Egypt. J. Chem. **Vol. 64,** No. 5 pp. 2369 - 2375 (2021)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Study of Viscous Behavior for Amino Acid L- Glutamine Aqueous N,N Dimethyl Formamide Solution at Different Temperatures

Suhair Abdulhadi Mahdi[a*], Ahlam Mohammed Farhan[b]

[a]*Department of Chemistry, College of Science, Mustansiriyah University, Baghdad, Iraq*

[b]*Department of Chemistry, College of science for Women, University of Baghdad, Baghdad, Iraq*

Abstract

The densities (ρ) and kinematic viscosities (ν) which was converted to the absolute viscosity (η) from the product of the kinematic viscosity and the density of L-Glutamine have been measured at different temperatures 298.15, 303.15 and 313.15K in aqueous 20% (w/w) dimethyl formamide (DMF) under atmospheric pressure. The value of apparent molar volume (ϕv), limiting apparent molar volume (ϕv°) and viscosity data have been analyzed by using Jones-Dole equation, the Jones-Dole coefficients (A and B) were calculated and excess Gibbs free energy of activation of viscous flow ($\Delta\mu^{\#}$) has been obtained to throw light on the mechanism of viscous flow. The results were interpreted strong ion-solvent interactions in these systems and also structure-maker in 20% DMF + 80% water mixed solvents.

Keywords: Volumetric; Viscometric; Amino Acid; L-glutamine; Dimethyl formamide.

1. Introduction

The main substance that has been used in the structure of protein formation is amino acids which were considered an important material for studying the interactions between protein molecules in different types of solutions. Glutamic acid is one of the kinds of amino acids that have an important role in nitrogen metabolism, and the production of purine bases by biological pathways. Moreover, the presence of glutamic acid helps increase immunity as well as the ability to remove practical toxins [1-3]. The main structural the molecule of L-glutamine contains carboxylic acid (-C=O) and (-NH2) side chain that called hydrophilic amino acids has ability to react with the aquatic environment as a result of their polar nature [2]. There are many works that have been studied for viscosity and volumetric behavior and thermodynamic properties, enthalpies, heat capacities of amino acids in aqueous solutions [4-11]. The behavior of solubility to amino acids in liquid solvents is affected by its weight percentages in a mixture. Accordingly, thermodynamic properties, a peptide in mixed of aqueous solvents, and viscosities of amino acids seem beneficial to investigate important information on different kinds of interactions in these solutions [1-2].

DMF is an organic solvent and it has wide applications in many pharmacology and biochemistry industries, furthermore, it contains an effective functional (-CONH) group [8].

Recently many studies presented the importance of L-glutamine presence on the behavior of aqueous solution, Valeriy and Valentin, 2019 [1], studied the effect of thermodynamics dissolution of many different amino acids in mixed solvents [water + (formamide, N-dimethylformamide, and N, N-dimethylformamide)] at 298.15 K, they founded the solubility entropy factor, side-chain structures and intermolecular interactions of glutamine was influenced in aqueous organic mixtures compared to with different amino acids. Gaba et al., 2019 [3], Presented the measured of densities and speeds of the sound of l-glutamic acid and l-aspartic acid in an aqueous solution of 1-methylimidazolium chloride at

*Corresponding author e-mail: suhear.a@uomustansiriyah.edu.iq ; (Suhair Abdulhadi Mahdi).
Receive Date: 31 August 2020, Revise Date: 19 January 2021, Accept Date: 06 February 2021
DOI: 10.21608/EJCHEM.2021.41180.2834

different temperatures are helpful to study the structure and solvents behavior and various interactions present in the ternary solutions of amino acid in aqueous of 1-methylimidazolium chloride . Daniel et al., 2018 [7], Studied dissociation enthalpies of many amino acids (L-asparagine, L-glutamine, L-aspartic acid, glutamic acid, arginine, lysine, histidine) in an aqueous solution of potassium chloride at 298.15K, the results showed the effects of hydrophobic- hydrophilic in a solute-solvent on the side chain of amino acid. Arsule et al., 2019 [15], densimetry and velocity of ultrasound of different amino acid concentrations in an aqueous solution of acetylsalicylic acid at different temperatures and atmospheric pressure, they deduced the acetylsalicylic acid has an effect on the hydration of amino acids and effect on solute-solvent interactions. Manuel et al., 2018 [21], measured both the density and viscosity of glycine in five aqueous solutions of sodium sulfate at different temperatures and they concluded that glycerin has a behavior maker on the solvent structure, as demonstrated by the studied thermodynamic functions that give a clear picture of the interactions between stable molecules in glycine with mixtures (water + sodium sulfate).

It seems a little information reported in the literature present the effect of temperature and L-glutamine concentrations on the viscous behavior of the aqueous solution of DMF. Accordingly, the present study focuses on the effect of different temperatures and L-glutamine concentrations on the intermolecular interactions in aqueous solution DMF.

2. Material and Methods

2.1. Materials

Amino acid L-glutamine obtained from Fluka Company and used without any further treatment. DMF (purity >99.7%) is an aprotic polar liquid with a high dielectric constant that was purchased from Fluka company and used without any further purification. The distilled water used for preparation was distilled twice (Sp.conductivity ~10^{-6}ohm^{-1}cm^{-1}).

A 20% w / w stock solution was prepared from DMF and different concentrations for glutamine (0.01, 0.04, 0.08, 0.12, 0.14) mol. L^{-1} dissolved in DMF.

2.2 Methods

The glutamine concentration in these mixtures was ranged from (0.01-0.14) mol.L^{-1}. The kinematic viscosities (ν) of samples was measured under different temperature using a suspended-level ubbelohde viscometer according to the procedure described by findly [10], in controlled temperature bathwater with accurate ±0.01K .

The Densities (ρ) of all solutions were measured under different temperatures using a vibrating tube with digital Anton Paar densimeter (DMA60/602) according to the procedure described by shuklu et al. [13], in a thermostated bath controlled with accurate ±0.01K.

3. Results and Discussion

The relevant results as shown in table (1) observe that densities (ρ) value were increasing at increase glutamine concentration in an aqueous solution that consists of 20% DMF+80% water, on the other hand, it decreased with temperature.

The obtained experimental results for densities were used to calculate the apparent molar volume of glutamine in 20% DMF+80% water solution and reported in the table (1) within a range of temperature of 298.15, 303.15 and 313.15 K, using equation (1) [4,5,9].

$$\phi v = \frac{M}{\rho} + \frac{1000\,(\rho_\circ - \rho)}{c\rho_\circ} \qquad (1)$$

Where:

ϕv Apparent molar volume ($cm^3.mol^{-1}$) of solution.

M Molar mass of glutamine (g·mol^{-1}).

$\rho_\circ$ Density of the solvent ($g.cm^{-3}$).

ρ Density of the solution ($g.cm^{-3}$).

c Molar concentration of solution ($mol.L^{-1}$).

The results of the calculation present that values of ϕv for the solution were increased with an increase in the L-glutamine concentrations and decrease with increasing temperature.

Figure (1) present the relation between the ϕv and the root square of the concentration of glutamine in aqueous 20% DMF at all different temperatures to provide as an information on the limiting apparent molar volume and experimental slope (volumetric pairwise interaction coefficient) S_v using equation (2) [14].

$$\phi v = \phi v^\circ + S_v \sqrt{c} \qquad (2)$$

Table 1:Value densities ρ, Absolute viscosity, the borders of Jones Doll and apparent molar volume of glutamine in 20%(w/w) DMF + 80% (w/w) water mixtures at different temperatures.

$c/mol.L^{-1}$	$\rho/g.cm^{-3}$	η/cP	$\frac{\eta_{rel-1}}{\sqrt{c}}$	$\phi v\ /(cm^3.mol^{-1})$
298.15K				
0.00	0.9923	1.4522		
0.01	0.9926	1.4786	0.1814	117.00
0.04	0.9931	1.5611	0.3747	127.00
0.08	0.9937	1.6354	0.4461	129.43
0.12	0.9943	1.680	0.4519	130.18
0.14	0.9949	1.7354	0.5212	128.17
303.15K				
0.00	0.9899	1.4631		
0.01	0.9902	1.5269	0.4362	117.28
0.04	0.9908	1.6226	0.5453	124.77
0.08	0.9915	1.7158	0.6108	127.19
0.12	0.9922	1.8380	0.7397	127.93
0.14	0.9928	2.0215	1.0201	126.27
313.15K				
0.00	0.9871	1.4662		
0.01	0.9875	1.5626	0.6576	107.47
0.04	0.9881	1.6542	0.6410	122.57
0.08	0.9889	1.7480	0.6795	124.99
0.12	0.9896	1.8886	0.8315	126.57
0.14	0.9902	2.2228	1.3791	125.15

Where ϕv° limiting apparent molar volume and S_v is the experimental slope also known as the volumetric pairwise interaction coefficient, these data are listed in a table (2). It was obtained from the intercept and slope from the extrapolation of the diagrams of ϕv versus $\sqrt{c}$ shown in Fig. (1). The positive S_v values in Masson's equation for l-glutamine of aqueous 20% DMF + 80% water at each the temperatures, refer to consist a stronger zwitterion-zwitterion and weak solute-solute interactions [15], its means a bigger size of hydrated zwitterions of l-glutamine with low in electrostriction, on other hand, a higher positive value of v° were founded with increasing temperature [3, 15]. The observed positive value of v° were higher than S_v, which indicate strong solute-solvent interactions than solute – solute interaction.

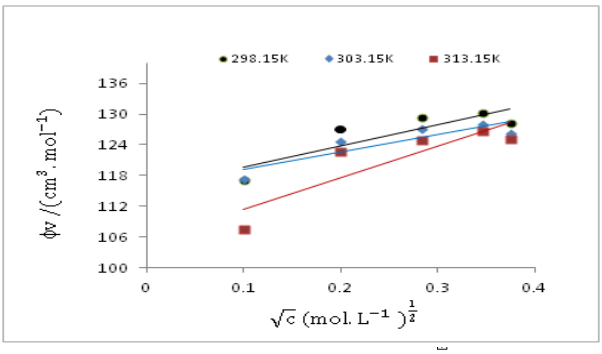

Fig.1. A change value apparent molar volume (v) against the square root of molar concentration glutamine.

Viscosity data was analyzed using Jones-Dole equation (3) [17], as shown in a table (2).

$$\frac{\eta_{rel}-1}{\sqrt{c}} = A + B\sqrt{c} \qquad (3)$$

Where:

$\eta_{rel} = \frac{\eta}{\eta^{\circ}}$ (relative viscosity).

η viscosities of the solution (cP).

η^{o} viscosities of the solvent (cP).

A, B are the Falkenhage and Jones-Dole coefficients respectively [17, 18].

The A and B coefficient refers to solute-solute interactions and effect of hydrogen bond ions respectively [16] moreover the B value gave an idea about the salvation of solutes, which show the (solute-solvent) interactions [17, 18, 19].

The relevant results in this study as shown in figure (2) noticed of A- and B-coefficients have a positive value and the value of A-coefficients were smaller than B- coefficients, which attributed to weak solute-solute and strong solute-solvent interactions in the solutions, the B-coefficients were increases with increasing L-glutamine concentration for all temperature, this explains that the activity of an L-glutamine toward the formation of self-association hydrogen bonds with aqueous solutions of DMF has increased with increases in its concentration that will be permitted to making clathrate – structure [9].

The positive B-coefficients values of solution which pointed out that the L-glutamine acts as a structure-maker when DMF was added to solutions [13].

The trend of A and B coefficients support the behaviors of v°, S_v which suggest a stronger solute-solvent interaction with comparison to solute-solute interactions.

The values of the excess activation free energy of viscous flow at different concentrations of L-glutamine in aqueous solutions were determined using the Eyring equation (4) [20].

$$\ln\eta = \ln\frac{hNA}{Vm} + \frac{\Delta\mu^{\#}}{RT} \qquad (4)$$

Where:

h is the Plank's constant (m^2 kg / s),

N_A is the Avogadro's number (mol^{-1}),

R is the gas constant ($Jmol^{-1}K^{-1}$).

V_m is the average molar volume of solution.

The slope of a straight line for the relationship between $\ln\eta$ and $\frac{1}{T}$ represent the value of $\frac{\Delta\mu^{\#}}{R}$ as shown in the figure (3), the determined values of $\Delta\mu^{\#}$ show in the table (3), has positive values and it increased with increasing L- glutamine concentration in the binary mixture (DMF + water), It is inferred that the dissolution of amino acid increases in aqueous solutions as the concentration of glutamine has increased, moreover, the interference between solute-solvent was stronger which attributed to hydrophilic groups, the positive value of excess activation free energy refers to the higher structure-making tendency of the solute, that will be leading to an increase in the friction preventing solution flow or decreased viscosity at increased L-glutamine concentrations [4,8].

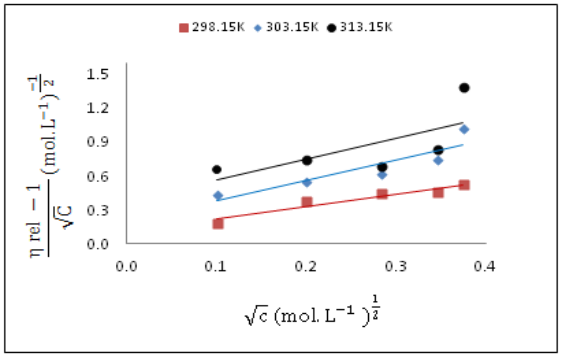

Fig.2. A change $\frac{\eta\,rel\,-1}{\sqrt{C}}$ against the square root of a concentration glutamine.

Table 2: Partial molar volume at infinite dilution ϕv^{o}, experimental slopes S_v Jones-Dole coefficients A and B of glutamine in 20 %(w/w) DMF + 80% (w/w) water mixtures at different temperatures.

T(K)	ϕv^{o} $(cm^3.mol^{-1})$	$S_v(cm^3mol^{-2}Kg)$	$A(mol.L^{-1})^{\frac{-1}{2}}$	$B(mol^{-1}.L)$	R
298.15	115.63	41.135	0.105	1.1125	0.9171
303.15	115.88	33.79	0.202	1.7943	0.7972
313.15	105.18	62.033	0.3793	1.8357	0.4732

Table 3

Value lnη and excess Gibbs free energy of activation of viscous flow ($\Delta\mu^{\#}$) of glutamine in 20 %(w/w) DMF + 80% (w/w) water mixtures at different temperatures.

$\frac{1}{T}_x 10^{-4}/K^{-1}$	0.00335	0.00330	0.00319	
c/mol.L^{-1}	lnη/cp			$\Delta\mu^*$/KJ. mol^{-1}
0.01	0.3911	0.01	0.4463	2.72
0.04	0.4454	0.08	0.5033	2.80
0.08	0.4919	0.14	0.5585	3.18
0.12	0.5066	0.5905	0.6358	5.55
0.14	0.5512	0.7038	0.7988	12.11

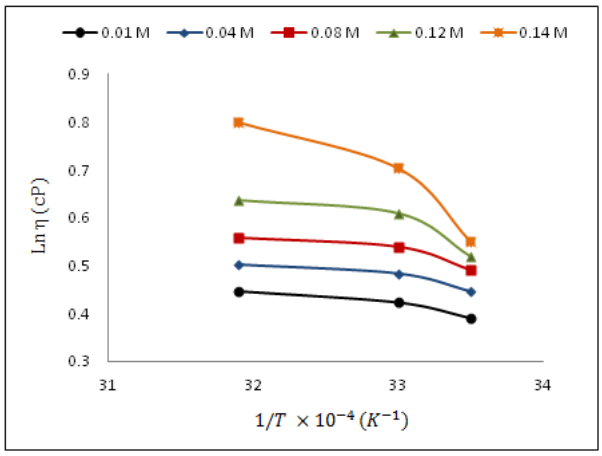

Fig. 3. A change value lnη as a function of the inverted temperature glutamine.

4. Conclusions

At different temperatures, both density and viscosity were measured for DMF aqueous solution with different concentration of L-glutamine. The following conclusions can be drawn from the attained results.

- The molar volume data in dilute solutions, it was found to be the largest from the experimental slope positive values, this indicates that the solute-solvent interactions are stronger than solute-solute interactions .
- For Jones-Doll coefficients, the values of B were greater than the values of A and also to be the values of B are positive, which is also indicates to interactions between solute-solvent are stronger than the interactions between solute - solute and its corresponds to the behaviors of ϕv°, S_v.
- The positive values of B prove that glutamine acts as a structure-maker with DMF in different solutions .
- The excess free activation energy of the viscous flow was determined and its values were found to be positive and increase with the increase in the amino acid concentration in aqueous solutions, which indicates that the dissolution of glutamine increases in aqueous solutions of DMF with increasing its concentration, and this confirms the behavior of Jones Doll's coefficient.

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دراسة السلوك اللزوجي للحامض الاميني كلوتامين –L في المحاليل المائية لداي مثيل فورمايد عند درجات حرارة مختلفة

سهير عبد الهادي مهدي [أ,*], احلام محمد فرحان [ب]

[أ] قسم الكيمياء, كلية العلوم, الجامعة المستنصرية, بغداد, العراق

[ب] قسم الكيمياء, كلية العلوم للبنات, جامعة بغداد, بغداد, العراق

الخلاصة

تم في هذه الدراسة قياس كل من الكثافة (ρ) واللزوجة الحركية والتي تم تحويلها الى اللزوجة المطلقة (η) من حاصل ضرب اللزوجة الحركية والكثافة لمحاليل من الحامض الاميني كلوتامين في مزيج (20%مذيب داي مثيل فورمايد و80%الماء) وزنا عند درجات حرارية مختلفة (298.15, 303.15 and 313.15) كلفن.

ومن تحليل تلك النتائج تم حساب الحجم المولاري الظاهري (ϕv) والحجم المولالي الظاهري المحدد (ϕv°) في المحاليل مخففة والميل (S_V) ومعاملات جونز دول (A, B) وطاقة التنشيط الحرة للجريان اللزج ($\Delta\mu^{\#}$).

تمت مناقشة طبيعة التداخلات من نوع مذاب -مذيب التي تكون اقوى من التداخلات بين مذاب -مذاب كما اظهرت النتائج ان حامض الاميني الكلوتامين يسلك سلوك مقوي للتركيب في المحاليل الثنائية للمزيج داي مثيل فورماميد + الماء.