Interaction Of Threonine Amino Acid In Aqueous Dimethyl Sulfoxide Solutions At Various Temperatures

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Abstract

Apparent molal volume Φ_v, apparent molal volumes at infinite dilution Φ^o_v ,the slope S_v and viscosity **B** and D coefficients for Threonine (Thr) in (2-10)% w/w aqueous Dimethyl Sulfoxide (DMSO) solvents have been calculated respectively from the density and viscosity measurements at different temperatures 298.15,303.15,308.15and 313.15 K. The results are discussed in the light of solute-solvent and solute-solute interaction, and shows that Threonine behave as structure-breaker in aqueous DMSO solvent.

Introduction

Amino acids which are the fundamental substances for building blocks of proteins are used as model compounds to study the interactions of proteins in water and different solutions.

A number of workers studied the volumetric and viscometric properties of amino acids in water [1-5].

In recent years interest has been directed to study the behavior of amino acids in mixed aqueous solvents, in aqueous electrolyte systems and in binary aqueous solutions of urea. Such works is important in understanding the factors that determine the stability of these acids [6-16].

Ogawa et al [10] studied the volume, adiabatic compressibility and viscosity of some amino acids in aqueous alkali-chloride. They showed all the apparent molal volume Φ^o_v, the apparent molal adiabatic compressibilities Φ^o_{ks} at infinite dilution, and Jones-Dole **B** values in a mixed solvents larger than the corresponding results in water, except in a few cases of **B** coefficient

Pal and Kumer [15] measured the volumetric and viscometric data of Urea in water and in aqueous solutions of many amino acids at various

temperatures. They concluded that L-Valine act as structure-mater, while L-alanine and L-glycine act as structure –breaker .

Ali and Shahjaham [17] studied the volumetric and viscometric behavior of L-serine, L-Threonine, L-glutamine, L-lysine, L-arginine and L-histidine amino acids and their group contributions in aqueous tetramethylammonium bromide at different temperatures. The Jones-Dole coefficient **B** for (NH^{+}_{3} ,COO^{-}) zwitterionic end groups and for CH_2 group are calculated. They found the $\partial \mathbf{B}/\partial T$ is positive for zwitterionic end groups (NH^{+}_{3}, COO^{-}) and negative for CH_2 groups ,inferring that (NH^{+}_{3}, COO^{-}) are structure-breakers ,where as CH_2 groups are structure-makers. The values of B (NH^{+}_{3}, COO^{-}) are greater than B (CH_2) values ,enhancing that all the amino acids studied are net structure-breaker.

In the continuation of our earlier work of viscosity and volumetric for some amino acids in water [18] and Cysteine in aqueous Dimethyltformamide solutions [19] at different temperatures studied. In this paper systematically the interaction of Threonine

[$CH_3CHOHCHCOO^{-}$] NH^{+}_{3}

With (2%and 10% by mass Dimethylsulfoxide +water) solutions at different temperatures investigated .Threonine was chosen because it is one of the important amino acids that maintain the proper protein equilibrium in body and needed to produce Glycine and Serine. Dimethylsulfoxide (DMSO)is the organ sulfur compound with the formula$(CH_3)_2SO$ having various uses. DMSO is an important dipolar, aprotic solvent because it has a wide range of applicability a solvent in chemical and biological processes . The liquid dissolves both polar and nonpolar compounds and is miscible in a wide range of organic solvent as well as water. So its extensively used as a solvent for polymers [20].

In this study, the densities ρ of Thr [0.1, 0.15 , 0.20 , 0.25 , 0.30 , 0.35 , 0.40] molar concentration c($mol.dm^{-3}$) in 2% and 10% by mass DMSO+ water mixture at 298.15,303.15,308.15 and 313.15 K are measured. Then the apparent molal volumes Φ_v , apparent molal volume at infinite dilution Φ^{o}_{v} ,the slope S_v and Jones-Dole coefficients (Band D) ,are calculated.

The aim of this work is to provide information about the solute-solvent and solute-solute interactions in the above solutions. Then a decision is made if Threonine in these solutions acts as structure-maker or structure-breaker.

Experimental

The Analar Threonine was obtained from Flukacompany ,it is used without further purification. Dimethylsulfoxide (colorless liquid) was obtained from Fluka company (purity>99.7%) and used without any futher treatment. Water used in these experiments doubly distilled (Sp. Conductivity ~10^{-6} $ohm^{-1}cm^{-1}$).

Viscosity η was measured by using a suspended-level Ubbelohde viscometer with a flow time of approximately 330 s for distilled water at 298.15 K [21]. Densities ρ of all solutions were evaluated by vibrating tube with digital Anton parr (DMA 60/602)[22] . A thermostatic control (±0.01K) was employed during all measurements.

Results and Discussion

The experimental data for the molar concentration c, density ρ and viscosity η of Threonine 2% and 10% w/w (DMSO + H2O) at various temperatures 298.15, 303.15, 308.15 and 313.15K were summarized in table 1.

The molality of solutions m was calculated applying the following relation:

m=1/ (ρ/c-M/1000) .... (1)

where ρ=density of solution ($g.cm^{-3}$)

M=molecular weight of solute (Threonine M=119 g mol^{-1})

The apparent molal volumes Φ_v were obtained from equation[4, 9]

$$\frac{10^3(\rho-\rho_\circ)}{m\rho\rho_\circ} - \frac{M}{\rho} = \Phi_V$$

Where ρ^o=is the density of solvent (g cm^{-3})

The calculated values of Φ_v for all solution at different temperatures were listed in table 1. Table 1 showed that the values of Φ_v decrease with increase Thr concentration and DMSO percent in solvent, but increase with elevated temperature. It indicated that the solute-solvent interactions decrease with increasing Thr concentration and DMSO content.

The apparent molal volume at infinite dilution Φ_v^o was found by computerized least-square fitting to the following linear equation [3]

$\Phi_{v}=\Phi_v^o + S_v m$ ……….. (3)

where S_v is the experimental slope [4]. The values of Φ_v° reflects the presence of solute-solvent interactions. Where as, S_v indicate solute-solute interactions. The obtained values of Φ_v^o and S_v were listed in Table2. These values revels that Φ_v^o are positive and increase with temperature, exhibit

the presence of solute-solvent interactions which become more pronounced at elevated temperature The Φ_v^o values was not effected by DMSO content.
Table 2 also illustrated that all temperatures investigated, S_v values were negative , suggesting weak solute –solute interaction and Sv value became more negative with elevated temperature. This reflect the reducing strength of solute-solute interactions .So the behavior of S_v supports that of Φ_v° for Threonine . The decrease in S_v rise temperature inflects that Thr act as structure-breaker [15, 17].

The viscosity of a solution η of a non-electrolyte or a dipolar ion can be related to the viscosity of the solvent η°, and to the molar concentration c of solution [2, 23] by equation (4)

$\eta_r=\eta/\eta°=1+B_c$ ………. (4)

η_r is a relative viscosity. B an empirical term ,has been found depend upon solvent-solute interactions, and on the relative size of the solute and solvent molecules. Equation (4) is valid only at low concentrations, but at higher concentrations a third term c^2 is required. The variation of the relative viscosity η_r with molarity c for solutions of dipolar ions or non-electrolytes is normally interpreted in term of the Jones-Dole equation24 of another form

$\eta_r=\eta/\eta°=1+ B_c + Dc^2$ ……….. (5)

where D is an empirical coefficient . The D, besides it reflection solute-solute interactions ,also induces the solute –solvent interactionwhich are not included in coefficient B [25].

The values of B and D have been obtained from the intercepts and slope of the plots (η/η^o-1) /c vs. molar concentration c respectively. The values of B and D were included in Table 2. A perusal of Table 2 suggested that the B-coefficients for all solutions were positive and increase with temperature ,and when the percent of DMSO increases from 2 to 10% by mass. This may be attributed to strong solute-solvent interaction in the system .

The sign of temperature derivatives of B-coefficient $(\partial B/\partial T)$ gives important information regarding the structure-making or structure-breaking ability of the solute in the solvent media [8, 15, 26].

The variation of B with T is illustrated in figure 1. The slope $\partial B/\partial T$ is positive for Thr in the two cases under study (2 and 10% DMSO content in solutions). Thus Threonine in these systems behave as structure-breakers. This conclusion are in a good agreement with that the drawn from S_v values (Table2)

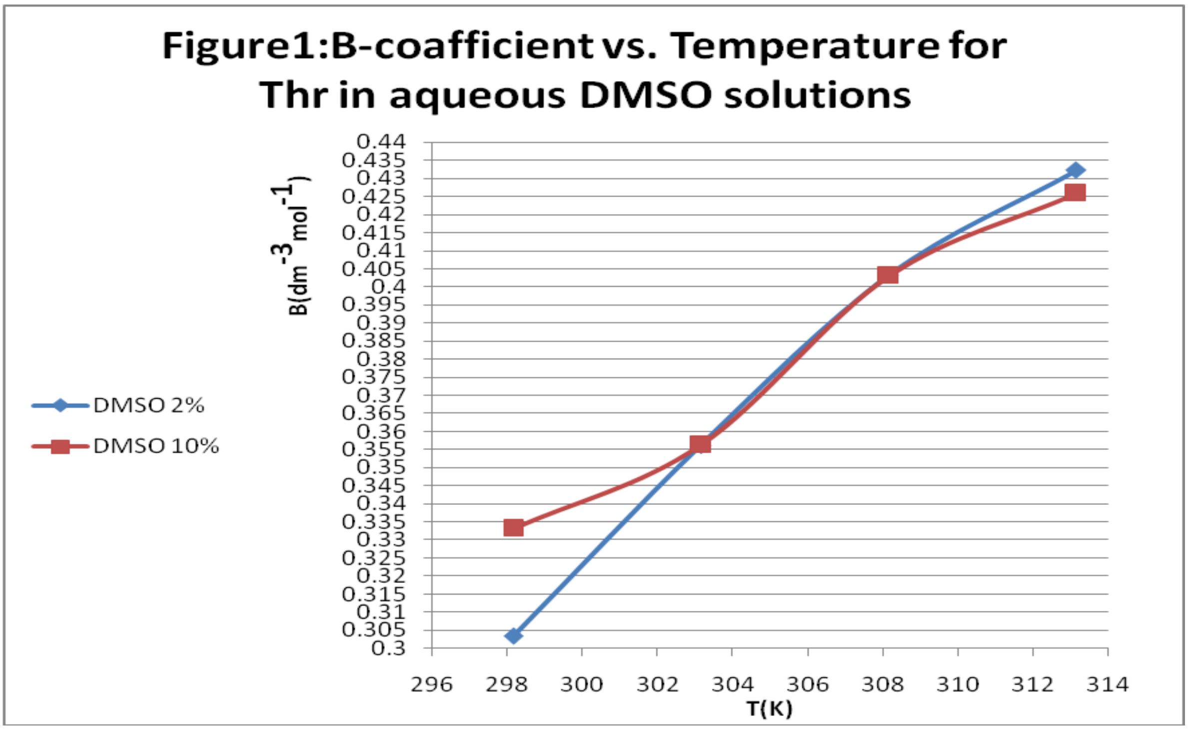

Table 1:Densities ρ ,Viscosities η ,and The calculated apparent molal volume Φ_V of Threonine in 2% and 10% (w/w) of DMSO + water mixtures at different temperatures.

Percent of DMSO in sol. 2%					10%			
C mol dm^{-3}	**m mol kg^{-1}**	**ρ g cm^{-3}**	**η cp**	**Φv cm^3mol^{-1}**	**m mol kg^{-1}**	**ρ g cm^{-3}**	**η cp**	**Φv cm^3mol^{-1}**
298.15 K								
0.00	0.0000	1.0552	0.9583		0.0000	1.0564	1.1484	
0.10	0.0954	1.0600	1.0026	67.2800	0.0952	1.0613	1.1980	66.2185
0.15	0.1435	1.0626	1.0455	65.9981	0.1433	1.0639	1.2500	65.2813
0.20	0.1920	1.0652	1.0931	65.3783	0.1917	1.0669	1.3078	62.9396
0.25	0.2408	1.0679	1.1504	64.6295	0.2403	1.0697	1.3748	62.2669
0.30	0.2899	1.0705	1.2182	64.4398	0.2893	1.0725	1.4425	61.8362
0.35	0.3392	1.0733	1.2887	63.7570	0.3386	1.0753	1.5112	61.5281
0.40	0.3889	1.0761	1.3592	63.2544	0.3881	1.0781	1.5772	61.2841
303.15K								
0.00	0.0000	1.0524	0.8460		0.0000	1.0517	1.0842	
0.10	0.0945	1.0571	0.8900	67.8662	0.0954	1.0595	1.1342	66.8321
0.15	0.1439	1.0597	0.9304	66.8079	0.1382	1.0618	1.1845	66.0981

0.20	0.1925	1.0623	0.9754	66.0192	0.1920	1.0647	1.2455	65.1863
0.25	0.2414	1.0650	1.0194	65.1660	0.2408	1.0675	1.3135	63.9711
0.30	0.2907	1.0676	1.0825	64.9256	0.2894	1.0704	1.3825	62.9652
0.35	0.3402	1.0702	1.1525	64.7374	0.3391	1.0733	1.4475	62.3283
0.40	0.3901	1.0728	1.2225	64.6051	0.3550	1.0744	1.5115	61.5824
308.15K								
0.00	0.0000	1.0503	0.7614		0.0000	1.0529	0.9882	
0.10	0.0959	1.0546	0.8018	72.3582	0.0956	1.0569	1.0382	70.2741
0.15	0.1442	1.0574	0.8458	68.2058	0.1439	1.0597	1.0882	66.8074
0.20	0.1929	1.0601	0.8908	65.2099	0.1925	1.0627	1.1382	64.1364
0.25	0.2420	1.0628	0.9408	65.6944	0.2414	1.0653	1.1982	64.0407
0.30	0.2913	1.0655	1.0008	65.0562	0.2906	1.068	1.2622	63.6609
0.35	0.3409	1.0682	1.0448	64.6006	0.3401	1.0706	1.3262	63.6565
0.40	0.3908	1.0710	1.1248	64.0215	0.3898	1.0736	1.3912	62.7056
313.15 K								
0.00	0	1.0486	0.6971		0	1.0505	0.9871	
0.10	0.096	1.0531	0.7411	73.5391	0.0958	1.0547	1.0371	73.2594
0.15	0.1445	1.0559	0.7815	69.061	0.1442	1.0577	1.0904	67.571
0.20	0.1932	1.0587	0.8265	66.7976	0.1929	1.0605	1.1504	65.678
0.25	0.2423	1.0615	0.8705	65.4602	0.2419	1.0631	1.2084	65.2957
0.30	0.2919	1.0641	0.9336	65.1948	0.2912	1.0658	1.2784	64.7215
0.35	0.3414	1.0667	0.9967	65.0018	0.3408	1.0684	1.3384	64.5823
0.40	0.3915	1.0693	1.0779	64.8644	0.3907	1.0712	1.4084	64.0077

Table 2: Partial molal volumes at infinite dilution Φ_v^o, S_v, and Jones-Dole coet (B ,D) of Thr. In 2% and 10% by mass DMSO aqueous solvent in different temperatures .

				2% DMSO
Temperature K	**Φ_v^o cm^3 mol^{-1}**	**S_v cm^3 mol^{-2} kg**	**B dm^3 mol^{-1}**	**D dm^6 mol^{-2}**
298.15	67.479	-10.925	0.3033	1.9345
303.15	68.366	-10.888	0.3561	1.9177
308.15	72.138	-23.451	0.4032	2.0249
313.15	73.41	-25.843	0.4323	2.3199
				10% DMSO
298.15	67.677	-18.266	0.3331	1.6355
303.15	68.303	-18.246	0.3562	1.73334
308.15	70.223	-18.2142	0.403	1.6509
313.15	72.539	-25.13	0.4259	1.7429

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دراسة تأثرات الحامض الاميني الثريونين في المحاليل المائية لداي ميثل سلفوكسايد بدرجات حرارة مختلفة

الخلاصة :

تم حساب الحجم المولاري الظاهري Φ_V ،الحجم المولاري الظاهري المحدد Φ^o_V ،الميل S_V ومعاملي اللزوجة **B** و D. نوقشت النتائج على ضوء التأثرات بين مذاب – مذيب و مذاب –مذاب حيث ظهر ان الحامض الاميني الثريونين يسلك سلوك المهدم – للتركيب في المحلول المائي لداي ميثل سلفوكسايد .