at all temperature. Since A is considered to be a measure of ion–ion interaction, the positive values may be indicating the presence of ionic interactions in the solutions concerned. The coefficient B is important for a number of reasons[15]. First, the viscosity B coefficient provides information about solvation of solute and its effects on the structure of the solvent in the near environment of the solute molecule. Furthermore, some active parameter of viscous flow can be obtained using the viscosity B coefficient.

The viscosity B coefficient, originally introduced as an empirical term, was found depend on solute – solvent interactions and on the relative size of solute and solvent [16]. It can be seen from Table (5) that the viscosity B coefficient are negative indicating the structure–breaking ability of alum chrom because solvent molecule attached to the ions (ion – solvent interaction) wrenched out of the bulk solvent and this breaking of the solvent causes a decrease in viscosity of solution .This conclusion is an excellent agreement with that drawn from the density measurement.

The sign of temperature derivative of B coefficient (dB/ d T) gives the information of structure making / breaking ability of the solute in the solvent media. In general the (dB/ d T) is negative for structure maker and positive for structure breakers [17] . The temperature coefficient (dB/ d T) are given in Table (5). From this table it can be seen that alum chrom act as structure breaker in aqueous PEG while it acts as structure maker in water this result is opposite to the result obtained from the density measurement .

The viscosity data were also analyzed on the basis of the transition state as suggested by Feakins, et al[18] .according to which the viscosity B- coefficient was computed from the following relation

$$B = 1/1000*[(V_1^{\square} - V_2^{\square}) + V_1^{\square} (\Delta\mu_2^{0*} - \Delta\mu_1^{0*})/RT \qquad (9)$$

Where $V_1^0 = M_{SOLVENT} / d$ is the partial molar volume of solvent and $V_1^0 = \theta_v^0$ is the partial molar volume of solute.Eyring and coworker[19] used the following relation for calculating $\Delta\mu_1^{0*}$, the free energy of activation of viscous flow per mole of pure solvent .

$$\eta_{\square} = hN/ V_1^{\square} \exp (\Delta\mu_1^{0*} /RT) \qquad (10)$$

This on rearrangement gives

$$\Delta\mu_1^{0*} = RT \ln \eta_0 V_1^0 / hN \qquad (11)$$

Eq. (9) can be rearranged to give:

$$\Delta\mu_2^{0*} = \Delta\mu_1^{0*} + (RT/ V_1^0) [1000B - (V_1^0 - V_2^0)] \qquad (12)$$

Where $\Delta\mu_2^{0*}$contribution per mole of solute to free energy of activation for viscous flow of the solution , R,h and N are gas constant , Planck' s ,Avogadro Constant respectively , T, is the absolute temperature . The $\Delta\mu_1^{0*}$ and $\Delta\mu_2^{0*}$ values calculated from above equations are given in Table (6).

It is clear from Table (6) that $\Delta\mu_2^{0*}$ values are negative as compared to those of $\Delta\mu_1^{0*}$. This is due to the fact the alum in water and aqueous PEG behaves as structure breaker. This conclusion is in an excellent agreement with the conclusion drawn from density measurement. In fact Feakins et al [20] have shown the electrolyte has $\Delta\mu_2^{0*} > \Delta\mu_1^{0*}$act as structure makers. According to transition state theory every solvent molecule in one mole of solution must pass through the transition and interact more or less strongly with solute molecule. The activation free energy $\Delta\mu_2^{0*}$contains contribution from two effects: first, the activation energy of solvent molecule is affected by the interaction between solute and surrounding solvent molecule in the transition state $\Delta G2^{0\,*}$ $(1\rightarrow 1')$.and the second, the solute moves through its own transition state $\Delta G_2^{0\,*}$ $(2\rightarrow 2')$. The $\Delta G_2^{\,*\circ}(1\rightarrow 1')$ values obtained by the subtracting $\Delta\mu_1^{0*}$ from $\Delta\mu_2^{0*}$ as $\Delta G_2^{\,0*}$ $(2\rightarrow 2')$ is equivalent to $\Delta\mu_1^{0*}$ [21.22] . It can be also noted that $\Delta G_2^{0\,*}$ $(1\rightarrow 1')$ (thermodynamic activation of transfer for alum from ground state to transition state in aqueous PEG) and $\Delta\mu_2^{0*}$ are negative except at 288.15 This can be explained by the fact that transfer of alum from ground state to transition state solvent is favored.

The free energy of activation of viscous flow of solution , $\Delta G^{0*}$was calculated by using the equation

$$\Delta G^{0*} = n_1 \Delta\mu_1^{0*} + n_2 \Delta\mu_2^{0*} \qquad (13)$$

Where n_1 and n_2 are the number of moles of solvent and solute respectively.

The enthalpy ΔH^{0*} and entropy, ΔS^{0*} of activation of viscous flow were computed using the equation

$$\Delta G^{0*} = \Delta H^{0*} - T\,\Delta S^{0*} \qquad (14)$$

The values, ΔH^{0*} and, ΔS^{0*} are obtained from the intercept and slop of $\Delta\mu^{0*}$ versus T. The ΔH^{0*} and, ΔS^{0*} are summarized in Table (7)

Table (7) shows positive ΔH^{0*} values and increase of with increase concentration of chrom alum in water and aqueous PEG. The values of ΔS^{0*} are positive for alum in water ΔS^{0*} are negative for alum in aqueous PEG and decrease with increase of concentration this may be due to the fact that formation of activated species necessary for viscous flow appears difficult (ions binds strongly to water molecule)..

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Table (1): Experimental densities ρ(g.cm^{-3}) and viscosities η (cp) for (alum + H_2O)

C mol.L^{-1}	(alum + H_2O)					
	288.15K		293.15K		298.15K	
	ρ(g.cm^{-3})	η (cp)	ρ(g.cm^{-3})	η (cp)	ρ(g.cm^{-3})	η (cp)
0.00	0.99910	1.224397	0.99821	1.002892	0.99704	0.888363
0.010	1.00242	1.250646	1.000561	1.109956	0.99922	1.009914
0.015	1.00361	1.260936	1.00203	1.119151	1.00094	1.017314
0.020	1.00483	1.270005	1.00335	1.129733	1.00287	1.02432
0.025	1.00638	1.282531	1.0047	1.133897	1.00416	1.031425
0.030	1.00757	1.289186	1.00602	1.144267	1.00533	1.038816
0.035	1.00934	1.298112	1.00738	1.153907	1.0069	1.047776

0.040	1.01053	1.310556	1.00894	1.16308	1.00883	1.053939

Table (2): Experimental densities ρ(g.cm^{-3}) and viscosities η (cp) for (alum + PEG)

C mol.L^{-1}	(alum +PEG)					
	288.15K		293.15K		298.15K	
	ρ(g.cm^{-3})	η (cp)	ρ(g.cm^{-3})	η (cp)	ρ(g.cm^{-3})	η (cp)
0.00	1.00194	1.235103	1.00086	1.050903	0.99983	0.936141
0.01	1.00472	1.360592	1.00321	1.194255	1.00122	1.082564
0.015	1.00594	1.366469	1.00405	1.20851	1.00277	1.098063
0.020	1.00753	1.381324	1.00579	1.223742	1.00422	1.112806
0.025	1.00902	1.390026	1.00747	1.230936	1.00542	1.122523
0.030	1.01038	1.402812	1.00899	1.249726	1.00695	1.137233
0.035	1.01152	1.413163	1.01132	1.261996	1.00879	1.141376
0.040	1.01346	1.424722	1.01191	1.275605	1.00998	1.151452

Table (3): Apparent molar volume of (alum + H_2O) and (alum + EG) at different temperature

C /mol.L^{-1}	V_0 (Alum + H_2O)		
	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^{-1}	V_0 (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

Table (4): Values of partial molar volume ($V\theta^{\circ}$) in ($cm^3.mol^{-1}$) experimental slop (Sv) in ($cm^3.mol^{-2}.L$) for (Alum + H_2O)and (alum + PEG) at different temperature.

T/K	Alum +H_2O	
	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

Table(5): values of parameters, A($L^{1/2}.mol^{-1/2}$)and B($L.mol^{1/2}$) of Jones–Dole equation in(alum+H_2O) and (alum + PEG) and the values of (dB/ d T)

T/K	Alum + H_2O		
	A($L^{1/2}.mol^{-1/2}$)	B($L.mol^{-1}$)	(dB/ d T)
288.15	0.081	1.322	-1.1076
293.15	1.284	-2.625	-0..6276

298.15	1.718	-4.165	-0.1476
T/K	Alum+PEG		
	A($L^{1/2}.mol^{-1/2}$)	B($L.mol^{-1}$)	(dB/ d T)
288.15	1.181	-2.249	0.3907
293.15	1.591	-2.834	0.2807
298.15	1.924	-4.008	0.1707

Table (6): Free energy of activation per mole of solvent, $\Delta\mu_1^{0*}$ and solute, $\Delta\mu_2^{0*}$ of alum in water and aqueous PEG at different temperatures

T/K	Alum + H_2O	
	$\Delta\mu_1^{0*}$(KJ $mole^{-1}$)	$\Delta\mu_2^{0*}$(KJ $mole^{-1}$)
288.15	59.25	197.50
293.15	59.80	-322.16
298.15	60.52	-526.87
T/K	Alum+PEG	
	$\Delta\mu_1^{0*}$(KJ $mole^{-1}$)	$\Delta\mu_2^{0*}$(KJ $mole^{-1}$)
288.15	69.87	-272.08
293.15	70.69	-348.27
298.15	71.61	-511.93

Table(7): enthalpies, ΔH^* and entropies, ΔS^* of activation of viscous flow of(alum + H_2O)and(alum+ EG)

C / mol.L^{-1}	Alum + H_2O	
	ΔH^{0*} (KJ mole^{-1})	ΔS^{0*} (J mole^{-1}K^{-1})
0.01	1633	5716
0.015	1776	5209
0.02	1818	5053
0.025	1941	4617
0.03	2032	4290
0.035	2176	3784
0.04	2244	3530
C / mol.L^{-1}	Alum+PEG	
	ΔH^{0*} (KJ mole^{-1})	ΔS^{0*} (J mole^{-1}K^{-1})
0.01	66.73	-238
0.015	100.0	-358
0.02	133.2	-478
0.025	166.5	-598
0.03	199.8	-718
0.035	233.0	-838
0.04	266.3	-958

لزوجة وكثافة شب الكروم في محلول بولي اثلين كلايكول بدرجات حرارية مختلفة

سندس هادي مرزا

قسم الكيمياء ، كلية التربية– ابن الهيثم ،جامعة بغداد

استلم البحث في :13 أيلول2011 قبل البحث في :16 تشرين الأول 2011

الخلاصة

استعملت المعلومات التي تم الحصول عليها من قياس الكثافة لمحاليل شب الكروم في الماء وفي المحلول المائي للبولي اثلين كلايكول ذي الوزن الجزيئي 1500 وبدرجات حرارة مختلفة (299.15,293.15,298.15) مطلقة لإيجاد الحجم المولاري الظاهري (V_θ)، والحجم الظاهري المحدد (V°_θ)، والميل (S_v)، والمشتقة الثانية للحجم المولاري المحدد مع درجة الحرارة بثبوت الضغط [$\delta^2 \theta^{\circ}_v / \delta T^2$]. استعملت معادلة جونز ودول لمعالجة المعلومات من قياسات اللزوجة لإيجاد المعاملA، ومعامل جونز ودول B، وطاقة التنشيط الحرة لكل مول من المذيب والمذاب $\Delta\mu_1^{0*}$, $\Delta\mu_2^{0*}$ وانثالبي التنشيط ΔH^{0*} وانتروبي التنشيط ΔS^{0*} للجريان اللزج . نوقشت هذه النتائج على أساس تأثيرات متبادلة من نوع ايون– مذيب، وعلى قابلية المذاب على الهدم والبناء في المحلول. .

الكلمات المفتاحية : شب الكروم ، الحجم المولاري الظاهري ، تأثيرات متبادلة مذاب– مذيب