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Interaction of Cysteine in aqueous Dimethylformamide Solutions at different temperatures.

تأثرات الحامض الاميني الستين في المحاليل المائية – لداي مثيل فورماميد في درجات حرارة مختلفة.

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Abstract:

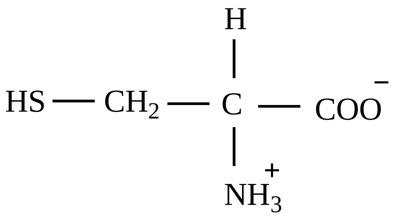
Densities ρ and viscosities η of cysteine (Cys) in 2.5% and 5%(w/w) Dimethylformamide (DMf)-water mixtures have been measured at different temperatures 298.15, 303.15, 308.15 and 313.15 K. From the experimental data molal volume ϕ_v , limiting partial molal volume ϕ_v° , the slop S_v , Jones-Dole B and D-coefficients, Gibbs free energy of activation for viscous flow of solution ΔG^*, enthalpy ΔH^* and entropy ΔS^* 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-coefficient.

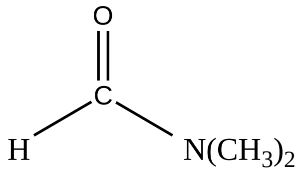
الخلاصة:

تم قياس كثافة ρ ولزوجة η محاليل مختلفة التراكيز للحامض الاميني الستين في مزيج (2.5 % , 5% بنسب وزنية) من داي مثيل فورماميد مع الماء . أجريت القياسات في درجات حرارة مختلفة. (298.15 , 303.15 , 308.15 و 313.15 مطلقة) أستخدمت النتائج في حساب الحجم المولالي الظاهري ϕ_v , الحجم المولالي الظاهري المحدد ϕ_v°, الميل S_v , معاملي جونس – دول D,B , طاقة كبس الحرة للانسياب اللزج للمحلول ΔG^* , الانثالبية ΔH^* والانتروبي ΔS^* . تمت مناقشة طبيعة التأثر من نوع مذاب – مذيب ومذاب – مذاب من خلال قيم ϕ_v° , S_v وقيمة معاملي جونس دول D,B .

Introduction:

It is well known that the mixed aqueous solvents (with different percent w/w) can influence the solubility behaviour of amino acids. Consequently thermodynamic properties, enthalpies, heat capacities, apparent molal volumes and viscosities of amino acids and peptide in mixed aqueous solvents is useful to obtain information about various types of interactions in these solutions [1-8]. Amino acids are high water solubities suggest, that they exist in anionic from (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[9]. Cysteine (abbreviated as Cys or C) is an α-amino acid and it is a non-essential amino acid, which means that humans can systhesize. Its codons are UGU and UGC with a thiol side chain cysteine is classified as ahydrophobic amino acid. Because of the high reactivity of this thiol, cysteine is an important structural and functional component of many proteins and enzymes[10].





Cysteine (CYS)

$M = 121$ g mole^{-1}

Dimethyl formamide (DMF)

$M= 73.1$ g mole $^{-1}$

In present work we measured the viscosities η and densities ρ of cysteine (0.1, 0.15, 0.20, 0.25, 0.30 and 0.35 molar concentration) in 2.5% and 5% (w/w) DMF + water mixture at 298.15, 303.15, 308.15 and 313.15 K. Then apparent molal volumes ϕ_v , limiting molal volumes at infinite dilution ϕ_v° , Jones- Dole coefficients B and D, Gibbs free energy ΔG^*, enthalpy ΔH^* and entropy ΔS^* were calculated.

Experimental:

Amino acid cysteine obtained from Fluka company is Analar and used without any further treatment. Dimethylformamide (DMF) is an aportic polar liquid with a high dielectric constant obtain from Fluka company (purity > 99%) used without further purification. Solutions doubly distilled water (SP. conductivity ~10^{-6} ohm^{-1} cm^{-1}) were used. The concentration in these mixtures ranged from 0.1 - 0.35 molar (mole dm^{-3}). The viscosity η were measured at different temperatures 298.15, 303.15, 308.15 and 313.15 K using a suspended – level ubbelohode viscometer described by findly [11], in a bath controlled to ± 0.01 K for all measurements. Densities ρ of all solution were measured at different temperatures 298.15, 303.15, 308.15 and 313.15K using avibrating tube with diqital Anton parr densimeter. (DMA 60/602) according to shukla et.al. procedure [12], in athermostated bath controlled to ± 0.01K.

Result and Discussion:

The density and viscosity data measured for the solutions of L-cysteine in aqueous dimethylformaimed (DMF + H_2O) at 298.15, 303.15, 308.15 and 313.15 K are listed in Table (1). The density data was used to compute apparent molar volumes ϕ_v , using the following relation.[13a].

$$\phi_v = \frac{M}{\rho} - \frac{1000(\rho - \rho_0)}{m\rho\rho_0} \quad ....(1)$$

Where M is the molecular weight of solute and m is the molality $[m = 1/(\frac{\rho}{c} - \frac{M}{1000})]$ of the solution, ρ_0 and ρ are the densities of solvent and solution respectively and c is the molar concentration. The results of ϕ_v are tabulated in table (1). The plot of ϕ_v against m in figure (1) shows a linear relationship where the slop equal S_v and the intercept, is ϕ_v° . Table (1) shows that the value of ϕ_v decrease with increase concentration of cysteine but ϕ_v increase with increase DMF content in the system suggesting that the solute-solvent interaction increase with increasing DMF%

in solution [13b]. The variation of apparent molal volumes ϕ_v with molal concentration can be adequately represented by equation [14a-14b]

$$\phi_v = \phi_v^{\circ} + S_v \text{m} \quad ....(2)$$

Where ϕ_v° is the apparent molar volume at infinite dilution and S_v is the experimental slop which also considered as the volumetric pairwise interactions coefficient [15]. The ϕ_v° reflects the presence of solute-solvent interactions, where as S_v , is indicated of the solute-solute interactions. Table(2) reveals that ϕ_v° positive and increases with increasing temperatures, indicating the presence of solute-solvent interactions which increase as the temperature of solution increases. The increase in ϕ_v° on going from 2.5% to 5% DMF demonstrate the rising trend of solute-solvent interaction. The S_v values are found to be negative. This illustrate weak solute-solute interactions and S_v values become more negative with increase in temperatures indicating a redaction of solute-solute interactions in solution and also shows the Cysteine behave as structure-breakers [16]. In fact negative S_v values are often obtained in solvent of high dielectric constant such as (DMF+ water) solvents [17].

The viscosity data was successfully analyzed according Jones-Dole equation [18-19].

$$\eta_r = \frac{\eta}{\eta_{\circ}} = 1 + \text{Bc} + \text{Dc}^2 \quad ....(3)$$

Where η and $\eta_{\circ}$ are the viscosities of solution and solvent respectively, B and D viscosity coefficient which are empirical constant characteristic of give solute-solvent pair. B is considered to reflect mainly the effect of the size shape of solute molecule, as well as the solute-solvent interactions on viscous flow. On the other hand, the D coefficient besides the solute – solute interactions, also induces the solute-solvent interactions which are not included in coefficient B.[20]. From table (2) the B coefficient for all solutions are quite positive and increase with increasing temperatures and DMF percent solutions, this may be attributed to strong solute-solvent interactions.

From transition state theory the Gibbs free energy of activation for viscous flow of solution, ΔG^* (J.mole^{-1}) at a given temperature and composition is given by the equation [21-22].

$$\Delta G^* = RT \ln \left(\frac{\bar{\text{V}}_{1,2}\,\eta}{hN_A} \right) \quad ....(4)$$

Where R is the gas constant, T is the absolute temperature, h is planks constant, N_A is Avogadro's number and volume of mole solution, $\bar{\text{V}}_{1,2}$ obtained from the following relation.

$$\bar{\text{V}}_{1,2} = (10^3 + mM_2) / \rho\left(\frac{10^3}{\text{M}_1} + m\right) \quad ....(5)$$

Where M_1 and M_2 are the molecular weight for solvent and solute respectively, the values of ΔG^* is calculated via equation (4) and given in table (3). Table (3) demonstrate that the values of ΔG^* increating with increasing DMF% in solution. The calculation of enthalpy, ΔH^* and entropy, ΔS^* of activation of viscous flow was done using the following equation:

$$\Delta G^* = \Delta H^* - T\,\Delta S^* \quad ....(6)$$

The ΔH^* and ΔS^* are deduced from linear relation of ΔG^* vs . temperature. ΔH^* gives the structural information of the solute species and ΔS^* provides information regarding solute-solvent interactions [23]. The sign of $\partial B / \partial T$ is more straight forward indicator of the structure- making or –braking ability of a solute rather than the sign or size of B- coefficient. The structure-makers will have negative $\partial B / \partial T$ values while structure-breakers will have a positive $\partial B / \partial T$ values [24-25]. The variation of B with T is depicted graphically in figure (2) revealed that the slope ($\partial B / \partial T$) is positive for all states under study. Therefore, cysteine in all solutions act as structure-breakers.

Table 1: Densities and Viscosities (η) with calculated apparent molal volume (ϕ_v), and the $\frac{\eta}{\eta_0} - 1/c$ of cysteine in water at different percent w/w of Dimethyl formamide mixtures at different temperatures.

2.5% DMF						5% DMF				
c mol. dm^{-3}	m mol.kg^{-1}	ρ g.cm^{-3}	η cρ	ϕ_v cm^{3}mol^{-1}	(η_{r-1}) /c	m mol.kg^{-1}	ρ g.cm^{-3}	η cρ	ϕ_v cm^{3}mol^{-1}	(η_{r-1}) /c
0.00	0.0000	1.0466	0.9017				1.0472	0.9834		
0.1	0.0962	1.0516	0.9394	67.8383	0.4185	0.0962	1.0520	1.0302	69.7273	0.4758
0.15	0.1448	1.0542	0.9642	67.2081	0.4621	0.1447	1.0545	1.0567	69.1375	0.4966
0.2	0.1937	1.0568	0.9944	66.8863	0.5140	0.1936	1.0571	1.0850	68.2705	0.5166
0.25	0.2429	1.0595	1.0262	66.3104	0.5523	0.2428	1.0598	1.1156	67.4130	0.5377
0.3	0.2924	1.0623	1.0618	65.6082	0.5918	0.2923	1.0625	1.1486	66.8376	0.5599
0.35	0.3422	1.0651	1.1048	65.1074	0.6435	0.3422	1.0653	1.1825	66.1709	0.5786

298.15 K

0.00	0.0000	1.0452	0.8391			0.0000	1.0461	0.9221		
0.1	0.0963	1.0501	0.8768	68.8673	0.4493	0.0963	1.0508	0.9737	70.7503	0.5596
0.15	0.1450	1.0527	0.9017	67.9330	0.4974	0.1449	1.0533	1.0098	69.7805	0.6341
0.2	0.1940	1.0553	0.9330	67.4585	0.5595	0.1939	1.0558	1.0493	69.3110	0.6897
0.25	0.2433	1.0580	0.9661	66.7920	0.6054	0.2431	1.0585	1.0965	68.2468	0.7565
0.3	0.2929	1.0607	1.0016	66.3417	0.6455	0.2927	1.0612	1.1437	67.5512	0.8011
0.35	0.3427	1.0635	1.0443	65.7355	0.6987	0.3425	1.0640	1.2007	66.7662	0.8632

303.15 K

0.00	0.0000	1.0438	0.7626			0.0000	1.0444	0.8375		
0.1	0.0965	1.0486	0.7983	69.9473	0.4681	0.0965	1.0490	0.8907	71.8376	0.6352
0.15	0.1452	1.0511	0.8234	69.2940	0.5315	0.1452	1.0515	0.9275	70.5477	0.7164
0.2	0.1943	1.0537	0.8499	68.5075	0.5724	0.1942	1.0540	0.9692	69.8930	0.7863
0.25	0.2437	1.0563	0.8810	68.0298	0.6210	0.2436	1.0566	1.0199	69.1340	0.8712
0.3	0.2933	1.0590	0.9185	67.3760	0.6814	0.2933	1.0593	1.0766	68.3081	0.9516
0.35	0.3433	1.0618	0.9565	66.6490	0.7265	0.3432	1.0621	1.1490	67.4325	1.0627

308.15 K

0.00	0.0000	1.0417	0.7215			0.0000	1.0426	0.7530		
0.1	0.0967	1.0464	0.7568	71.0453	0.4893	0.0966	1.0471	0.8030	72.8869	0.6640
0.15	0.1455	1.0489	0.7796	70.0703	0.5368	0.1454	1.0495	0.8405	71.9238	0.7747
0.2	0.1946	1.0514	0.8083	69.5966	0.6015	0.1946	1.0520	0.8808	70.9780	0.8486
0.25	0.2442	1.0541	0.8379	68.5461	0.6453	0.2441	1.0546	0.9344	70.0255	0.9636
0.3	0.2950	1.0568	0.8711	67.8428	0.6912	0.2939	1.0572	0.9907	69.3839	1.0522
0.35	0.3441	1.0596	0.9080	67.0647	0.7385	0.3439	1.0601	1.0488	68.0991	1.1224

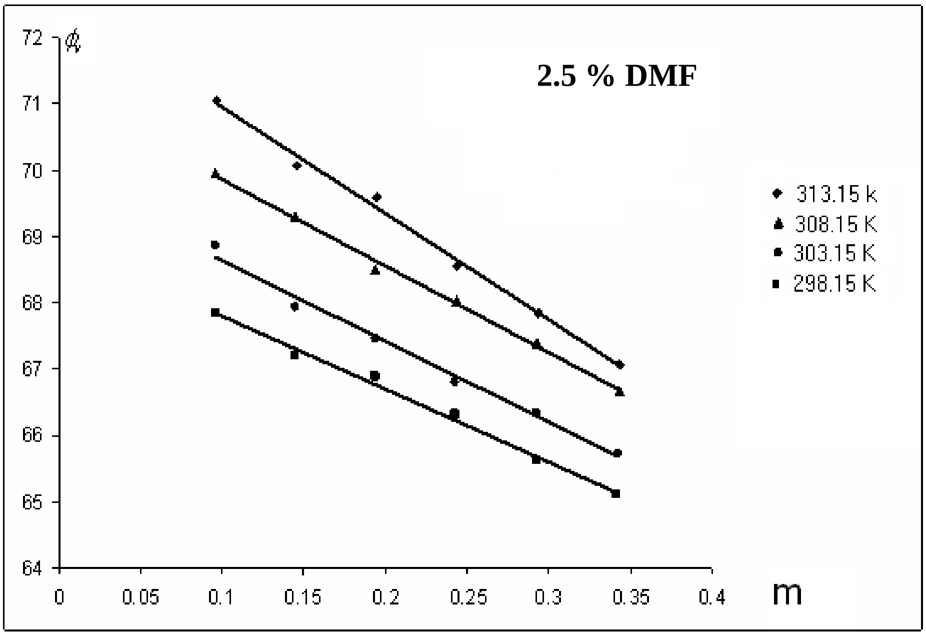
313.15 K

Table 2: Partial molal volume at infinit dilution ϕ_v° , S_v , Jones- Dole Cofficients B and D of Cysteine in various water + DMF mixtures at different temperatures.

	298.15 K	303.15 K	308.15 K	313.15 K
Solu.	**CYS + H_2O + 2.5 % DMF**			
ϕ_v° **cm³ mol⁻¹**	68.910	69.866	71.186	72.535
S_v cm^3 mol^{-2}kg	-11.053	-12.227	-13.152	-15.955
B dm^3 mol^{-1}	0.3308	0.3526	0.3700	0.3917
D $dm^6$$mol^{-2}$	0.8871	0.9927	1.0230	1.0017
CYS + H_2O + 5 % DMF				
ϕ_v° **cm^3 mol^{-1}**	71.168	72.248	73.271	74.676
S_v cm^3 mol^{-2}kg	-14.829	-16.052	-17.078	-18.777
B dm^3 mol^{-1}	0.4343	0.4492	0.4608	0.4877
D $dm^6$$mol^{-2}$	0.4143	1.1919	1.6731	1.8511

Table3: Thermodynamic functions Viscous flow $\Delta G^*, \Delta H^* and \Delta S^*$ of Cysteine in water with 2.5% and 5% of DMF at different temperatures.

2.5% DMF						
	ΔG^* **J.mol⁻¹**				ΔH^* **J.mol⁻¹**	ΔS^* **J/mol.K**
c mol.dm⁻³	**298.15 K**	**303.15 K**	**308.15K**	**313.15 K**		
0.00	63915	64809	65636	66562	11632	175.36
0.1	64016	64919	65753	66687	11225	177.06
0.15	64080	64989	65832	66764	11041	177.9
0.2	64156	65075	65913	66857	10844	178.82
0.25	64233	65162	66004	66950	10613	179.86
0.3	64315	65252	66110	67051	10262	181.32
0.35	64414	65356	66213	67158	10224	181.78
5% DMF						
0.00	64128	65044	65870	66671	13714	169.2
0.1	64243	65182	66033	66839	12764	172.78
0.15	64330	65273	66136	67958	12204	174.94
0.2	64371	65369	66249	67080	10707	180.14
0.25	64439	65480	66379	67233	9148	185.62
0.3	64511	65585	66517	67385	7595.9	191.08
0.35	64582	65707	66682	67532	6065.5	196.5



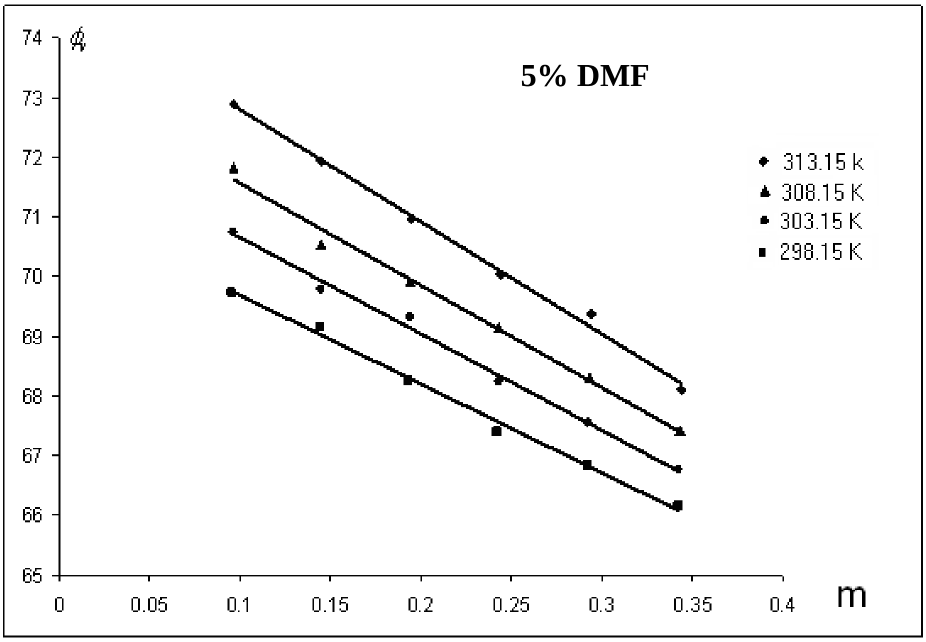


Figure 1: ϕ_v vs.m for Cys inaquaus DMF.

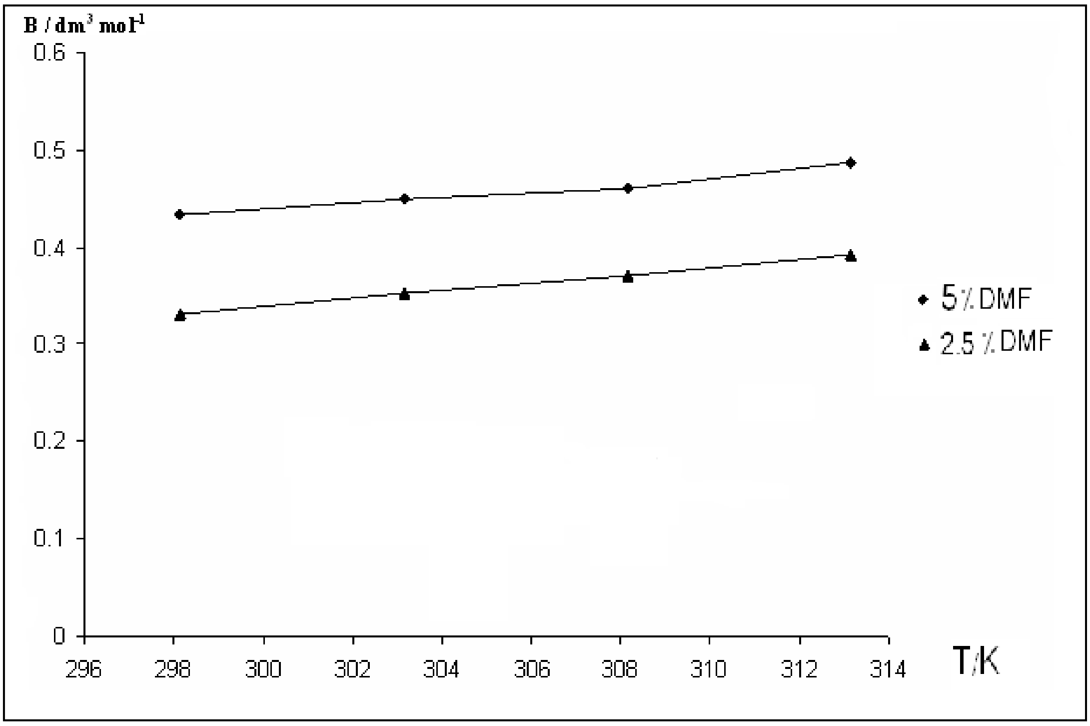


Figure2: B-coefficient verses T for Cys inaquous DMF.

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