

Viscosity and Density study of Caffeine Citrate in Aqueous Solution at 298.15, 303.15 and 308.15 K

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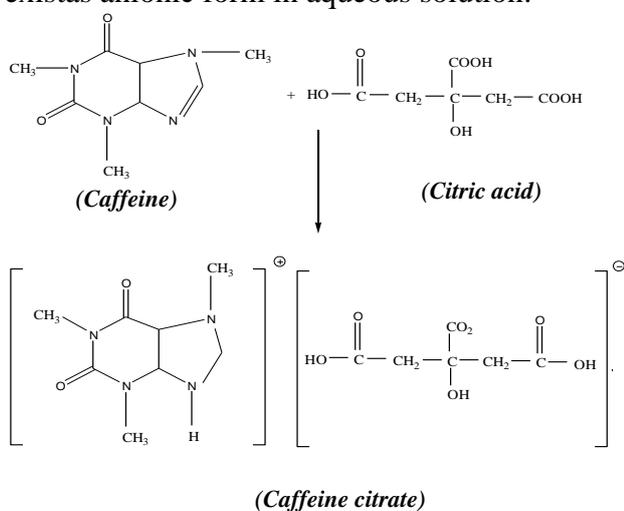
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Abstract

Densities (ρ) and viscosities (η) of caffeine citrate at different temperature (298.15, 303.15, 308.15) K have been measured from these experimental data, The apparent molar volumes (ϕ_v) and limiting partial molar volumes (ϕ_v°), slope (S_v), Gibbs free energy of activation for viscous flow of solution $\Delta G_{1,2}$ and Jones-Doles A and B Coefficients were calculated, The results shows a strong ion-ion interactions and weak ion-solvent interactions and also indicate that caffeine citrate acts as structures maker in aqueous solution .

Introduction

Caffeine citrate is a compound produced from mixing caffeine and citric acid. It's high solubility in water suggests that this compound existas anionic form in aqueous solution.



.....(1)

Also it has the actions of caffeine^[1]. Caffeine is the trimethyl derivative of xanthine (2-6-di-oxopurine) which is minor purine bases which could be found in a small amounts in nucleic acids^[2]. Caffeine belongs to the group of alkaloids^[3], found naturally in foods (i.e., coffee, tea, cacao, beans, kola, nuts, gaur Ana, etc.)^[4]. It can acts an effective anti oxidant. It is a stimulant drug acting on the central nervous system^[5], on muscles including the cardiac muscle, and on kidneys) used in a wide range of pharmaceutical preparations^[6]. It has been found that caffeine inhibits phosphodiesterase, causes prolonged action of cyclic AMP and increases the activity of hormone sensitive lipase^[2]. Citric

acid is one of the citrus fruits content^[7], which plays important role in metabolism^[8].

To investigate the interactions of dissolved caffeine citrate in aqueous solution we will involve study of density (ρ) and viscosity (η) of its solution at different concentrations and temperatures then we can get the information about the structural effects for solute and solvent, thermodynamic properties and the nature of interactions in amount solute particles.

Experimental

Caffeine citrate ($C_8H_{10}N_4O_2 \cdot C_6H_8O_7$) is Analar and used without further treatment the water used (specific conductance = 10^{-6} scm^{-1}) was deionized and distilled. The solutions were prepared in molar concentration by dissolving (5g) of caffeine citrated in (1 dm^3) volumetric flask which sated as a stock solution, from this solution a series of nine concentrations were made by dilution then converted to molality units through the relation $m = 1000 C / (1000 \rho - CM)$(2)

Where C is the molar concentration of solute, M is the molecular weight of the solute densities (ρ) of all solutions were measured by using 50 ml pycnometers. The volume of pycnometers were calibrated with deionized and doubly distilled water at (298.15, 303.15, 308.15) K. The densities of caffeine citrate solutions determined from the weight of the solutions in the pycnomter after reaching thermal equilibrium in a water bath at the studied temperatures, divided by the volume of pycnometer.

Sartorius BL-2105 Germany electronic balance with an accuracy of (10⁻⁴g) used for the weight determination. The viscosities η were measured by using suspended-level ubbel hode temperature which controlled by using a Scott- Gerate model 300 AVS thermostat with a precision of (± 0.01 K) for all measurements.

Results and Discussion

The results of absolute viscosities (η) and densities (ρ) are listed in Table (1).

Table (1)
Densities ρ and Viscosities η with calculated apparent molal volume ϕ_v of caffeine citrate in water at different temperatures.

at 298.15 K				
C/ mol. d ⁻³ m	m/ mol.kg ⁻¹	ρ / g.cm ⁻³	η /cp	ϕ_v cm ³ .mol ⁻¹
0.000	0.000	0.99704	0.89200	
0.002588527	0.002597984	0.99736	0.89305	263.4773309
0.003882791	0.003898099	0.997573	0.89463	249.7868859
0.005177055	0.005199026	0.997774	0.89604	245.2664634
0.006471319	0.006500806	0.997964	0.897821	244.259058
0.007765582	0.007803084	0.998194	0.89928	238.4212396
0.009059846	0.009105886	0.998444	0.90059	232.0372768
0.01035411	0.010409133	0.998714	0.901822	225.3119621
0.011648374	0.011713218	0.998964	0.903417	221.8032312
0.012942638	0.013018366	0.999183	0.905111	221.3985572

at 303.15 K			
m/ mol.kg ⁻¹	ρ / g.cm ⁻³	η /cp	ϕ_v cm ³ .mol ⁻¹
0.000	0.995650	0.80100	
0.002601561	0.995990	0.80368	256.0852158
0.003903534	0.996186	0.80469	249.3597135
0.005206335	0.996376	0.8057	247.1610048
0.006509706	0.996603	0.80692	240.0992549
0.007813856	0.996822	0.80797	236.4261020
0.009118634	0.997053	0.809261	232.4721312
0.010423814	0.997313	0.809871	226.6935836
0.011729672	0.997569	0.811462	222.5440532
0.013036711	0.997784	0.812761	222.4061015

at 308.15 K			
m/ mol.kg ⁻¹	ρ / g.cm ⁻³	η /cp	ϕ_v cm ³ .mol ⁻¹
0.000	0.994060	0.72300	
0.002605672	0.994420	0.72521	248.7223258
0.003909591	0.994645	0.72575	237.0635028
0.005214264	0.994864	0.72621	232.3998900
0.006519603	0.995094	0.72665	227.8917842
0.007825534	0.995339	0.72710	222.9932368
0.009132366	0.995559	0.72751	222.1844470
0.010439884	0.995784	0.7279	221.1296208
0.011748364	0.995989	0.72842	222.0364163
0.013057149	0.99623	0.72891	219.063725

The apparent molal volumes ϕ_v of caffeine citrate in liquid water were calculated using equation (3):

$$\phi_v = \frac{1}{m} \left[\left(\frac{10^3 + mM}{\rho} \right) - \left(\frac{10^3}{\rho_0} \right) \right] \dots\dots\dots(3)$$

where ρ and ρ_0 are the densities of solution and solvent respectively; M is the molecular weight of solute and m is the molality of solution.

The results of ϕ_v at different concentrations and temperatures are given in Table (1). This table shows that the value of ϕ_v decrease with increase concentrations of caffeine citrate and temperatures suggest that the ion-solvent interaction decrease with increase concentrations and temperature^[9], limiting value of apparent molar volume at infinite dilution ϕ_v° was calculated from relation:

$$\phi_v = \phi_v^\circ + S_v m \dots\dots\dots(4)$$

Which is equal to the partial molar volume at infinite dilution^[10]. ϕ_v° considered as a measure of ion-solvent interactions and a measure of molecular volume of solute^[11]. (S_v) is the experiment at slope which is a parameter of ion-ion interactions^[12]. The value of ϕ_v versus m are plotted for caffeine citrate at different temperatures shown in Fig. (1) and these values are tabulated in Table (2). This table reveals. That values of ϕ_v° are positive for the whole range of concentrations and at different temperatures under study, that suggesting strong ion-solvent interaction.

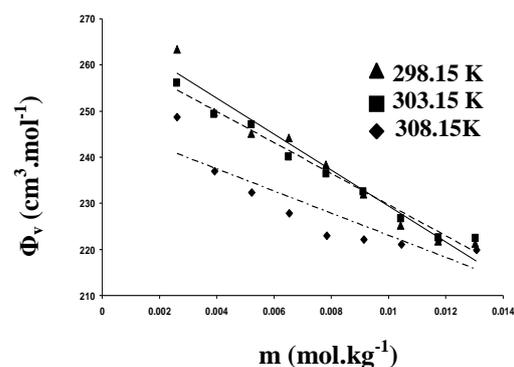


Fig.(1) plots of apparent molar volume (Φ_v) versus m of caffeine citrate in Aqueous solution at different temperature.

Table (2)
Partial molal volumes at infinite dilution ϕ_v° , experimental slope S_v , At different temperature.

T/K	ϕ_v° cm ³ -mol ⁻¹	S_v cm ³ -mol ⁻² .kg
298.15	268.3	-3894
303.15	263.3	-3369
308.15	247.07	-2402

The ϕ_v° values decrease with increase in temperature indicating that the ion-solvent interaction decrease with increase in temperature.

The S_v values are found to be large and negative indicating the presence of weak ion-ion interactions. The values of S_v become less negative with increase temperature suggesting increase ion-ion interaction in solution with rise in temperature. In fact negative S_v values are often obtained in solvents of high dielectric constant^[10].

The viscosity data were analyzed by using the Jones-Dole equation:

$$\frac{\eta_r - 1}{\sqrt{m}} = A + B\sqrt{m} \dots\dots\dots(5)$$

Where η_r is the relative viscosity of the solution which obtained from dividing the viscosity of the solutions that contain caffeine citrated on the viscosity of water as solvent A and B are Jones-Dole constants where A accounts for the ion-ion interactions and B is a measure of structural modifications induced by the ion-solvent interactions^[13], from the linear plots of $(\eta_{ra} - 1)/\sqrt{m}$ versus \sqrt{m} presented in Fig.(2).

A and B are obtained respectively from slope and intercept of the straight line presented in Fig. (2) and included in Table (3). This table shows the increase of A value with increasing temperature at the same time that decrease B coefficient with increasing temperature this mean the ion-ion interactions become strong by increasing temperature while the ion-solvent become weak. This

supports our earlier conclusion drawn from apparent molal ϕ_v° and S_v results.

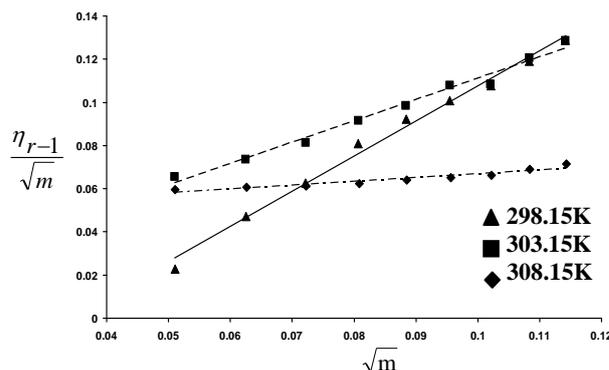


Fig.(2) $\frac{\eta_{r-1}}{\sqrt{m}}$ against \sqrt{m} For caffeine citrate solution at different temperature.

Table (3)
Partial molal volumes at infinite dilution ϕ_v° , experimental slope S_v , A and B with B constant with B derivative.

T/K	A / 1/2 -1/2 kg. mol	B/-1 Kg.mol	$\frac{\partial B}{\partial T}$
298.15	-0.055	1.626	0.1871
303.15	0.012	0.988	0.1571
308.15	0.049	0.175	0.1271

The temperature derivatives of B coefficient $\left(\frac{\partial B}{\partial T}\right)$ have also been calculated its sign provide important in formation regarding the structure-making or structure-breaking ability of the solute insolvent media^[14] in general. The $\left(\frac{\partial B}{\partial T}\right)$ is negative for structure-maker and positive for structure-breaker solute in solution^[15,16].

The negative $\left(\frac{\partial B}{\partial T}\right)$ values for caffeine citrate studied indicate that caffeine citrate acts as structure-makers in aqueous solution.

The activation free energy of viscose flow has been calculated by using the Eyring relation^[17,18].

$$\Delta G^* = RT \ln \frac{\eta V_{1,2}^-}{h N_A} \dots\dots\dots(6)$$

where ΔG^* is the free energy of activation (R) gas constant (T) absolute temperature (η) viscosity of solution (h) Planck's constant. (N_A) Avogadro number, ($V_{1,2}$) is the molar volume of solution which obtained from the relation $V_{1,2} = (10^3 + mM_2) / \rho \left(\frac{10^3}{M_1} + m \right)$

Where M_1 and M_2 are molecular weight for solvent and solute respectively. The entropies (ΔS^*) and enthalpies (ΔH^*) of activation of viscous flow have been calculated from the free energy of activation by using the relations.

$$\Delta S^* = -d(\Delta G^*)/dT \dots\dots\dots(7)$$

$$\Delta H = \Delta G + T\Delta S^* \dots\dots\dots(8)$$

Equations (6) and (7) applied at constant pressure. The value of (ΔG^*), (ΔH^*) and (ΔS^*) are listed in table (4).

This table shows the (ΔS^*) value decrease with increase concentration when the (ΔH^*) value increase with increase concentration suggesting that the arrangement state for caffeine citrate molecules increase this mean the contact between the liquid layers increase with increase the concentration therefore the viscous liquid need additional activation energy for viscous flow as a result the (ΔG^*) value increase with increase concentration and temperature.

Table (4)

Thermodynamic function for viscous flow ΔG^* and ΔH^* in J/mol, ΔS^* in J/mol.K the ΔG^* that shown for three temperatures while ΔH^* at 298.15 K and ΔS^* constant with temperature and molar concentration is used here because it is constant with temperature.

C/mol. d ³ m	$\Delta G^*/J.$ mol ⁻¹ at 298.15K	$\Delta G^*/J.$ mol ⁻¹ at 303.15K	$\Delta G^*/J.$ mol ⁻¹ at 308.15K	$\Delta S^*/J.$ mol ⁻¹ .K ⁻¹	$\Delta H^*/J.$ mol ⁻¹
0.002588527	20586.326	20669.266	20750.995	-16.47425	15677
0.003882791	20591.364	20673.142	20753.551	-16.22605	15756
0.005177055	20595.954	20677.031	20756.403	-16.05231	151812
0.006471319	20601.590	20681.477	20758.028	-15.64963	15938
0.007765582	20606.230	20685.408	20760.212	-15.40345	16016
0.009059846	20610.403	20690.055	20762.284	-15.19262	16083
0.01035411	20614.307	20692.504	20764.342	-15.00774	16142
0.011748374	20619.527	20698.011	20766.873	-14.73666	16228
0.012942638	20624.538	20702.707	20769.205	-14.46825	16313

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الخلاصة

تضمنت هذه الدراسة قياس كثافة ولزوجة سترات الكافئين في المحلول المائي بدرجات حرارية مختلفة (298.15، 303.15، 308.15) درجة مطلقة. استخدمت هذه النتائج لحساب الحجم المولالي الظاهري ϕ_v ، الحجم المولالي الظاهري المحدد ϕ_v° ، الميل S_v ، طاقة كبس الحرة للانسياب اللزج للمحلول $\Delta G_{1,2}$ ومعامل جونز - دول A و B.

أشارت النتائج إلى وجود تأثير قوي من نوع أيون - أيون وضعيف من نوع أيون- مذيب وبينت الدراسة إن سلوك سترات الكافئين من النوع البانية للتركيب في المحلول المائي.