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Viscosity and Volumetric studies of some amino acids in solutions at different temperatures.

الكثافة واللزوجة لعدد من محاليل الحوامض الأمينية بدرجات حرارة مختلفة .

Zainab Abbas H.Al-Dulaimy, Asal Ahmed Al- Jawary, Dr.Shatha Fadil Al-saidi .
Department of Chemistry, College of Education (Ibn-Al-Haitham)
University of Baghdad
P.O. Box 4150, Baghdad , Iraq.

Abstract :

Densities ρ and viscosities η for several concentrations of amino acids (Serine, Cysteine and Threonine) at different temperatures (298.15, 303.15 and 308.15K) have been measured. On the basis of these data, the apparent molal volumes ϕ_v , partial molal volumes at infinite dilution ϕ_v°, slope S_v , Gibbs free energy of activation for viscous flow of solution $\Delta G_{1,2}^*$ and Jones – Dole B-coefficients were calculated the nature of solute-solvent and solute-solute interactions have been discussed in terms of the values of ϕ_v , ϕ_v° , S_v and B-coefficents.

الخلاصة :

شملت هذه الدراسة قياس الكثافة واللزوجة الى عدد من محاليل الحوامض الامينية (سيرين , سستين , ثريونين) بدرجات حرارة مختلفة (298,15 , 303,15 , 308,15 مطلقة) . أستخدمت 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 جونس – دول B- . تمت مناقشة طبيعة التأثر من نوع مذاب – مذيب ومذاب – مذاب من خلال قيم ϕ_v° و S_v وقيمة معامل اللزوجة B .

Introduction :

All proteins are polymers consisting of chains of amino acid chemically bound to each other. The amino acid in proteins are called α-amino acid. Each amino acid has a characteristic side chain (R group) that imparts chemical individuality to the molecule. The polarity of the R groups is an important characteristic and is the basis for classifying amino acids into four groups[1]. Amino acids are high water solubilities suggests that they exist in an ionic form (zwitter ion). In physiological media such as blood, membranes, cellular fluids, etc. , where happens to be involved in an important manner, the zwitter ionic (dipolar) character of these compounds has an important bearing on their biological functions[2].

It has been known for sometimes that viscosity measurements can provide direct evidence regarding size and state of solvation of molecules in solution[3]. The variation of relative viscosity with molarity (c) for solutions of dipolar ions or non-electrolytes is normally interpreted in term Jones-Dole equation :-

$$\eta_r = \frac{\eta}{\eta_0} = 1 + Bc + Dc^2 \qquad \text{…….. (1)}$$

where η and η_0 are the viscosities of the solution and the solvent respectively, B and D are empirical coefficients. B is an adjustable parameter which related to the size and shape of the solute molecules and to different solute- solvent interactions. While D coefficient is generally positive. The Dc^2 term is usually small for dilute solutions and its significance is not completely understood[4-7]. In recent years interest has been directed to study the behavior of amino acids, peptides and polypeptides in mixed aqueous solvents. Such work is important in understanding the factors that determine the stability of biopolymer[8-11]. From the literature survey it appears that the studies of viscosity and density for α-amino acid solutions are abundant[6-8, 12-14], but on those Serine, cysteine and threonine are few. With this in view, the title study has been undertaken in the light of the following aspects :-

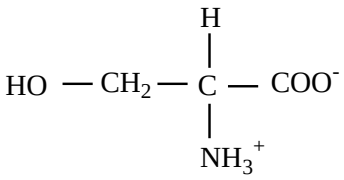
1- Determination of apparent molal volume ϕ_v from density data as a function of molal concentration m.

2- Calculate of limiting apparent molal volume ϕ_v° or partial molal volume at infinite dilution.

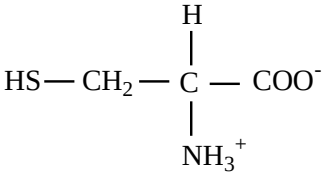
3- Estimating the Gibbs free energy of activation for viscous flow of solution , $\Delta G^*_{1,2}$ from the viscosity and density data.

4- Estimating the Jones-Dole coefficient B(empirical coefficient) from viscosity measurements.

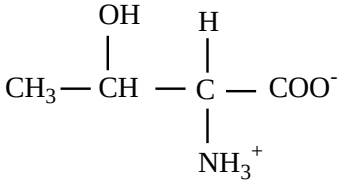
These parameters are used to discuss the solute-solvent and solute-solute interactions in the α-amino acids (Serine, Cysteine and Threonine) solutions.



Serine (Ser)
M=105.1 g mol^{-1}



Cysteine (Cys)
M=121 g mol^{-1}



Threonine (Thr.)
M=119 191 g mol^{-1}

All amino acids under study with uncharged polar R group.

Experimental :

Three α-amino acids selected in this work serine, Cysteine and Threonine form Fluka company. They are Analar and used without further treatment. All solutions were prepared with water redistilled (sp.conductivity ~10^{-6} ohm^{-1} cm^{-1}). An electrical balance with at least count of 1.0×10^{-4} g was used for measurement of mass.

The concentrations of amino acids were in range of 0.1 – 0.35 molar (mol dm^{-3}).

The densities ρ of the solutions were measured at different temperatures 298.15, 303.15 and 308.15K using a vibrating tube digital densimeter (DMA- 60/602 ; Anton Paar). The operational was described by Shukla et.al.[15].

The viscosity of solutions were measured with an Ostwald suspended level type viscometer as per details described by Findly [16].

Densities and viscosities were measured at 298.15, 303.15 and 308.15K, and carried out in a thermostatted bath, whose temperature was controlled to ± 0.01K for all measurements.

Results and discussion :

The experimental values of densities and absolute viscosities of the Ser, Cys and Thr solutions as a functions of amino acid concentration and temperature are listed in Tables 1,2 and 3 respectively .

Table 1: Densities (ρ) and viscosities (η) with calculated apparent molal volume (ϕ_v^*) , Gibbs free energy of activation for viscous flow ($\Delta G^*_{1,2}$) and viscosity B-coefficient of Serine in water at different temperatures.

c mol dm^{-3}	m mol kg^{-1}	ρ g cm^{-3}	η cp	ϕ_v^* cm^3mol^{-1}	$\Delta G^*_{1,2}$ kJ mol^{-1}	B dm^3mol^{-1}
298.15K						
0.00	0.0000	0.9907[a]	0.890[a]			
0.10	0.1009	1.0009	0.894	66.31	60.552	0.0220
0.15	0.1496	1.0030	0.901	64.68	60.577	0.0673
0.20	0.2032	1.0052	0.909	64.19	60.605	0.0953
0.25	0.2548	1.0075	0.918	63.29	60.634	0.1166
0.30	0.3066	1.0100	0.925	61.95	60.658	0.1233
0.35	0.3587	1.0125	0.935	60.99	60.689	0.1377
303.15K						
0.00	0.0000	0.9956[a]	0.798[a]			
0.10	0.1011	0.9997	0.812	64.38	61.328	0.1754
0.15	0.1521	1.0019	0.821	63.37	61.361	0.1921
0.20	0.2034	1.0042	0.828	62.37	61.388	0.1880
0.25	0.2550	1.0065	0.834	61.78	61.412	0.1805
0.30	0.3069	1.0090	0.841	60.69	61.438	0.1796
0.35	0.3590	1.0117	0.846	59.36	61.457	0.1719
308.15K						
0.00	0.000	0.9940[a]	0.719[a]			
0.10	0.1011	0.9992	0.733	63.40	62.079	0.1947
0.15	0.1522	1.0014	0.739	62.75	62.106	0.1852
0.20	0.2035	1.0038	0.749	61.40	62.145	0.2086
0.25	0.2552	1.0062	0.758	60.59	62.180	0.2170
0.30	0.3070	1.0087	0.766	59.73	62.213	0.2179
0.35	0.3592	1.0113	0.773	58.82	62.240	0.2146

a-ref.(17)

Table 2: Densities (ρ) and viscosities (η) with calculated apparent molal volume (ϕ_v^*) , Gibbs free energy of activation for viscous flow ($\Delta G^*_{1,2}$) and viscosity B-coefficient of Cysteine in water at different temperatures.

c mol dm^{-3}	m mol kg^{-1}	ρ g cm^{-3}	η cp	ϕ_v^* cm^3mol^{-1}	$\Delta G^*_{1,2}$ kJ mol^{-1}	B dm^3mol^{-1}
298.15K						
0.10	0.1011	1.0017	0.931	74.25	60.652	0.4372
0.15	0.1521	1.0042	0.939	73.21	60.683	0.3513
0.20	0.2036	1.0067	0.948	72.73	60.713	0.3139
0.25	0.2553	1.0093	0.958	72.01	60.744	0.2959
0.30	0.3075	1.0119	0.969	71.56	60.780	0.2877
0.35	0.3600	1.0145	0.978	71.21	60.810	0.2755
303.15K						
0.10	0.1012	1.0004	0.825	73.33	61.370	0.3383
0.15	0.1523	1.0029	0.834	72.64	61.405	0.3008
0.20	0.2038	1.0054	0.845	72.31	61.444	0.2943
0.25	0.2557	1.0080	0.854	71.71	61.478	0.2807
0.30	0.3079	1.0106	0.865	71.31	61.516	0.2799
0.35	0.3605	1.0132	0.875	71.03	61.552	0.2757
308.15K						
0.10	0.1012	0.9999	0.749	72.35	62.136	0.4173
0.15	0.1524	1.0025	0.758	71.36	62.174	0.3616
0.20	0.2039	1.0051	0.765	70.86	62.204	0.3198
0.25	0.2558	1.0077	0.773	70.56	62.238	0.3004
0.30	0.3080	1.0104	0.779	70.02	62.264	0.2782
0.35	0.3605	1.0131	0.788	69.63	62.300	0.2742

Table 3: Densities (ρ) and viscosities (η) with calculated apparent molal volume (ϕ_v) , Gibbs free energy of activation for viscous flow ($\Delta G_{1,2}^{\neq}$) and viscosity B-coefficient of Threonine in water at different temperatures.

c mol dm^{-3}	m mol kg^{-1}	ρ g cm^{-3}	η cp	ϕ_v cm^3mol^{-1}	$\Delta G_{1,2}$ kJ mol^{-1}	B dm^3mol^{-1}
298.15K						
0.10	0.1010	1.0016	0.919	73.20	60.622	0.3027
0.15	0.1521	1.0046	0.925	72.55	60.650	0.2466
0.20	0.2035	1.0065	0.934	71.71	60.675	0.2354
0.25	0.2553	1.0090	0.940	71.21	60.698	0.2152
0.30	0.3075	1.0115	0.948	70.89	60.725	0.2093
0.35	0.3599	1.0143	0.955	69.99	60.750	0.2018
303.15K						
0.10	0.1012	1.0003	0.819	72.34	61.352	0.2632
0.15	0.1523	1.0027	0.828	72.00	61.386	0.2506
0.20	0.2038	1.0052	0.836	71.31	61.427	0.2381
0.25	0.2556	1.0077	0.844	70.91	61.448	0.2306
0.30	0.3079	1.0102	0.854	70.65	61.484	0.2339
0.35	0.3604	1.0129	0.862	69.88	61.513	0.2291
308.15K						
0.10	0.1014	0.9998	0.742	71.46	62.112	0.3198
0.15	0.1524	1.0023	0.749	70.70	62.143	0.2782
0.20	0.2039	1.0048	0.755	70.36	62.170	0.2503
0.25	0.2557	1.0074	0.762	69.75	62.200	0.2392
0.30	0.3079	1.0101	0.769	69.01	62.229	0.2318
0.35	0.3604	1.0127	0.774	68.77	62.252	0.2186

The densities which were required for determination of the apparent molal volumes ϕ_v are given by this equation [12].

$$\phi_v = \frac{1}{m}\left[\left(\frac{10^3 + mM}{\rho}\right) - \left(\frac{10^3}{\rho_0}\right)\right] \quad \text{..... (2)}$$

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

[$m=1/(\frac{\rho}{c} - \frac{M}{1000})$] . The calculated values of the ϕ_v for three amino acids with different temperatures are also reported in Tables 1,2 and 3.

In general, ϕ_v values decrease with increase temperature and concentration for all amino acids under study with the sequence of ϕ_v values : Cys > Thr > Ser . It indicates that the solute-solvent interactions decrease with increasing concentration [18].

The variation of the apparent molal volumes ϕ_v wih molal concentration m can be adequately represented by the relation:

$$\phi_v = \phi_v^{\circ} + S_v\, m \qquad \text{……. (3)}$$

where ϕ_v° is the limiting value of the apparent molal volume (equal to partial molal volume at infinite dilution) and S_v is experimental slope (empirical constant) [8,12,13]. The values of ϕ_v vs. m are plotted for Ser,Cys and Thr at different temperatures shown in Figure 1. The plot of ϕ_v against m should be linear with a slope S_v and an intercept of ϕ_v° when m→o.

The values of ϕ_v° and S_v are listed in Table 4 .

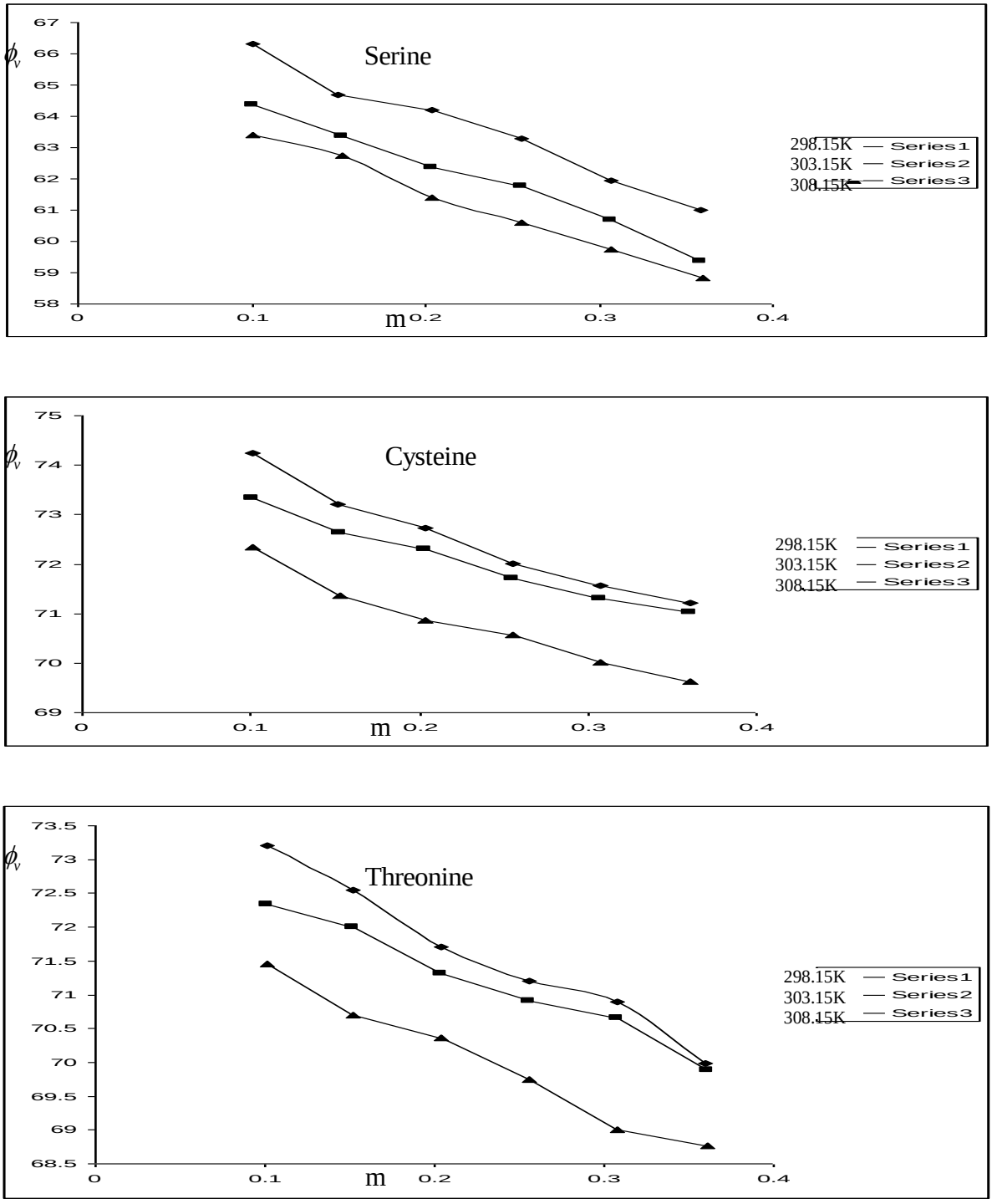


Figure 1 : Plot of ϕ_v vs. m for amino acids at different temperatures

Table 4 : Values of apparent molal volume at infinite dilution ϕ_v° and experimental slope S_v of Ser, Cys and Thr at 298.15, 308.15 and 308.15K.

Solute	298.15K		303.15K		308.15K	
	ϕ_v° cm^3mol^{-1}	S_v $cm^3mol^{-2}kg$	ϕ_v° cm^3mol^{-1}	S_v $cm^3mol^{-2}kg$	ϕ_v° cm^3mol^{-1}	S_v $cm^3mol^{-2}kg$
Serine	68.07	-19.678	66.28	-18.685	65.28	-18.137
Cystein	75.14	-11.508	74.09	-8.859	73.07	-9.865
Threonine	74.32	-11.876	73.31	-9.237	72.44	-10.547

Table 4 shows that all the values of S_v are negative, indicating the presence of weak solute- solute interactions in solution[19-21]. Moreover, the values of S_v become less negative with increase temperature for the three amino acids, suggesting increased solute-solute interaction with increase temperature. In fact negative S_v values are often obtained in solvents of high dielectric constant [19]. A perusal of Table 4 reveals that the values of ϕ_v° are positive for all the three amino-acid solutions, suggesting strong solute-solvent interactions[20,21]. For Cysteine the value obtained for ϕ_v° at 298.15K (75.14 cm^3 mol^{-1}) is in reasonable agreement with the (73.44 cm^3 mol^{-1}) obtained by Millero et.al.[22].In general, ϕ_v° values are in the sequence : Cys > Thr > Ser. The ϕ_v° values decrease with increase in temperature for all amino acids under study (Table 4), indicating that the solute-solvent interaction decreases with increase in temperature[18-21].

From transition state theory the Gibbs free energy of activation for viscous flow of solution, $\Delta G^*_{1,2}$ (J mol^{-1}) at a given temperature and composition is given by [23,24]

$$\Delta G^*_{1,2} = RT \, Ln \left(\frac{\bar{V}_{1,2} \, \eta_{1,2}}{hN} \right) \qquad \ldots\ldots\ldots (4)$$

Where R is the gas constant, T is the absolute temperature, h is plank's constant, N is Avogadro's constant and the volume of mole of solution is $V_{1,2}$ obtained from the relation $V_{1,2} = (10^3 + mM_2) / \rho$ ($\frac{10^3}{M_1} + m$) .Where M_1 and M_2 are molecular weight for solvent and solute respectively. The values for $\Delta G^*_{1,2}$ calculated via the equation (4) for Ser, Cys and Thr are given in Table 1,2 and 3 respectively. Tables 1,2 and 3 shows that the values of $\Delta G^*_{1,2}$ increase with increase of concentrations and temperature for Ser, Cys and Thr.

Jones-Dole coefficient B is a measure of structural modification induced by solute- solvent interactions [25,26].

The values of B coefficient have been obtained by using the following equation .

$$\eta_r = 1 + Bc \qquad \ldots\ldots\ldots\ldots (5)$$

The values of B are included in Tables 1,2 and 3 . These Tables indicate that the values of B-coefficients are positive, for all amino acids studied and follow the order $B_{Cys} > B_{Thr} > B_{Ser}$ suggesting solute- solvent interactions.

Thus the values of coefficient B support the behaviours of ϕ_v° and S_v. which all suggest solute- solvent interactions compared to solute-solute interactions in these amino acid systems. Also, the increasing value of B-coefficients with the rise in temperature further support our earlier conclusion (drawn from the variation of ϕ_v° and S_v with temperature) that solute- solvent interactions decrease while solute-solute interactions increase with a rise temperature.

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