Physiochemical Studies of Some Amino Acids in Aqueous and Acidic Media at Four Temperatures

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Abstract. This work is concerned with the study of solute-solvent interaction of amino acids: [DL-Valine, DL-Methionine and L-Arginine] as solutes in water and in hydrochloric acid solution (0.1 mol.L. -1) as solvents. This study covered experimental measurements of partial molal volume from precise density measurements using Anton Paar (DMA 60/602) densimeter, as well as theoretical calculations concerning partial molal volume, and some related parameters, a comparison and discussion was made in the light of these measurements. Measurements of the dynamic viscosities of amino acids solutions have been done over concentration variation from (0.04-0.2 mol.L.-1) at four temperatures in the range of (293.15-308.15)K. The resulting data have been utilized to verify the validity of Jones and Dole equation, and the viscous behaviour of the systems have been interpreted with regard to the contributions of the various viscosity components and the arrangements of solvent molecules. It was found that B-coefficient of amino acids in this study flow the order: Methionine > Valine > Arginine > . This study clarifies that each of B-Coefficient, Partial Molal Volume, Van der Waal’s Volume and Effective Flow Volume can be considered as parameters to account for solute-solvent interaction.

Key words: Apparent molar volume. Density. Solute-solute and solute-solvent interactions. Amino acids. Viscosity

Introduction

The study of solutions is of great importance because most of the interesting and useful chemical and biological processes occur in liquid solutions. Generally, a solution is defined as a homogeneous mixture of two or more components that form a single phase. All biological and many chemical systems are aqueous solutions containing various ions. The stability of biomolecules and the rate of many biochemical reactions are very much dependent on the type and concentration of ions present. It is important to have at least a qualitative understanding of the behaviour of ions in solutions. Aqueous solution of simple polar non-electrolytes are very interesting since many of them are components of biological fluids or very similar to the monomeric units of biological macromolecules. (1, 2) The study of the behaviour of the amino acids...
acids in aqueous solutions is useful models for understanding the thermodynamics behavior of proteins, especially in determining the polar group contributions to the biopolymer.\(^3\)\(^,\)\(^4\)

Every proteins molecule can be viewed as polymer of amino acid, at the center is tetrahedral carbon atom called the alpha (\(\alpha\)) carbon (C\(_\alpha\)) it is covalently bonded on one side to an amino group (NH\(_2\)) and one the other side to carboxyl group (COOH). A third bond is always to hydrogen and the fourth bond is a variable side (R). In neutral solution (PH=7) the carboxyl group loses a proton and amino group gains one, thus an amino acid in solution, while neutral overallis doubly charged in species called (Zwitter ion).

There are 20 common amino acids, and we divide the amino acids into three categories the first category contains eight amino acids with a polar (R) group, the second category contains seven amino acids with uncharged polar (R) group, and the third category contains five amino acids with (R) groups that normally exist in the charged state. The proteins represents the main component for all living cells, and because amino acids are the structural units of the proteins. The importance of studying physical properties for these acids are emerged due to it is main role for understanding it is behavior and mechanism.\(^5\)\(^,\)\(^6\)\(^,\)\(^7\) For this reason the purpose of the current study to understand the physical interaction between some amino acids molecules and solvent system molecules (water-hydrochloric acid) and this is can be achieved. Through the relation between practical measurements for the partial molal volume and viscosity with theoretical computation for the partial molal volume and van der waal’s volume to best understand the partial interactions between amino acids molecules and solvent system molecules.

**Experimental**

1. **Material:**

   The amino acids that used in this research DL-Valine, DL-Methionine and L-Arginine (99%) of molar mass 117.15, 149.21, 174.20 g mol\(^{-1}\) respectively was supplied by Fluka AG. Hydrochloric acid with chemical formula (HCL) and specific gravity (1.16) and the molecular weight (36.46 g. / mol.) produced from (Fluka AG) company in percent (36%). Deionized water was used in all experiments. The solvent used was Deionized water and 0.1 M HCl. The experiments were carried out at 293.15, 298.15, 303.15 and 308.15 K.

2. **Density and Viscosity Measurements**

   The amino acids solutions were prepared by dissolving exact balanced quantity of amino acid in aqueous and acidic solution (0.04-0.2 mol.L\(^{-1}\)). The sample densities were measured by an Anton Paar DMA 60/602 vibrating-tube digital densimeter. The density data determined are reproducible to 2 × 10\(^{-5}\) g.cm\(^{-3}\). The temperature around the density meter cell was controlled by circulating water from the Haak DIG thermostat. Viscosity measurements were carried out with a suspended level Ostwald viscometer. Flow time measurements are performed by a Schott AVS 310 photoelectric time unit with a resolution of 0.01 s. At least three time recordings were obtained, and the average value was used as the experimental flow time. The reproducibility of flow time was ± 0.01S. The viscometer was thermo stated in Hewlett-Packard a quartz thermostat, the temperature of which was controlled to be 293.15, 298.15, 303.15 and 308.15 with accuracy in temperature ± 0.01K. The viscosities were calculated by using the formula \(\frac{\eta}{\eta^0}=t^0/\rho^0\) where, \(\eta\), \(t\) and \(\rho\) are the absolute viscosity, time of flow and density of solution, while \(\eta^0\), \(t^0\) and \(\rho^0\) are same quantities for the solvent water and (0.1M HCl). The absolute viscosities and densities of water at 298.15, 303.15, 308.15 and 313.15 K were taken as 0.8904, 0.7975, 0.7194 and 0.6893 centi- poise, 0.9983, 0.99707, 0.9956 and 0.9947 g. cm\(^{-3}\) respectively. The densities of water were taken as 0.9982, 0.99565 and 0.9922 g.cm\(^{-3}\) respectively.\(^7\)\(^,\)\(^8\)
Result and Discussion:
The experimental results of densities (\(\rho\)) and viscosities (\(\eta\)) measurements of amino acids solutions (DL-Valine, DL-Methionine and L-Arginine) in water and 0.1M HCl at different molarities at (293.15, 298.15, 303.15 and 308.15 K) are presented in Table (1) and (2).

### Table (1): Densities and viscosities of amino acids solutions in water at different temperatures.

| C (mol.L\(^{-1}\)) | 293.15K | 298.15K | 303.15K | 308.15K | \(\rho\) (g.cm\(^{-3}\)) | 293.15K | 298.15K | 303.15K | 308.15K | \(\eta\) (mPas.s) |
|---------------------|---------|---------|---------|---------|----------------|---------|---------|---------|---------|----------------|
| Solvent H2O         | 0.99832 | 0.99707 | 0.99568 | 0.99406 | 1.0027        | 0.8904  | 0.7975  | 0.7194  |         |                |
| 0.04                | 0.99927 | 0.99853 | 0.99635 | 0.99461 | 1.057812      | 0.93575 | 0.848672| 0.750817|         |                |
| 0.06                | 0.99927 | 0.99910 | 0.99673 | 0.995271 | 1.065071      | 0.95793 | 0.857600| 0.757214|         |                |
| 0.08                | 0.99977 | 0.999475| 0.997347| 0.995759| 1.069297      | 0.96336 | 0.864512| 0.762204|         |                |
| 0.1                 | 1.000309| 0.999767| 0.997854| 0.996259| 1.075199      | 0.96814 | 0.876809| 0.770510|         |                |
| 0.12                | 1.000968| 1.000527| 0.998464| 0.996911| 1.079572      | 0.97445 | 0.872628| 0.774979|         |                |
| 0.14                | 1.001580| 1.001031| 0.998962| 0.997415| 1.084620      | 0.97781 | 0.878068| 0.779997|         |                |
| 0.16                | 1.002126| 1.001570| 0.999444| 0.997898| 1.088270      | 0.98179 | 0.883449| 0.783092|         |                |
| 0.18                | 1.003635| 1.002110| 0.999990| 0.998608| 1.094443      | 0.98685 | 0.889708| 0.787548|         |                |
| 0.2                 | 1.004574| 1.002564| 1.000508| 0.999166| 1.099193      | 0.99092 | 0.892317| 0.793286|         |                |

### Table (2): Densities and viscosities of amino acids solutions in 0.1M HCl at different temperatures.

| C (mol.L\(^{-1}\)) | 293.15K | 298.15K | 303.15K | 308.15K | \(\rho\) (g.cm\(^{-3}\)) | 293.15K | 298.15K | 303.15K | 308.15K | \(\eta\) (mPas.s) |
|---------------------|---------|---------|---------|---------|----------------|---------|---------|---------|---------|----------------|
| Solvent 0.1 M HCl   | 1.000055| 0.99876 | 0.997421| 0.996266| 1.0027        | 0.8904  | 0.7975  | 0.7194  |         |                |
| 0.04                | 1.001055| 1.000010| 0.998072| 0.996535| 1.092063      | 0.977607| 0.893178| 0.810927|         |                |
| 0.06                | 1.001451| 1.000362| 0.998482| 0.997149| 1.100665      | 0.985993| 0.904795| 0.818894|         |                |
| 0.08                | 1.001843| 1.000724| 0.998859| 0.997523| 1.105184      | 1.00163 | 0.912371| 0.827501|         |                |
| 0.1                 | 1.002233| 1.001148| 0.999314| 0.997897| 1.112156      | 1.00765 | 0.920828| 0.832798|         |                |
| 0.12                | 1.002627| 1.001517| 0.999775| 0.998309| 1.128954      | 1.01289 | 0.926885| 0.838652|         |                |
| 0.14                | 1.003040| 1.001935| 0.990179| 0.98683 | 1.135148      | 1.022180| 0.929675| 0.845082|         |                |
| 0.16                | 1.003414| 1.002234| 1.000706| 0.999053| 1.151127      | 1.028218| 0.933386| 0.855371|         |                |
Density values showed a substantial increase with increasing molar concentration at all temperatures of study. The density for a solution of a certain concentration decreases on increasing temperature and this decrease of density on increasing temperature. May be ascribed to Hydrogen bonds breaking between water molecules in the bulk state and extra formation of water molecules in the dense state. (10)

Available data in Tables (1) and (2) indicate that for all amino acids solutions (studied here), viscosity decreases as the temperature increases from 293.15K to 308.15K for a definite concentration, and increase with increasing the concentration at constant temperature.

The decreasing of viscosity on increasing temperature can be explained according to the “Hole Theory” that there are vacancies in a liquid, and the molecules are continually moving into these vacancies so that the vacancies move around. This process permits flow, but requires energy, because there is an activation energy that a molecule has to have to move in a vacancy. The activation energy is more readily available at higher temperatures so the liquid can flow more easily at higher temperatures. (9)

The increase in the viscosity of a solution as the concentration increased is caused by the structural effect induced by the solute-solvent interactions. In addition, the solute particles lying across the fluid stream lines under torsional forces. These particles will tend to rotate, thus requiring absorption of energy which correspond to an increase in the viscosity of solution. (10)

Apparent molar volume ($\Phi_V$) were determined from the measured densities of solvent ($\rho_0$) , and of solution ($\rho$), using the following equation:

$$\Phi_V = \frac{M}{\rho_0} - 1000(\rho - \rho_0) / \rho_0^2 C(1)$$

Where is, (C) the molarity of the solution and (M) is the molecular weight of amino acids studied here. Solvent was taken as water and 0.1 M HCl solution. Values are included in table (3)and (4). The apparent molar volumes were least squares fitted to Masson’s empirical relation (9):
\[ \Phi_v = \Phi_v^0 + am \quad (2) \]

Where is \( \Phi_v \) the apparent molar volume at infinite dilution of amino acids studied here, were obtained [using equation (2)] by extrapolating the plot \( (\Phi_v) \) versus the molal concentration \( (C) \), to zero concentration at each temperature of study is given in figure (1). The obtained data are presented in Tables (5,6).

**Table (3)** Apparent Molar Volume \( (\Phi_v \text{ ml. mol}^{-1}) \) values for different concentrations of aqueous DL-Valine, DL-Methionine, and L-Arginine solution at temperature range from (293.15-308.15) K.

| C mol.L^{-1} Solvent H_2O | 293.15K | DL-Valine in water | 298.15K | 303.15K | 308.15K |
|-----------------------------|-----------------|---------------------|---------|---------|---------|
|                             | m | \( \Phi_v \) | M | \( \Phi_v \) | M | \( \Phi_v \) | M | \( \Phi_v \) | M |
| 0.04 | 0.0402 | 131.593 | 0.04032 | 129.8633 | 0.04041 | 146.7120 | 0.04045 | 134.0774 |
| 0.06 | 0.0605 | 131.6958 | 0.06065 | 130.82182 | 0.06078 | 143.3290 | 0.06083 | 133.3402 |
| 0.08 | 0.0809 | 131.8101 | 0.08108 | 130.53889 | 0.08126 | 140.4230 | 0.08135 | 132.4989 |
| 0.1  | 0.1015 | 131.8903 | 0.10162 | 131.24262 | 0.10181 | 135.4814 | 0.10195 | 132.1117 |
| 0.12 | 0.1221 | 131.9406 | 0.12226 | 130.55839 | 0.12250 | 134.7780 | 0.12260 | 131.5284 |
| 0.14 | 0.1428 | 131.9517 | 0.14303 | 130.79724 | 0.14330 | 134.4874 | 0.14346 | 131.2905 |
| 0.16 | 0.1637 | 132.0308 | 0.16390 | 130.83724 | 0.16422 | 134.3400 | 0.16443 | 130.0673 |
| 0.18 | 0.1846 | 132.1506 | 0.18489 | 131.06321 | 0.18524 | 133.7909 | 0.18519 | 128.7159 |
| 0.2  | 0.2057 | 132.2537 | 0.20599 | 131.22010 | 0.20618 | 128.9306 | 0.20664 | 127.6464 |

| C mol.L^{-1} Solvent H_2O | 293.15K | DL-Methionine in water | 298.15K | 303.15K | 308.15K |
|-----------------------------|-----------------|---------------------|---------|---------|---------|
|                             | m | \( \Phi_v \) | M | \( \Phi_v \) | M | \( \Phi_v \) | M | \( \Phi_v \) | M |
| 0.04 | 0.0402 | 131.593 | 0.04032 | 129.8633 | 0.04041 | 146.7120 | 0.04045 | 134.0774 |
| 0.06 | 0.0605 | 131.6958 | 0.06065 | 130.82182 | 0.06078 | 143.3290 | 0.06083 | 133.3402 |
| 0.08 | 0.0809 | 131.8101 | 0.08108 | 130.53889 | 0.08126 | 140.4230 | 0.08135 | 132.4989 |
| 0.1  | 0.1015 | 131.8903 | 0.10162 | 131.24262 | 0.10181 | 135.4814 | 0.10195 | 132.1117 |
| 0.12 | 0.1221 | 131.9406 | 0.12226 | 130.55839 | 0.12250 | 134.7780 | 0.12260 | 131.5284 |
| 0.14 | 0.1428 | 131.9517 | 0.14303 | 130.79724 | 0.14330 | 134.4874 | 0.14346 | 131.2905 |
| 0.16 | 0.1637 | 132.0308 | 0.16390 | 130.83724 | 0.16422 | 134.3400 | 0.16443 | 130.0673 |
| 0.18 | 0.1846 | 132.1506 | 0.18489 | 131.06321 | 0.18524 | 133.7909 | 0.18519 | 128.7159 |
| 0.2  | 0.2057 | 132.2537 | 0.20599 | 131.22010 | 0.20618 | 128.9306 | 0.20664 | 127.6464 |
Table (4) Apparent Molal Volume ($\Phi_v$ m. mol$^{-1}$) values for different concentrations of acidic DL-Valine, DL-Methionine, and L-Arginine solution at temperature range from (293.15-308.15) K.

| C mol.L$^{-1}$ Solvent 0.1M HCl | DL-Valine in 0.1 M HCl | | | DL-Methionine in 0.1 M HCl | | | L-Arginine in 0.1 M HCl | | |
|---|---|---|---|---|---|---|---|---|
| | 293.15K | 298.15K | 303.15K | 308.15K | | 293.15K | 298.15K | 303.15K | 308.15K | |
| m | $\Phi_v$ | m | $\Phi_v$ | m | $\Phi_v$ | m | $\Phi_v$ | m | $\Phi_v$ |
| 0.04 | 0.04015 | 95.82397 | 0.04019 | 96.62849 | 0.04026 | 101.1465 | 0.04038 | 110.8394 |
| 0.06 | 0.06034 | 97.28266 | 0.06041 | 96.56103 | 0.06051 | 99.71588 | 0.06059 | 102.8208 |
| 0.08 | 0.08061 | 96.46748 | 0.08070 | 96.31995 | 0.08085 | 99.42923 | 0.08095 | 101.8195 |
| 0.1 | 0.10096 | 96.14780 | 0.10107 | 96.11410 | 0.10125 | 98.47856 | 0.10139 | 100.2623 |
| 0.12 | 0.12188 | 95.80031 | 0.12152 | 95.96058 | 0.12173 | 97.78790 | 0.12193 | 101.2205 |
| 0.14 | 0.14188 | 95.36306 | 0.14204 | 95.39966 | 0.14229 | 97.87912 | 0.14252 | 100.1027 |
| 0.16 | 0.16245 | 94.79786 | 0.16266 | 94.14560 | 0.16291 | 96.86762 | 0.16319 | 99.19205 |
| 0.18 | 0.18302 | 92.15597 | 0.18337 | 96.56929 | 0.18366 | 96.71572 | 0.18395 | 99.04036 |
| 0.2 | 0.20381 | 93.89071 | 0.20393 | 91.38597 | 0.20452 | 96.04877 | 0.20486 | 100.4976 |

| C mol.L$^{-1}$ Solvent 0.1M HCl | DL-Methionine in 0.1 M HCl | | | L-Arginine in 0.1 M HCl | | |
|---|---|---|---|---|---|
| | 293.15K | 298.15K | 303.15K | 308.15K | |
| m | $\Phi_v$ | m | $\Phi_v$ | m | $\Phi_v$ | m | $\Phi_v$ |
| 0.04 | 0.0401 | 107.1033 | 0.04021 | 106.06282 | 0.04028 | 116.2093 | 0.04035 | 126.4939 |
| 0.06 | 0.0603 | 107.5488 | 0.06045 | 107.21772 | 0.06057 | 115.3224 | 0.06066 | 121.1600 |
| 0.08 | 0.0806 | 107.4145 | 0.08078 | 108.01243 | 0.08094 | 114.6523 | 0.08091 | 118.6641 |
| 0.1 | 0.1010 | 107.8483 | 0.10121 | 108.14376 | 0.10141 | 114.0867 | 0.10156 | 117.5569 |
| 0.12 | 0.1215 | 108.0437 | 0.12171 | 108.81325 | 0.12195 | 113.6086 | 0.12215 | 116.1934 |
| 0.14 | 0.1422 | 108.0997 | 0.14242 | 109.32190 | 0.12168 | 112.5538 | 0.14281 | 114.6502 |
| 0.16 | 0.1628 | 108.9173 | 0.16292 | 109.11770 | 0.16331 | 110.8741 | 0.16366 | 117.0731 |
| 0.18 | 0.1835 | 110.4111 | 0.18376 | 109.54517 | 0.18418 | 112.3117 | 0.18430 | 112.6686 |
| 0.2 | 0.2043 | 112.0290 | 0.20462 | 114.17686 | 0.20503 | 110.2939 | 0.20537 | 109.3795 |

| C mol.L$^{-1}$ Solvent 0.1M HCl | L-Arginine in 0.1 M HCl | |
|---|---|
| | 293.15 K | 298.15 K | 303.15 K | 308.15 K |
| m | $\Phi_v$ | m | $\Phi_v$ | m | $\Phi_v$ | m | $\Phi_v$ |
| 0.04 | 0.0402 | 130.2549 | 0.04025 | 131.48623 | 0.04032 | 138.2755 | 0.04039 | 151.5200 |
| 0.06 | 0.0604 | 130.0493 | 0.06053 | 130.80152 | 0.06064 | 136.7146 | 0.06074 | 146.2978 |
| 0.08 | 0.0808 | 130.1164 | 0.08092 | 130.75861 | 0.08010 | 135.9148 | 0.08120 | 144.6867 |
| 0.1 | 0.0808 | 128.6967 | 0.10141 | 129.30485 | 0.10160 | 135.1662 | 0.10175 | 142.9798 |
| 0.12 | 0.1012 | 127.7848 | 0.12200 | 128.69793 | 0.12223 | 134.2180 | 0.12244 | 140.9950 |
| 0.14 | 0.1425 | 128.6842 | 0.14272 | 129.21623 | 0.14299 | 132.7356 | 0.14320 | 138.9796 |
| 0.16 | 0.1633 | 125.0191 | 0.16354 | 129.27301 | 0.16386 | 131.8670 | 0.16410 | 135.5427 |
| 0.18 | 0.1840 | 122.3800 | 0.18460 | 132.89705 | 0.18386 | 131.3627 | 0.18550 | 133.8129 |
| 0.2 | 0.2052 | 127.1585 | 0.20542 | 127.05824 | 0.20622 | 131.0017 | 0.20680 | 133.5663 |
Figure (1) Limited Apparent Molal Volume ($\Phi_0v$) for Aqueous and Acidic Amino Acid DL-Valine, DL-Methionine, L-Arginine Solution at Four Temperatures.
Table (5) Limited Apparent Molal Volume ($\Phi^0_v$) for Aqueous Amino Acid Solutions at Four Temperature (293.15, 298.15, 303.15, and 308.15) K.

| Amino acid    | $\Phi^0_v$ $\text{cm}^3 \cdot \text{mol}^{-1}$ |
|---------------|-----------------------------------------------|
|               | 293.15 K | 298.15 K | 303.15 K | 308.15 K |
| DL-Valine     | 95.671   | 92.078   | 100.331 | 101.529  |
| DL-Methionine | 105.688  | 104.671  | 109.493 | 108.926  |
| L-Arginine    | 131.479  | 129.751  | 135.728 | 149.164  |

Table (6) Limited Apparent Molal Volume ($\Phi^0_v$) for Acidic Amino Acid Solutions at Four Temperature (293.15, 298.15, 303.15, and 308.15) K.

| Amino acid    | $\Phi^0_v$ $\text{cm}^3 \cdot \text{mol}^{-1}$ |
|---------------|-----------------------------------------------|
|               | 293.15 K | 298.15 K | 303.15 K | 308.15 K |
| DL-Valine     | 98.031   | 92.777   | 101.708 | 107.475  |
| DL-Methionine | 105.475  | 105.066  | 117.464 | 127.231  |
| L-Arginine    | 132.215  | 130.895  | 139.613 | 153.879  |

The clear dependence of apparent molal volume on molality show that the presence of solute-solute interactions, meaning that in non-infinitely dilution mixtures solute-solute, a part from solute-solvent and solvent-solvent interactions will be present. Available results indicate that dense water structure are formed around polar groups, and bulky structure around non polar groups, and that extent of these various types of “solvation phenomena” depends strongly on the concentration. The apparent molal volume was found to have a lower value at 298.15K, then after that it increases. This behaviour may be attributed to the size, geometry and polarity of the amino acid molecule at this temperature as well as the solvent molecular arrangements due to polarity and possibility of hydrogen bonds formation. These effects may lead to the incorporation of the amino acid molecule with the solvent molecular arrangements giving rise to lower value of the apparent molal volume and an appreciable shrinkage is expected to take place.

Jones and Dole equation was applied to amino acids solutions [in water and 0.1M HCl] over concentration range from (0.04-0.2 mol.L.-1) for Valine, Methionine and Arginine, The obtained data (Jones-Dole terms) are presented in Tables (7) and (8), using the following equation:

$$\frac{(\eta - 1)}{c} = A + B\sqrt{c}$$

Where, ($\eta$) The relative viscosity, ($\eta$) The measured viscosity of the amino acid solution, ($\eta$) The viscosity of the pure solvent at the same temperature, (A) constant correspond the electrostatic interaction of the solute particles with one another, (B) constant corresponds to the interaction between the solvent and solute particles and (C) Molar concentration (mol.L$^{-1}$).
Table (7) Values of $\eta_r - 1/\sqrt{C}$ and $\sqrt{C}$ for the aqueous amino acids solutions at four different temperatures in the range from (293.15-308.15) K.

| C Mol.L-1 | $\sqrt{C}$ | 293.15 K | 298.15 K | 303.15 K | 308.15K |
|-----------|------------|-----------|-----------|-----------|---------|
| DL-Valine in water |           |           |           |           |         |
| 0.04      | 0.200000   | 0.25030   | 0.322664  | 0.312431  | 0.233924 |
| 0.06      | 0.244949   | 0.247184  | 0.301204  | 0.302389  | 0.229612 |
| 0.08      | 0.282843   | 0.231350  | 0.296175  | 0.295237  | 0.226409 |
| 0.1       | 0.316228   | 0.228792  | 0.286653  | 0.289826  | 0.224622 |
| 0.12      | 0.346410   | 0.225664  | 0.278031  | 0.279894  | 0.222606 |
| 0.14      | 0.374166   | 0.225660  | 0.269693  | 0.270888  | 0.221537 |
| 0.16      | 0.400000   | 0.219615  | 0.259593  | 0.270423  | 0.220039 |
| 0.18      | 0.424264   | 0.217713  | 0.255764  | 0.269331  | 0.216797 |
| 0.2       | 0.447214   | 0.214142  | 0.247860  | 0.265607  | 0.215292 |

| DL-Methionine in water | | | | | |
| 0.04      | 0.200000   | 0.335024  | 0.282026  | 0.194226  | 0.294795 |
| 0.06      | 0.244949   | 0.322466  | 0.277333  | 0.185927  | 0.280322 |
| 0.08      | 0.282843   | 0.301127  | 0.273833  | 0.180353  | 0.268117 |
| 0.1       | 0.316228   | 0.281835  | 0.267007  | 0.173555  | 0.257253 |
| 0.12      | 0.346410   | 0.273116  | 0.265665  | 0.162601  | 0.248792 |
| 0.14      | 0.374166   | 0.265177  | 0.259655  | 0.155699  | 0.385668 |
| 0.16      | 0.400000   | 0.253992  | 0.258264  | 0.152948  | 0.230238 |
| 0.18      | 0.424264   | 0.242637  | 0.257250  | 0.148334  | 0.222414 |
| 0.2       | 0.447214   | 0.233590  | 0.253829  | 0.146358  | 0.215057 |

| L-Arginine in water | | | | | |
| 0.04      | 0.200000   | 0.350249  | 0.593842  | 0.298485  | 0.244484 |
| 0.06      | 0.244949   | 0.334732  | 0.552007  | 0.280185  | 0.246199 |
| 0.08      | 0.282843   | 0.312985  | 0.511862  | 0.264741  | 0.223514 |
| 0.1       | 0.316228   | 0.299577  | 0.467363  | 0.244122  | 0.213994 |
| 0.12      | 0.346410   | 0.289263  | 0.434372  | 0.226266  | 0.210598 |
| 0.14      | 0.374166   | 0.288461  | 0.399813  | 0.215401  | 0.203202 |
| 0.16      | 0.400000   | 0.279035  | 0.390438  | 0.211332  | 0.198908 |
| 0.18      | 0.424264   | 0.271298  | 0.364144  | 0.202827  | 0.197286 |
| 0.2       | 0.447214   | 0.265279  | 0.349862  | 0.180749  | 0.191900 |
### Table (8) Values for the acidic amino acids solutions at four different temperatures in the range from (293.15-308.15) K.

| C MoLL-1 | √C | 293.15 K | 298.15 K | 303.15 K | 308.15K |
|----------|-----|----------|----------|----------|---------|
| DL-Valine in 0.1 M HCl | | | | | |
| 0.04 | 0.200000 | 0.252046 | 0.316614 | 0.312430 | 0.231924 |
| 0.06 | 0.244949 | 0.247181 | 0.301243 | 0.298237 | 0.229122 |
| 0.08 | 0.282843 | 0.237836 | 0.290175 | 0.288624 | 0.226409 |
| 0.1 | 0.316228 | 0.231357 | 0.276653 | 0.288624 | 0.226409 |
| 0.12 | 0.346410 | 0.223795 | 0.273031 | 0.279896 | 0.222737 |
| 0.14 | 0.374166 | 0.206065 | 0.262936 | 0.274888 | 0.224606 |
| 0.16 | 0.400000 | 0.217713 | 0.257593 | 0.273313 | 0.221039 |
| 0.18 | 0.424264 | 0.214147 | 0.255674 | 0.270423 | 0.218797 |
| 0.2 | 0.447214 | 0.212515 | 0.252867 | 0.266607 | 0.217292 |
| DL-Methionine in 0.1 M HCl | | | | | |
| 0.04 | 0.200000 | 0.265299 | 0.405522 | 0.451001 | 0.294585 |
| 0.06 | 0.244949 | 0.255149 | 0.355811 | 0.426443 | 0.271048 |
| 0.08 | 0.282843 | 0.251866 | 0.322083 | 0.388124 | 0.270896 |
| 0.1 | 0.316228 | 0.246554 | 0.323841 | 0.364866 | 0.269833 |
| 0.12 | 0.346410 | 0.242244 | 0.312839 | 0.360826 | 0.269051 |
| 0.14 | 0.374166 | 0.232575 | 0.301588 | 0.360257 | 0.269505 |
| 0.16 | 0.400000 | 0.229081 | 0.299022 | 0.351673 | 0.267852 |
| 0.18 | 0.424264 | 0.228110 | 0.293736 | 0.350826 | 0.267564 |
| 0.2 | 0.447214 | 0.224870 | 0.291073 | 0.347578 | 0.258302 |
| L-Arginine in 0.1 M HCl | | | | | |
| 0.04 | 0.200000 | 0.247258 | 0.336000 | 0.380268 | 0.507960 |
| 0.06 | 0.244949 | 0.236842 | 0.335156 | 0.364916 | 0.485976 |
| 0.08 | 0.282843 | 0.228719 | 0.323014 | 0.344429 | 0.421007 |
| 0.1 | 0.316228 | 0.221356 | 0.320857 | 0.327477 | 0.423129 |
| 0.12 | 0.346410 | 0.217486 | 0.314098 | 0.327222 | 0.402248 |
| 0.14 | 0.374166 | 0.214100 | 0.307873 | 0.321044 | 0.399191 |
| 0.16 | 0.400000 | 0.205227 | 0.307335 | 0.319556 | 0.390473 |
| 0.18 | 0.424264 | 0.199686 | 0.301343 | 0.316534 | 0.390385 |
| 0.2 | 0.447214 | 0.192843 | 0.299597 | 0.313227 | 0.382810 |

By plotting the left hand term of equation (3) as a function of , a straight line is obtained with a slope B and an intercept A on the ordinate. Equation (3), though applied successively on behaviour of strong and weak electrolytes, may also describe the viscous behaviour of a number of non-electrolytic solution. (12,13) The extent of the interaction between the amino acid particles and solvent molecules was investigated through the estimation of B-coefficients, Tables (9) represent B-coefficient values for Jones and Dole equation in water and 0.1M HCl solution.

In Figures (2) we display the variation of (ηr-1)/ against for the amino acids solutions in this study at four temperatures range according to Jones and Dole equation of the form (12).
Figure (2) $\eta^{-1/\sqrt{C}}$ against $\sqrt{C}$ for aqueous and acidic amino acids solutions at four temperatures rang

In Figures (2), we present the variation of $(\eta^{-1/\sqrt{C}})$ versus $\sqrt{C}$, for the solutions of amino acids valine, Methionine, arginine in aqueous and in 0.1M HCl solution in temperature range from (293.15-308.15)K. These Figures show linear relationships between the values of $(\eta^{-1/\sqrt{C}})$ and the corresponding values of $\sqrt{C}$ indicating the validity of Jones and Dole equation in describing the viscous behaviour of aqueous and acidic amino acids solutions at four temperatures over the range from (293.15-308.15)K.
Table (9) B-coefficient values for aqueous and acidic amino acids solutions at temperature range (293.15-303.15) K.

| Amino acid | H2O Solvent | 0.1 M HCl |
|------------|-------------|-----------|
|            | 293.15 K    | 298.15 K  | 303.15 K  | 293.15 K    | 298.15 K  | 303.15 K  | 308.15 K  |
| DL-Valine  | -0.1058     | -0.3062   | -0.1939   | -0.0710     | -0.2627   | -0.1919   | -0.0579   |
| DL-Methionine | -0.4167   | -0.1166   | -0.2075   | -0.3227     | -0.1665   | -0.4079   | -0.3285   | -0.1272   |
| L-Arginine | -0.3397     | -100233   | -0.4476   | -0.2103     | -0.2099   | -0.1541   | -0.2815   | -0.5222   |

It was found that B-coefficient values displayed in Tables (9) are negative for all amino acids studied here at all temperatures of this study, this may be attributed to the (Structure Breaking Effect) of solvent by solute particles (amino acids) that cause the destruction of water arrangement molecules, then increasing disorder of the solution. We can observe that B-coefficient values at 298.15K listed in Tables (9) for the amino acids DL-Valine, and L-Arginine have a value in 0.1M HCl larger than that in aqueous medium, while for DL-Methionine the B-coefficients have larger values in water than that corresponding values in 0.1M HCl solutions. This indicates that the non polar groups present in DL-Valine are usually located in the interior of the protein, having little contact with water; while for DL-Methionine which has relatively some polarity in their structures showed different behaviour of interaction with solvent (water or 0.1M HCl solution).

It is clear from the obtained data listed in Tables (9) and represented in Figures (3a, b, c) that B-coefficient values are very sensitive to temperature. It was found that: in water as solvent B-values for DL-Methionine increase between 293.15K and 298.15K, then after decrease i.e. this amino acid has the maximum value of B at 29815K. while B-values for DL-Valine and L-Arginine show decreasing between (293.15-298.15)K, then increasing over the temperature (298.15-308.15)K; while In 0.1M HCl solution B-values for DL-Valine, DL-Methionine and decrease between 293.15K and 298.15K then increase with increasing temperature over the range of (298.15-308.15)K i.e. B-values have its minimum value at 298.15K. While the corresponding values for L-Arginine show increasing between (293.15-298.15)K then decrease over the temperature (293.15-308.15)K. This behaviour may be explained as follow:

The values of (η_E) does not markedly depend on temperature and (η_or) slightly decreases with increasing temperature. On the other hand,(η_st) suffers a relatively greater reduction as the solvent (water) structure is more and more broken with increasing temperature of the amino acid solution. The decrease of B-values as indicating in Figures (3a,b,c) should be associated with the net variation of (η_E), (η_or) and (η_st) equation (η_E + η_or + η_st = η_0 BC). The effect of the charges in these three types of viscosities is the observed decrease of B-values over the temperatures (293.15-298.15)K Figures (3a,b,c). Hydration can increase with increasing temperature since the ratio of monomeric water molecules increases, giving rise to the increase of (η_E) and (η_or) and a consequent increase of B-values over temperatures (293.15-308.15) K.
Figure (3) (B) viscosity coefficient for aqueous amino acid a)DL-Valine b) DL-Methionine c) L-Arginine

Effective flow volume \((V_h)\) was calculated for solutions of amino acids studied here at four different temperatures in the range of \((293.15-303.15)\) K according to equation

\[ B = \frac{\alpha}{V_h} \]

Effective flow volume was calculated also through the equation (5), that modified by Egland and Pilling:

\[ C/\text{Log} \eta_l = 2.303/V_h - 2.303QC/\alpha \]

The obtained data of \((V_h)\) are presented in tables (12) and display in Figure (4).

Table (10) \(V_h\) values that calculated from equation (4) for aqueous and acidic amino acid solutions at four temperature \((293.15-308.15)\) K.

| Amino acid | H2O Solvent | \(V_h\) (L.mol\(^{-1}\)) | \(V_h = B/a\) | 0.1 M HCl |
|------------|-------------|--------------------------|---------------|-----------|
| DL-Valine  | 293.15 K    | -0.0614                  | -0.1224       | -0.0775   | -0.0283   | -0.0683   | -0.105    | -0.076    | -0.023    |
| DL-Methionine | 298.15 K    | -0.1666                  | -0.0466       | -0.0830   | -0.1290   | -0.066    | -0.163    | -0.131    | -0.050    |
| L-Arginine | 303.15 K    | -0.1358                  | -0.4093       | -0.1790   | -0.0841   | -0.083    | -0.061    | -0.112    | -0.208    |
Table (11) $C / \log \eta_r$ values for aqueous and acidic amino acid solutions at four temperatures range (293.15-308.15) K.

|            | DL-Valine in H2O | DL-Valine in 0.1M HCl | DL-Methionine in H2O | DL-Methionine in 0.1M HCl |
|------------|------------------|-----------------------|-----------------------|--------------------------|
| **MoL$^{-1}$** |                  |                       |                       |                          |
| 0.04       | 1.69605          | 1.33678               | 1.47384               | 1.98981                  |
| 0.06       | 2.26141          | 1.88623               | 1.89122               | 2.55422                  |
| 0.08       | 2.82946          | 2.33529               | 2.27459               | 3.15902                  |
| 0.1        | 3.26110          | 2.74549               | 2.71561               | 3.32983                  |
| 0.12       | 3.70070          | 3.05748               | 3.05897               | 3.68747                  |
| 0.14       | 4.06348          | 3.43529               | 2.33904               | 3.96088                  |
| 0.16       | 4.62238          | 3.75674               | 3.86969               | 4.31665                  |
| 0.18       | 4.69129          | 4.03721               | 3.77774               | 4.53513                  |
| 0.2        | 4.96897          | 4.29865               | 4.08836               | 4.68751                  |

Figure (4) $C / \log \eta_r$ against $C$ for aqueous and acidic amino acids at 298.15K.
Table (12) $V_h$ values that calculated from equation (5) for aqueous and acidic amino acids solutions at four temperature (293.15-308.15) K.

| Amino acid | 293.15K | 298.15K | 303.15K | 308.15K | 293.15K | 298.15K | 303.15K | 308.15K |
|------------|---------|---------|---------|---------|---------|---------|---------|---------|
| H2O Solvent | 0.1 M HCl | 0.1 M HCl | 0.1 M HCl | 0.1 M HCl | 0.1 M HCl | 0.1 M HCl | 0.1 M HCl | 0.1 M HCl |
| DL-Valine  | 0.8458  | 1.1451  | 0.9445  | 0.5223  | 0.5601  | 1.0336  | 1.3573  | 1.2906  |
| DL-Methionine | 0.5790  | 1.0427  | 1.3919  | 0.9662  | 1.1679  | 0.7342  | 0.2793  | 1.7111  |
| L-Arginine  | 1.0790  | 2.1471  | 0.3576  | 0.4077  | 0.3823  | 1.1256  | 1.0792  | 1.4737  |

Van der Waal’s volume may be defined as the occupied volume of a molecule that is unaffected by other molecules, and it represents the intrinsic volume of a solute molecule (assumed spherical) that is dissolved in water. It's considered as one of the important quantities to study physical properties. Theoretical calculations have been done to estimate Van der Waal’s volumes ($V_w$) and partial molal volumes ($\Phi_0v$) of the amino acids in this study. ($V_w$) was found by utilizing the principle of additivity as reported by bondi\(^\text{(15,16)}\) and Edward.\(^\text{(17)}\) ($V_w$) may be dissected into contributions from individual atoms or groups of atoms measured in (ml/mol.).

The partial molal volume ($\Phi v$) can be estimated\(^\text{(18,19)}\) as well as the detection of solute-solvent interaction provided that the intrinsic volume of a molecule is made equal to its Van der Waal’s volume ($V_w$). If a molecule (assumed spherical) is dissolved in water, the volume is increased by ($v^0$) where ($v^0 = \Phi v / N$); (N) is the Avogadro’s constant. The value of ($v^0$) is greater than ($v_w$) by an amount associated void or empty volume \(^\text{(18)}\) as given by the equation:

$$v^0 = \frac{4}{3} \pi (r_w + \Delta)^3 \quad (6)$$

Where: $r_w$: the radius of Van der Waal’s volume which is equal to $\Delta$: is the thickness of spherical shell which is the empty volume ($v^0$).

Terasawa et. Al\(^\text{(19)}\) has reported the relation between ($\Phi v$) and ($V_w$) according to:

$$\Phi v = a V_w + b \quad (7)$$

Where, $V_w$: is the molar Van der Waal’s volume ($V_w = N v_w$) which represents the volume occupied by one mole of a compound and (b) are empirical constants.

Experimental values of ($\Phi v$) at (298.15K), then calculated values of ($V_w$) by additivity and ($r_w$), have been introduced into equation

$$\left(\frac{v^0}{v_w}\right)^{\frac{3}{5}} = 1 + \frac{\Delta}{r_w} \quad (8),$$

Then ($\Delta$) can be estimated for each amino acids. Then by introducing the values of ($\Delta$) and ($r_w$) into equation (6), the theoretical value of ($\Phi v$) can be obtained. The obtained data of theoretical partial molal
volumes with those corresponding experimental values have been listed in Tables (13 a,b). It can be noticed that there is good agreement between the theoretical and experimental values of \( \Phi_v \) which indicate strong solute-solvent interaction which coincide with other parameter for determination of molecular interaction.

**Table (13 a) Theoretical and experimental values for limited apparent molal volume \( \Phi^0_v \), Van der Waals volume \( V_w \), Van der Waals radius \( r_w \) and \( \Delta \) values for aqueous amino acids solutions**

| Amino acids | \( \Phi^0_v \) Theoretical | \( \Phi^0_v \) Experimental | \( r_w \) (cm) | \( V_w \) | \( \Delta \) (cm) |
|-------------|-----------------|-----------------|-------------|--------|------------|
| DL-Valine   | 92.082          | 92.078          | 2.5714×10^{-8} | 71.18  | 0.2304×10^{-8} |
| DL-Methionine | 105.066        | 105.066        | 2.6987×10^{-8} | 81.41  | 0.2290×10^{-8} |
| L-Arginine  | 129.751         | 129.751         | 2.9032×10^{-8} | 79.76  | 0.2379×10^{-8} |

**Table (13b) Theoretical and experimental values for limited apparent molal volume \( \Phi^0_v \), Van der Waals volume \( V_w \), Van der Waals radius \( r_w \) and \( \Delta \) values for acidic amino acids solutions**

| Amino acids | \( \Phi^0_v \) Theoretical | \( \Phi^0_v \) Experimental | \( r_w \) | \( V_w \) | \( \Delta \) |
|-------------|-----------------|-----------------|--------|--------|-------|
| DL-Valine   | 97.781          | 92.777          | 2.5714×10^{-8} | 71.18  | 0.2870×10^{-8} |
| DL-Methionine | 104.671        | 104.671        | 2.6987×10^{-8} | 81.41  | 0.2253×10^{-8} |
| L-Arginine  | 130.895         | 130.895         | 2.9032×10^{-8} | 79.76  | 0.2471×10^{-8} |

**Conclusions**

In this work the volumetric and viscometric behaviour of aqueous solutions of amino acids [DL-Valine, DL-Methionine and L-Arginine] were investigated from density and viscosity data.

From this work we can conclude that: The apparent molal volume for all solutes (amino acids) is concentration dependent and increase with increasing temperature in the range (298.15 - 308.15) K. The apparent molal volume has its minimum value at 293.15 K indicating an appreciable shrinkage at this temperature due to more incorporation taking place.

The extent of molecular interaction between solute and solvent depends largely on the structure of amino acids showed specific interaction with solvent (water). Methionine showed higher degree of interaction. Viscosity data reported for all amino acids solutions (studied here) indicate that the values of the viscosity coefficient (B) are negative which means that these amino acids particles are structure breaking for solvent.

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