Chapter One

1

Solvent – Solute Interactions and the Properties of Amino Acids

(1-1) 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 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)

(1-2) Solubility

Solubility is a statement of how much solute can dissolve in some given amount of solvent at a given temperature. When a solid or liquid dissolves, the structural units-ions or molecules become separated from each other and the spaces in between become occupied by solvent molecules **(solvation process)**.(5)

In dissolution, as in melting and boiling, energy must be supplied to overcome the interionic or intermolecular forces. The energy required to break the bonds between solute particles is supplied by the formation of bonds between the solute particles and the solvent molecules, the old attractive forces are replaced by new ones. In solution each ion is surrounded by a cluster of solvent molecules, and is said to be **solvated;** if the solvent happens to be water, the ion said to be **hydrated.** In solution, as in the solid and liquid states, the unit of substance like sodium chloride is the ion; although in this case its solvated ion(6), as shown in Figure (1-1).

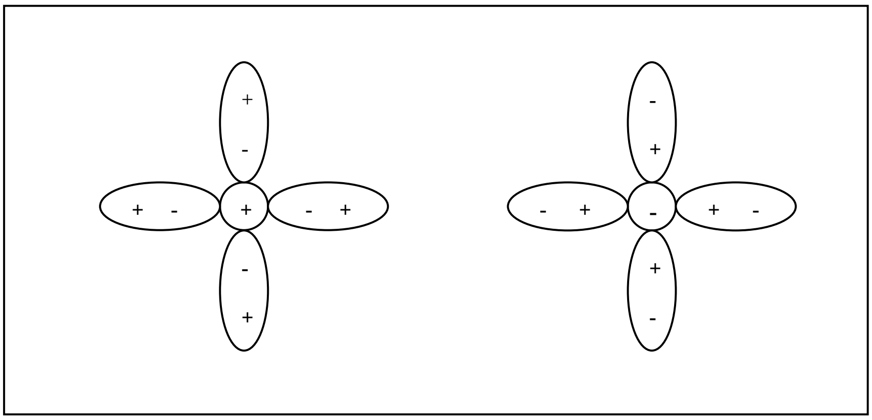


Figure (1-1) Ion-dipole interaction solvated cation and anion

To dissolve ionic compound, a solvent must also have a high dielectric constant, that is, have high insulating properties to lower the attraction between oppositely charged ions once they are solvated. Water owes its superiority as a solvent for ionic substance not only to its polarity and its high dielectric constant but to another factor as well; it contains the –OH group and thus can form hydrogen bonds. Water solvate both cations and anions. Cations, at its negative pole (its unshared electrons, essentially); anions through hydrogen bonding. The solubility characteristics of non-ionic compounds are determined chiefly by their polarity. Non-polar or weak polar compounds dissolve in non-polar or weakly polar solvents; highly polar compound dissolve in highly polar solvents.**" Like dissolves like"** is extremely useful rule of thumb. (6)

Solubility depends on the nature of intermolecular forces that include solvent-solute, solute-solute, and solvent-solvent interactions. Whenever a chemical reaction occurs, there is an energy change. When heat is released, we can regard heat as product. A reaction in which heat is product is called **"Exothermic reaction"** (Exo, means "out", and thermic means "heat". Hence, heat, or enthalpy, comes out or released.). Note that the potential energy of the chemical products is less than that of the reactant since energy has been given off in the form of heat. Sometimes heat must be supplied for a reaction in order to occur. In this case we can regard heat as a reactant. A reaction in which heat is a reactant is called an **"Endothermic reaction"**. (Endo, means "in" indicating that heat is put in or is absorbed.). In the case of an endothermic reaction the potential of the chemical products is higher than that of the reactants since energy has been added. Solubility is the effected by various factors such as nature of solute and solvent, temperature, external pressure, particle size, and stirring of solution.(7)

Studies on solubilitys of amino acids in different solvents are often of great importance as these studies many suggest suitable conditions for the separations and purifications of amino acids.(8)

(1-3) Types of Interactions of Solute and Solvent in Aqueous Solution

There are several types of intermolecular forces between solute particles and solvent molecules that play a role in determining the three-dimensional structure of protein.(1) These are electrostatic forces :

1. Van der waals forces:

These van der waals forces are a short range forces; they act only between the portions of different molecules that are in close contact, that is, between surfaces of molecules. Van der Waals forces have attractive and repulsive forces and this important to our understanding of molecular structure.(9) Van der Waals involves three types of effects:

Dipole-Dipole forces: is the attraction of the positive end of one polar molecule with the negative end of another molecule.

Dipole-induced dipole forces: is the attraction between two molecules, if one of this molecules has a dipole moment this creates an electric filed which polarize the charge on the second molecule.

London forces or (dispersion forces): it occurs even when the molecules have no permanent dipole moment, and it can be visualized as the interaction between the fluctuating charge distribution on molecule (A) with that of molecule (B).(9)

2. *Hydrogen Bonds:*

The intermolecular force that is called **"Hydrogen bond"** occurs between a hydrogen covalently bonded (N, O, or F) in one molecule and nonbonding pair of electron on (N, O, or F) in another molecule(5).

Water, (H_2O), is the most commonly encountered molecule that shows hydrogen bonding. The electron pair in the covalent bond between (O) and (H) is shifted toward the more electronegative Oxygen, leaving the hydrogen partially positive charge. Because of the small size of the hydrogen atom, it positive charge is concentrated, and this lead to a strong intermolecular attraction with nonbonding pair of electrons on oxygen of a nearby water molecule. This attraction known as the (**hydrogen bond)** as shown: (5)

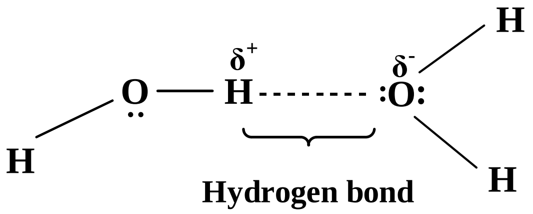


Figure (1-2) Hydrogen bond

Each oxygen offers two nonbonding pairs of electrons for hydrogen bonding with hydrogen's of two nearby water molecule.

The hydrogen bond is stronger than other dipole-dipole attraction or London forces, but much weaker than the normal covalent bond.

In Figure (1-2) the covalent bond are shown by the dash (**—**) and the hydrogen bonds by dots (---).

Many of the special physical properties of water (compared with molecules of similar molecular weigh and polarity) arise from the strong hydrogen bonding between water molecules. Hydrogen bond leads to increase viscosity, boiling point, surface tension, and solubility for the compound having hydrogen bond. (5)

Hydrogen bonding is very important in biological molecules, because hydrogen bonds effect the three-dimensional shape of proteins and act as “hook-and eyes” that hold together the two chains of the genetic material DNA. (5)

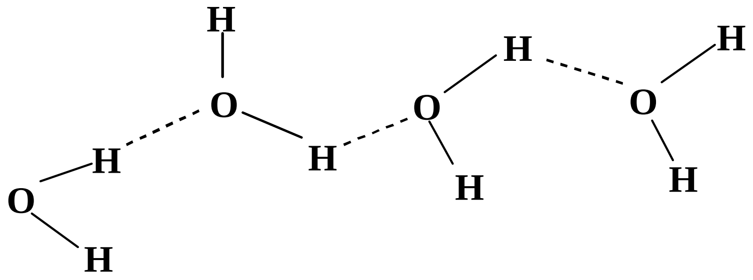


Figure (1-3) Cluster hydrogen bond

(1-4) Water

Water is the major component of living systems, it makes about (65%) of the lean body mass of the human body. Interest in water is great because of its importance in chemical and biological systems. All the fluids in the body have water as the medium. Water is of fundamental importance to all tissues, both structurally and functionally.(10, 11)

Water is so common a substance that we often overlook its unique properties. It should be a gas at room temperature, but because of hydrogen bonding, it has a high boiling point of (373.15K) at (1 atm.) so it has high values for boiling point, melting point, dielectric constant and specified heat.(1)

An individual water molecule has a significant dipole that due to the grater electronegativity of the oxygen atom over the hydrogen atom. This dipole leads to a strong interaction between water molecules in the form of hydrogen bonds. The dipolar properties of water molecules affect the interaction between water molecule and other molecule.(10)

Because of high heat capacity of water, large changes in heat production can undergo inside the body with very little alteration in body temperature. A constant circulation of water in blood is important in maintaining a constant temperature of the body. (12)

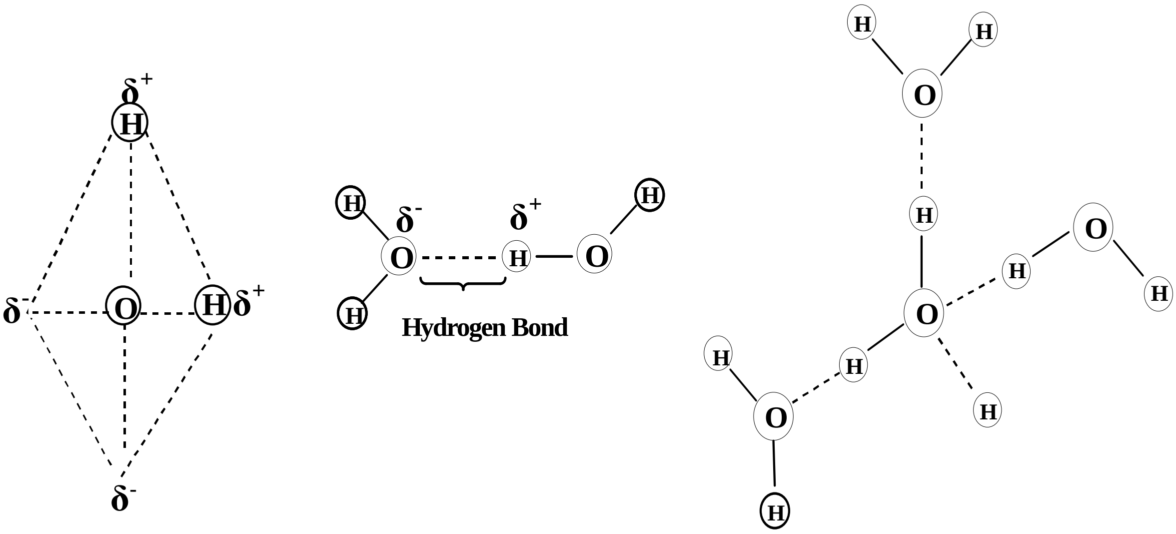
Numerous structural models have been proposed for water. Although none of the existing theories can account satisfactorily for all the observed properties of water, good progress has been made toward a detailed explanation of its structure and properties.(1) The structure of liquid water is best described in term of mixture of low density hydrogen-bonded clusters with non hydrogen bonded molecules in ratio of (4.4) to (1.0) rearrangements within the system are known to be extremely rapid, (1 micro second). The open hydrogen-bonded framework of the clusters represents the **(bulky)** ice-like structure, in water with non molecules **(dense water)** occupying the cavities (13-17). The equilibrium between bulk and dense states can be represented as:

$$\mathbf{(H_2O)_b \rightleftharpoons (H_2O)_d}$$

Where **b**, and **d** represent bulk and dense states respectively.

The interaction or the substance that shift the equilibrium towards dense (right direction) can be considered as **(Water Structure Breaker)**, while those shifted the equilibrium towards bulk (left direction) can be considered as **(Water Structure Maker).** (13-17)

The addition of polar solute and elevation of temperature causes destruction of the bulk shape and increasing the dense type water molecules. While with non polar molecules we will have formation hydrophobic effect that leads to increase in hydrogen bonds four coordination, i.e. increasing in bulk type water molecules.(11)



a) Singal Water Molecule

b) two interacting water molecules

c) cluster of interacting water molecule

Figure (1-4) Structural Building of water molecule and interaction of water molecule with another water molecule

(1-5) Amino Acids

Proteins are the most abundant organic molecules in animals playing important role in all aspects of cell structures and functions. The physical and chemical properties of proteins are determined by its constituent amino acids. The term amino acids, suggests, every amino acids has an amine group and carboxylic acid group. Both of these functional groups are attached to the same carbon atom which usually also hydrogen atom and another variable group. There are 20 α-amino acids, called the standard amino acids that are found in nearly all proteins. The 20 standard amino acids, grouped according to chemical properties of their side chain (18).

(1-5-1) The Dominant Amino Acids in Proteins

The Figure (1-5) shows the general structural formula for the 20 α-amino acids that commonly found in natural proteins, which contain both amino group and carboxylate group in ionic form, attached to α-carbon atom, and each amino acid has a characteristics side chain, or (R) group that imparts chemical individuality to the molecules attached to the same α-carbon atom.(19)

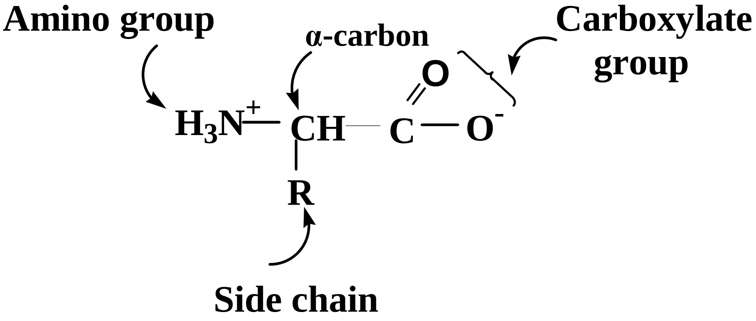


Figure (1-5) Structure Formula for Amino Acids

All amino acids having a free α-amino group except proline, the structure differ slightly from general formula because the amino group and (R) group are part of ring, and this give strength to the proline in peptides that contain it, as show in Figure (1-6).

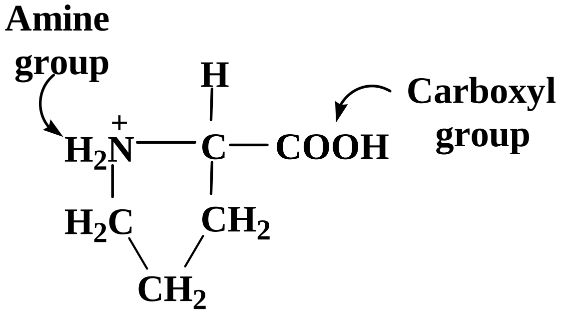


Figure (1-6) Proline

The side chain for amino acids contains different structure features, such as aromatic rings,-OH group, -$^+NH_3$ group, and –COO^- group.
This variety in side chains causes difference in the properties of individual amino acids and the properties containing different combinations of them. (19)

Amino acids classified as shown in Table (1-1). (18)

جمهورية العــراق
وزارة التعليم العالي والبحث العلمي
جامعــة النهرين

دراسة بعض الخصائص الفيزيائية لمحاليل بعض الحوامض الأمينية في أوساط مائية و حامضية بدرجات حرارية مختلفة من (٢٩٣,١٥ – ٣٠٨,١٥) كلفن

رسالــة
مقدمة إلى كلية العلوم / جامعة النهرين كجزء من متطلبات نيل درجة
ماجستير علوم في الكيمياء

من قبل
زينـة شكـر محمـود
(بكالوريوس علوم كيمياء ٢٠٠٢)

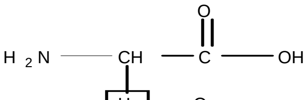
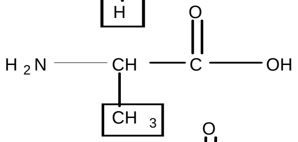
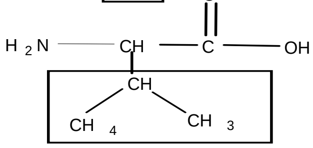
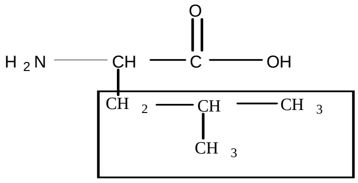
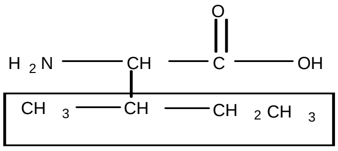
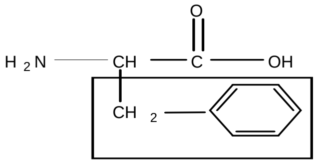
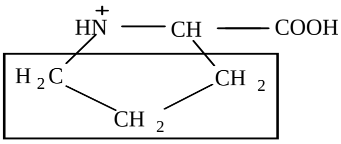
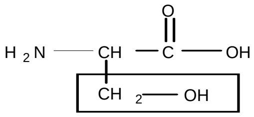
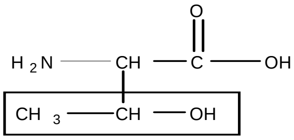
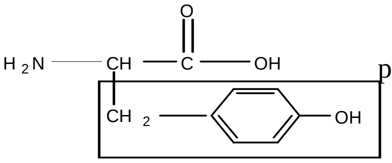
جمادى الأول	١٤٢٦
حزيران	٢٠٠٥

بسم الله الرحمن الرحيم

وأن ليس للإنسان ألا ما سعى {٣٩} وأن سعيه سوف يرى {٤٠} ثم يجزى الجزاء الأوفى {41}

صدق الله العظيم

سورة النجم

Name	Symbol	Abbreviation	Structure	Functional group In side chain	Isoelectric point
Side chain is (H) or alkyl (nonpolar)					
Glycine	G	Gly		none	6.0
Alanine	A	Ala		alkyl group	6.0
Valine	V	Val		alkyl group	6.0
Leucine	L	leu		alkyl group	6.0
Isolucine	I	IIe		alkyl group	6.0
Phenylalanin	F	Phe		aromatic group	5.5
Proline	P	Pro		rigid cyclic structure	6.3
Side chain contains an –OH					
Serine	S	Ser		hydroxyl group	5.7
Theronine	T	Thr		hydroxyl group	5.7
Tyrosine	Y	Tyr		phenolic –OH group	5.7

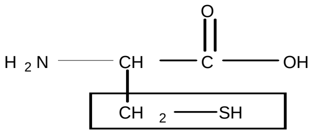
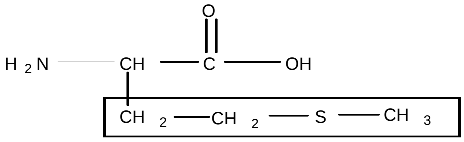
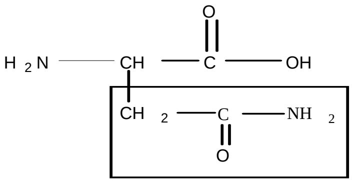
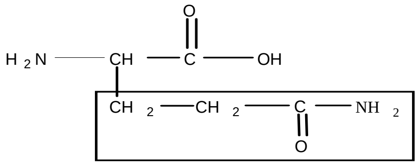
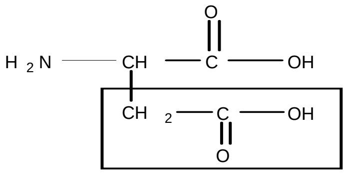
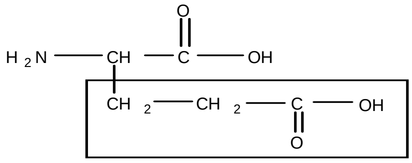
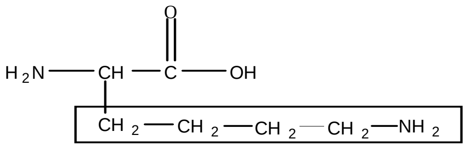
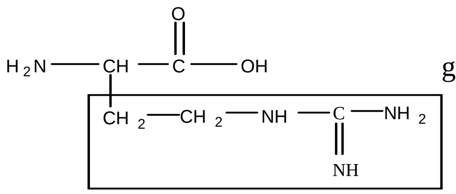
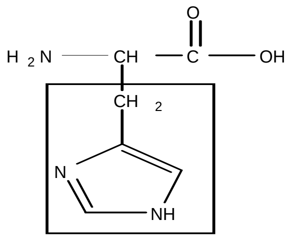
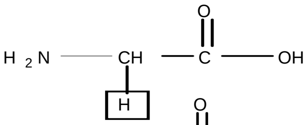
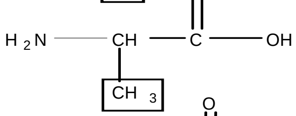
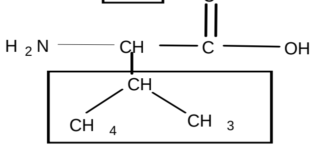
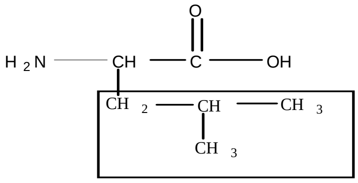
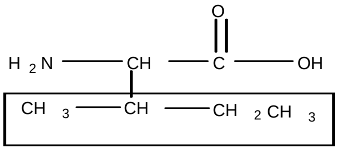
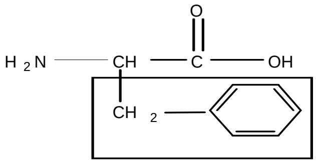
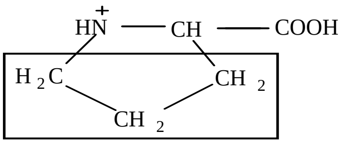
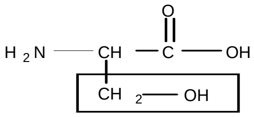
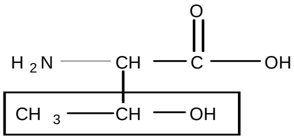
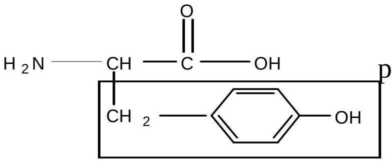
Side chain contains sulfur					
Cysteine	C	Cys		thiol	5.0
Mehionine	M	Met		sulfide	5.7
Side chain contains nonbasic nitrogen					
Aspargine	N	Asn		amid	5.4
Glutamine	Q	Gln		amid	5.7
Side chain is acidic					
Aspartic acid	D	Asp		carboxylic acid	2.8
Glutamic acid	E	Glu		carboxylic acid	3.2
Sid chain is basic					
Lysine	K	Lys		amino group	9.7
Arginine	R	Arg		guanidno group	10.8
Histidine	H	His		imidazole ring	7.6

Table (1-1)
The Standard Amino Acids

Name	Symbol	Abbreviation	Structure	Functional group In side chain	Isoelectric point
Side chain is (H) or alkyl (nonpolar)					
Glycine	G	Gly		none	6.0
Alanine	A	Ala		alkyl group	6.0
Valine	V	Val		alkyl group	6.0
Leucine	L	leu		alkyl group	6.0
Isolucine	I	IIe		alkyl group	6.0
Phenylalanin	F	Phe		aromatic group	5.5
Proline	P	Pro		rigid cyclic structure	6.3
Side chain contains an –OH					
Serine	S	Ser		hydroxyl group	5.7
Theronine	T	Thr		hydroxyl group	5.7
Tyrosine	Y	Tyr		phenolic –OH group	5.7

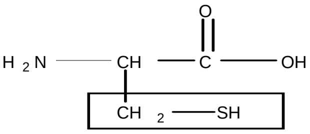
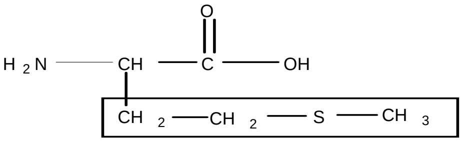
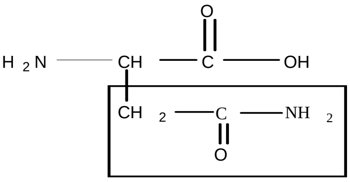
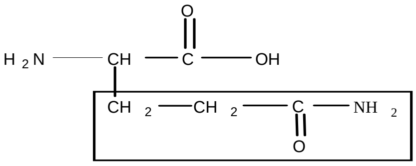
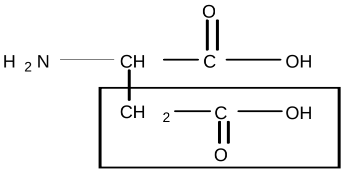
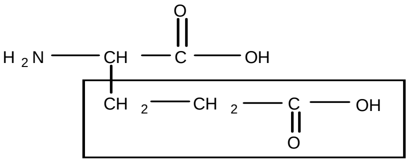
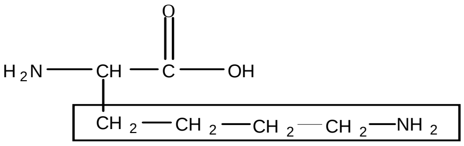
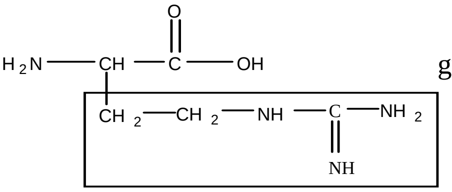
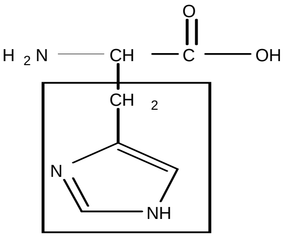
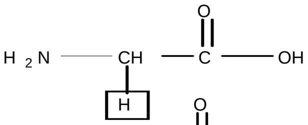
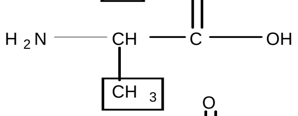
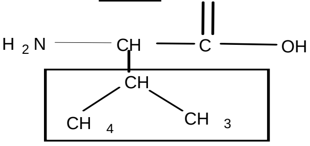
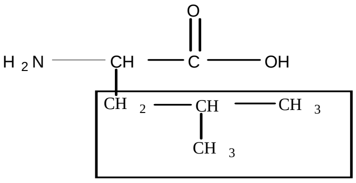
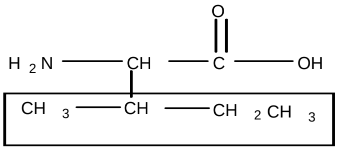
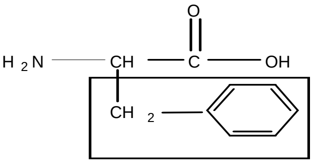
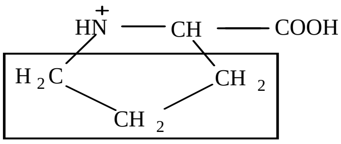
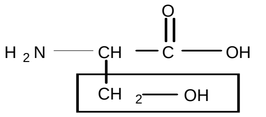
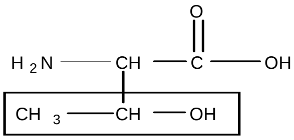
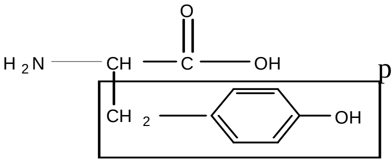
Side chain contains sulfur					
Cysteine	C	Cys		thiol	5.0
Mehionine	M	Met		sulfide	5.7
Side chain contains nonbasic nitrogen					
Aspargine	N	Asn		amid	5.4
Glutamine	Q	Gln		amid	5.7
Side chain is acidic					
Aspartic acid	D	Asp		carboxylic acid	2.8
Glutamic acid	E	Glu		carboxylic acid	3.2
Sid chain is basic					
Lysine	K	Lys		amino group	9.7
Arginine	R	Arg		guanidno group	10.8
Histidine	H	His		imidazole ring	7.6

Table (1-1)
The Standard Amino Acids

Name	Symbol	Abbreviation	Structure	Functional group In side chain	Isoelectric point
Side chain is (H) or alkyl (nonpolar)					
Glycine	G	Gly		none	6.0
Alanine	A	Ala		alkyl group	6.0
Valine	V	Val		alkyl group	6.0
Leucine	L	leu		alkyl group	6.0
Isolucine	I	IIe		alkyl group	6.0
Phenylalanin	F	Phe		aromatic group	5.5
Proline	P	Pro		rigid cyclic structure	6.3
Side chain contains an –OH					
Serine	S	Ser		hydroxyl group	5.7
Theronine	T	Thr		hydroxyl group	5.7
Tyrosine	Y	Tyr		phenolic –OH group	5.7

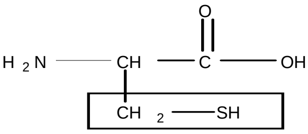
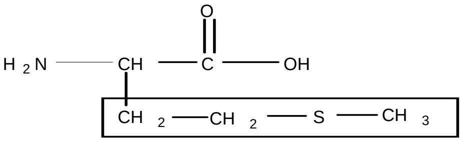
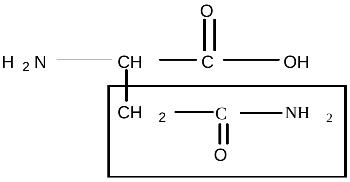
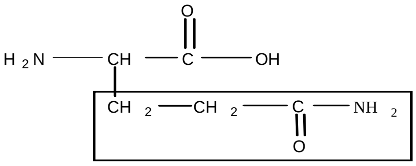
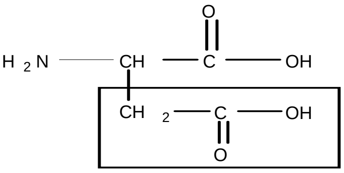
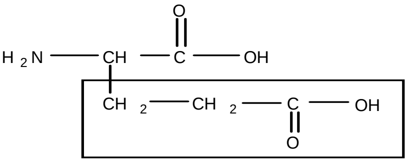
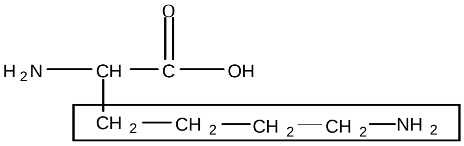
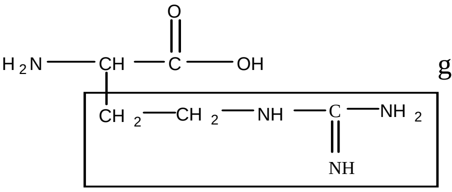
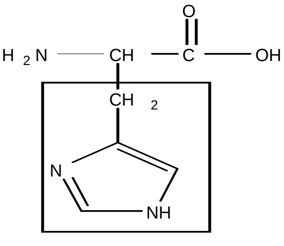
Side chain contains sulfur					
Cysteine	C	Cys		thiol	5.0
Mehionine	M	Met		sulfide	5.7
Side chain contains nonbasic nitrogen					
Aspargine	N	Asn		amid	5.4
Glutamine	Q	Gln		amid	5.7
Side chain is acidic					
Aspartic acid	D	Asp		carboxylic acid	2.8
Glutamic acid	E	Glu		carboxylic acid	3.2
Sid chain is basic					
Lysine	K	Lys		amino group	9.7
Arginine	R	Arg		guanidno group	10.8
Histidine	H	His		imidazole ring	7.6

Table (1-1)
The Standard Amino Acids

(1-5-2) Stereochemistry of the α-Amino Acids

The inspection in the structure of amino acids except glycine, we can see that the attachment of carboxyl, amine, (R) group, and hydrogen to central carbon makes that carbon **(chiral)** so the amino acid is optically active.(20)

There are two possible arrangements for molecules with chiral carbon. (Molecules that have only in special arrangement of their atoms are called **stereoisomers**). There are two types of stereoisomer (21) of molecules with chiral carbon, **D-isomers, L-isomers**.

The atoms of two isomers are bonded together in the same pattern except for position of amino group and hydrogen atom. Careful examination reveals that the two isomers in Figure (1-7) are mirror images of each other, such molecules called **(enantiomers)**, can not be superimposed on each other.

a) L-amino acid **b) D-amino acid**

Figure (1-7) The structural formula (L, D) for alinine amino acid

Some of amino acids contain equal quantity from (D) and (L) and this mixture called **(Racemic Mixtures)**.

The genetic code use only (L-amino acids) in constructing proteins, although (D-amino acids) may occur as a modification after the genetic code has been transcribed in to proteins, or they are formed by nongenatically directed processes.(D-amino acids) occur mainly in to lower organisms such as bacteria.$^{(20)}$

(1-5-3) Acidic and Basic Properties for Amino Acids

The term “amphoteric” is applied to all substance which is capable of exhibiting both acidic and basic functions.

Among these must, therefore, be include water, alcohols, and other amphiprotic solvents and a number of metallic hydroxides, e.g. lead and aluminum hydroxides. $^{(22)}$

In these compounds it is generally the same group, such as, -OH, which is responsible for the acidic and basic properties; the most familiar examples of this type of ampholyte are provide by the amino acids, which may be represented by the general formula **NH_2RCO_2H.**

Until relatively recent times these substance were usually regarded as having this particular structure in the neutral state, and it was assumed that the addition of acid resulted in the neutralization of the $–NH_2$ group such as:

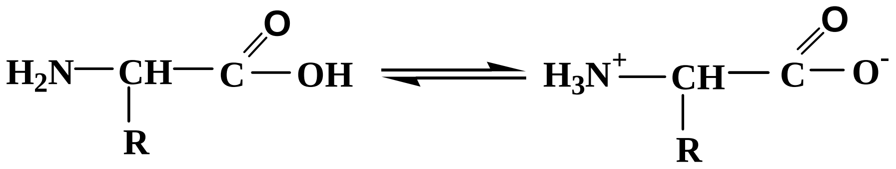
$$NH_2RCO_2H + \overset{+}{H_3}O \rightleftharpoons {}^{+}NH_3RCO_2H + H_2O$$

Whereas a strong base was believed to react with the $–CO_2H$ group such as:

$$NH_2RCO_2H + {}^{-}OH \rightleftharpoons NH_2RCO_2^{-} + H_2O$$

It has been long realized, however, that in addition to the uncharged molecules NH_2RCOOH, a solution of an amino acid might contain molecules carring positive charge at one end and a negative charge at the other, thus constituting and an electrically neutral system, such as, $^+NH_3RCO^-_2$.$^{(22)}$

These particles have been variously called **"Zwitterion"** $^{(19)}$ a dipolar ion that carries both a positive and negative charge as result of internal acid-base reaction in an amino acid molecules.



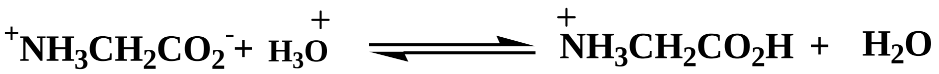
non ionized form dos not exist

Zwitter ion present in soilds state and solution

The suggestion was made by Bjerrume$^{(23)}$, however that nearly the whole of neutral aliphatic amino acid is present in solution in the form of the dipolar ion, and that reaction with acids and bases is of a different type form that represented before.

A solution of glycine, for example, i.e., $NH_2CH_2CO_2H$ is compared with one of ammonium acetate; if a strong acid is added to the latter, the reaction is with basic $CH_3CO_2^-$ ion and CH_3CO_2H is formed, but a strong base reacts with the acidic $^+NH_4$ ion to yield NH_3.

In the same way, the addition of strong acid to glycine consisting mainly of the dual ion $^+NH_3CH_2CO_2^-$, result in the reaction.



$$^+NH_3CH_2CO_2^- + \overset{+}{H_3O} \rightleftharpoons \overset{+}{N}H_3CH_2CO_2H + H_2O$$

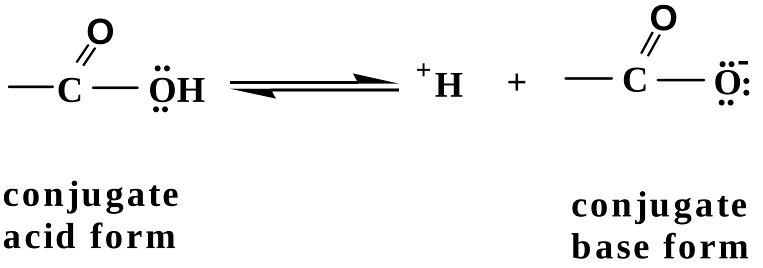
While reaction with alkali is:

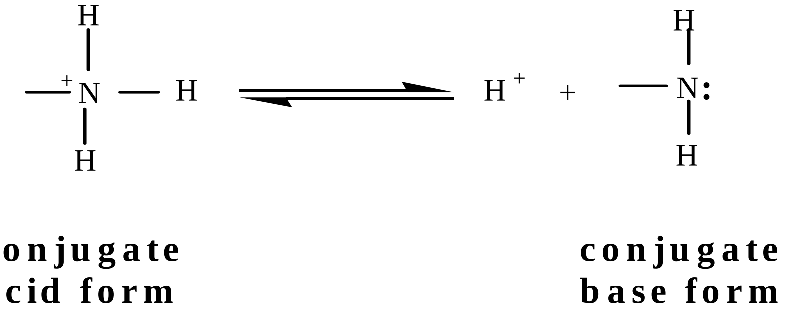
$$^{+}NH_3CH_2CO_2^{-} + {}^{-}OH \rightleftharpoons NH_2CH_2CO_2^{-} + H_2O$$

The products are of course, the same as in the alternative representation since there are no a doubt that in acid solution the amino acids form $^{+}NH_3CH_2CO_2H$ ions while in alkaline solution the anions $NH_2CH_2CO_2^{-}$ are formed. It should be noted, however, that the exhibiting the acidic and basic functions are the reverse of those accepted in the original treatment of amino acids; the basic property of the ampholyte is due to the $–CO_2^{-}$ group whereas the acidic property is that of the $–^{+}NH_3$ group.(24)

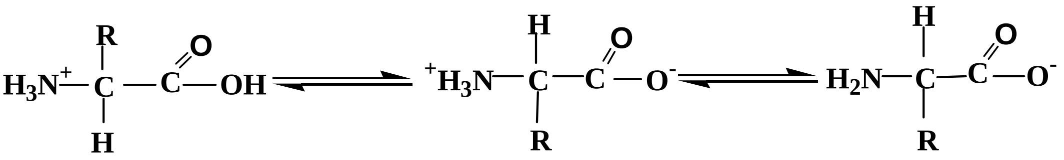
The structure of an amino acid in solution varies with the pH of the solution, amine and carboxylic acid have conjugate acid-base forms in water that are dependent upon the pH of solution in which find themselves(20).

The ionization constant, **K_aS.** for these group are about 10^{-2} for carboxyl and 10^{-9} for the amine group. Therefore the **pK_aS.** are **2** and **9**, respectively. This means that at pH of 2, 50% of the carboxyl groups are in the conjugate base form.





When the pH less than 2, most of the carboxyl are in the uncharged acid form, above a pH of 2 most are in the (-1) charged conjugate base form. Overall then, an amino acid has several charged forms that are pH dependent.



pH below 2
amine and carboxyl
in conjugate acid form
NET CHARGE = +1

pH between 2 and 9
amine group as conjugate acid,
carboxyl as conjgate base
NET CHARGE =0

pH above 9
amine and carboxyl
conjugate base form
NET CHARGE =-1

The pH at which an amino acid or protein will not move in an electric filed is called **“Isoelectric point”** or **“Isoionic”** pH_I the pI. a rough idea of the pI can be calculated by averting the pK_a going from the 0 to the -1 form.(20)

For our genetic amino acid:

$$pI = \frac{pK_{a\,(+1 \longrightarrow 0)} + pK_{a\,(0 \longrightarrow -1)}}{2} = \frac{2 + 9}{2} = 5.5$$

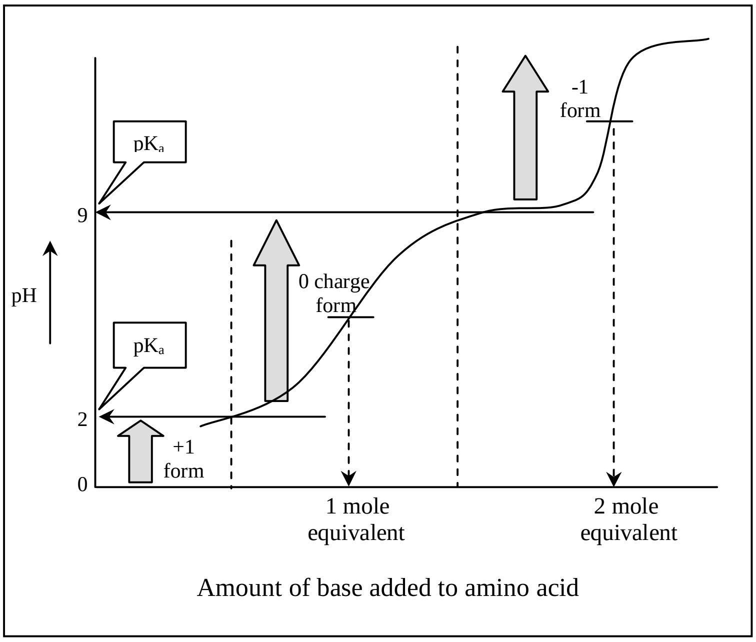


Figure (1-8)
Titration curve for an amino acid

This mean that at pH 5.5 almost our generic amino acid molecules would be in the (0) net charge or Zwitterion having an equal number of (+1) and (-) charges.

If (R) group contains a functional group that has conjugate acid- base properties, its ionization must be considered along with those of amine and carboxyl group. The pI is calculate in the same way as for the generic amino acid; the pK_a values used for the calculation must be those of the $+1 \rightarrow 0$ transition and the $0 \rightarrow -1$ transition. (20)

There are several other properties of amino acids(25) which are in agreement with the dipolar ion type of structure these are the high melting point, the sparing solubility in alcohol and acetone, and increased solubility in presence of natural salts, all of which properties associated with ionized substance. Emotion of crystals of glycine by the method of X-ray diffraction indicates that the substance has the structure ($^{+}NH_3CH_2CO_2^{-}$) in the solid state. The high dielectric constant of aqueous solution of aliphatic amino acids lead to the conclusion that the molecules have very large dipole moments; such large values can only be explained by the presence within the molecule of unit charges of opposite sign separated by several atomic diameters, as would be expected for dipolar ions.

(1-6) Literature survey

In view of the large number of papers describing the physical properties for amino acids solutions in water and another different solvents, and from investigations to be interested for density studies that consider very important physical properties and we can use this characteristic to determine another physical properties such as apparent molal volume and molar polarization.

Partial molal volume ($\overline{V}^0$), apparent molal volume (ϕ_v), limiting apparent molal volume (ϕ_v^0) and apparent molal adiabatic compressibilies (ϕ_{ks}) determined for aqueous amino acids solutions at 298.15K. The results discussed in terms of solute-solvent interactions.(26-37)

The density, viscosity and B-coefficient for aqueous amino acids solutions calculated at different temperatures, and the results discussed in terms of structure breaker or maker.(38, 39)

Saadoon et al., study (39, 40) the solute-solvent interaction, using different amino acids as solute and an aqueous solution of dimethyl formimide (DMF) and aqueous ethylene glycol as solvent at 298.15K. The study covered theoretical calculation concerning partial molal volume, van der waals volume, and some related parameters as well as experimental measurements. Viscosity measurements have been done for the above system. Interpretation and discussion of the results were presented on the bases of Jones-Dole equation and then related to the partial molal volume result.

Sasahara and Uedaira, (41) measure the solubility of amino acids in water and aqueous polyethylene glycol (PEG) solutions as function of temperature and (PEG) concentration. the equilibrium constant of the binding of amino acids to (PEG) chain were estimated from the solubility data. Amino acids with larger hydrophobicity are bond more strongly to (PEG) chain due to the hydrophobic interaction between the methylene groups of (PEG) and side chain of amino acids.

Dey and Lahiri,(42) estimate the solubility of amino acids in different mixed solvent (methanol + water, ethanol + water and 2-propanol + water mixture) spectrophotometrically. Then the results have been interpreted in terms of solute-solvent interactions and structural changes of amino acids in solvent mixture.

Heang and Haedi,(43) used (HPLC) with gradient elution for analyzing (19) different amino acids at Pico mol level using flurometric detection. The amino acids in natural waters were preconcentrated prior to their analysis. Calicume ions interfere in the determination of amino acids and a way to overcome this effect has been described.

Densities of solutions of glycine, L-seriene, L-alanine have been measured respectively, in ethylene glycol + water in 298.15K studied by Qingwaang Liu et. al. (44)

The experimental data, apparent molar volumes, and limiting partial molar volumes of each amino acids in the mixtures have been calculated. The trends of transfer volumes are interpreted by cosphere overlap model.

The first and second dissociation constants and the related thermodynamic quantities of both amino acids glycine and DL-alanine in both solvent mixtures by Jamal Saleh ;(45) The study also covered the thermodynamic quantities of transfer of the amino acids from water to glycol-water or to ethylene glycol water mixtures.

Chapter Two

Some Physical Properties of Solutions

2

A knowledge of chemical and physical properties of systems containing two or more components liquids is often required in theoretical studies (46, 47) and for chemical processes at wide range of temperatures. (48-50)

The intensive properties may include density, viscosity (or fluidity), refractive index, speed sound, and relative permittivity.

Theoretical studies of binary and ternary mixtures reveal the importance of molecular interactions (hydrogen bonding, charge-transfer complexes, dipole-dipole, and dipole-induced dipole etc.) on the physical properties of these mixtures. (51) It is important to have at least a qualitative understanding of the behavior of ions in solution.

Physical properties can be considered as a probe of a molecular interaction, some of these properties are density, and viscosity.

(2-1) Density

Density (ρ) refers to the mass contained within a unit volume under specified conditions. (52)

$$\rho = \frac{W}{V} \qquad \text{………… (2-1)}$$

Where: **W** is the weight of the liquid, **V** is the volume of the liquid, its units ($g.cm^{-3}$).

The density is one of the important physical properties which are used to distinguish between the materials with single and multicontinous.

The density of the liquid materials is in the middle between the densities of solid and gases this mean that the average space between the molecules of the liquid is larger than the average space of solid and smaller than the average space of gas material. (52)

The density of most liquids decreases on increasing temperature. As liquid expanded when heated, so its volume increase then its density decrease at specific temperature the density of different liquids are clearly different, with considering the relative forces between the molecules, whenever this force large, molecules become closer to each other which make density larger. (53, 54)

The first studies by Martin and Chick (55), for proteins density in solution, shows that the protein leads to limiting contractions to solution. We can benefit from this property in recognizing other physical properties like apparent molar volume, and excess molar volume. (56)

(2-2) Viscosity

Viscosity (internal friction) is a measure of the resistance against flow that a fluid offers to an applied shearing force. (57) The fluid between parallel planes is moved in the Y-direction at a constant velocity relative to the other while maintaining a constant distance between the planes (coordinate Z).The layer of the fluid immediately adjacent to the moving plane moves with velocity of this plane. The layer next to the stationary plane is the stationary; in between the velocity usually changes linearly with distance as shown. The velocity gradient, that is, the rate of change of velocity with respect to distance measured perpendicular to the direction of flow, is represented by dv/dz.

The coefficient of viscosity (η) is defined by the equation: (9)

$$F = -\eta \frac{d\ \nu Y}{dZ} \qquad \text{………… (2-2)}$$

Where: **F** is the force per unit area required to move one plane relative to the other.

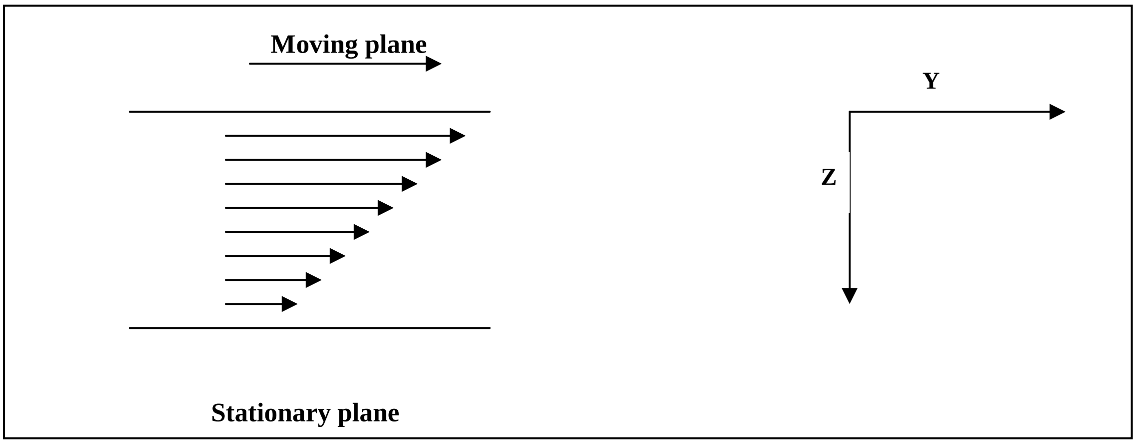


Figure (2.1) Velocity gradient in a fluid due to a shearing action

The SI units of viscosity is the Pascal second, **($N.m^{-2}.s=Kg.s^{-1}.m^{-1}$)**. A fluid has a viscosity of 1 Pa.s. If a force of 1N is required to move a plane of ($1m^2$) at a velocity of ($1ms^{-1}$) with respect to a plane surface a meter a way and parallel with it. Viscosity is related to the ease which individual molecules of the liquid can move with respect to one another. It thus depends on the attractive forces between molecules and structural features exist that cause the molecules to become entangled. (9)

The viscosity decreases with increasing temperature, because at higher temperature, the greater average kinetic energy of the molecules more easily overcomes the attractive forces between molecules.(58)

The variation of the coefficient of viscosity with temperature may represented by:

$$\eta = Ae^{Ea/RT} \qquad \text{………… (2-3)}$$

Where **A** pre-exponential factor (Arrhenius factor), **Ea** activation energy for viscous flow, **R** gas constant, **T** temperature in Kelvin.

The quantitative measurement of absolute viscosity can be done by indirect measurements in which the viscosity of a liquid is determined relative to that of another liquid whose viscosity has been obtained by an absolute method, by passing a certain quantity of a liquid through a capillary tube measuring the time that consumed and making use of the relationship: (59)

$$\frac{\eta_1}{\eta_2} = \frac{t_1 \rho_1}{t_2 \rho_2} \qquad \text{…………(2-4)}$$

Where: $\boldsymbol{\eta_{1,\ 2}}$ represent the viscosity (poise) of solution (solvent) and reference solution, $\boldsymbol{\rho_{1,\ 2}}$ density (g. cm^{-3}) of solution (solvent) and reference solution, **t** flow time (sec).

(2-3) Theories of Viscosity

Several theories have been developed on the viscosity of liquid. Some of them give more or less qualitative interpretation of the factor in the empirical equation, while others, partly on the basis of quantum mechanics, try to correlate the phenomena of viscous flow with the properties of the atoms or molecules using extensive mathematical treatment.(57) Some of these studies and theories are:

(2-3-1) *Eyring Theory*

In the theory of the viscosity of liquids, Eyring considered that molecules displaced relative to one another in the course of viscous flow have to overcome the energy barrier between the adjacent positions.(57)
The rate of this process is determined by factors similar to those acting of the absolute reaction rate theory with suitable modifications.
The viscosity coefficient is, by definition:

$$\eta = f\lambda_1/\Delta u \qquad \text{………… (2-5)}$$

Where: $\boldsymbol{\lambda_1}$ is the distance between two liquids layers of unit surface area, $\boldsymbol{f}$ is the shear force, and $\boldsymbol{\Delta u}$ is the relative velocity.

In the mechanism of viscous flow, the displacement of liquid layer with respect to adjacent one can be described as the movement of the molecules of the layer from their equilibrium positions to the adjacent once within the same layer.

However, a molecule can jump to the adjacent equilibrium position only when there is a hole to be occupied. Therefore, a hole must be formed in the liquid by pushing away the molecules, which requires a certain amount of energy. Thus, the jump of the molecule from its equilibrium position to an adjacent one can be regarded as a process accompanied by overcoming a potential energy barrier.(57)

(2-3-2) *Holes Theory*

In liquid the molecules are rather tightly fitted to one another, although there are some gaps between them. Owing to this, the molecules can only vibrate around their equilibrium position and translational displacement, i.e. transport of the molecules, can occur only when an empty place, i.e. a hole (a vacancy) if formed in their vicinity. (57)

Thermal fluctuation results in continuous formation of holes in the liquid which are quickly occupied and new ones formed. The molecules move in the “empty space” in gases; in a certain sense, holes “move” similarly in liquids. The holes play the same role in liquids as molecules do in gases. The majority of the holes formed in the liquids, however, have probably a size smaller than the volume of one molecule.(57)

Many basic studies had investigated in details.(60 - 64) The change in viscosity as a consequence of solute-solvent interaction. Other studies are also available (65, 66) regarding the concentration dependence of viscosity of aqueous and non aqueous solutions.

The solvent structure is influenced by the size and shape of dissolved ions, and the viscosity is altered by this effect as well.

The first treatment was given by Einstein. His result, restricted to the case of small volume fraction of spherical particles, is

$$\frac{\eta}{\eta_0} = 1 + 2.5\,\Phi \qquad \text{………… (2-6)}$$

Where: **η** and **η_0** are the viscosities of solution and pure solvent respectively, and **Φ** volume fraction occupied by the particles.

(Φ) Involves also the solvent molecules bound to the surface of the particles and moving together with it.

On the bases of experimental investigation of dilute solutions, Jones and Dole (54, 67) have achieved to an empirical correlation valid at constant temperature revealing the variation of relative viscosity (η/η_0) with molarity (C) for dilute and moderate concentration.

$$\eta_r = \frac{\eta}{\eta_0} = 1 + A\sqrt{C} + BC \qquad \text{………… (2-7)}$$

(2-4) Partial Molal Quantities

Partial molal quantities tell us how the properties of solutions change with concentration. We need to know partial molal quantities for all the extensive properties of a solution, including V, G, H, S , and A.(68) The partial molal Gibbs Free energy, which is called the chemical potential, is central to the study of solutions. for a two-component solution with n_1 moles of component 1 and n_2 moles of component 2. The change in Gibbs Free Energy with concentration at constant temperature and pressure is:

$$dG = \left(\frac{\partial G}{\partial n_1}\right)_{n_2} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{n_1} dn_2 \qquad \text{………… (2-8)}$$

The partial molal Gibbs Free Energy with respect to changes in the number of moles of Component 1 is:

$$\left(\frac{\partial G}{\partial n_1}\right)_{n_2} = \mu_1 \qquad \text{………… (2-9)}$$

The partial molal Gibbs Free Energy is the Gibbs Free Energy per mole of compound in the solution. The partial molal Gibbs Free Energy with respect to changes in the number of moles of component 2 is

$$\left(\frac{\partial G}{\partial n_2}\right)_{n_1} = \mu_2 \qquad \text{………… (2-10)}$$

Substituting these definitions into Equation (2-8) gives:

$$dG = \mu_1 dn_1 + \mu_2 dn_2 \qquad \text{………… (2-11)}$$

Which determines the change in Gibbs Free Energy for changes in concentration. The important point is that the partial molal properties depend on concentration. Hence knowing the concentration dependence is crucial for understanding solutions.(69)

Of all the extensive thermodynamic properties, the volume is the easiest to visualize; this also holds true for the partial molal volumes, which are defined as

$$\left(\frac{\partial V}{\partial n_1}\right)_{n_2} = V_1 \qquad \text{and} \qquad \left(\frac{\partial V}{\partial n_2}\right)_{n_1} = V_2 \qquad \text{………… (2-12)}$$

V_1 the partial molal volume of component 1 is the volume per mole of compound 1 in the solution. Similarly, V_2 the partial molal volume of component 2 is the volume per mole of compound 2 in the solution. The total change in volume for changes in the concentration of the solution is

$$dV = \left(\frac{\partial V}{\partial n_1}\right)_{n_2} dn_1 + \left(\frac{\partial V}{\partial n_2}\right)_{n_1} dn_2 \qquad \text{………… (2-13)}$$

More compactly, using Equation (2-13) we write:

$$dV = V_1 dn_1 + V_2 dn_2 \qquad \text{............ (2-14)}$$

we need to note that V_1 and V_2 depend on concentration, so the integration of equation (2.14) is done in a way that keeps the concentration of the solution constant. Since V_1 and V_2 are constants, the integrated from of this equation is

$$V = n_1V_1 + n_2V_2 \qquad \text{………… (2-15)}$$

for ideal solution, volume is just the same of the volume of the pure solute and pure solvent

$$V=n_1V_{m1}+n_2V_{m2} \qquad \text{………… (2-16)}$$

where **Vm_1** is the molar volume of pure component 1, **Vm_2** is the molar volume of component 2.

The experimental determination of partial molal volumes is quite simple and involves the careful measurement of the densities of solutions of known concentrations.

(2-5) Partial Molal Volume

The partial molal volume is important in oceanography and aquatic environmental science, which is why we measure the partial molal volume of NaCl solutions in the lab., partial molal volume is needed in biochemistry for careful calculations of the molecular weights of proteins and nucleic acids using ultracentrifugation. (68)

The density ρ for a solution of total volume V in liters containing n_1 moles solvent with molecular mass M_1 and n_2 moles solutes with molecular mass M_2 is (70):

$$\rho = \frac{n_1 M_1 + M_2}{1000\ V} \qquad \text{………… (2-17)}$$

$$n_1 = \frac{1000\ \rho V - M_2}{M_1} \qquad \text{………… (2-18)}$$

on differentiation at constant temperature and pressure:

$$dn_1 = \frac{1000(\rho dV + V d\rho)}{M_1} \qquad \text{………… (2-19)}$$

So:

$$\frac{dV}{dn_1} = \frac{M_1}{1000\left[\rho + V\left(\frac{d\rho}{dV}\right)\right]} \qquad \text{………… (2-20)}$$

Since $\left(\frac{dV}{dn_1}\right)_{n_2}$ denotes to constant quantity (one mole) of component 2, then it will be equivalent to:

$$\left(\frac{dV}{dn_1}\right)_{T,P,n_2} = \bar{V}_1 \qquad \text{………… (2-21)}$$

Where $\bar{\mathbf{V}}$: partial molal volume in liters for component.

On substituting of V in the right hand side by $\frac{1}{c}$, where c: concentration (mol. /L) then:

$$\bar{V}_1 = \frac{M_1}{1000\left[\rho - \left(\frac{d\rho}{dc}\right)\right]} \qquad \text{………… (2-22)}$$

Since

$$V\left(\frac{d\rho}{dv}\right) = c\left(\frac{d\rho}{dc}\right) \qquad \text{………… (2-23)}$$

We need to know serious of solutions to estimate $\bar{V}_1$ densities for plotting curve of density versus concentration to know $\frac{d\rho}{dc}$ from the slope $\frac{\rho}{c}$.

By inserting value of concentration and density at the slope $\frac{d\rho}{dc}$ in equation (2-22) we can estimate $\bar{V}_{1.}$

(2-6) Apparent Molal Volume

The apparent molal volume represents the volume of a solution as n_2 moles of a solute are added to fixed n_1 moles of solvent. $^{(71)}$ The volume of the solution changes as shown in Figure (2-2). The volume due to the added solute (per mol) is called the apparent molal volume **(Φ_v)**.

The total volume of a solution (V) depends on the volume of the pure solvent and the apparent molal volume of the solute (Φ_v).

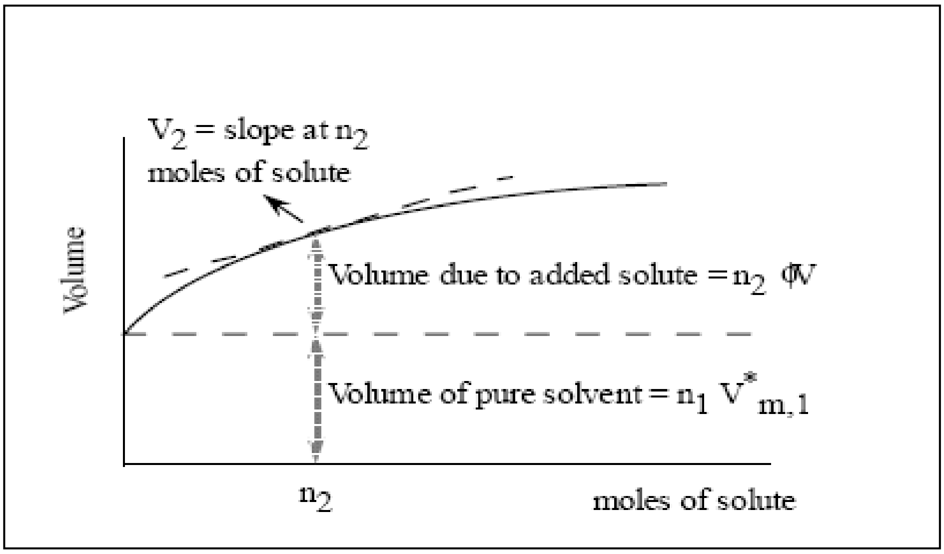


Figure (2-2) Show how the total volume of a solution (V) depends on the volume of the pure solvent and the apparent molal volume of the solute (Φ_v).

Figure (2-2) shows that:

$$\Phi_v = \frac{V_{solution} - V_{solvent}}{\text{moles of solute}} \qquad \text{……….. (2-24)}$$

Or

$$\Phi_v = \frac{V_{n_1} V^*_{m,1}}{n_2} \qquad \text{…………. (2-25)}$$

Thus, in Figure (2-2), the volume V of the solution at any particular added n_2 moles of solute is given by a rearrangement of Equation (2-25):

$$V = n_1 V_{m,1} + n_2 \Phi_v \qquad \text{………… (2-26)}$$

The apparent molal volume had calculated for the amino acids solutions by applying the relationship. (72)

$$\phi_v = \frac{1}{m}\left[\frac{1000 + mM}{\rho} - \frac{1000}{\rho_0}\right] \qquad \text{………… (2-27)}$$

Where (**Φ_v**) apparent molal volume for amino acid solution in water and in (0.1M) HCl, (**m**) molality of the solution, (**M**) molecular weight of the solute, (**ρ_0, ρ**) density of the solvent and the amino acid solution respectively.

The apparent molal volume relates linearly with the molality of the solute (m) according to (73, 74)

$$\Phi_v = \Phi_v^0 + am \qquad \text{………… (2-28)}$$

Where (ϕ^0_v) is the apparent molal volume at infinite dilution (limiting apparent molal volume)

(2-7) Application of Jones and Dole Equation

The viscosity of water is altered by dissolved substance, namely they increase or decrease viscosity depending on the properties of the particles, mainly their size and charge. It was found that this effect varies approximately linearly with concentration in dilute (about 0.02 to 0.1M) solutions. At very low concentration, however (< 0.02 M) an appreciable deviation from linearity appears. (54, 57)

Electrolytic solutions of moderate concentration generally have relative viscosities which obey the empirical equation of Jones and Dole.(54)

$$\eta_r = \frac{\eta}{\eta_0} = 1 + A\sqrt{c} + BC \qquad \text{………… (2-29)}$$

Where: $\boldsymbol{\eta}$ is the measured viscosity of the electrolyte solution, $\boldsymbol{\eta_0}$ is the viscosity of the pure solvent at the same temperature, **A** and **B** are empirical constant independent of the concentration of the given system.

Equation (2.29) relates the relative viscosity (η_r) of the electrolyte solution to the concentration (C) of the electrolyte in the solution.

The parameter (A) in interaction of the solute particles with one another, while the parameter (B) corresponds to the interaction between the solvent and solute particles.(75)

In practice the A term in equation (2-29) is dominant at low solute concentration (< 0.02M). The linear term, which rapidly swamps the $A\sqrt{c}$ term concentrations above (0.02M) measure the effect of the solute particles on the solvent structure. Equation (2-29) is generally in agreement with experiment up to above (≤0.2M) concentration, its validity can be extended to higher concentrations (>0.2M) as well. Equation (2-29), through applied successively on the behavior of strong and weak electrolytes, may also describe the viscous behavior of a number of non- electrolytic solutions (54, 57). Equation (2-29) may be written as:

$$(\eta_r - 1)/\sqrt{c} = A + B\sqrt{c} \qquad \ldots\ldots\ldots\ldots (2\text{-}30)$$

By plotting the left-hand term of equation (2-29) as a function of $\sqrt{c}$, a straight line is obtained with a slope (B) and an intercept (A) on the ordinate.

(2-8) Effective Flow Volume

The Effective Flow Volume is defined as the volume which includes the immobilized solvent molecules inside the cavities of the solute molecules as well as the solvent molecules in the primary salvation layer .

The effective flow volume (V_h) may be considered as one of the important parameters that discuss the type of solute-solvent interaction. The equation reported by Vand (76) and modified by Eagland and Pilling (77):

$$C/[Log\,\eta/\eta_0] = 2.303/aV_h - 2.303QC/a \qquad \ldots\ldots\ldots (2\text{-}31)$$

Was investigated to calculated effective flow volume (V_h).

Where (**V_h)** Effective Flow Volume ($L.mol^{-1}$), (**Q)** Particle interaction coefficient, (**a)** Shape factor assumed equal 2.5 for spherical solute particles in normal solvent, (**C)** The molar concentration.

A plot of C/ [Log η/ η_0] versus (C) should be linear with a slope of 2.303Q/2.5 and an intercept of 2.303/2.5V_h, as C→o. Hence the limiting value of the effective flow volume (V^0_h) as C→o can be calculated.

Another general method of obtaining (V^0_h) is related the B-coefficient from Jones and Dole equation to the limiting value of effective flow volume (V^0_h) by the relationship (2):

$$B = V_h / a \qquad \ldots\ldots\ldots\ldots (2\text{-}32)$$

(2-9) The Aim of the Work

The most versatile biomolecules in living organisms are the amino acids which make up proteins. Proteins acts as catalysts, structural support, protection, transport agent, chemical messengers, and cell recognition factors to name only a few function.

The effect of elevated amounts of free amino acids as solutes in body fluids is of significant importance; certain diseases developed as a result of increasing the concentration of some amino acids in blood. This fact leads to:

- Provide information on the nature of the molecular interaction between some of amino acids molecules (the solute) and the solvent molecules (water or 0.1M HCl solution).

- Investigate the volumetric and viscometric behaviours of the system through correlation of the experimental measurements of the partial molal volume and viscosity to theoretical calculations of the partial molal volume and Van der Waals volume.

Chapter Three

3

Experimental

(3-1) Materials

1. The amino acids that used in this research were reported in Table (3-1) with some physical properties and suppliers of all chemicals used in this study.

Table (3-1) Some amino acids that used in this research and some physical properties [(78)]

Substance	Source	M.W.	Purity	M.P.	Solubility g.L. at $20^{o}c$
DL- Valine	Fluka AG	117.15	99 %	295-297	68.1
DL-Isolucine	Fluka AG	131.18	99 %	-----	21.1
DL- Methionine	Fluka AG	149.21	99 %	271-273	30.0
DL-Glutamine	BDH Co.	146.15	99 %	185	------
L-Arginine	BDH Co.	174.20	98 %	232-224	------
DL-Histidine	BDH Co.	155.16	98 %	273	------

2. 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%).

(3-2) Preparation of Amino Acids Solutions

The amino acids solutions were prepared by dissolving an appropriate mount of the amino acids DL-Valine, , DL-Methionine and L-Arginine in the solvent [the solvent is either deionized doubly distilled water or 0.1 mol.L^{-1} HCl solution] over concentration variation from (0.04 - 0.2 mol.L^{-1}) and from (0.06 - 0.28 mol.L^{-1}) for DL-Isolucine. For the two amino acids (DL-Glutamine and DL-Histidine) the concentration variation was from (0.002 - 0.02 mol.L^{-1}) due to limited solubility for them.

(3-3) Density Measurements

The Density measurement apparatus shown in Figure (3-1).This apparatus composed of three blocks which are density measurement system, temperature measurement system and temperature control system (79).

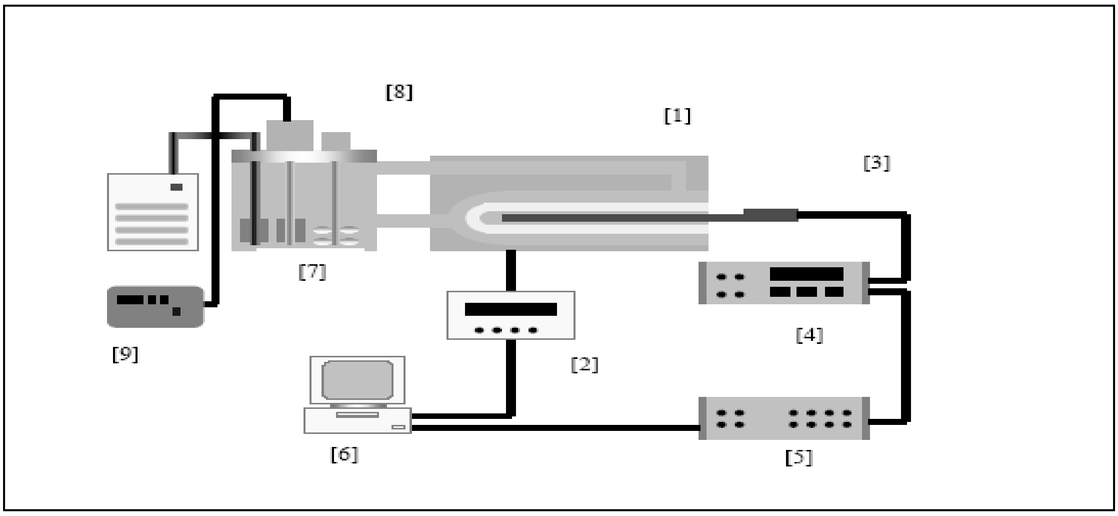


Figure (3-1) Density measurement apparatus

[1] Density measuring cell [2] Density meter [3] Sheathed Platinum resistance thermometer [4] Thermometry bridge [5] Standard resistor [6] Computer [7] Thermostat controlled Circulatory bath [8] Stirrer [9] Temperature control unit [10] Cooler.

Density meter [1, 2] an Anton Paar digital densimeter (model DMA 60/602) was employed for the determination of the densities of the amino acids solutions. The meter has a glass U-tube that is filled with the sample. The U-tube is made to vibrate and the vibration frequency is measured. The viubration frequency is a sensitive measure of the density of the solution. The more dense the solution, the smaller vibration frequency. The meter is computer controlled, and the computer converts the vibration frequency into the measured density using a calibration equation. The meter also determines the temperature and applies a correction for the density calculation.

To cause the U-tube to vibrate, a small magnet is glued into the end of the U-tube. The magnet is placed in a coil that has an oscillating current as shown in Figure (3-2).

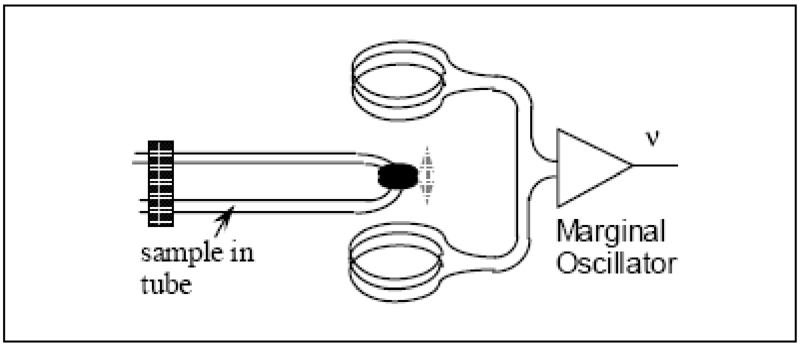


Figure (3-2) Operation of the densimeter

The frequency of oscillating current is varied until the natural frequency that is resonance frequency of the U-tube is found. By measuring the period of oscillation (τ) of the vibrating U-shaped tube, filled with the sample (air, water) and determining the constant (K) by using the standard values of the densities of water and air in the relation:

$$K_0 = \frac{\rho_{H_2O} - \rho_{air}}{\tau_{H_2O} - \tau_{air}} \qquad \text{......... (3-1)}$$

Where (**ρ**) represents the density and (**τ**) the oscillation period.

Then density (**ρ**) is estimated for every sample by measuring its period (**τ**) of oscillation and applying the following relation:

$$\rho\ (\text{g.cm}^{-3}) = K_0\ t \qquad \text{........... (3-2)}$$

The Table (3-2) refers to density of water and air at the temperatures used in this research.

Table (3-2) Density of water and air at four temperatures (293.15, 298.15, 303.15 and 308.15)K [(80)]

Temp. (K)	**Density of water (g.cm^{-3}**	**Density of air (g.cm^{-3})**
293.15	0.99832	0.001205
298.15	0.99707	0.001184
303.15	0.99568	0.001165
308.15	0.99406	0.001146

All measurements were carried out at atmospheric pressure. A time interval of 15 minutes was chosen to attain a satisfactorily temperature constancy and oscillation period stability (fluctuations are restricted to the sixth decimal digits). The temperature of the water bath was kept constant to within 0.01K with Haak DIG thermostat. The precision of density measurements is estimated to be better than 2×10^{-5} (g.cm^{-3}).

(3-4) Viscosity Measurements

In the present research, the viscosity (η) of the amino acids solutions was measured using **"Ostwald"** viscometer as shown in Figure (3-3). This viscometer had a flow volume of about 3 cm^3, a capillary length of about 8 cm. and a capillary diameter of about (0.36-0.63mm).

The viscosity of the solution was calculated at certain temperature according to this equation:

$$\frac{\eta}{\eta_0} = \frac{\rho\, t}{\rho_0\, t_0} \quad \text{........ (3-3)}$$

Where **η, ρ,** and **t** represent the viscosity, density, and flow time of amino acids solutions respectively, and **η_o, ρ_o** and **t_o** represent the viscosity, density, and flow time of reference solution or (solvent) respectively.

Table (3-3) refers to the density and viscosity of water at the temperature used in this research.

Table (3-3) Density and viscosity of water at four temperatures (293.15, 298.15, 303.15 and 308.15)K [(80)].

Temp.(K)	Density of water (g.cm^{-3})	Viscosity of water (cp)
293.15	0.99832	1.002
298.15	0.99707	0.8904
303.15	0.99568	0.7975
308.15	0.99406	0.7194

(3-4-1) *Operation of Viscometer*

A volume of about 15cm^3 of the liquid sample was introduced in to the clean and dry Ostwald viscometer immersed in a constant temperature bath. The liquid sample inside the Ostwald viscometer was allowed to reach thermal equilibrium with the water bath about 10 minutes. The sample liquid was then drawn up into bulb (A) until the sample liquid level was above the mark (a), the sample liquid then starts draining. The time necessary for the liquid level to fall from (a) to (b) was measured with a precision of ± 0.01 second.

A constant temperature water bath with a basic control unit was used. The temperature of the water bath was measured by a Hewlett-Packard a quartz thermometer. The temperature fluctuations were limited to ± 0.01K.

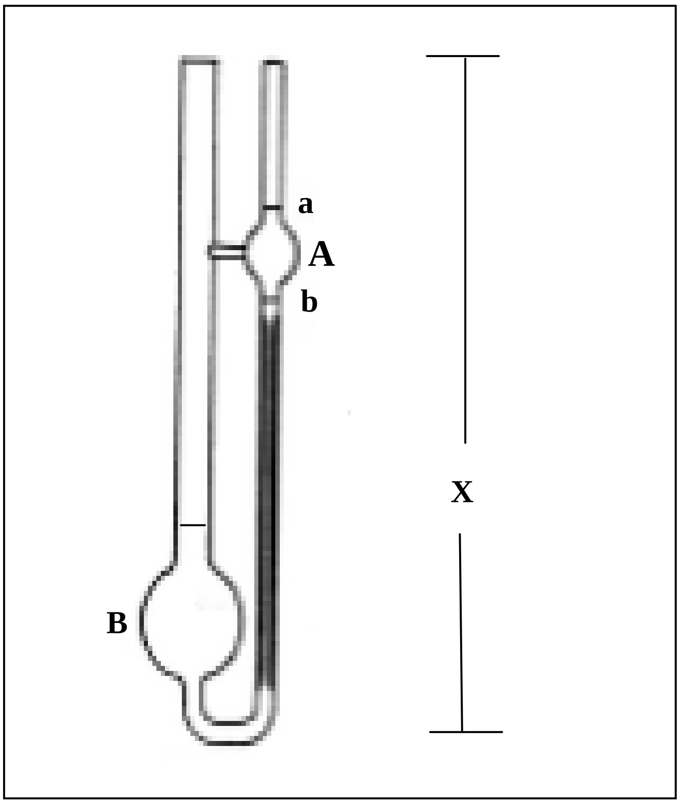


Figure (3-3) Ostwald viscometer

(3-4-2) *Calibration of Viscometer*

The viscometer used in this study was calibrated with deionized doubly distilled water. The flow time of water at each of the four experimental temperatures (293.15, 298.15, 303.15, and 308.15K) was measured. The data for the kinamatic viscosity of water at these temperature and the experimentally dented flow times were filled to the following equation:

$$\nu = ct \qquad \text{……… (3-4)}$$

where (ν) is the kinematic viscosity of the deionized water, (t) is the flow time in seconds and (c) is the viscometer constant. The value of c (0.0024 cm^2/S^2) each time value was an average of three measurements. The uncertainty of the viscosity measurements was ±0.01%.

Chapter Four

4

Results and Discussions

(4-1) Density

The experimental measured densities (ρ) in units of ($g.cm^{-3}$) of the amino acids solutions [Valine, Isolucine, Methionine, Glutamine, Arginine, and Histidine as solutes in water and /or 0.1M HCl solution as solvent] at (293.15, 298.15, 303.15, and 308.15)K in the concentration range from (0.04-0.2 mol. L^{-1}) for Valine, , Methionine and Arginine, from (0.06-0.28 mol.L^{-1}) for Isolucine and from (0.002-0.02 mol.L^{-1}) for Glutamine and Histidine are listed in Tables (4-1a, b, c, d, e, f) and (4-1a$^{/}$, b$^{/}$, c$^{/}$, d$^{/}$, e$^{/}$, f$^{/}$) respectively.

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.

Table (4-1a) Experimental Densities (ρ/g.cm^{-3}) of DL-Valine Solution in water as a function of molar concentration at different Temperatures in the range of (293.15-308.15)K

C (mol.L^{-1})	ρ(g.cm^{-3})			
	293.15K	298.15K	303.15K	308.15K
Solvent H_2O	0.998324	0.997071	0.995683	0.994063
0.04	0.999273	0.998533	0.996351	0.994661
0.06	0.999273	0.999101	0.996873	0.995271
0.08	0.999774	0.999475	0.997347	0.995759
0.1	1.000309	0.999976	0.997854	0.996259
0.12	1.000968	1.000527	0.998464	0.996911
0.14	1.001580	1.001031	0.998962	0.997415
0.16	1.002126	1.001570	0.999444	0.997989
0.18	1.003635	1.002110	0.999990	0.998608
0.2	1.004574	1.002564	1.000508	0.999166

Table (4-1b) Experimental Densities (ρ/g.cm^{-3}) of DL-Isolucine Solution in water as a function of molar concentration at different Temperatures in the range of (293.15-308.15) K .

C (Mol.L^{-1})	ρ(g.cm^{-3})			
	293.15K	298.15K	303.15K	308.15K
Solvent H_2O	0.998324	0.997071	0.995683	0.994063
0.06	1.000673	0.999753	0.99728	0.996197
0.08	1.001811	1.001082	0.998806	0.997322
0.11	1.002894	1.001633	0.999982	0.998443
0.14	1.004084	1.002771	1.001132	0.999538
0.17	1.005229	1.003865	1.002259	1.000672
0.19	1.006370	1.004980	1.003356	1.001835
0.22	1.007380	1.006096	1.004499	1.002946
0.25	1.008495	1.007175	1.005655	1.004075
0.28	1.009312	1.008199	1.006904	1.007335

Table (4-1c) Experimental Densities (ρ/g.cm^{-3}) of DL-Methionine Solution in water as a function of molar concentration at different Temperatures in the range of (293.15-308.15) K.

C (mol.L^{-1})	ρ (g.cm^{-3})			
	293.15K	**298.15K**	**303.15K**	**308.15K**
Solvent H_2O	0.998324	0.997071	0.995683	0.994063
0.04	0.999462	0.998970	0.997030	0.995690
0.06	1.001030	0.999907	0.998190	0.996622
0.08	1.001960	1.000802	0.999149	0.997508
0.1	1.002874	1.001723	1.000090	0.998389
0.12	1.003781	1.002594	1.000976	0.999471
0.14	1.004707	1.003501	1.001872	1.000239
0.16	1.005548	1.004377	1.002717	1.001126
0.18	1.006534	1.005263	1.003618	1.002149
0.2	1.007518	1.002209	1.004541	1.003139

Table (4-1d) Experimental Densities (ρ/g.cm^{-3}) of DL-Glutamine Solution in water as a function of molar concentration at different Temperatures in the range of (293.15-308.15)K

C Mol.L^{-1}	ρ (g.cm^{-3})			
	293.15K	**298.15K**	**303.15K**	**308.15K**
Solvent H_2O	0.998324	0.997071	0.995683	0.994063
0.002	0.998468	0.997206	0.995709	0.994257
0.004	0.998595	0.997337	0.995723	0.994368
0.006	0.998723	0.997456	0.995757	0.994434
0.008	0.998815	0.997583	0.995816	0.994559
0.01	0.998920	0.997700	0.995940	0.994691
0.012	0.999020	0.997816	0.996038	0.994827
0.014	0.999090	0.997935	0.996107	0.994964
0.016	0.999189	0.998050	0.996238	0.995118
0.018	0.999407	0.998160	0.996324	0.995255
0.02	0.999447	0.998184	0.996485	0.995406

Table (4-1e) Experimental Densities (ρ/g.cm^{-3}) of L-Arginine Solution in water as a function of molar concentration at different Temperatures in the range of (293.15-308.15) K.

C Mol.L^{-1}	ρ (g.cm^{-3})			
	293.15K	298.15K	303.15K	308.15K
Solvent H_2O	0.998324	0.997071	0.995683	0.994063
0.04	0.999999	0.998858	0.996805	0.998660
0.06	1.000862	0.999732	0.997569	0.999359
0.08	1.001711	1.000593	0.998430	0.999459
0.1	1.002567	1.001473	0.999610	0.999648
0.12	1.003418	1.002319	1.000481	0.999836
0.14	1.004274	1.003201	1.001321	1.000134
0.16	1.005130	1.004033	1.002150	1.001103
0.18	1.006024	1.004875	1.003058	1.002503
0.2	1.006886	1.005738	1.004845	1.004334

Table (4-1f) Experimental Densities (ρ/g.cm^{-3}) of DL-Histidine Solution in water as a function of molar concentration at different Temperatures in the range of (293.15-308.15) K.

C Mol.L^{-1}	ρ (g.cm^{-3})			
	293.15K	298.15K	303.15K	308.15K
Solvent H_2O	0.998324	0.997071	0.995683	0.994063
0.002	0.998415	0.997758	0.994230	0.993811
0.004	0.998467	0.997960	0.995734	0.994526
0.006	0.998488	0.997988	0.995831	0.994677
0.008	0.998562	0.997997	0.995944	0.994819
0.01	0.998661	0.998407	0.996045	0.994923
0.012	0.998795	0.998731	0.996159	0.995039
0.014	0.998876	0.998825	0.996212	0.995131
0.016	0.998983	0.998933	0.996399	0.995259
0.018	0.999101	0.999068	0.996511	0.995349
0.02	0.999133	0.999110	0.996589	0.995608

Table (4-1a$^{/}$) Experimental Densities (ρ/g.cm^{-3}) of DL-Valine Solution in (0.1M HCl) as a function of molar concentration at different Temperatures in the range of (293.15-308.15) K.

C Mol.L^{-1}	ρ (g.cm^{-3})			
	293.15K	**298.15K**	**303.15K**	**308.15K**
Solvent 0.1M HCl	1.000055	0.998767	0.997421	0.996266
0.04	1.001055	1.000010	0.998072	0.996535
0.06	1.001451	1.000362	0.998482	0.997149
0.08	1.001843	1.000724	0.998859	0.997523
0.1	1.002233	1.001148	0.999314	0.997897
0.12	1.002627	1.001517	0.999775	0.998309
0.14	1.003040	1.001935	1.000179	0.998683
0.16	1.003414	1.002324	1.000706	0.999053
0.18	1.003774	1.002699	1.001151	0.999565
0.2	1.004025	1.003096	1.001692	0.999963

Table (4-1b$^{/}$) Experimental Densities (ρ/g.cm^{-3}) of DL-Isolucine Solution in (0.1M HCl) as a function of molar concentration at different Temperatures in the range of (293.15-308.15)K

C Mol.L^{-1}	ρ (g.cm^{-3})			
	293.15K	**298.15K**	**303.15K**	**308.15K**
Solvent 0.1M HCl	1.000055	0.998767	0.997421	0.996266
0.06	1.001685	1.000908	0.999108	0.998273
0.08	1.00295	1.002000	1.001161	0.999518
0.11	1.003642	1.003119	1.001094	1.000608
0.14	1.005122	1.004286	1.002576	1.001724
0.17	1.006164	1.005363	1.003634	1.002852
0.19	1.007243	1.006485	1.004703	1.003948
0.22	1.008414	1.007613	1.005932	1.005095
0.25	1.009597	1.008720	1.008266	1.006235
0.28	1.010658	1.009830	1.009693	1.007924

Table (4-1c$^{/}$) Experimental Densities (ρ/g.cm^{-3}) of DL-Methionine Solution in (0.1M HCl) as a function of molar concentration at different Temperatures in the range of (293.15-308.15)K

C Mol.L^{-1}	ρ (g.cm^{-3})			
	293.15K	**298.15K**	**303.15K**	**308.15K**
Solvent 0.1M HCl	1.000055	0.998767	0.997421	0.996266
0.04	1.001739	1.000700	0.998753	0.997194
0.06	1.002579	1.001499	0.999472	0.997980
0.08	1.003396	1.002339	1.000209	0.998745
0.1	1.004221	1.003101	1.000963	0.999475
0.12	1.004994	1.003912	1.001728	1.000174
0.14	1.005820	1.004645	1.002596	1.000948
0.16	1.006583	1.005400	1.003369	1.001866
0.18	1.007031	1.006169	1.004375	1.002915
0.2	1.007328	1.006923	1.005266	1.004319

Table (4-1d$^{/}$) Experimental Densities (ρ/g.cm^{-3}) of DL-Glutamine Solution in (0.1M HCl) as a function of molar concentration at different Temperatures in the range of (293.15-308.15) K.

C Mol.L^{-1}	ρ(g.cm^{-3})			
	293.15K	**298.15K**	**303.15K**	**308.15K**
Solvent 0.1M HCl	1.000055	0.998767	0.997421	0.996266
0.002	1.008433	0.999035	0.997622	0.996688
0.004	1.008492	0.999104	0.997637	0.996778
0.006	1.008661	0.999173	0.997648	0.996822
0.008	1.008682	0.999256	0.997662	0.996865
0.01	1.008699	0.999329	0.997670	0.996906
0.012	1.009117	0.999416	0.997676	0.997029
0.014	1.009227	0.999504	0.997683	0.997117
0.016	1.009356	0.999585	0.997697	0.997363
0.018	1.009367	0.999704	0.997711	0.997448
0.02	1.009382	0.999899	0.997721	0.997507

Table (4-1e$^{/}$) Experimental Densities (ρ/g.cm^{-3}) of L-Arginine Solution in (0.1M HCl) as a function of molar concentration at different Temperatures in the range of (293.15-308.15) K.

C Mol.L^{-1}	**ρ(g.cm^{-3})**			
	293.15K	**298.15K**	**303.15K**	**308.15K**
Solvent 0.1M HCl	1.000055	0.998767	0.997421	0.996266
0.04	1.001825	1.000633	0.998872	0.997196
0.06	1.002699	1.001547	0.999691	0.997973
0.08	1.003586	1.002459	1.000475	0.998671
0.1	1.004603	1.003333	1.001318	0.999439
0.12	1.005515	1.004328	1.002259	1.000551
0.14	1.006553	1.005280	1.003357	1.001686
0.16	1.007582	1.006195	1.004297	1.002530
0.18	1.008902	1.007196	1.005199	1.003640
0.2	1.010428	1.008430	1.006093	1.004513

Table (4-1f$^{/}$) Experimental Densities (ρ/g.cm^{-3}) of DL-Histidine Solution in (0.1M HCl) as a function of molar concentration at different Temperatures in the range of (293.15-308.15) K.

C Mol.L^{-1}	**ρ(g.cm^{-3})**			
	293.15K	**298.15K**	**303.15K**	**308.15K**
Solvent 0.1M HCl	1.000055	0.998767	0.997421	0.996266
0.002	1.000078	0.998954	0.997931	0.997556
0.004	1.000082	0.998976	0.997944	0.997567
0.006	1.000089	0.998977	0.997958	0.997581
0.008	1.000096	0.998978	0.997965	0.997621
0.01	1.000108	0.998979	0.997973	0.997635
0.012	1.000119	0.998981	0.997998	0.997647
0.014	1.000128	0.998995	0.998115	0.997662
0.016	1.000136	0.999010	0.998134	0.997711
0.018	1.000145	0.999021	0.998166	0.997720
0.02	1.000167	0.999044	0.998222	0.997738

(4-2) Apparent Molal Volume

The apparent molal volume (Φ_v ml. mol^{-1}) of all amino acids in this study was calculated from the density data using equation (2-27) that mentioned before:

$$\Phi_v = \frac{1}{m}\left[\frac{1000+mM}{\rho} - \frac{1000}{\rho_0}\right] \qquad \text{………… (2-27)}$$

Where:

m: molal concentration of the solution.

M: molecular weight of the solute.

ρ: the density of solution.

ρ_0: the density of solvent.

The experimental values of the apparent molal volumes (Φ_v) for the amino acids that calculated by using equation (2-27) in the range of studied molalities and temperatures in water and (0.1M HCl) are given in Tables (4-2a, b, c, d, e, f) and (4-2a$^{/}$, b$^{/}$, c$^{/}$, d$^{/}$, e$^{/}$, f$^{/}$) respectively.

The data of these Tables are presented in graphical forms for each amino acid at the temperatures (293.15, 298.15, 303.15and 308.15)K and shown in Figures (4-1-1 a, b, c, d, e, f), (4-1-2 a, b, c, d, e, f), (4-1-3 a, b, c, d, e, f), (4-1-4 a, b, c, d, e, f), (4-1-5 a, b, c, d, e, f), (4-1-6 a, b, c, d, e, f), (4-1-1 a$^{/}$, b$^{/}$, c$^{/}$, d$^{/}$, e$^{/}$, f$^{/}$), (4-1-2 a$^{/}$, b$^{/}$, c$^{/}$, d$^{/}$, e$^{/}$, f$^{/}$), (4-1-3 a$^{/}$, b$^{/}$, c$^{/}$, d$^{/}$, e$^{/}$, f$^{/}$), (4-1-4 a$^{/}$, b$^{/}$, c$^{/}$, d$^{/}$, e$^{/}$, f$^{/}$), (4-1-5 a$^{/}$, b$^{/}$, c$^{/}$, d$^{/}$, e$^{/}$, f$^{/}$), (4-1-6 a$^{/}$, b$^{/}$, c$^{/}$, d$^{/}$, e$^{/}$, f$^{/}$).

Table (4-2a) Apparent Molal Volume (Φ_v ml. mol^{-1}) values for different concentrations of aqueous DL-Valine solution at temperature range from (293.15-308.15) K.

C mol.L^{-1} Solvent H_2O	**293.15K**		**298.15K**	
	m	**Φ_v**	**m**	**Φ_v**
0.04	0.040218	93.590373	0.040248	89.939761
0.06	0.060044	93.076235	0.060479	89.412256
0.08	0.080732	92.447293	0.080800	89.287415
0.1	0.101072	90.859921	0.101204	89.116533
0.12	0.121526	90.223545	0.121642	88.400185
0.14	0.141980	90.104609	0.142175	88.102669
0.16	0.161437	89.224448	0.162791	87.239775
0.18	0.183276	87.782409	0.183478	85.843021
0.2	0.203844	86.025482	0.204240	84.841127

C mol.L^{-1} Solvent H_2O	**303.15K**		**308.15K**	
	m	**Φ_v**	**m**	**Φ_v**
0.04	0.040336	98.016641	0.040405	102.739455
0.06	0.060616	97.683122	0.060714	97.547317
0.08	0.080969	96.733685	0.081099	96.483703
0.1	0.101415	95.999309	0.101578	95.729002
0.12	0.121901	94.785836	0.122094	93.947351
0.14	0.142485	94.114309	0.142678	93.740198
0.16	0.163149	94.033124	0.163407	93.147883
0.18	0.183879	93.612882	0.184163	92.436888
0.2	0.204692	93.413965	0.204985	92.167744

Table (4-2b) Apparent Molal Volume (Φ_v ml. mol^{-1}) values for different concentrations of aqueous DL-Isolucine solution at temperature rang from (293.15-308.15) K.

C mol.L^{-1} Solvent H_2O	293.15K		298.15K	
	m	Φ_v	m	Φ_v
0.06	0.056148	111.161559	0.056181	109.466822
0.08	0.084399	109.899613	0.084516	109.202621
0.11	0.111294	108.996374	0.113101	108.993910
0.14	0.141562	108.801474	0.141751	108.865679
0.17	0.170459	108.703391	0.170696	108.573890
0.19	0.199454	108. 093462	0.199734	108.570682
0.22	0.228577	107.981463	0.228881	108.941791
0.25	0.258131	107.731572	0.258931	106.344370
0.28	0.287579	107.578671	0.287325	106.344370

C mol.L^{-1} Solvent H_2O	303.15K		308.15K	
	m	Φ_v	m	Φ_v
0.06	0.056294	112.249623	0.056378	111.506246
0.08	0.084647	111.069004	0.084788	110.799122
0.11	0.113275	110.535674	0.1133466	110.527939
0.14	0.141981	110.520572	0.1422199	110.510121
0.17	0.171158	110.350172	0.171255	110.298397
0.19	0.200055	110.304806	0.200381	109.974841
0.22	0.229276	110.079456	0.229651	109.960231
0.25	0.258780	109.874482	0.259242	109.899601
0.28	0.288470	109.377239	0.288260	108.133108

Table (4-2c) Apparent Molal Volume (Φ_v ml. mol.$^{-1}$) values for different concentrations of aqueous DL-Methionine solution at temperature range from (293.15-308.15) K.

C mol.L^{-1} Solvent H_2O	293.15K		298.15K	
	m	**Φ_v**	**m**	**Φ_v**
0.04	0.040361	105.871529	0.040282	104.774922
0.06	0.060653	103.421573	0.060548	104.001739
0.08	0.081036	103.114595	0.080901	103.847868
0.1	0.101505	103.848627	0.101551	103.573814
0.12	0.122066	103.876271	0.121860	103.453729
0.14	0.142714	103.763078	0.142475	103.075561
0.16	0.163428	104.209319	0.163186	102.855566
0.18	0.184283	103.749472	0.183968	102.852275
0.2	0.205192	103.391952	0.204831	102.220271
C mol.L^{-1} Solvent H_2O	**303.15K**		**308.15K**	
	m	**Φ_v**	**m**	**Φ_v**
0.04	0.040262	110.969629	0.040415	109.119216
0.06	0.060476	107.837961	0.060749	107.143651
0.08	0.080801	106.304963	0.081171	106.744878
0.1	0.101219	105.566442	0.101390	106.549877
0.12	0.121719	105.531157	0.122254	105.695988
0.14	0.142303	105.439038	0.142952	105.674897
0.16	0.162987	106.684327	0.163724	104.896026
0.18	0.183734	105.568066	0.184560	104.743782
0.2	0.20456	105.359272	0.205487	104.435234

Table (4-2d) Apparent Molal Volume (Φ_v ml. mol.$^{-1}$) values for different concentrations of aqueous DL-Glutamine solution at temperature range from (293.15-308.15) K.

C mol.L^{-1} Solvent H_2O	**293.15K**		**298.15K**	
	m	**Φ_v**	**m**	**Φ_v**
0.002	0.002004	111.370211	0.0020063	108.986424
0.004	0.004008	113.611408	0.004013	109.541427
0.006	0.006014	107.263322	0.006022	110.130299
0.008	0.008021	112.577823	0.008031	110.008063
0.01	0.010028	114.387117	0.010040	110.367751
0.012	0.012037	116.071994	0.012051	111.421531
0.014	0.014047	119.409885	0.014063	112.315804
0.016	0.016058	120.117340	0.016076	113.320669
0.018	0.018069	119.772765	0.018089	113.394895
0.02	0.020082	120.072822	0.020104	114.331443
C mol.L^{-1} Solvent H_2O	**303.15K**		**308.15K**	
	m	**Φ_v**	**m**	**Φ_v**
0.002	0.002011	191.281027	0.002013	120.578642
0.004	0.004020	182.028054	0.004026	118.048468
0.006	0.006033	171.082300	0.006040	112.564668
0.008	0.008046	167.938444	0.008055	112.486816
0.01	0.010058	148.834438	0.010071	111.715043
0.012	0.012073	144.976981	0.012087	110.931230
0.014	0.014089	144.349329	0.014106	110.263277
0.016	0.016105	139.947551	0.016124	108.722111
0.018	0.018124	139.008930	0.018144	108.483897
0.02	0.020141	134.510858	0.020165	107.531132

Table (4-2e) Apparent Molal Volume (Φ_v ml. mol.$^{-1}$) values for different concentrations of aqueous L-Arginine solution at temperature range from (293.15-308.15) K.

C mol.L^{-1} Solvent H_2O	293.15K		298.15K	
	m	Φ_v	m	Φ_v
0.04	0.040281	131.593122	0.040327	129.886315
0.06	0.060581	131.695855	0.060652	130.821820
0.08	0.080987	131.810122	0.081082	130.538895
0.1	0.101508	131.890326	0.101628	131.242620
0.12	0.122131	131.940640	0.122268	130.558399
0.14	0.142875	131.951790	0.143030	130.797247
0.16	0.163723	132.030882	0.163901	130.837247
0.18	0.184692	132.150665	0.184891	131.063217
0.2	0.205764	132.253734	0.205994	131.220101
C mol.L^{-1} Solvent H_2O	303.15K		308.15K	
	m	Φ_v	m	Φ_v
0.04	0.040411	144.712003	0.040453	134.077402
0.06	0.060783	142.329004	0.060839	133.340238
0.08	0.081260	140.423039	0.081351	132.498913
0.1	0.101813	139.481453	0.101957	132.111792
0.12	0.122502	134.778005	0.122600	131.528450
0.14	0.143306	136.487431	0.143467	131.290513
0.16	0.164224	134.340099	0.164432	130.067327
0.18	0.185242	131.790915	0.185197	128.715987
0.2	0.206184	129.930697	0.206643	127.646422

Table (4-2f) Apparent Molal Volume (Φ_v ml. mol.$^{-1}$) for different concentrations of aqueous DL-Histidine solution at temperature range from (293.15-303.15) K.

C mol.L^{-1} Solvent H_2O	293.15K		298.15K	
	m	**Φ_v**	**m**	**Φ_v**
0.002	0.002004	156.791492	0.002007	131.118162
0.004	0.004009	152.224309	0.004014	129.960767
0.006	0.006015	150.061681	0.006022	127.718443
0.008	0.008023	144.182847	0.008031	125.206106
0.01	0.010031	141.361335	0.010045	122.860198
0.012	0.012040	139.844447	0.012053	121.628653
0.014	0.014050	136.679883	0.014065	120.628056
0.016	0.016061	133.751023	0.016078	119.478567
0.018	0.018073	132.971600	0.018092	119.092883
0.02	0.020087	131.012063	0.020108	117.592759
C mol.L^{-1} Solvent H_2O	**303.15K**		**308.15K**	
	m	**Φ_v**	**m**	**Φ_v**
0.002	0.002012	163.881951	0.002013	109.380659
0.004	0.004020	160.494472	0.004025	103.206644
0.006	0.006031	150.751309	0.006038	98.826839
0.008	0.008044	147.874454	0.008253	95.283075
0.01	0.010057	141.293773	0.010069	90.042269
0.012	0.012072	139.856156	0.012085	86.347959
0.014	0.014088	129.819980	0.014103	88.381235
0.016	0.016103	129.770785	0.016122	79.778739
0.018	0.018120	129.297123	0.018141	71.812121
0.02	0.020139	127.616474	0.020159	65.384716

Table (4-2a$^{/}$) Apparent Molal Volume (Φ_v ml. mol.$^{-1}$) for different concentrations of acidic DL-Valine solution at temperature range from (293.15-308.15) K.

C mol.L^{-1} Solvent 0.1M HCl	**293.15K**		**298.15K**	
	m	**Φ_v**	**m**	**Φ_v**
0.04	0.040152	97.282663	0.040192	96.628493
0.06	0.060349	96.467483	0.060410	96.561031
0.08	0.080618	96.147804	0.080706	96.319952
0.1	0.100965	95.823973	0.101076	96.114101
0.12	0.121889	95.800315	0.121522	96.569291
0.14	0.141887	95.363065	0.142041	95.960583
0.16	0.162455	94.797868	0.162666	95.399661
0.18	0.183026	93.890710	0.183372	94.145603
0.2	0.203817	92.155976	0.203932	91.385979

C mol.L^{-1} Solvent 0.1M HCl	**303.15K**		**308.15K**	
	m	**Φ_v**	**m**	**Φ_v**
0.04	0.040266	101.146549	0.040387	110.839450
0.06	0.060517	99.715884	0.060599	102.820814
0.08	0.080850	99.429238	0.080959	101.819520
0.1	0.101256	98.478561	0.101391	100.262319
0.12	0.121739	97.787904	0.121931	101.220584
0.14	0.142292	97.879124	0.142522	100.102773
0.16	0.162917	96.867626	0.163190	100.497670
0.18	0.183663	96.715725	0.183954	99.192050
0.2	0.204521	96.048775	0.204867	99.040369

Table (2-4b$^{/}$) Apparent Molal Volume (Φ_v ml. mol.$^{-1}$) for different concentrations of acidic DL-Isolucine solution at temperature range from (293.15-303.15) K.

C mol.L^{-1} Solvent 0.1M HCl	293.15K		298.15K	
	m	Φ_v	m	Φ_v
0.06	0.056044	117.597752	0.056095	114.623257
0.08	0.084350	116.972610	0.084414	113.117684
0.11	0.112759	112.798149	0.112895	112.121640
0.14	0.141394	112.637382	0.141548	111.184124
0.17	0.170249	112.320638	0.170384	111.092616
0.19	0.199222	111.930647	0.199365	110.790350
0.22	0.228443	111.683158	0.228593	110.440042
0.25	0.257804	111.132605	0.257992	110.547285
0.28	0.287350	111.126711	0.287551	110.341968

C mol.L^{-1} Solvent 0.1M HCl	303.15K		308.15K	
	m	Φ_v	m	Φ_v
0.06	0.056197	119.218558	0.056226	122.571288
0.08	0.084569	117.247475	0.084622	119.687672
0.11	0.112985	116.492001	0.113179	119.634328
0.14	0.141700	112.441965	0.141922	111.414464
0.17	0.170828	112.337920	0.170835	110.198438
0.19	0.199736	112.132614	0.199874	110.194127
0.22	0.229053	111.298557	0.229182	109.979153
0.25	0.258499	106.269529	0.258669	109.842040
0.28	0.288077	105.477094	0.288599	108.809319

Table (4-2c$^{/}$) Apparent Molal Volume (Φ_v ml. mol.$^{-1}$) for different concentrations of acidic DL-Methionine solution at temperature range from (293.15-303.15) K.

C mol.L^{-1} Solvent 0.1M HCl	**293.15K**		**298.15K**	
	m	**Φ_v**	**m**	**Φ_v**
0.04	0.040170	107.103374	0.040213	106.062825
0.06	0.060387	107.548822	0.060456	107.217722
0.08	0.080693	107.414596	0.080789	108.012439
0.1	0.101090	107.848311	0.101211	108.143766
0.12	0.121570	108.043791	0.121717	108.813254
0.14	0.142239	108.099774	0.142420	109.321904
0.16	0.162868	108.917373	0.162929	109.117701
0.18	0.183540	110.411127	0.183762	109.545178
0.2	0.204368	112.029099	0.204625	114.176861

C mol.L^{-1} Solvent 0.1M HCl	**303.15K**		**308.15K**	
	m	**Φ_v**	**m**	**Φ_v**
0.04	0.040289	116.209338	0.040354	126.493936
0.06	0.060572	115.322441	0.060666	121.160090
0.08	0.080946	114.652361	0.08001069	118.664149
0.1	0.101411	114.086764	0.101569	117.556961
0.12	0.121957	113.608668	0.122153	116.193474
0.14	0.121683	112.553873	0.142817	114.650286
0.16	0.163311	110.874101	0.163665	117.073118
0.18	0.184189	112.311795	0.184303	112.668611
0.2	0.205039	110.293950	0.205378	109.379511

Table (4-2d$^{/}$) Apparent Molal Volume (Φ_v ml. mol.$^{-1}$) for different concentrations of acidic DL-Glutamine solution at temperature range from (293.15-303.15) K.

C mol.L^{-1} Solvent 0.1M HCl	293.15K		298.15K	
	m	**Φ_v**	**m**	**Φ_v**
0.002	0.002001	230.843593	0.002003	141.982733
0.004	0.004003	220.270761	0.004006	140.637043
0.006	0.006007	205.751982	0.006011	140.186396
0.008	0.008012	192.410451	0.008017	138.182183
0.01	0.010018	181.421684	0.010024	138.477868
0.012	0.012025	178.112440	0.012032	137.102187
0.014	0.014033	169.764483	0.014041	136.216102
0.016	0.016041	164.364112	0.016052	135.338425
0.018	0.018051	161.120137	0.018064	133.590679
0.02	0.020063	150.582272	0.020077	132.852704

C mol.L^{-1} Solvent 0.1M HCl	303.15K		308.15K	
	m	**Φ_v**	**m**	**Φ_v**
0.002	0.002007	259.401178	0.002010	293.528521
0.004	0.004014	236.437528	0.004020	272.152894
0.006	0.006024	222.692305	0.006032	251.478518
0.008	0.008039	214.103571	0.008045	236.096907
0.01	0.010045	199.662124	0.010059	215.098016
0.012	0.012057	182.082409	0.012075	204.936461
0.014	0.014071	176.280844	0.014089	185.506386
0.016	0.016086	172.072621	0.016103	168.774150
0.018	0.018102	168.672376	0.018121	164.715670
0.02	0.020121	160.494461	0.020141	148.311229

Table (4-2e$^{/}$) Apparent Molal Volume (Φ_v ml. mol.$^{-1}$) for different concentrations of acidic L-Arginine solution at temperature range from (293.15-308.15) K.

C mol.L^{-1} Solvent 0.1M HCl	**293.15K**		**298.15K**	
	m	**Φ_v**	**m**	**Φ_v**
0.04	0.040207	130.714998	0.040253	132.197058
0.06	0.060469	130.256429	0.060537	131.486230
0.08	0.080837	129.649335	0.080929	130.801528
0.1	0.080837	128.696725	0.101414	130.458615
0.12	0.101260	128.154223	0.122007	129.730859
0.14	0.142561	127.384890	0.142725	129.304014
0.16	0.163355	126.308531	0.163547	129.016231
0.18	0.184044	125.019127	0.184600	128.197938
0.2	0.205208	122.380073	0.205425	127.858249
C mol.L^{-1} Solvent 0.1M HCl	**303.15K**		**308.15K**	
	m	**Φ_v**	**m**	**Φ_v**
0.04	0.040324	138.27556	0.040395	151.520014
0.06	0.060649	136.714612	0.060746	146.297865
0.08	0.080108	135.914819	0.081203	144.668794
0.1	0.101602	135.166228	0.101759	142.979899
0.12	0.122235	134.218092	0.122441	140.995047
0.14	0.142992	132.735677	0.143208	138.979604
0.16	0.163863	131.867089	0.164108	135.542702
0.18	0.183863	131.362788	0.185505	133.812917
0.2	0.206220	131.001744	0.206800	133.566379

Table (4-2f$^{/}$) Apparent Molal Volume (Φ_v ml. mol.$^{-1}$) for different concentrations of acidic DL-Histidine solution at temperature range from (293.15-303.15) K.

C mol.L^{-1} Solvent 0.1M HCl	293.15K		298.15K	
	m	Φ_v	m	Φ_v
0.002	0.002000	123.419881	0.002003	120.027211
0.004	0.004001	121.891459	0.004006	119.372519
0.006	0.006004	120.416441	0.006010	118.097130
0.008	0.008007	119.989909	0.008010	117.924082
0.01	0.010011	118.769120	0.010022	116.933613
0.012	0.012017	117.230930	0.012029	116.854655
0.014	0.014022	116.147029	0.0140371	115.942392
0.016	0.016030	114.702912	0.016046	115.090777
0.018	0.018038	114.366851	0.0180057	114.775945
0.02	0.020047	112.044629	0.020067	113.867679

C mol.L^{-1} Solvent 0.1M HCl	303.15K		308.15K	
	m	Φ_v	m	Φ_v
0.002	0.002007	228.919943	0.002006	219.229113
0.004	0.004015	220.905743	0.004019	212.408860
0.006	0.006024	214.047363	0.006031	202.738836
0.008	0.008034	209.111881	0.008043	196.375025
0.01	0.010045	194.551956	0.010056	183.780479
0.012	0.014072	189.995630	0.012070	172.889056
0.014	0.014072	180.366928	0.014085	167.412267
0.016	0.016086	173.788881	0.016101	162.153075
0.018	0.018101	167.273970	0.018119	156.910927
0.02	0.20118	164.350290	0.020137	153.17767

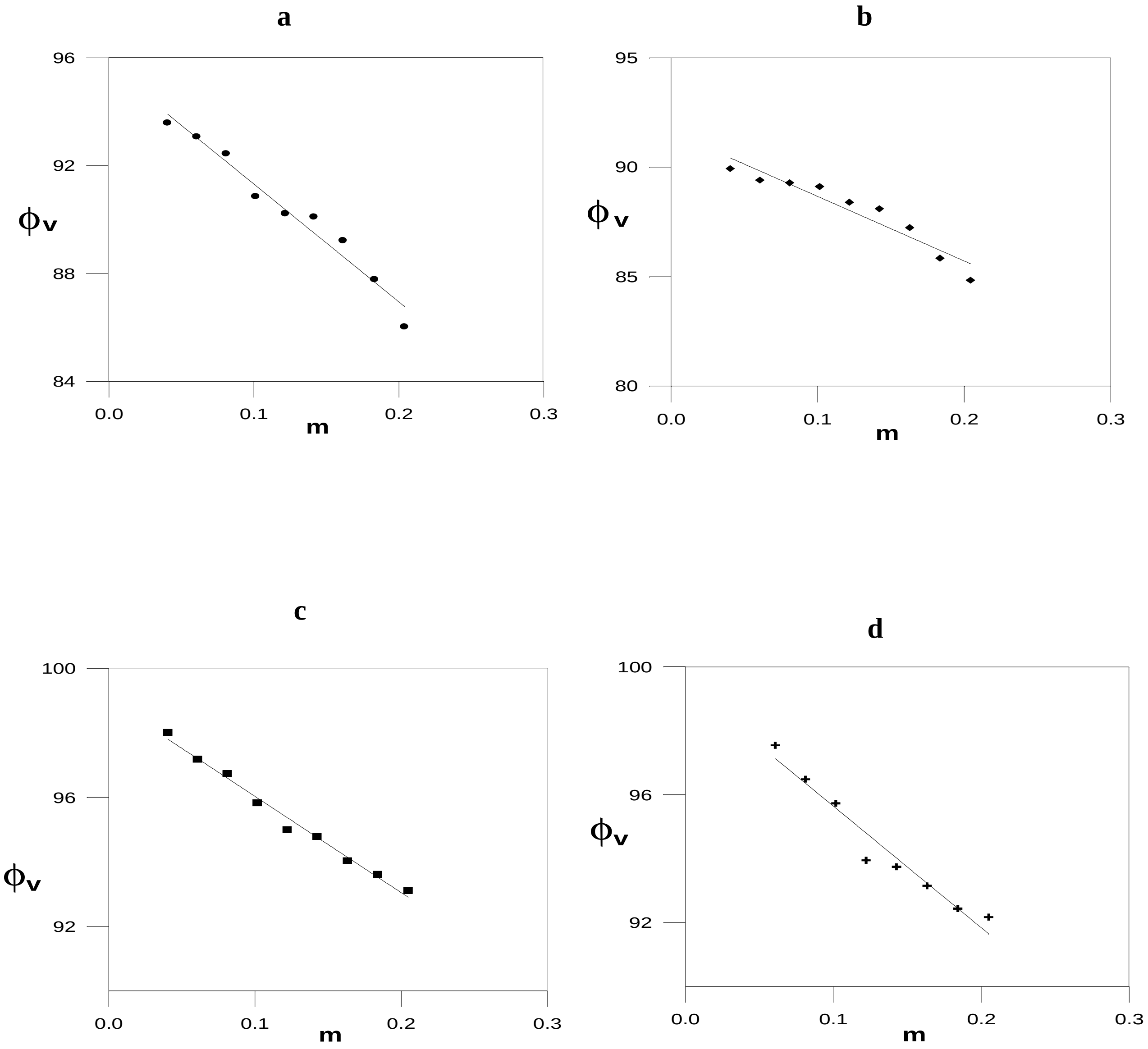


Figure (4-1-1) Limited Apparent Molal Volume (Φ_v^0) for Aqueous Amino Acid DL-Valine Solution at different Temperatures
a) 293.15K b) 298.15K c) 303.15K d) 308.15K

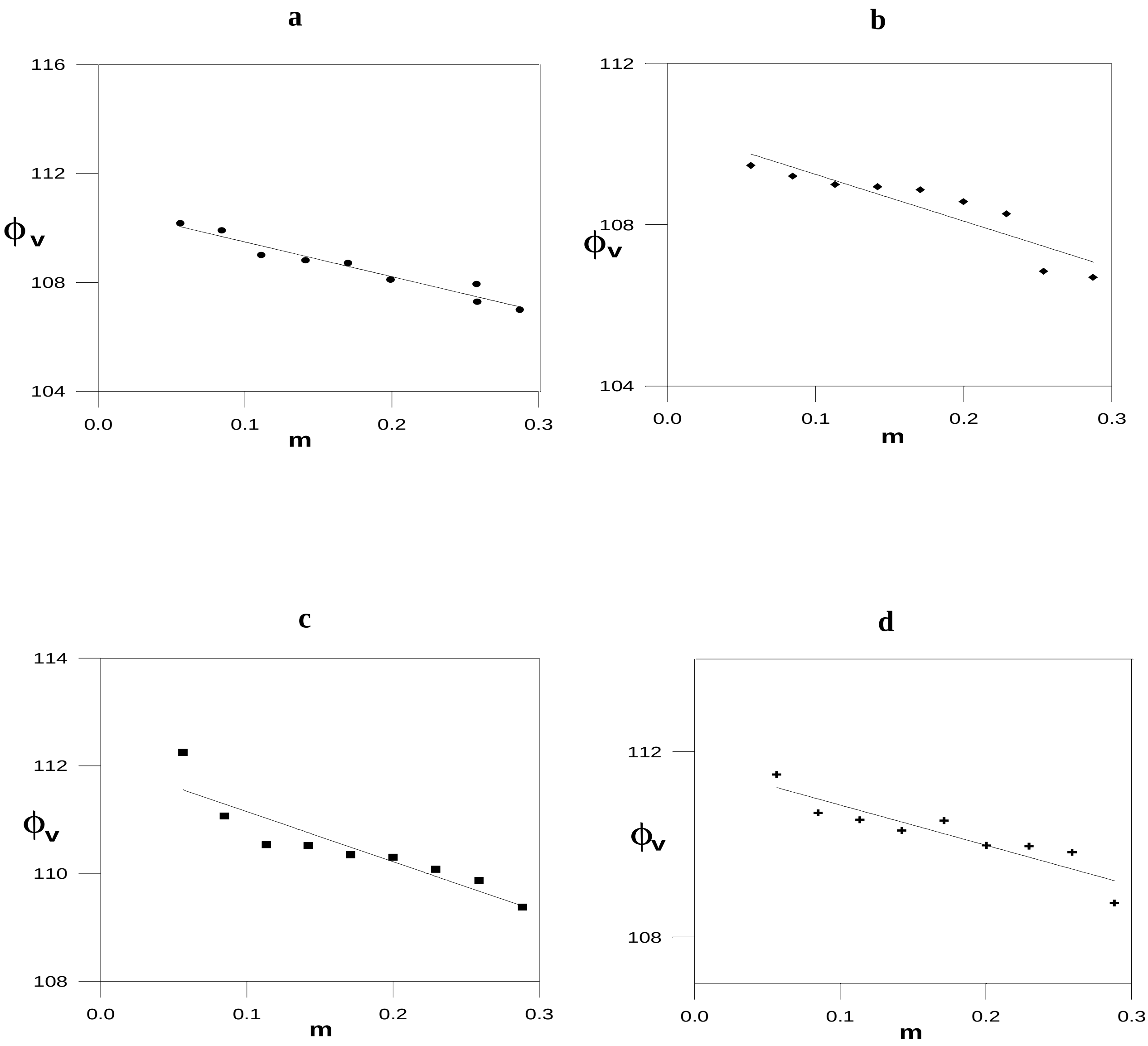


Figure (4-1-2) Limited Apparent Molal Volume (Φ_v^0) for Aqueous Amino Acid DL-Isolucine Solution at different Temperatures
a) 293.15K b) 298.15K c) 303.15K d) 308.15K

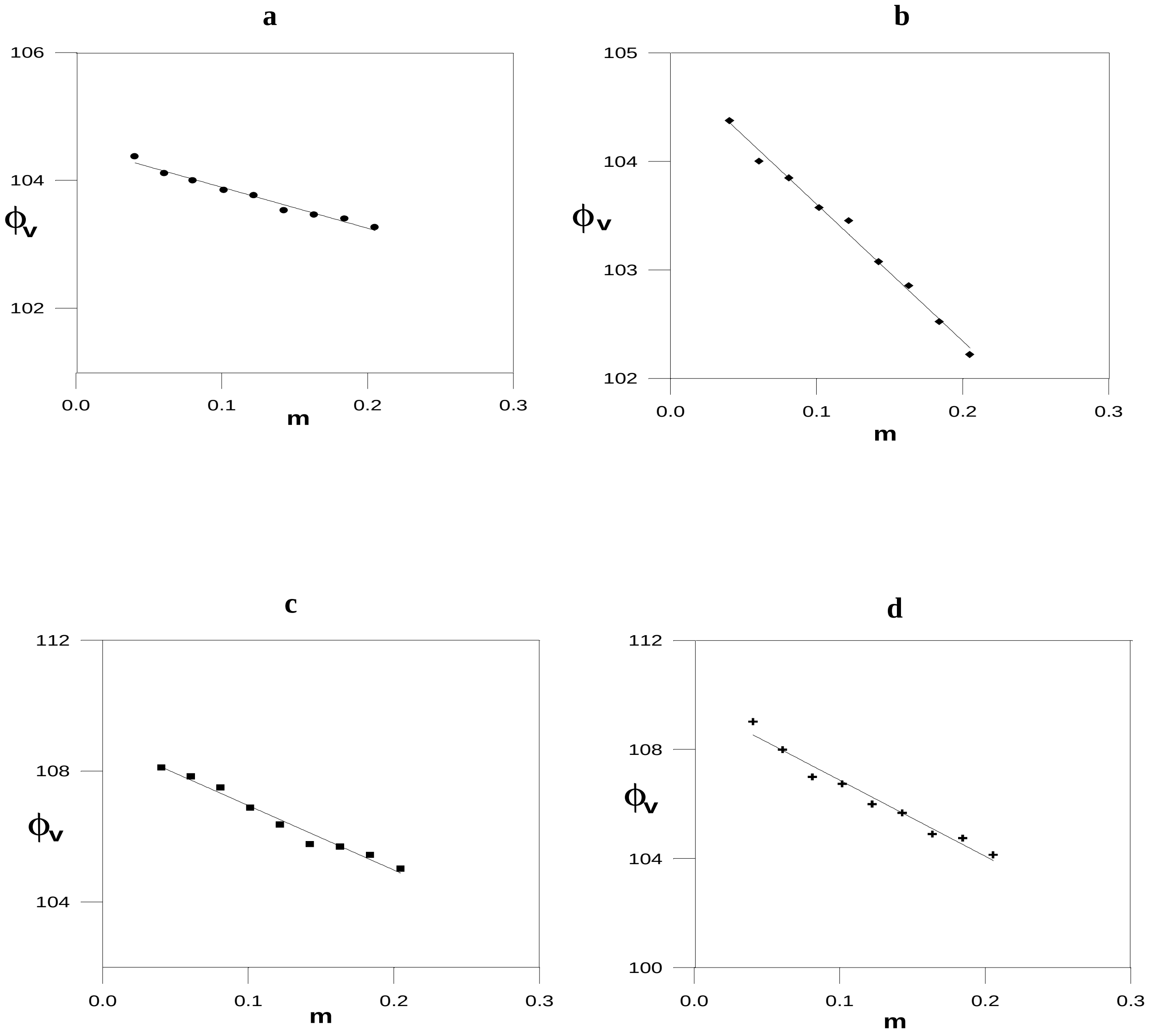


Figure (4-1-3) Limited Apparent Molal Volume (Φ_v^0) for Aqueous Amino Acid DL-Methionine Solution at differentTemperatures
a) 293.15K b) 298.15K c) 303.15K d) 308.15K

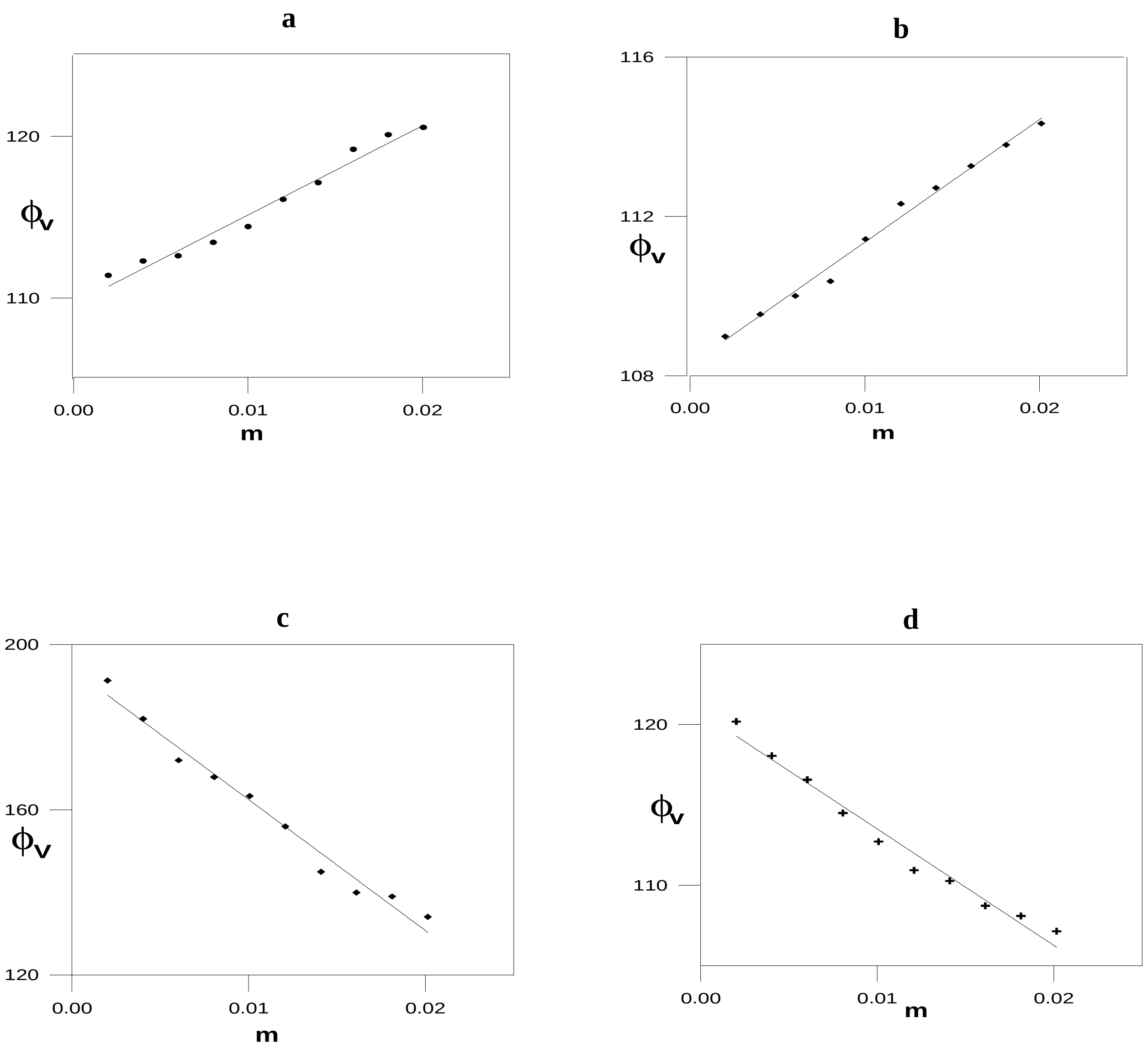


Figure (4-1-4) Limited Apparent Molal Volume (Φ_v^0) for Aqueous Amino Acid DL-Glutamine Solution at different temperatures
a) 293.15K b) 298.15K c) 303.15K d) 308.15K

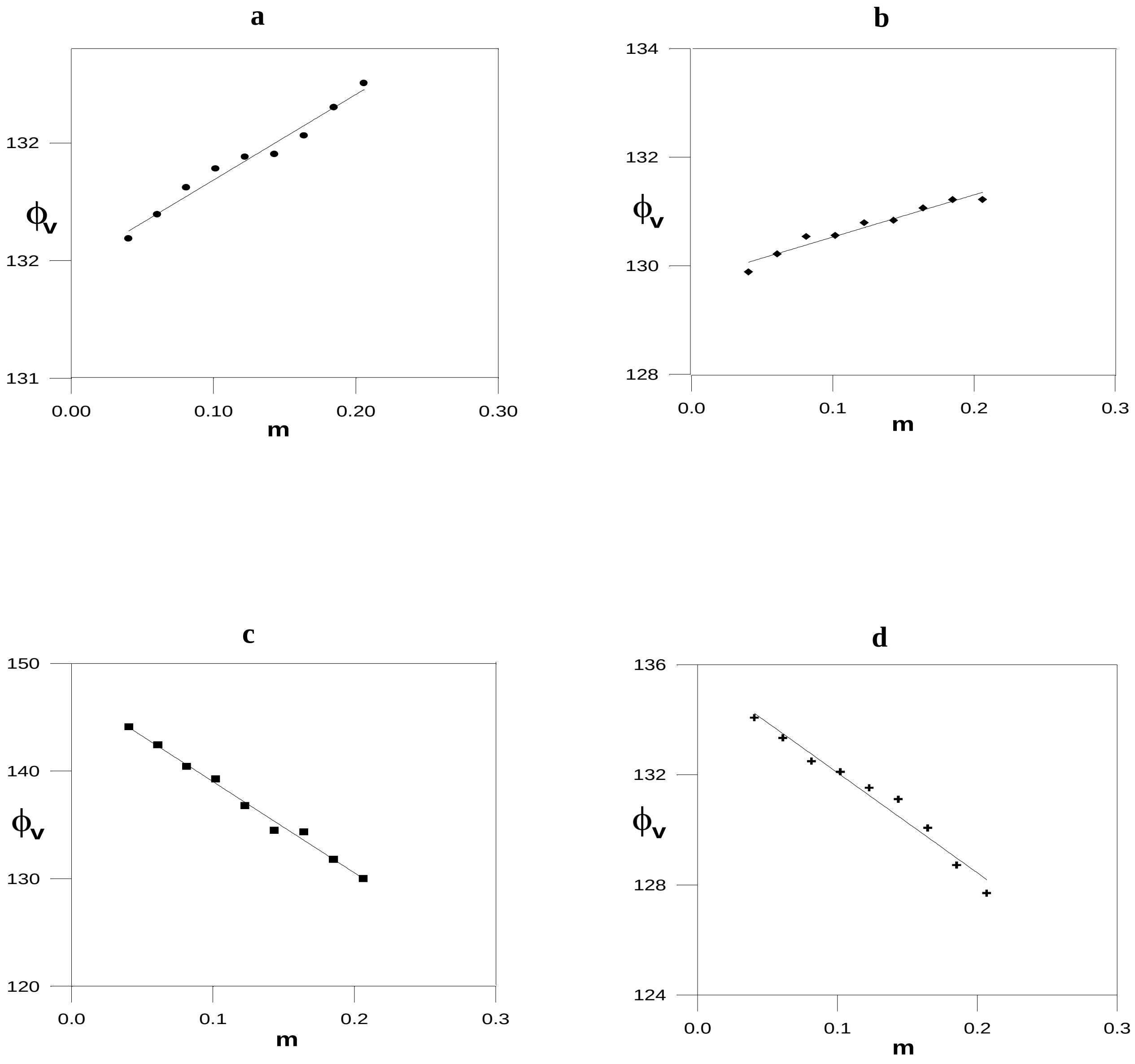


Figure (4-1-5) Limited Apparent Molal Volume (Φ_v^0) for Aqueous Amino Acid L-Arginine Solution at different Temperatures a) 293.15K b) 298.15K c) 303.15K d) 308.15K

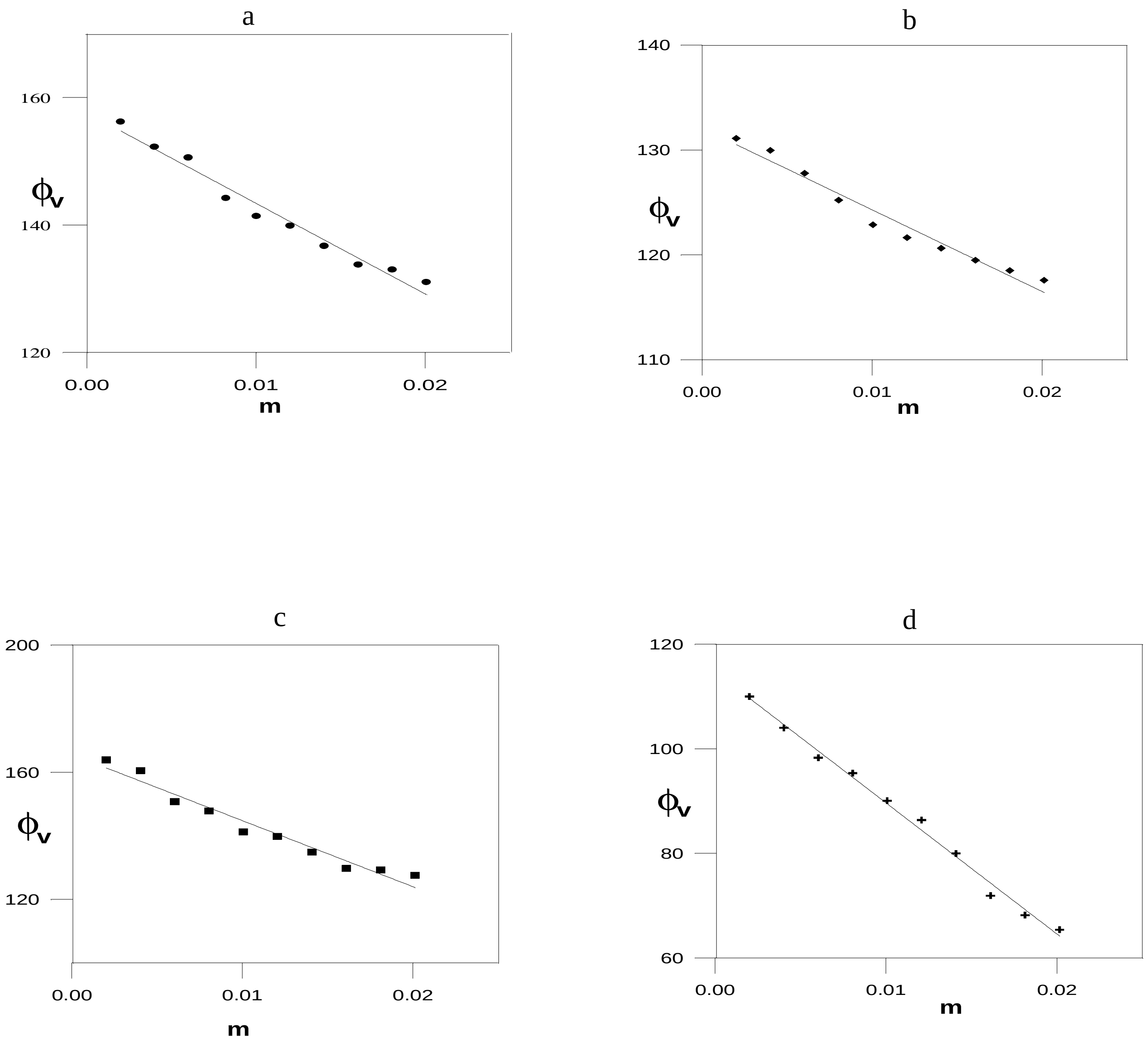


Figure (4-1-6) Limited Apparent Molal Volume (Φ_v^0) for Aqueous Amino Acid DL-Histidine Solution at different Temperatures
a) 293.15K b) 298.15K c) 303.15K d) 308.15K

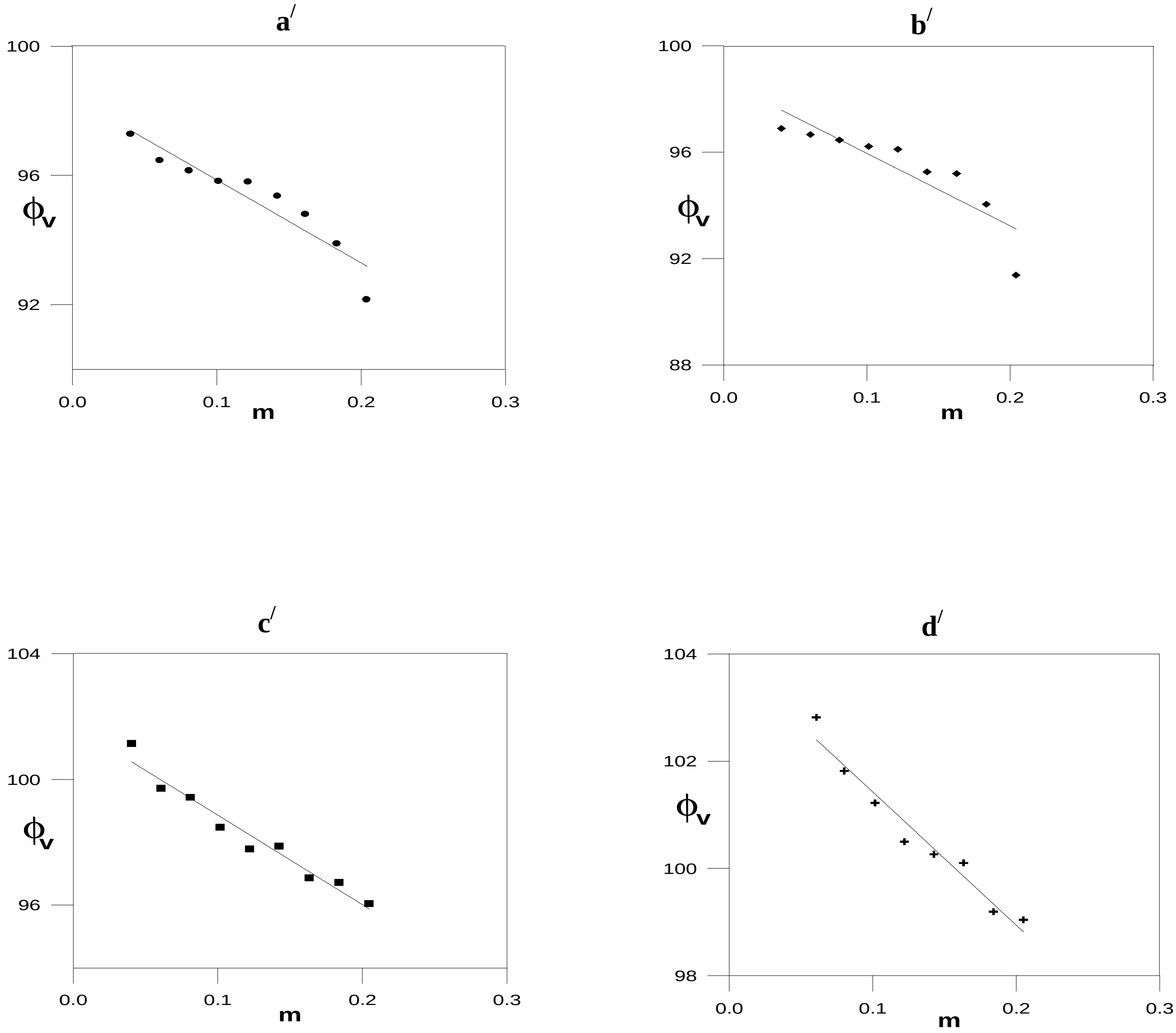


Figure (4-1-1) Limited Apparent Molal Volume (Φ_v^0) for Acidic Amino Acid DL-Valine Solution at different Temperatures
$a^{/}$) 293.15K $b^{/}$) 298.15K $c^{/}$) 303.15K $d^{/}$) 308.15K

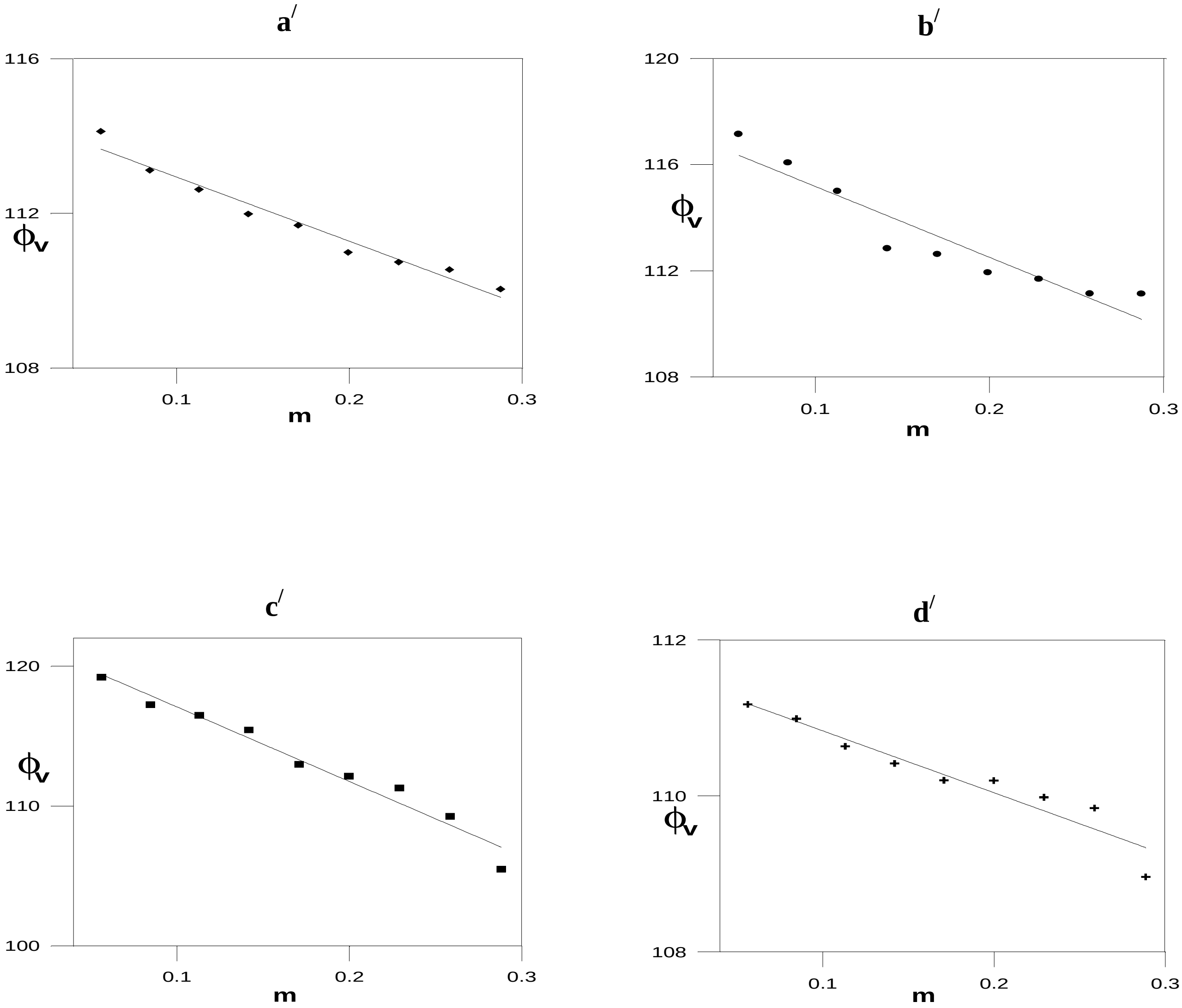


Figure (4-1-2) Limited Apparent Molal Volume (Φ_v^0) for Acidic Amino Acid DL-Isolucine Solution at different Temperatures
a) 293.15K b) 298.15K c) 303.15K d) 308.15K

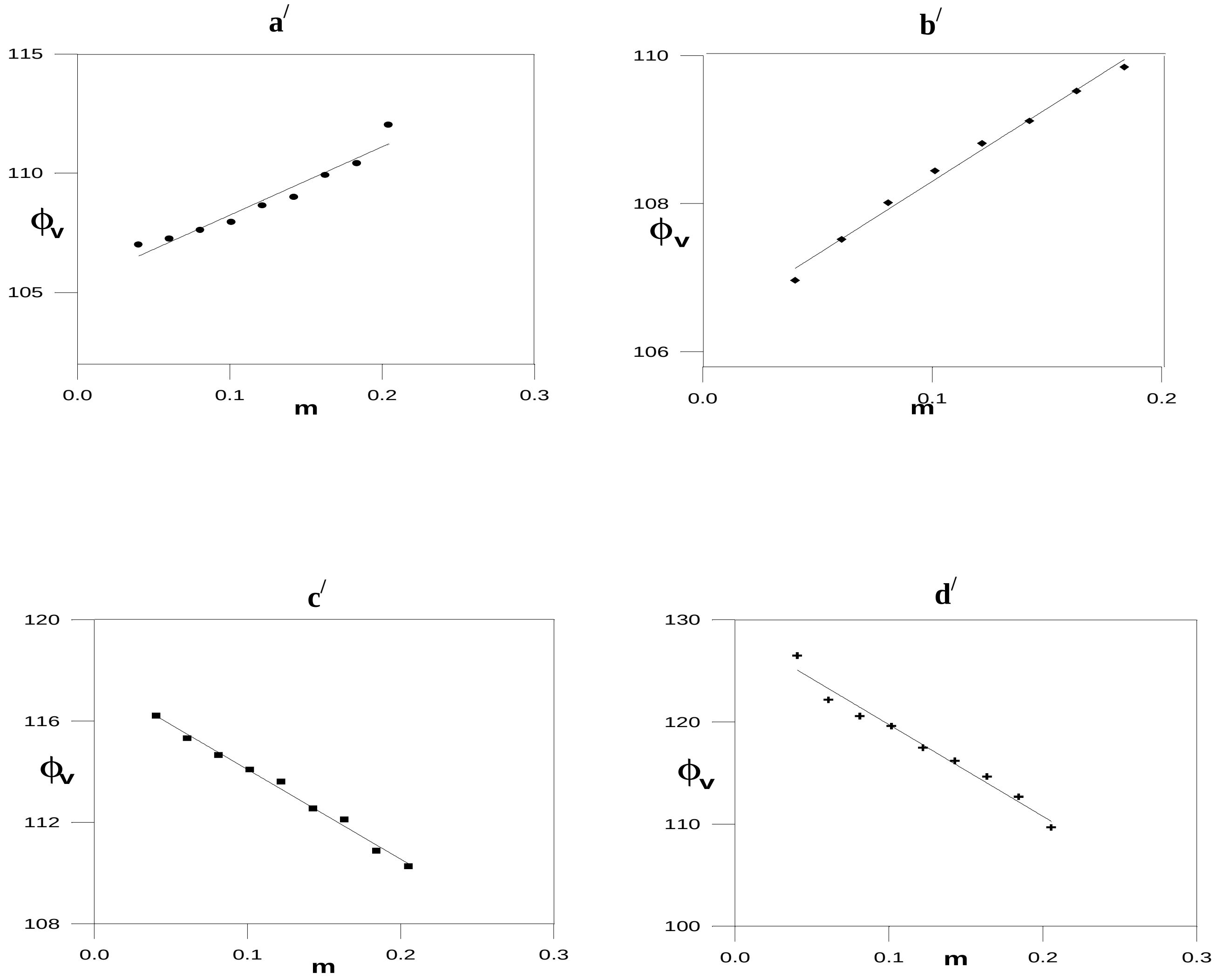


Figure (4-1-3) Limited Apparent Molal Volume (Φ_v^0) for Acidic Amino Acid DL-Methionine Solution at different Temperatures a) 293.15K b) 298.15K c) 303.15K d) 308.15K

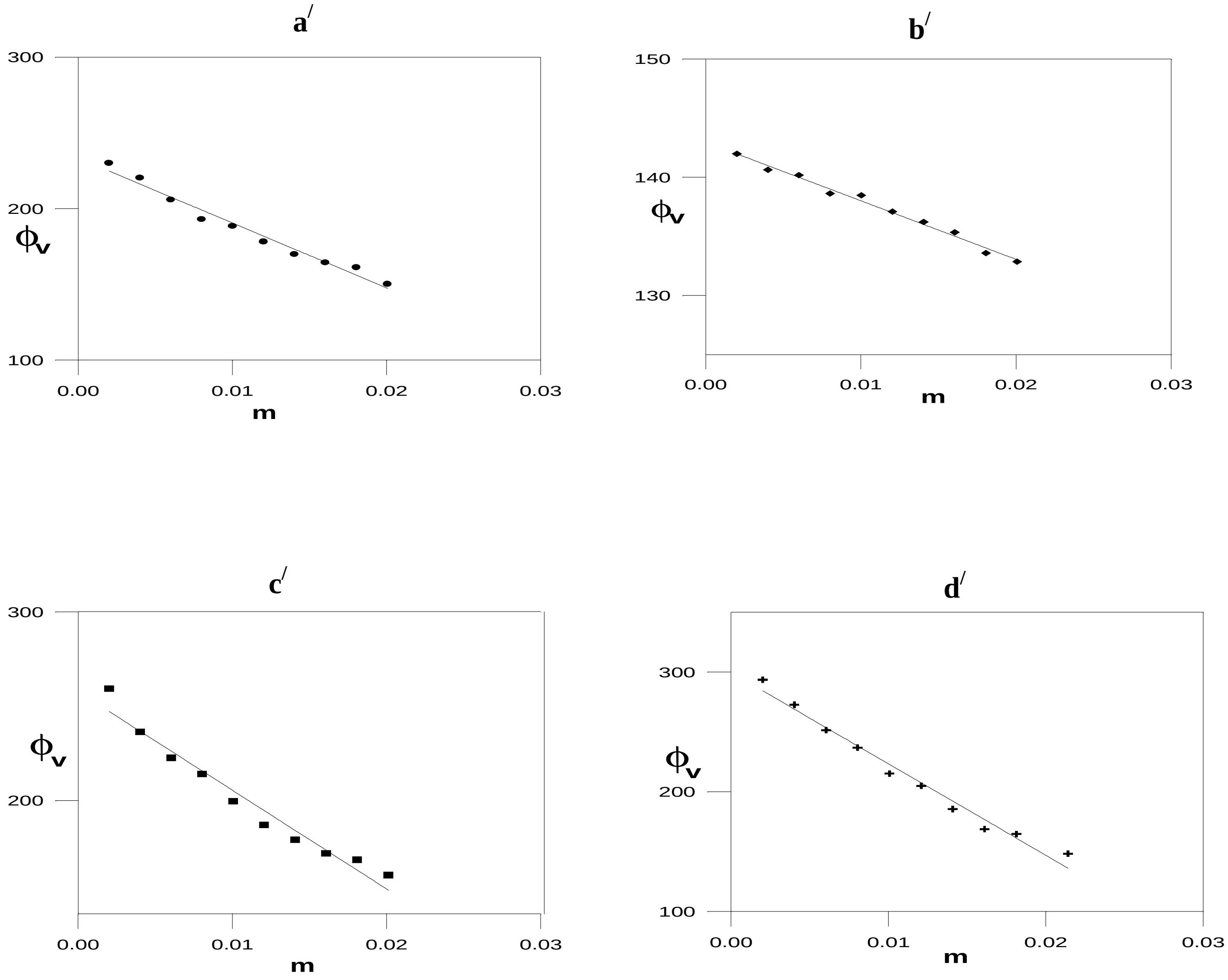


Figure (4-1-4) Limited Apparent Molal Volume (Φ_v^0) for Acidic Amino Acid DL-Glutamine Solution at different Temperatures $a^{/}$) 293.15K $b^{/}$) 298.15K $c^{/}$) 303.15K $d^{/}$) 308.15K

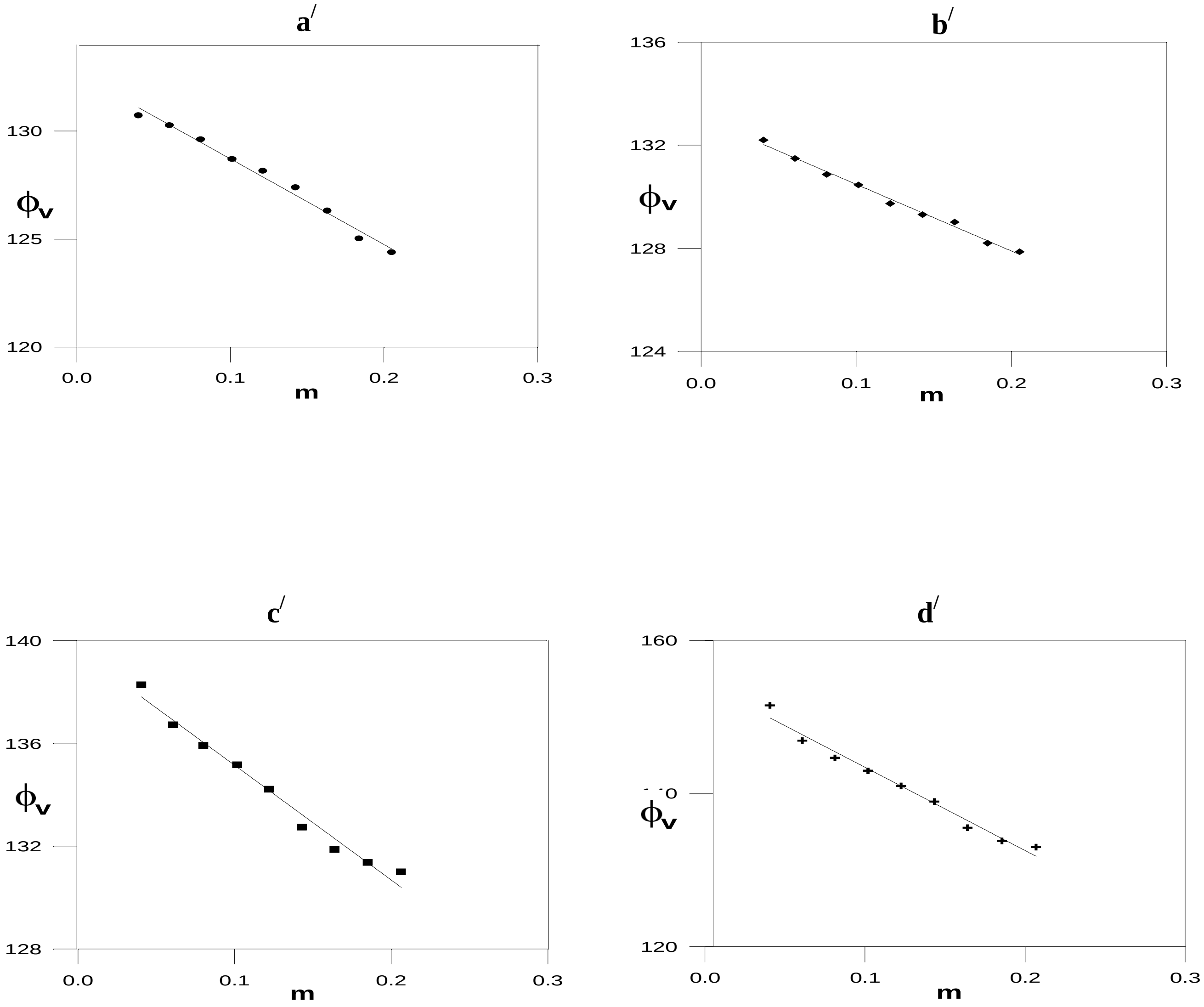


Figure (4-1-5) Limited Apparent Molal Volume (Φ_v^0) for Acidic Amino Acid L- Arginine Solution at different Temperatures
$a^{/}$) 293.15K $b^{/}$) 298.15K $c^{/}$) 303.15K $d^{/}$) 308.15K

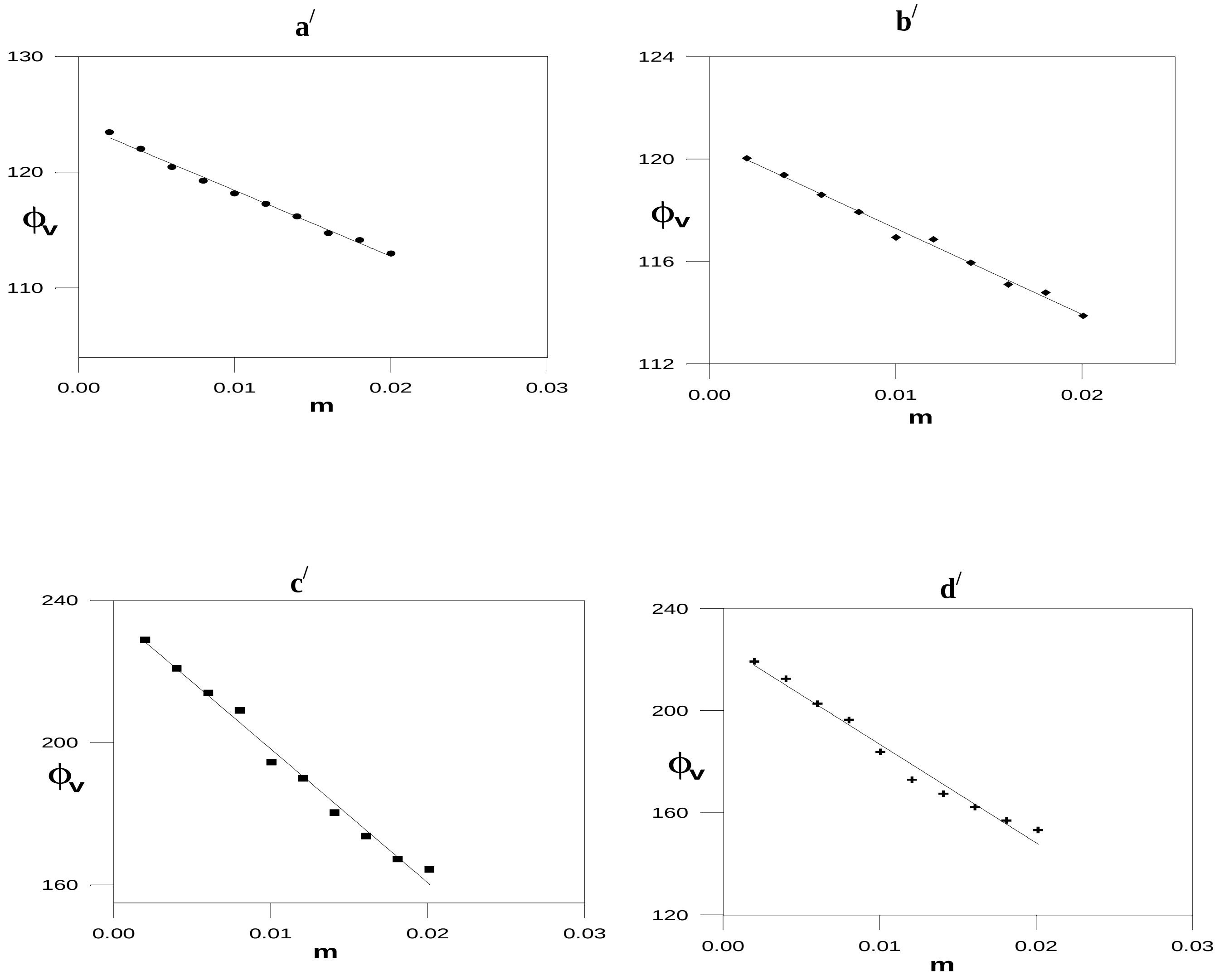


Figure (4-1-6) Limited Apparent Molal Volume (Φ_v^0) for Acidic Amino Acid DL-Histidine Solution at different Temperatures
a) 293.15K b) 298.15K c) 303.15K d) 308.15K

Limiting partial molal volume (Φ_v^0) for the amino acids solutions studied here were obtained [using equation (2-28)] by extrapolating the plot (Φ_v) versus the molal concentration (m), to zero concentration at each temperature of study. The obtained data are presented in Tables (4-3a and 4-3b).

Table (4-3a) Limited Apparent Molal Volume (Φ_v^0) for Aqueous Amino Acid Solutions at Four Temperature (293.15, 298.15, 303.15, and 308.15) K.

Amino acid	**Φ_v^0 cm^3 .mol^{-1}**			
	293.15K	**298.15K**	**303.15K**	**308.15K**
DL-Valine	95.671	92.078	100.331	101.529
DL-Isolucine	111.976	110.409	111.769	113.530
DL-Methionine	105.688	104.671	109.493	108.926
DL-Glutamine	108.542	106..555	189.031	117.692
L-Arginine	131.479	129.751	135.728	149.164
DL-Histidine	165.250	130.476	165.831	166.787

Table (4-3b) Limited Apparent Molal Volume (Φ_v^0) for Acidic Amino Acid Solutions at Four Temperature (29315, 298.15, 303.15, and 308.15) K.

Amino acid	**Φ_v^0 cm^3 .mol^{-1}**			
	293.15K	**298.15K**	**303.15K**	**308.15K**
DL-Valine	98.031	92.777	101.708	107.475
DL-Isolucine	116.551	114.392	122.175	123.91
DL-Methionine	105.475	105.066	117.464	127.231
DL-Glutamine	243.272	143.559	265.004	306.869
L-Arginine	132.215	130.895	139.613	153.879
DL-Histidine	124.409	121.307	224.236	201.722

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(81).

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 limited apparent molal volume values that are listed in tables (4-3a, b) were found to have a lower value at 298.15K. 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, then after that it increases when increasing temperature.

(4-3) Viscosity

Experimental data on viscosity measurements of the all amino acids solutions studied here in water and (0.1M HCl) solution are presented in Tables (4-4 a, b, c, d, e, f) and (4-4 $a^/$, $b^/$, $c^/$, $d^/$, $e^/$, $f^/$) and by using the following relationship(57, 59):

$$\frac{\eta}{\eta_0} = \frac{t\rho}{t_0\rho_0} \qquad \text{………… (2-4)}$$

where η, t and ρ represent the viscosity, flow time and density of the amino acid solution, and η_0, t_0 and ρ_0 represent the viscosity of the solvent [water or 0.1M HCl] and its flow time and density respectively.

Available data in Tables (4-4 a, b, c, d, e, f) and (4-4 $a^/$, $b^/$, $c^/$, $d^/$, $e^/$, $f^/$) 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(57).

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. (82)

Table (4-4a) Measured absolute viscosity (η) values for aqueous amino acid DL-Valine solution over concentration (C) ranging from (0.04-0.2 mol L^{-1}) at four temperatures in range (293.15-308.15) K.

C Mol.L^{-1}	η(cP)			
	293.15K	**298.15K**	**303.15K**	**308.15K**
Solvent H_2O	1.0027	0.8904	0.7975	0.7194
0.04	1.057812	0.953750	0.848672	0.750817
0.06	1.065017	0.957903	0.857680	0.757214
0.08	1.069297	0.963316	0.864512	0.762204
0.1	1.075199	0.968143	0.867809	0.770510
0.12	1.079572	0.974450	0.872628	0.774979
0.14	1.084620	0.977831	0.878068	0.779997
0.16	1.088270	0.981979	0.883449	0.783092
0.18	1.094443	0.986852	0.889708	0.787548
0.2	1.099193	0.990922	0.892317	0.793286

Table (4-4b) Measured absolute viscosity (η) values for aqueous amino acid DL-Isolucine solution over concentration (C) ranging from (0.06-0.28 mol L^{-1}) at four temperatures in range (293.15-308.15) K.

C Mol.L^{-1}	η(cP)			
	293.15K	**298.15K**	**303.15K**	**308.15K**
Solvent H_2O	1.0027	0.8904	0.7975	0.7194
0.06	1.03206	0.939463	0.852699	0.785225
0.08	1.039755	0.946073	0.859853	0.790500
0.11	1.044144	0.950427	0.868449	0.796513
0.14	1.051105	0.956879	0.874764	0.802517
0.17	1.057214	0.962532	0.878029	0.809297
0.19	1.063328	0.970522	0.882034	0.813911
0.22	1.068496	0.977759	0.887611	0.817755
0.25	1.071319	0.988827	0.893209	0.824656
0.28	1.077939	0.994461	0.898900	0.831674

Table (4-4c) Measured absolute viscosity (η) values for aqueous amino acid DL- Methionine solution over concentration (C) ranging from (0.04-0.2mol L^{-1}) at four temperatures in range (293.15-308.15) K.

C Mol.L^{-1}	η(cP)			
	293.15K	298.15K	303.15K	308.15K
Solvent H_2O	1.0027	0.8904	0.7975	0.7194
0.04	1.075645	0.940472	0.820597	0.771903
0.06	1.081089	0.948475	0.826228	0.776735
0.08	1.087300	0.955026	0.832370	0.782910
0.1	1.091194	0.963038	0.835831	0.791150
0.12	1.096639	0.969588	0.847958	0.794067
0.14	1.100625	0.975462	0.852739	0.800865
0.16	1.106757	0.987762	0.855471	0.805012
0.18	1.114547	0.996508	0.859597	0.815480
0.2	1.118620	0.995622	0.866438	0.820422

Table (4-4d) Measured absolute viscosity (η) values for aqueous amino acid DL-Glutamine solution over concentration (C) ranging from (0.002-0.02mol L^{-1}) at four temperatures in range (293.15-308.15) K.

C Mol.L^{-1}	η(cP)			
	293.15K	298.15K	303.15K	308.15K
Solvent H_2O	1.0027	0.8904	0.7975	0.7194
0.002	1.044866	0.906289	0.837249	0.749949
0.004	1.053543	0.909538	0.8611075	0.765274
0.006	1.067351	0.917523	0.867337	0.767007
0.008	1.073423	0.921576	0.884171	0.770313
0.01	1.076964	0.927340	0.887815	0.772823
0.012	1.083055	0.931248	0.895854	0.776942
0.014	1.092535	0.937662	0.901217	0.788548
0.016	1.102902	0.943286	0.903986	0.791620
0.018	1.109015	0.945755	0.918204	0.804576
0.02	1.113405	0.949684	0.928076	0.807108

Table (4-4e) Measured absolute viscosity (η) values for aqueous amino acid L-Arginine solution over concentration (C) ranging from (0.04-0.2mol L^{-1}) at four temperatures in range (293.15-308.15) K.

C Mol.L^{-1}	η(cP)			
	293.15K	**298.15K**	**303.15K**	**308.15K**
Solvent H_2O	1.0027	0.8904	0.7975	0.7194
0.04	1.073486	0.992096	0.832900	0.745023
0.06	1.084048	1.001870	0.836357	0.754753
0.08	1.090595	1.007932	0.42720	0.762430
0.1	1.095547	1.012535	0.847247	0.767309
0.12	1.098892	1.015623	0.850811	0.772897
0.14	1.105470	1.021729	0.856467	0.785515
0.16	1.113670	1.029285	0.862314	0.799614
0.18	1.122732	1.037608	0.880633	0.802842
0.2	1.126925	1.041485	0.885041	0.812760

Table (4-4f) Measured absolute viscosity (η) values for aqueous amino acid DL-Histidine solution over concentration (C) ranging from (0.002-0.02mol L^{-1}) at four temperatures in range (293.15-308.15) K.

C Mol.L^{-1}	η(cP)			
	293.15K	**298.15K**	**303.15K**	**308.15K**
Solvent H_2O	1.0027	0.8904	0.7975	0.7194
0.002	1.049051	0.922420	0.815567	0.748442
0.004	1.06116	0.929277	0.820045	0.756876
0.006	1.074941	0.938416	0.830569	0.763784
0.008	1.079945	0.940719	0.853220	0.767619
0.01	1.082203	0.946063	0.858495	0.771522
0.012	1.084663	0.949874	0.860760	0.779244
0.014	1.087877	0.952923	0.863727	0.787024
0.016	1.091918	0.961309	0.867566	0.802470
0.018	1.093535	0.964375	0.872083	0.815738
0.02	1.096781	0.973534	0.887175	0.827350

Table (4-4a/) Measured absolute viscosity (η) values for acidic amino acid DL-Valine solution over concentration (C) ranging from (0.04-0.2 mol L^{-1}) at four temperatures in range (293.15-308.15) K.

C $Mol.L^{-1}$	η(cP)			
	293.15K	**298.15K**	**303.15K**	**308.15K**
Solvent (0.1M) HCl	1.0027	0.8904	0.7975	0.7194
0.04	1.092063	0.977607	0.893178	0.810927
0.06	1.100665	0.985993	0.904795	0.818894
0.08	1.105184	1.001636	0.912371	0.827501
0.1	1.112156	1.007651	0.920828	0.832798
0.12	1.128954	1.012897	0.926885	0.838652
0.14	1.135148	1.022180	0.929675	0.845082
0.16	1.151127	1.028218	0.933386	0.855371
0.18	1.154817	1.035858	0.941053	0.863294
0.2	1.160840	1.041912	0.943980	0.875286

Table (4-4b/) Measured absolute viscosity (η) values for acidic amino acid DL-Isolucine solution over concentration (C) ranging from (0.06-0.28 mol L^{-1}) at four temperatures in range (293.15-308.15) K.

C $Mol.L^{-1}$	η(cP)			
	293.15K	**298.15K**	**303.15K**	**308.15K**
Solvent (0.1M) HCl	0.916741	0.822335	0.734194	0.643628
0.06	1.108123	0.969382	0.913725	0.815899
0.08	1.121391	0.990775	0.925349	0.828469
0.11	1.132878	1.001654	0.936142	0.838459
0.14	1.149337	1.012602	0.948257	0.848491
0.17	1.158372	1.022666	0.959998	0.858554
0.19	1.168328	1.036064	0.980042	0.879384
0.22	1.178415	1.045409	0.987865	0.896155
0.25	1.211260	1.066207	0.997628	0.904647
0.28	1.219532	1.078037	1.022312	0.915319

Table (4-4c$^{/}$) Measured absolute viscosity (η) values for acidic amino acid DL- Methionine solution over concentration (C) ranging from (0.04-0.2mol L^{-1}) at four temperatures in range (293.15-308.15) K.

C Mol.L^{-1}	**η(cP)**			
	293.15K	**298.15K**	**303.15K**	**308.15K**
Solvent (0.1M) HCl	0.916741	0.822335	0.734194	0.643628
0.04	1.092932	0.984605	0.874636	0.805211
0.06	1.100616	0.987885	0.880106	0.815741
0.08	1.104899	0.993707	0.888828	0.819671
0.1	1.111739	1.001127	0.896768	0.826879
0.12	1.121076	1.009437	0.899879	0.830764
0.14	1.127090	1.013512	0.908752	0.835543
0.16	1.133040	1.016777	0.915122	0.841277
0.18	1.148843	1.024238	0.920902	0.848789
0.2	1.161078	1.032530	0.925776	0.859080

Table (4-4d$^{/}$) Measured absolute viscosity (η) values for acidic amino acid DL-Glutamine solution over concentration (C) ranging from (0.002-0.02mol L^{-1}) at four temperatures in range (293.15-308.15) K.

C Mol.L^{-1}	**η(cP)**			
	293.15K	**298.15K**	**303.15K**	**308.15K**
solvent (0.1M) HCl	0.916741	0.822335	0.734194	0.643628
0.002	1.066512	0.950285	0.871996	0.800398
0.004	1.072024	0.957371	0.882765	0.809213
0.006	1.085123	0.960947	0.887302	0.818084
0.008	1.094352	0.964537	0.892781	0.822648
0.01	1.100926	0.973385	0.902809	0.831702
0.012	1.111565	0.976103	0.905590	0.836228
0.014	1.114060	0.981456	0.910179	0.847186
0.016	1.119733	0.987682	0.912048	0.850090
0.018	1.129079	0.994822	0.914826	0.855555
0.02	1.141247	1.010826	0.919424	0.860998

Table (4-4e$^{/}$) Measured absolute viscosity (η) values for acidic amino acid L-Arginine solution over concentration (C) ranging from (0.04-0.2mol L^{-1}) at four temperatures in range (293.15-308.15) K.

C Mol.L^{-1}	η(cP)			
	293.15K	**298.15K**	**303.15K**	**308.15K**
solvent (0.1M) HCl	0.916741	0.822335	0.734194	0.643628
0.04	1.083079	0.982689	0.890607	0.813625
0.06	1.090109	0.989604	0.899802	0.814275
0.08	1.094545	0.993947	0.906438	0.826540
0.1	1.103474	1.000843	0.911441	0.835549
0.12	1.114912	1.007877	0.916540	0.841507
0.14	1.123890	1.015730	0.925191	0.850014
0.16	1.132897	1.022701	0.929459	0.856609
0.18	1.142227	1.027177	0.937954	0.860920
0.2	1.156931	1.032764	0.947307	0.865035

Table (4-4f$^{/}$) Measured absolute viscosity (η) values for acidic amino acid DL-Histidine solution over concentration (C) ranging from (0.002-0.02mol L^{-1}) at four temperatures in range (293.15-308.15) K.

C Mol.L^{-1}	η(cP)			
	293.15K	**298.15K**	**303.15K**	**308.15K**
solvent (0.1M) HCl	0.916741	0.822335	0.734194	0.643628
0.002	1.107297	0.967695	0.906019	0.770936
0.004	1.112924	0.971278	0.911310	0.778497
0.006	1.120420	0.974840	0.915696	0.780933
0.008	1.131667	0.978402	0.919177	0.783401
0.01	1.134476	0.981964	0.925541	0.787650
0.012	1.139206	0.987306	0.934558	0.792774
0.014	1.142960	0.995334	0.944568	0.801290
0.016	1.154241	1.004253	0.952075	0.807257
0.018	1.159879	1.008714	0.957305	0.823492
0.02	1.168542	1.021202	0.973661	0.829468

(4-4) Application of Jones and Dole Equation

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 and from (0.06- 0.28 mol.L.$^{-1}$) for Isolucine and from (0.002-0.02 mol.L.$^{-1}$) for Glutamine and Histidine due to limited solubility for them at four different temperatures in the range from (293.15-308.15)K.

The obtained data (Jones-Dole terms) are presented in Tables (4-5 a, b, c, d, e, f) and (4-5 a$^{/}$, b$^{/}$, c$^{/}$, d, e$^{/}$, f$^{/}$).

In Figures (4-2a and a$^{/}$) we display the variation of $(\eta_r\text{-}1)/\sqrt{C}$ against $\sqrt{C}$ for the amino acids solutions in this study at 298.15K according to Jones and Dole equation of the form $^{(54)}$:

$$(\eta_r - 1)/\sqrt{c} = A + B\sqrt{c} \qquad \text{...........} \; (2\text{-}30)$$

Where:

η_r: The relative viscosity

η: The measured viscosity of the amino acid solution.

$\eta_{0:}$ 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.

C: Molar concentration (mol.L.$^{-1}$).

By plotting the left hand term of equation (2-30) as a function of $\sqrt{C}$, a straight line is obtained with a slope B and an intercept A on the ordinate.

Equation (2-30), though applied successively on behaviour of strong and weak electrolytes, may also describe the viscous behaviour of a number of non electrolytic solution. (54, 57)

The extent of the interaction between the amino acid particles and solvent molecules was investigated through the estimation of B-coefficients, Tables (4-6 a, b) represent B-coefficient values for Jones and Dole equation in water and 0.1M HCl solution.

Table (4-5a) Values of $\eta_r - 1/\sqrt{C}$ and $\sqrt{C}$ for the aqueous amino acid DL-Valine solution in the concentration range from (0.04-0.2 mol.L.$^{-1}$) at four different temperatures in the range of from (293.15-308.15)K.

C Mol.L^{-1}	$\sqrt{C}$	η_r-1/$\sqrt{C}$			
		293.15K	**298.15K**	**303.15K**	**308.15K**
0.04	0.200000	0.253030	0.322664	0.312431	0.233924
0.06	0.244949	0.247184	0.310240	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	0.266963	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

Table (4-5b) Values of $\eta_r - 1/\sqrt{C}$ and $\sqrt{C}$ for the aqueous amino acid DL-Isolucine solution in the concentration range from (0.06-0.28 mol.L.$^{-1}$) at four different temperatures in the range from (293.15-308.15) K.

C Mol.L^{-1}	$\sqrt{C}$	η_r-1/$\sqrt{C}$			
		293.15K	**298.15K**	**303.15K**	**308.15K**
0.06	0.235966	0.143831	0.234270	0.2984691	0.350149
0.08	0.289016	0.140837	0.221841	0.271648	0.343921
0.11	0.333721	0.138895	0.221200	0.267565	0.322901
0.14	0.373109	0.138414	0.216963	0.267544	0.313194
0.17	0.408718	0.135075	0.212276	0.255866	0.307148
0.19	0.441429	0.131626	0.207276	0.249606	0.298933
0.22	0.471953	0.130732	0.202551	0.245884	0.296895
0.25	0.500590	0.127559	0.200589	0.240414	0.293204
0.28	0.527665	0.126344	0.198647	0.238122	0.282922

Table (4-5c) Values of $\eta_r - 1/\sqrt{C}$ and $\sqrt{C}$ for the aqueous amino acid DL-Methionine Solution in the concentration range from (0.04-0.2 mol.L.$^{-1}$) at four different temperatures in the range from (293.15-308.15)K.

C Mol.L^{-1}	$\sqrt{C}$	η_r-1/$\sqrt{C}$			
		293.15K	**298.15K**	**303.15K**	**308.15K**
0.04	0.200000	0.335024	0.282026	0.194226	0.294795
0.06	0.244949	0.322466	0.277233	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

Table (4-5d) Values of $\eta_r - 1/\sqrt{C}$ and $\sqrt{C}$ for the aqueous amino acid DL-Glutamine solution in the concentration range from (0.002-0.02 mol.L.$^{-1}$) at four different temperatures in the range from (293.15-308.15)K.

C Mol.L^{-1}	$\sqrt{C}$	η_r-1/$\sqrt{C}$			
		293.15K	**298.15K**	**303.15K**	**308.15K**
0.002	0.044721	0.902925	0.487069	1.206236	1.016903
0.004	0.063246	0.863368	0.470978	1.200129	0.9651539
0.006	0.077460	0.845005	0.454709	1.160232	0.889985
0.008	0.089443	0.828233	0.440103	1.155826	0.876178
0.01	0.100000	0.799980	0.431401	1.134557	0.861406
0.012	0.109545	0.796870	0.416627	1.130706	0.844053
0.014	0.118322	0.786963	0.402352	1.127908	0.799126
0.016	0.126491	0.764553	0.395492	1.120569	0.787409
0.018	0.134164	0.749218	0.393433	1.102016	0.774136
0.02	0.141421	0.739439	0.382566	1.098305	0.755237

Table (4-5e) Values of $\eta_r - 1/\sqrt{C}$ and $\sqrt{C}$ for the aqueous amino acid L-Arginine solution in the concentration range from (0.04-0.2 mol.L.$^{-1}$) at four different temperatures in the rang from (293.15-308.15)K.

C Mol.L^{-1}	$\sqrt{C}$	η_r-1/$\sqrt{C}$			
		293.15K	298.15K	303.15K	308.15K
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 (4-5f) Values of $\eta_r - 1/\sqrt{C}$ and $\sqrt{C}$ for the aqueous amino acid DL-Histidine solution in the concentration range from (0.002-0.02 mol.L.$^{-1}$) at four different temperatures in the range from (293.15-308.15)K.

C Mol.L^{-1}	$\sqrt{C}$	η_r-1/$\sqrt{C}$			
		293.15K	298.15K	303.15K	308.15K
0.002	0.044721	1.052330	0.738023	0.839478	1.063243
0.004	0.063246	0.951161	0.698481	0.784754	1.002487
0.006	0.077460	0.935298	0.694980	0.768064	0.937416
0.008	0.089443	0.870917	0.673142	0.727079	0.904675
0.01	0.100000	0.801512	0.661506	0.704594	0.852220
0.012	0.109545	0.754084	0.633817	0.659517	0.823541
0.014	0.118322	0.725261	0.631027	0.637162	0.799212
0.016	0.126491	0.710303	0.626931	0.599372	0.764464
0.018	0.134164	0.681714	0.620605	0.583468	0.755519
0.02	0.141421	0.669634	0.611393	0.557881	0.7300035

Table (4-5a$^{/}$) Values of $\eta_r - 1/\sqrt{C}$ and $\sqrt{C}$ for the acidic amino acid DL-Valine solution in the concentration range from (0.04-0.2 mol.L.$^{-1}$) at four different temperatures in the range from (293.15-308.15) K.

C Mol.L^{-1}	$\sqrt{C}$	η_r-1/$\sqrt{C}$			
		293.15K	**298.15K**	**303.15K**	**308.15K**
0.04	0.200000	0.252046	0.316614	0.312430	0.231924
0.06	0.244949	0.247181	0.301243	0.303389	0.229122
0.08	0.282843	0.237836	0.290175	0.298237	0.226409
0.1	0.316228	0.231357	0.276653	0.288826	0.226462
0.12	0.346410	0.223795	0.273031	0.279896	0.222737
0.14	0.374166	0.220665	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

Table (4-5b$^{/}$) Values of $\eta_r - 1/\sqrt{C}$ and $\sqrt{C}$ for the acidic amino acid DL-Isolucine solution in the concentration range from (0.06-0.28 mol.L.$^{-1}$) at four different temperatures in the range from (293.15-308.15) K.

C Mol.L^{-1}	$\sqrt{C}$	η_r-1/$\sqrt{C}$			
		293.15K	**298.15K**	**303.15K**	**308.15K**
0.06	0.235966	0.274066	0.279824	0.387336	0.711753
0.08	0.289016	0.278267	0.291084	0.398823	0.732151
0.11	0.333721	0.283854	0.299777	0.405121	0.743746
0.14	0.373109	0.288570	0.309641	0.421125	0.752187
0.17	0.408718	0.289538	0.314119	0.431793	0.788490
0.19	0.441429	0.296810	0.321697	0.463511	0.781468
0.22	0.471953	0.299685	0.333328	0.469120	0.894114
0.25	0.500590	0.301598	0.340999	0.452059	0.931014
0.28	0.527665	0.313586	0.348145	0.451491	1.036097

Table (4-5c$^{/}$) Values of $\eta_r - 1/\sqrt{C}$ and $\sqrt{C}$ for the acidic amino acid DL-Methionine solution in the concentration range from (0.04-0.2 mol.L.$^{-1}$) at four different temperatures in the range from (293.15-308.15) K.

C Mol.L^{-1}	$\sqrt{C}$	η_r-1/$\sqrt{C}$			
		293.15K	**298.15K**	**303.15K**	**308.15K**
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	0.378008	0.270190
0.12	0.346410	0.242244	0.312839	0.364866	0.269833
0.14	0.374166	0.232575	0.301588	0.360257	0.269051
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

Table (4-5d$^{/}$) Values of $\eta_r - 1/\sqrt{C}$ and $\sqrt{C}$ for the acidic amino acid DL-Glutamine solution in the concentration range from (0.002-0.02 mol.L.$^{-1}$) at four different temperatures in the range from (293.15-308.15) K.

C Mol.L^{-1}	$\sqrt{C}$	η_r-1/$\sqrt{C}$			
		293.15K	**298.15K**	**303.15K**	**308.15K**
0.002	0.044721	0.703846	0.903665	1.145862	1.701235
0.004	0.063246	0.654676	0.809712	1.086705	1.511869
0.006	0.077460	0.644015	0.777077	0.998452	1.459498
0.008	0.089443	0.623057	0.711697	0.943267	1.372426
0.01	0.100000	0.619889	0.688120	0.930267	1.299673
0.012	0.109545	0.613812	0.687784	0.879948	1.272765
0.014	0.118322	0.606918	0.667519	0.861622	1.202637
0.016	0.126491	0.606775	0.660556	0.823870	1.193471
0.018	0.134164	0.585833	0.646235	0.801819	1.180362
0.02	0.141421	0.569340	0.615160	0.769377	1.151899

Table (4-5e$^{/}$) Values of $\eta_r - 1/\sqrt{C}$ and $\sqrt{C}$ for the acidic amino acid L-Arginine solution in the concentration range from (0.04-0.2 mol.L.$^{-1}$) at four different temperatures in the range from (293.15-308.15) K.

C Mol.L^{-1}	$\sqrt{C}$	η_r-1/$\sqrt{C}$			
		293.15K	**298.15K**	**303.15K**	**308.15K**
0.04	0.200000	0.247258	0.336000	0.380268	0.507960
0.06	0.244949	0.236842	0.333516	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

Table (4-5f$^{/}$) Values of $\eta_r - 1/\sqrt{C}$ and $\sqrt{C}$ for the acidic amino acid DL-Histidine solution in the concentration range from (0.002-0.02 mol.L.$^{-1}$) at four different temperatures in the range from (293.15-308.15) K.

C Mol.L^{-1}	$\sqrt{C}$	η_r-1/$\sqrt{C}$			
		293.15K	**298.15K**	**303.15K**	**308.15K**
0.002	0.044721	1.204357	2.034758	1.118378	0.975089
0.004	0.063246	1.142394	1.688600	1.050994	0.879943
0.006	0.077460	1.025991	1.552388	0.998632	0.856794
0.008	0.089443	1.009690	1.297625	0.857639	0.834320
0.01	0.100000	0.930156	1. 294341	0.860626	0.798125
0.012	0.109545	0.890716	1.283502	0.841739	0.734994
0.014	0.118322	0.889802	1.213403	0.801829	0.717459
0.016	0.126491	0.885895	1.205482	0.785017	0.678317
0.018	0.134164	0.884521	1.200101	0.782050	0.669694
0.02	0.141421	0.835215	1.183515	0.747468	0.664238

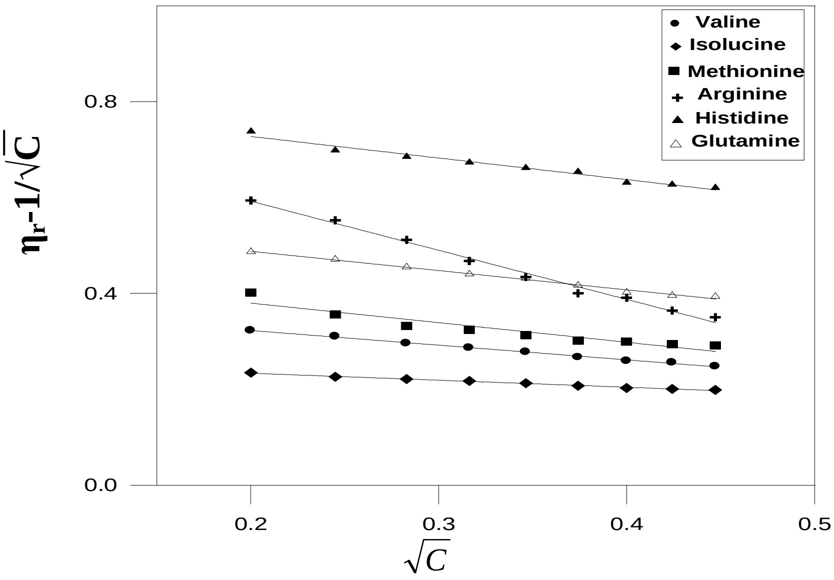


Figure (4-2a) η_r-1/$\sqrt{C}$ against $\sqrt{C}$ for aqueous amino acids solutions at 298.15K

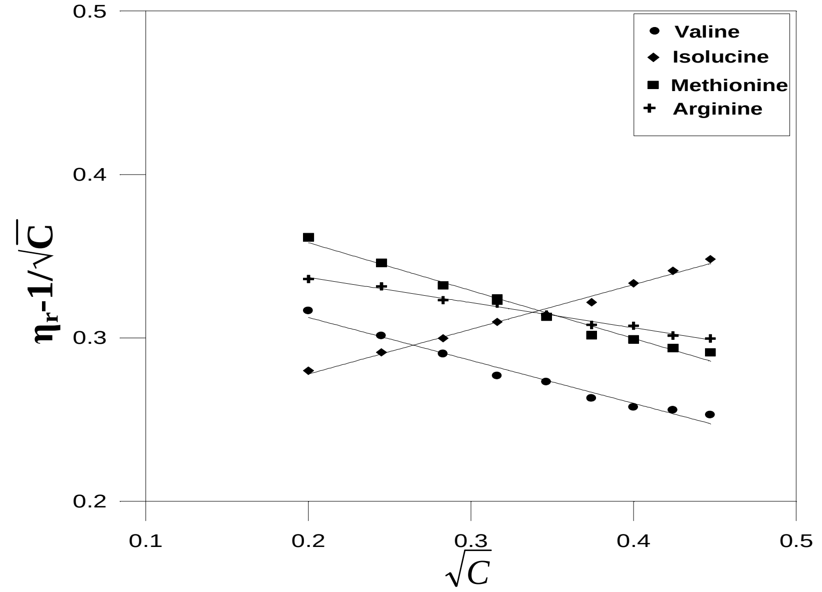


Figure (4-2a$^{/}$) η_r-1/$\sqrt{C}$ against $\sqrt{C}$ for acidic amino acids solutions at 298.15K

Table (4-6a) B-coefficient values for aqueous amino acids solutions at temperature range (293.15-303.15) K.

Amino acids	**B (L.mol^{-1})**			
	293.15K	**298.15K**	**303.15K**	**308.15K**
DL-Valine	-0.1058	-0.3062	-0.1939	-0.0710
DL-Isolucine	-0.0608	-0.1240	-0.1565	-0.2300
DL-Methionine	-0.4167	-0.1166	-0.2075	-0.3227
DL-Glutamine	-1.6401	-1.1150	-1.1704	-2.6069
L-Arginine	-0.3397	-1.0233	-0.4476	-0.2103
DL-Histidine	-4.1157	-1.2456	-3.0025	-3.5031

Table (4-6b) B-coefficient values for acidic amino acids solutions at temperature range (293.15-303.15) K.

Amino acids	**B (L.mol^{-1})**			
	293.15K	**298.15K**	**303.15K**	**308.15K**
DL-Valine	-0.1709	-0.2627	-0.1919	-0.0579
DL-Isolucine	0.1219	0.2302	0.4391	0.9370
DL-Methionine	-0.1665	-0.4079	-0.3285	-0.1272
DL-Glutamine	-1.1685	-2.7604	-3.8650	-3.3511
L-Arginine	-0.2099	-0.1541	-0.2815	-0.5222
DL-Histidine	-4.0959	-8.4264	-3.9490	-3.3511

In Figures (4-3 a, b, c), we display the variation of (η_r-1/ $\sqrt{C}$) as a function of $\sqrt{C}$ for the aqueous solutions of the amino acids Valine, Isolucine, and Arginine at four temperatures ranging from (29315-308.15)K. In Figures (4-3 a$^{/}$, b$^{/}$, c$^{/}$), we present the variation of (η_r-1/$\sqrt{C}$) versus $\sqrt{C}$,for the solutions of amino acids Methionine, Glutamine and Histidine in 0.1M HCl solution in temperature range from (293.15-308.15)K. These Figures show linear relationships between the values of (η_r-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.

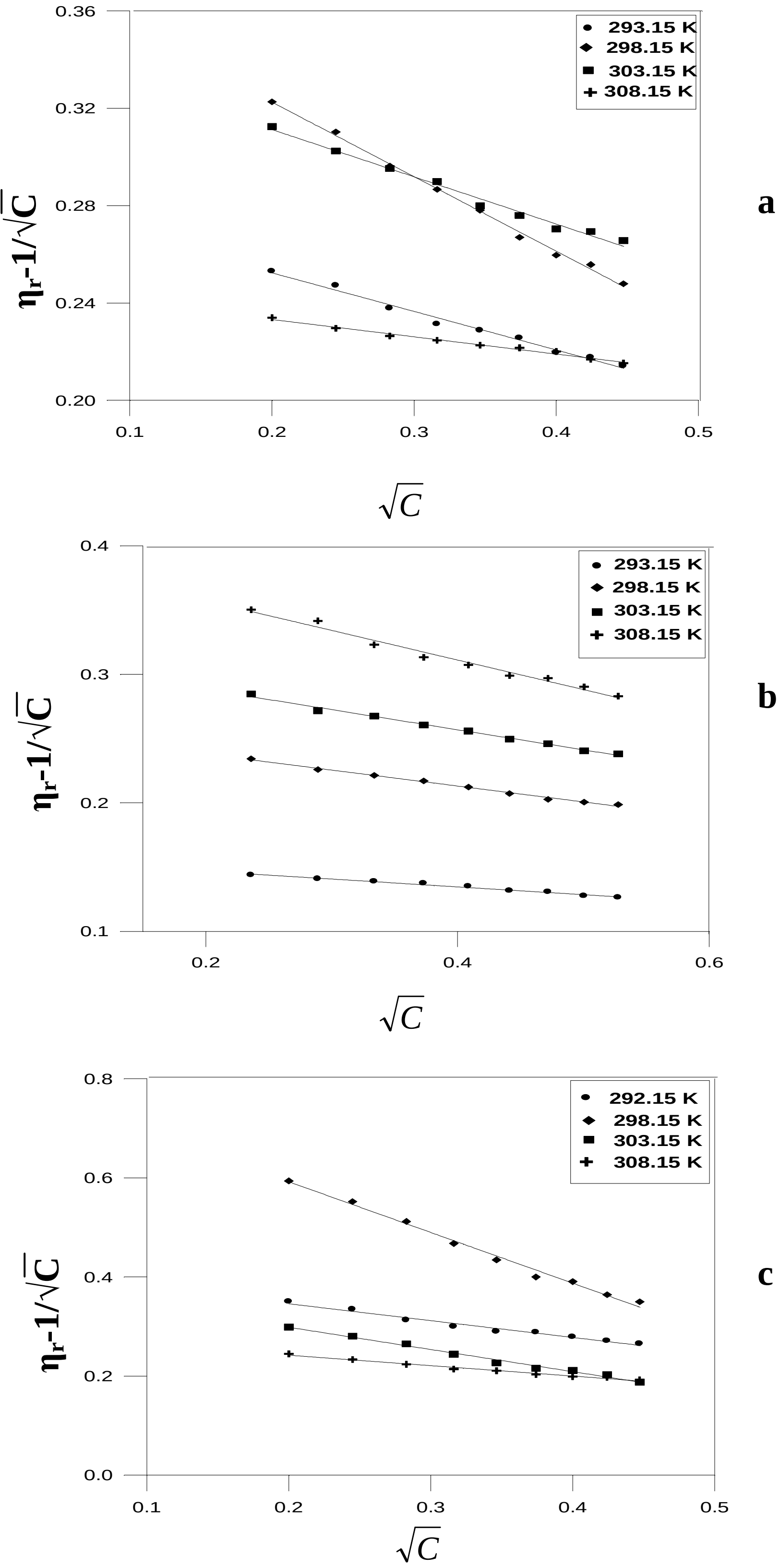


Figure (4-3) η_r-1/$\sqrt{C}$ against $\sqrt{C}$ for aqueous amino acids solutions at four temperatures

a) Valine b) Isolucine c) Arginine

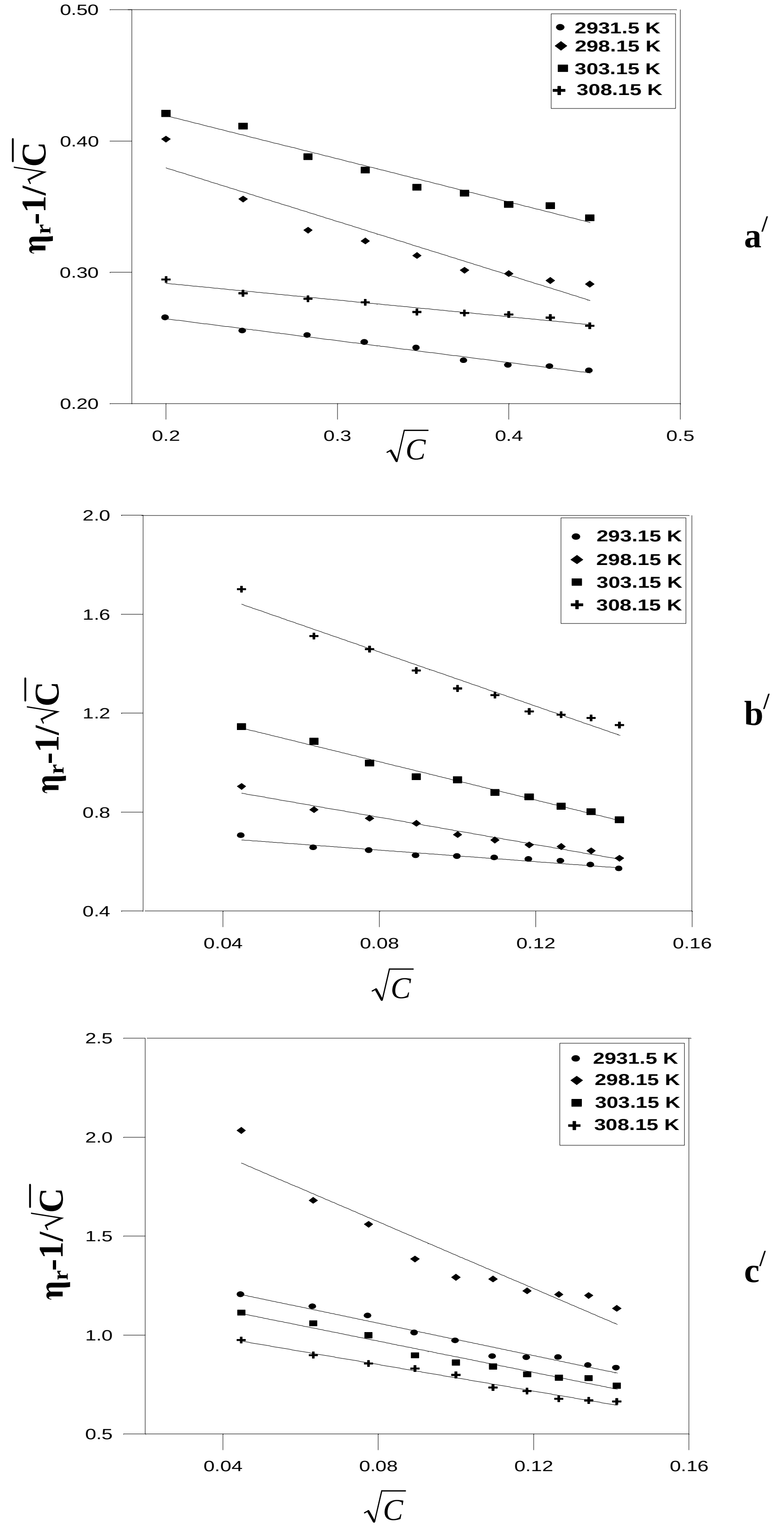


Figure (4-3) η_r-1/$\sqrt{C}$ against $\sqrt{C}$ for acidic amino acids solutions at four temperatures

$a^{/}$) Methionine $b^{/}$) Glutamine $c^{/}$) Histidine

The viscosity of a solution involves four different components in addition to the viscosity η_0 of the solvent $^{(83, 84)}$:

1. An increase in the viscosity due to the size and shape of the dissolved particles, called Enstien effect **(η_E)**; this is always positive and is larger the larger the size of the solute particles.
2. The orientation of the polar molecules of the solvent by the electric filed of the charged solute particles, called orientation effect **(η_{or})**; this usually increases viscosity since the mobility of the oriented molecules decreases.
3. The structural component **(η_{st})**; corresponding to the structural decomposition of the solvent which decreases viscosity.
4. The increases in viscosity due to the electrostatic interaction between the solute particles **(η_{el})**.

The viscosity (η) of a solution should therefore consists of these five terms:

$$\eta = \eta_0 + \eta_E + \eta_{or} + \eta_{st} + \eta_{el} \qquad \text{………… (4-1)}$$

comparing with Jones and Dole equation (2-29) one can obtain:

$$\eta_E + \eta_{or} + \eta_{st} + \eta_{el} = \eta_0 \, (A\sqrt{C} + BC) \qquad \text{………… (4-2)}$$

Since the coefficient (A) correspond to the electrostatic interaction between the charged solute particles, then:

$$\eta_{el} = \eta_0 \, A\sqrt{C} \qquad \text{………… (4-3)}$$

These terms can be eliminated from both sides of equation (4-2) to obtain:

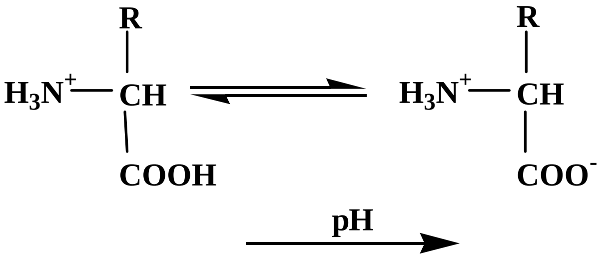
$$\eta_E + \eta_{or} + \eta_{st} = \eta_0\, BC \qquad \text{………… (4-4)}$$

According to equation (4-4), the coefficient (B) is thus related to the size of the solvated solute particles, orientation of the solvent molecules, and the change in the solvent structure; it is related to the effects of these phenomena on viscosity.

It was found that B-coefficient values displayed in Tables (4-6 a, b) are negative for all amino acids studied here (except acidic Isolucine) 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 (4-6 a, b) for the amino acids DL-Valine, DL-Isolucine, and L-Arginine have a value in 0.1M HCl larger than that in aqueous medium, while for DL-Methionine, DL-Glutamine, and DL-Histidine; 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 and DL-Isolucine are usually located in the interior of the protein, having little contact with water; while for DL-Methionine and DL-Glutamine which has relatively some polarity in their structures showed different behaviour of interaction with solvent (water or 0.1M HCl solution).

The presence of amino acids in acidic medium (presence of HCl) shifts the equilibrium to the cationic form:



In the absence of HCl we will have the Zwitterion which predominates in solution. The two different forms of amino acids due to different pHs leads to various types of molecular interactions between solvent and solute and numerous mechanisms of interactions.

(4-5) Effect of Temperature on B-Coefficient Values

It is clear from the obtained data listed in Tables (4-6a) and (4-6b) and represented in Figures (4-6 a, b) and (4-6 $a^{/}$, $b^{/}$) that B-coefficient values are very sensitive to temperature. It was found that:

1. *In water as solvent*

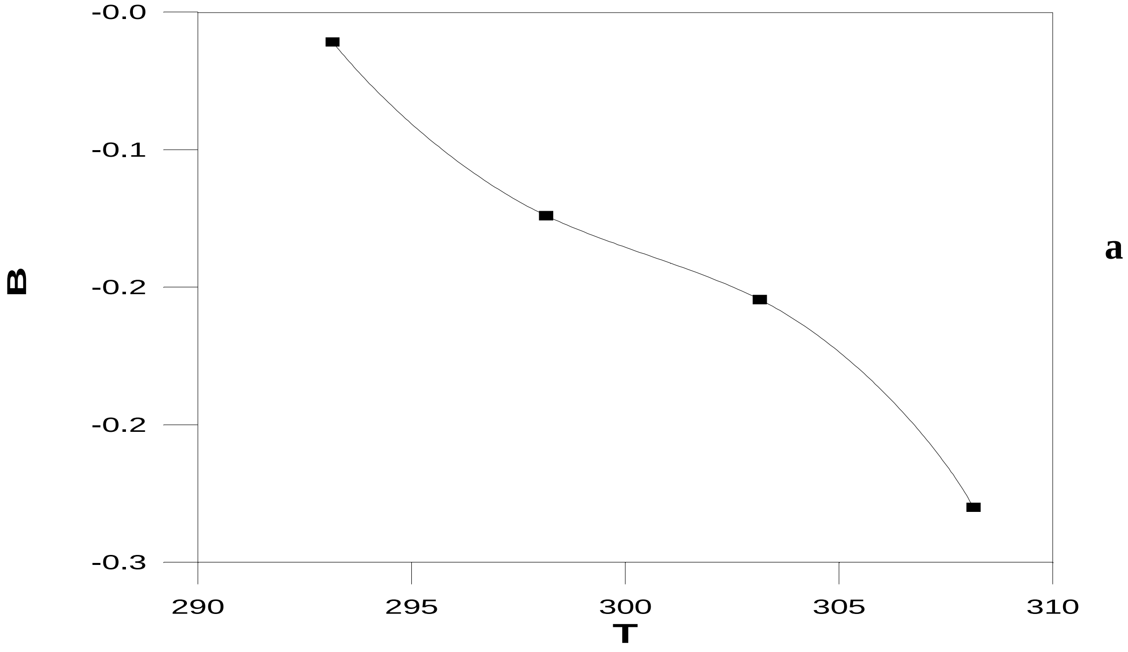
B-values for DL-Isolucine, DL-Methionine, DL-Glutamine and DL-Histidine increase between 293.15K and 298.15K, then after decrease i.e. these amino acids have the maximum value of B at 29815K. while B-values for DL-Valine and L-Arginine show decreasing between (293.15-298.15)K, then increasing over the temperature (298.15-308.15)K.

2. In 0.1M HCl solution

B-values for DL-Valine, DL-Isolucine, DL-Methionine and DL-Histidine 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 DL-Glutamine and L-Arginine show increasing between (293.15-298.15)K then decrease over the temperature (298.15-308.15)K. This behaviour may be explained as follow:

The values of (η_E) dose 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 (4-4 a, b, c) and (4-4 $a^{/}$, $b^{/}$, $c^{/}$) should be associated with the net variation of (η_E), (η_{or}) and (η_{st}) equation (4-4). 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 (4-4 a, b, c) and (4-4 $a^{/}$, $b^{/}$, $c^{/}$).

Hydration can increase with increasing temperature (85) 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 (298.15-308.15) K.



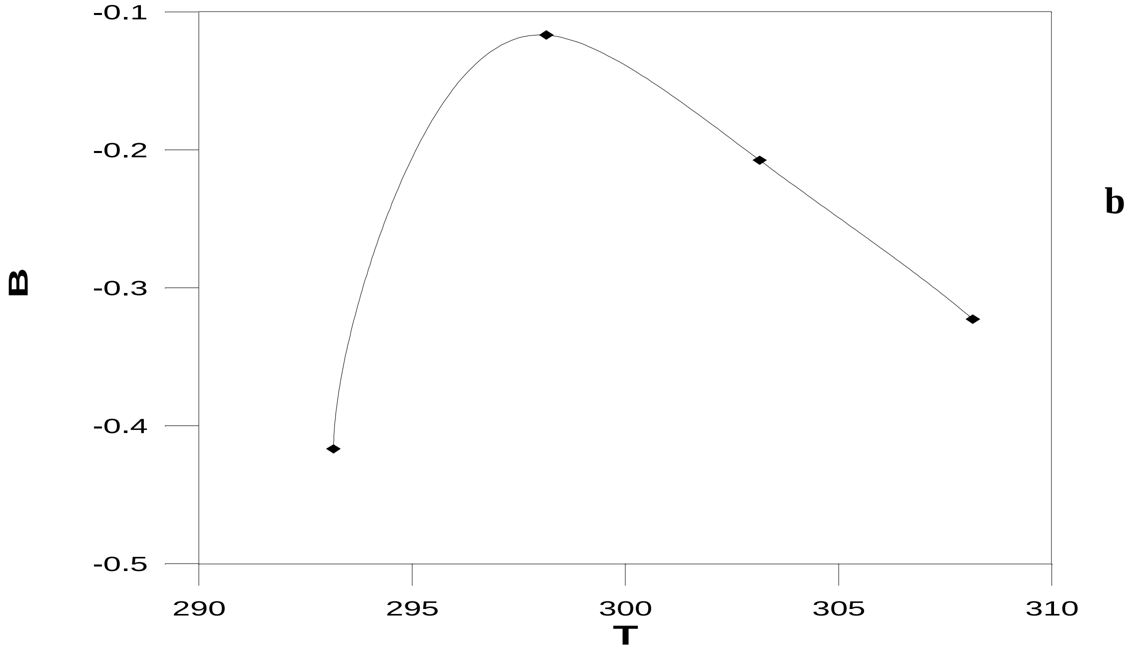


Figure (4-4) (B) Viscosity coefficient for aqueous amino acid against temperature a) Isolucine b) Methionine

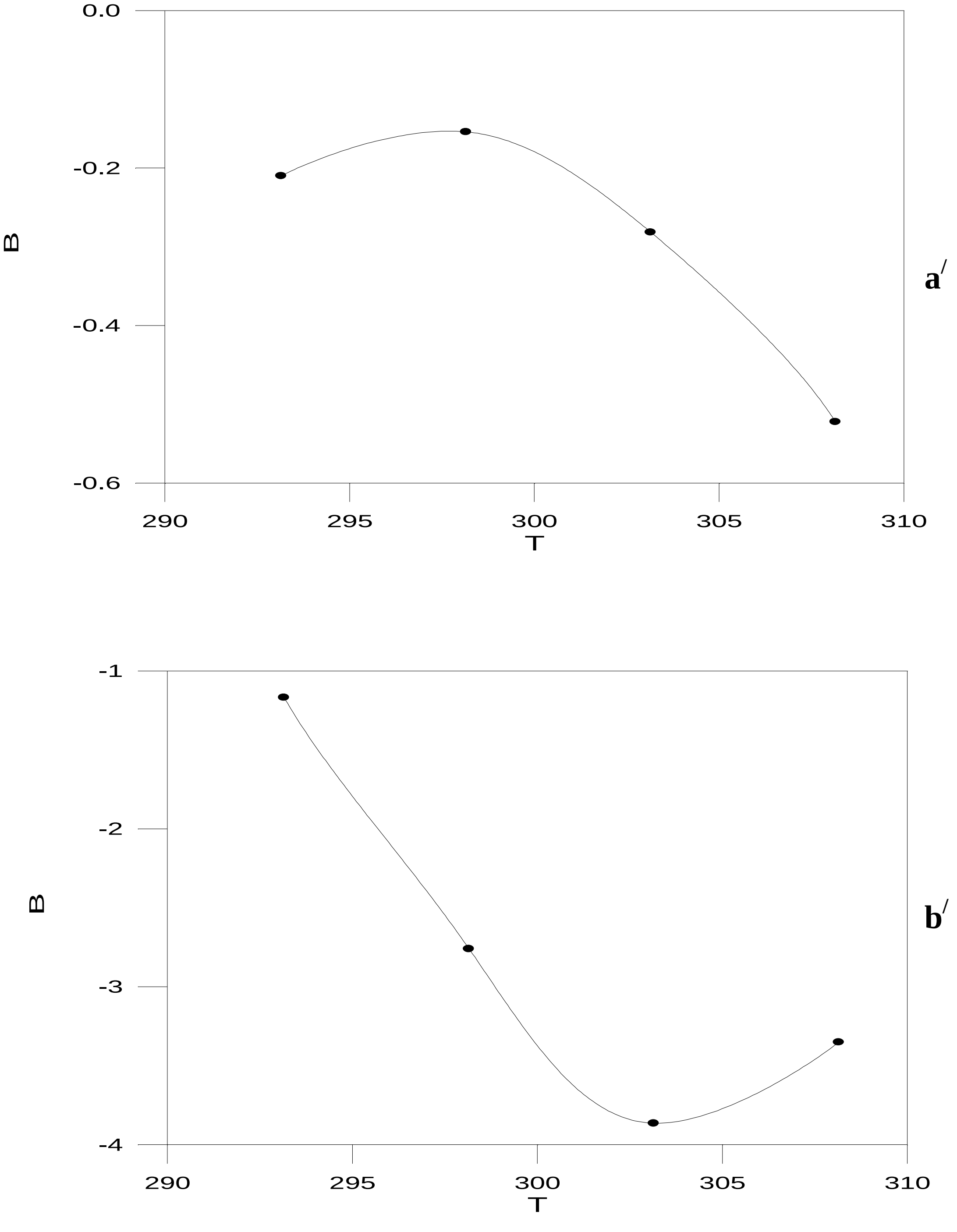


Figure (4-4) (B) Viscosity coefficient for acidic amino acid against temperature
a/)Glutamine b/) Arginine

(4-6) Effective Flow Volume

Effective flow volume (V_h) was calculated for solutions of amino acids (DL-Valine, DL-Isolucine, DL-Methionine, DL-Glutamine, L-Arginine and DL-Histidine) studied here at four different temperatures in the range of (293.15-303.15)K according to equation (2-32)

$$B = V_h / a \qquad \text{………… (2-32)}$$

as obtained in Tables (4-7 a, b).

Effective flow volume was calculated also through the equation (2-31) that modified by Egland and Pilling:

$$C / [Log\, \eta / \eta_0] = 2.303 / aV_h - 2.303QC / a \qquad \text{………… (2-31)}$$

The obtained data of (V_h) are presented in tables (4-8 a, b, c, d, e, f) and (4-8 $a^{/}$, $b^{/}$, $c^{/}$, $d^{/}$, $e^{/}$, $f^{/}$) and display in Figure (4-5 a, b, c) and (4-5 $a^{/}$, $b^{/}$, $c^{/}$)

Table (4-7a) V_h values that calculated from equation (2-32) for aqueous amino acid solutions at four temperature (293.15-308.15) K.

Amino acids	**V_h (L.mol^{-1}) V_h =B/a**			
	293.15K	**298.15K**	**303.15K**	**308.15K**
DL-Valine	-0.04234	-0.122476	-0.07757	-0.028384
DL-Isolucine	-0.012432	-0.04961	-0.06258	-0.092016
DL-Methionine	-0.16669	-0.046635	-0.08301	-0.12906
DL-Glutamine	-0.65606	-0.44602	-0.46814	-1.04275
L-Arginine	-0.13587	-0.40930	-0.17904	-0.08410
DL-Histidine	-1.64629	-0.49824	-1.20100	-1.40122

Table (4-7b) V_h values that calculated from equation (2-32) for acidic amino acid solutions at four temperature (293.15-308.15) K.

Amino acids	**V_h (L.mol^{-1}) V_h =B/a**			
	293.15K	**298.15K**	**303.15K**	**308.15K**
DL-Valine	-0.06834	-0.10509	-0.07675	-0.02318
DL-Isolucine	0.04871	0.09208	0.1757	0.3748
DL-Methionine	-0.0666	-0.16316	-0.13141	-0.05087
DL-Glutamine	-0.4674	-1.10416	-1.54649	-1.34044
L-Arginine	-0.08397	-0.06165	-0.11262	-0.20889
DL-Histidine	-1.63822	-3.37056	-1.57960	-1.34204

Table (4-8a) C / logη_r values for aqueous amino acid DL-Valine solution at concentration range from (0.04-0.2) mol.L^{-1} at four temperatures range (293.15-308.15) K.

C Mol.L^{-1}	C / log η_r			
	293.15K	**298.15K**	**303.15K**	**308.15K**
0.04	1.696056	1.336789	1.473842	2.191772
0.06	2.261417	1.886232	1.891224	2.670077
0.08	2.829465	2.335292	2.274596	3.159021
0.1	3.261102	2.745497	2.715617	3.329838
0.12	3.700579	3.057488	3.058972	3.687473
0.14	4.063486	3.435296	2.339048	3.960881
0.16	4.622385	3.756743	3.586962	4.316652
0.18	4.691291	4.037212	3.777746	4.535133
0.2	4.968972	4.298656	4.088362	4.687512

Table (4-8b) C / logη_r values for aqueous amino acid DL-Isolucine solution at concentration range from (0.06-0.28) mol.L^{-1} at four temperatures range (293.15-308.15) K.

C Mol.L^{-1}	C / log η_r			
	293.15K	**298.15K**	**303.15K**	**308.15K**
0.06	4.323229	2.997786	1.907104	1.455792
0.08	5.186060	3.362476	2.544771	2.030376
0.11	6.209287	3.920522	2.968185	2.505757
0.14	6.068604	4.441362	2.998276	2.918087
0.17	7.157740	4.927297	3.455238	3.252483
0.19	7.540175	5.197159	3.985982	3.619936
0.22	7.969699	5.470042	4.777484	3.986319
0.25	8.612788	5.594313	5.077441	4.213118
0.28	8.763986	5.891493	5.342962	4.405119

Table (4-8c) C / logη_r values for aqueous amino acid DL-Methionine solution at concentration range from (0.04-0.2) mol.L^{-1} at four temperatures range (293.15-308.15) K.

C Mol.L^{-1}	C / log η_r			
	293.15K	**298.15K**	**303.15K**	**308.15K**
0.04	1.296827	1.678525	3.792298	1.607772
0.06	1.817267	2.180715	3.871031	1.423016
0.08	2.253611	2.518842	4.274348	2.520013
0.1	2.697066	2.622695	4.482261	2.943805
0.12	3.057828	2.929826	4.793142	3.358733
0.14	3.430038	3.236862	4.874876	3.770236
0.16	3.696645	3.544511	5.226041	4.181674
0.18	3.887523	3.675823	5.503751	4.596386
0.2	4.176929	4.116717	5.534396	5.015900

Table (4-8d) C / logη_r values for aqueous amino acid DL-Glutamine solution at concentration range from (0.002-0.02) mol.L^{-1} at four temperatures range (293.15-308.15) K.

C Mol.L^{-1}	C / log η_r			
	293.15K	**298.15K**	**303.15K**	**308.15K**
0.002	0.139673	0.298228	0.09409	0.179380
0.004	0.183252	0.429698	0.119555	0.197765
0.006	0.218317	0.457849	0.163987	0.214048
0.008	0.267111	0.532625	0.178030	0.267379
0.01	0.318713	0.564108	0.214029	0.319152
0.012	0.354751	0.613700	0.236980	0.349292
0.014	0.372244	0.621324	0.263014	0.356704
0.016	0.383579	0.636652	0.293246	0.368698
0.018	0.408046	0.685286	0.293449	0.383050
0.02	0.436409	0.712577	0.303106	0.397527

Table (4-8e) C / logη_r values for aqueous amino acid L-Arginine solution at concentration range from (0.04-0.2) mol.L^{-1} at four temperatures range (293.15-308.15) K.

C Mol.L^{-1}	C / log η_r			
	293.15K	**298.15K**	**303.15K**	**308.15K**
0.04	1.334583	0.850313	2.793591	2.793606
0.06	1.731531	1.169609	2.849419	2.985776
0.08	2.171623	1.483698	3.143057	3.321817
0.1	2.576863	1.788974	3.423155	3.476464
0.12	2.990236	2.097149	3.513155	4.017167
0.14	3.276943	2.340234	3.645118	4.408815
0.16	3.483401	2.538733	3.752768	4.696782
0.18	3.639909	2.705903	3.859145	4.499372
0.2	3.916142	2.935093	3.954768	4.796782

Table (4-8f) C / logη_r values for aqueous amino acid DL-Histidine solution at concentration range from (0.002-0.02) mol.L^{-1} at four temperatures range (293.15-308.15) K.

C Mol.L^{-1}	C / log η_r			
	293.15K	**298.15K**	**303.15K**	**308.15K**
0.002	0.100139	0.129729	0.252841	0.199869
0.004	0.160335	0.214671	0.271545	0.249554
0.006	0.196335	0.262198	0.311162	0.258803
0.008	0.245570	0.334183	0.326860	0.281702
0.01	0.298646	0.378676	0.337541	0.301785
0.012	0.348124	0.426223	0.360555	0.328178
0.014	0.411915	0.473842	0.402573	0.328447
0.016	0.428188	0.479745	0.430947	0.335558
0.018	0.473577	0.518226	0.435940	0.373592
0.02	0.508964	0.594946	0.462039	0.396768

Table (4-8a/) C / logη_r values for acidic amino acid DL-Valine solution at concentration range from (0.04-0.2) mol.L^{-1} at four temperatures range (293.15-308.15) K.

C Mol.L^{-1}	C / log η_r			
	293.15K	298.15K	303.15K	308.15K
0.04	1.898033	1.299931	1.177420	0.98981
0.06	2.554224	1.740537	1.515727	1.333761
0.08	2.734126	1.937361	1.851584	1.620406
0.1	3.201700	2.272533	2.118044	1.918132
0.12	3.333694	2.590157	2.397088	2.169789
0.14	3.559164	2.719732	2.725555	2.388695
0.16	3.600490	3.073599	3.013412	2.507156
0.18	3.889994	3.219217	3.177480	2.656451
0.2	4.214950	3.508015	3.448432	2.741099

Table (4-8b/) C / logη_r values for acidic amino acid DL-Isolucine solution at concentration range from (0.06-0.28) mol.L^{-1} at four temperatures range (293.15-308.15) K.

C Mol.L^{-1}	C / log η_r			
	293.15K	298.15K	303.15K	308.15K
0.06	1.989243	2.245459	0.586077	1.587906
0.08	2.486856	2.383411	0.831179	1.874843
0.11	2.719809	2.695137	1.055349	2.002059
0.14	3.114045	3.023473	1.252879	2.212644
0.17	3.303951	3.318637	1.434471	2.355803
0.19	3.536298	3.480067	1.553449	2.566606
0.22	3.791237	3.661032	1.728217	2.601734
0.25	3.967815	3.719215	1.881883	2.752357
0.28	4.340386	3.851644	1.936611	2.988449

Table (4-8c/) C / logη_r values for acidic amino acid DL-Methionine solution at concentration range from (0.04-0.2) mol.L^{-1} at four temperatures range (293.15-308.15) K.

C Mol.L^{-1}	C / log η_r			
	293.15K	**298.15K**	**303.15K**	**308.15K**
0.04	1.893799	1.381074	1.066491	1.698884
0.06	2.353915	1.699137	1.390540	2.176321
0.08	2.949848	2.112816	1.768497	2.511595
0.1	3.354318	2.435474	2.039220	2.799947
0.12	3.585725	2.683468	2.349529	3.224159
0.14	3.911429	3.050851	2.613639	3.375128
0.16	4.084698	3.345892	2.830071	3.594413
0.18	4.178844	3.528957	2.980308	3.809666
0.2	4.507426	3.669153	3.046722	4.037080

Table (4-8d /) C / logη_r values for acidic amino acid DL-Glutamine solution at concentration range from (0.002-0.02) mol.L^{-1} at four temperatures range (293.15-308.15) K.

C Mol.L^{-1}	C / log η_r			
	293.15K	**298.15K**	**303.15K**	**308.15K**
0.002	0.179840	0.108674	0.08935	0.057302
0.004	0.284879	0.199819	0.138564	0.100858
0.006	0.311311	0.257454	0.192888	0.135151
0.008	0.347999	0.300904	0.236830	0.170901
0.01	0.390788	0.346005	0.258860	0.202111
0.012	0.405321	0.367409	0.300253	0.222547
0.014	0.455436	0.401081	0.332057	0.241657
0.016	0.489838	0.454500	0.371640	0.262030
0.018	0.493231	0.470030	0.405651	0.281936
0.02	0.542306	0.498733	0.429640	0.300306

Table (4-8e$^{/}$) C / logη_r values for acidic amino acid L-Arginine solution at concentration range from (0.04-0.2) mol.L^{-1} at four temperatures range (293.15-308.15) K.

C Mol.L^{-1}	**C / log η_r**			
	293.15K	**298.15K**	**303.15K**	**308.15K**
0.04	2.763191	1.211336	1.222734	0.951909
0.06	2.816771	1.663574	1.613695	1.332561
0.08	3.468478	2.106990	1.981542	1.637311
0.1	3.740384	2.440714	2.338463	1.866772
0.12	3.862424	2.726636	2.655678	2.118107
0.14	4.051191	2.954595	2.841714	2.294233
0.16	4.208446	3.177492	3.511183	2.485281
0.18	4.328636	3.444911	3.259907	2.704354
0.2	4.591276	3.662548	3.359913	2.914165

Table (4-8f$^{/}$) C / logη_r values for acidic amino acid DL-Histidine solution at concentration range from (0.002-0.02) mol.L^{-1} at four temperatures range (293.15-308.15) K.

C Mol.L^{-1}	**C / log η_r**			
	293.15K	**298.15K**	**303.15K**	**308.15K**
0.002	0.071186	0.049835	0.078918	0.157892
0.004	0.132029	0.093847	0.143118	0.198570
0.006	0.180646	0.134205	0.203123	0.248361
0.008	0.213052	0.172288	0.255047	0.292561
0.01	0.258889	0.202304	0.295798	0.308044
0.012	0.296784	0.218746	0.312289	0.340906
0.014	0.334430	0.239063	0.369385	0.360297
0.016	0.346872	0.258015	0.399925	0.395555
0.018	0.373106	0.280877	0.425644	0.426854
0.02	0.392219	0.279947	0.462275	0.454419

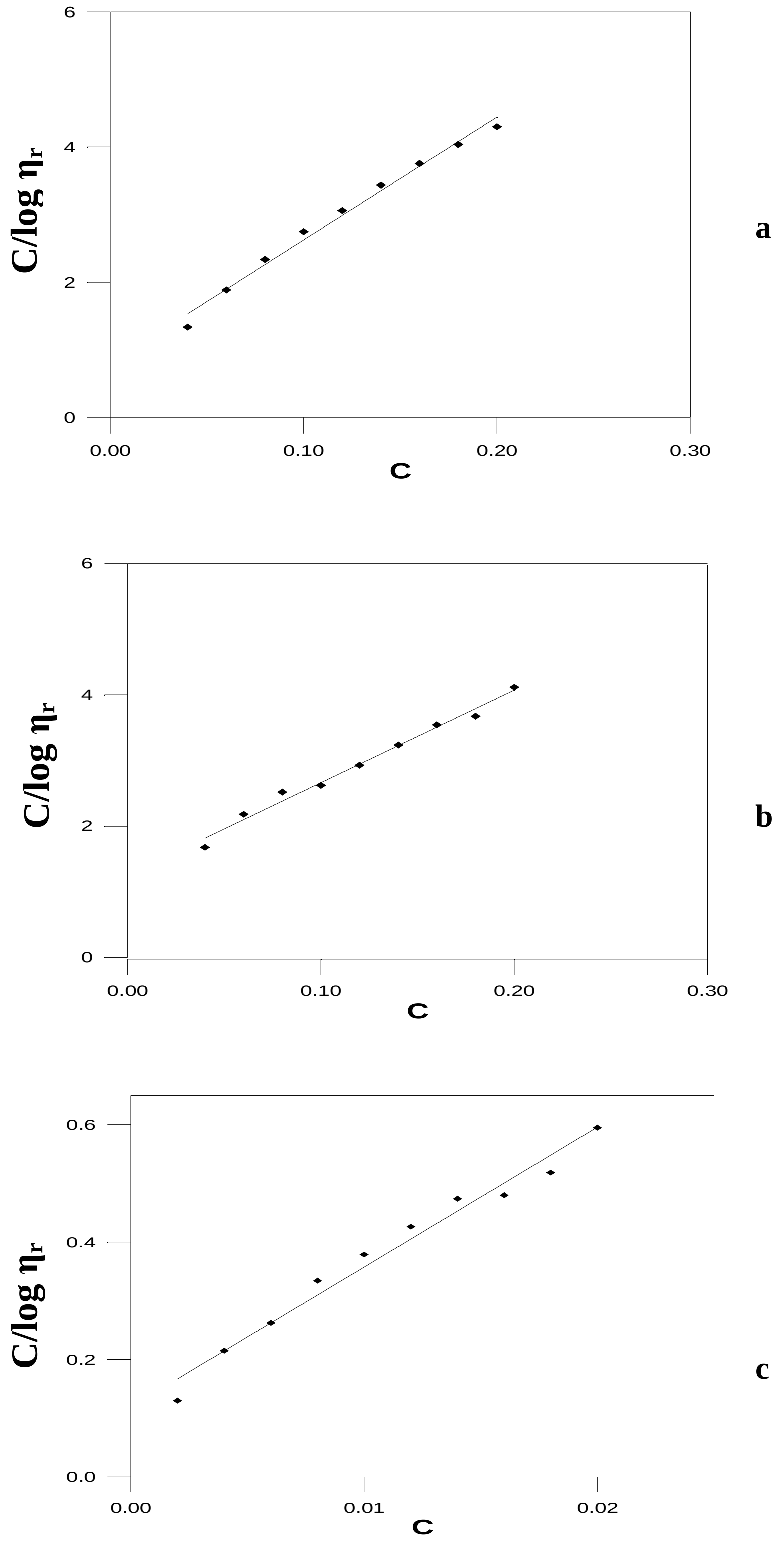


Figure (4-5) **C/log η_r against C for aqueous amino acids at 298.15K**
a) Valine b) Methionine c) Histidine

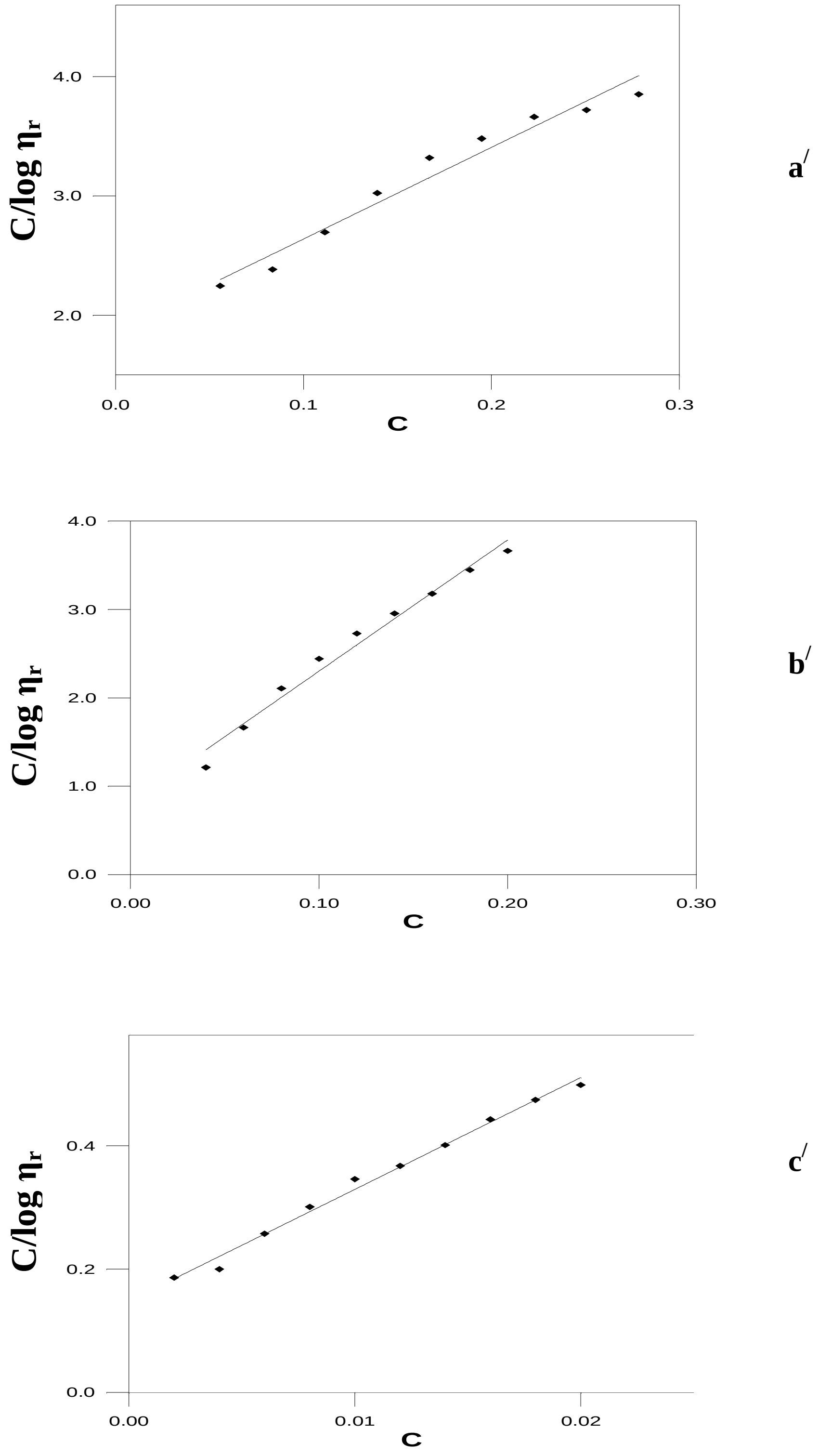


Figure (4-5) C/log η_r against C for aqueous amino acids at 298.15K
$a^{/}$) Isolucine $b^{/}$) Glutamine $c^{/}$)Arginine

Table (4-9a) V_h values that calculated from equation (2-31) for aqueous amino acids solutions at four temperatures (293.15-308.15) K.

Amino acids	V_h L.mol^{-1}			
	C/(log η/η_0)= 2.303/a V_h- 2.303 Q C / a			
	29315K	**298.15K**	**303.15K**	**308.15K**
DL-Valine	0.84581	1.14519	0.94459	0.52239
DL-Isolucine	0.24902	0.37756	0.85429	0.96629
DL-Methionine	0.57905	1.04274	1.39198	0.96629
DL-Glutamine	7.22628	2.78359	11.25309	5.90097
L-Arginine	1.07900	2.14715	0.35761	0.40773
DL-Histidine	14.28326	7.73851	4.00907	4.62139

Table (4-9b) V_h values that calculated from equation (2-31) for acidic amino acids solutions at four temperature (293.15-308.15) K.

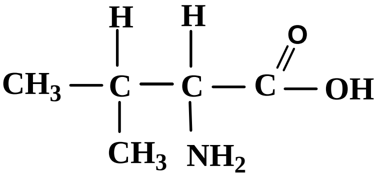
Amino acids	V_h L.mol^{-1}			
	C/(log η/η_0)= 2.303/a V_h- 2.303 Q C / a			
	2931.5K	**298.15K**	**303.15K**	**308.15K**
DL-Valine	0.56010	1.03363	1.35375	1.29062
DL-Isolucine	0.38235	1.12564	1.07925	1.47374
DL-Methionine	1.16796	0.73426	0.27934	1.71112
DL-Glutamine	4.78518	6.22252	13.40795	17.2433
L-Arginine	0.38235	1.12564	1.07925	1.47374
DL-Histidine	13.90388	20.75794	13.38205	6.40969

(4-7) Van der Waal's Volume

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. Its 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 $(\Phi^0_v)_{theo.}$ of the amino acids in this study. (v_w) was found by utilizing the principle of additivity as reported by bondi(86, 87) and Edward.(88) (v_w) may be dissected into contributions from individual atoms or groups of atoms measured in (ml/mol.). Table (4-10) indicates the contribution of group for determining (v_w).

(v_w) of Valine, for example is calculated from contributions of :



of	$-NH_2$	$>C=O$	$-OH$	$2\ {>}CH-$	$2\ -CH_3$	
by	**10.54**	**11.70**	**8.04**	**6.78**	**13.67**	**ml/mol.**

respectively and is equal to 71.18 ml/mol. Similarly v_w for other amino acids were estimated and tabulated in Table (4-11 a, b).

Table (4-10) group contributions to the Van der Waals volume

Group	**v_w, ml.mol^{-1}**
$-NH_2$	10.54
$>NH$	8.08
CH_4	17.12
$-CH_3$	13.67
$>CH_2$	10.23
$-\overset{\vert}{\underset{\vert}{C}}H$	6.78
$-OH$	8.04
$>C=O$	11.70
$-SH$	14.80
$>C=C<$	10.02
$=C-H$	8.06
$=C-$ (alkyl)	5.54
Phenyl group	45.8

The partial molal volume (Φ_v) can be estimated(89,90) 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 ($\overline{\upsilon}^0$) where ($\overline{\upsilon}^0 = \Phi^0_v / N$); (N) is the Avogadro's constant.

The value of ($\overline{\upsilon}^0$) is greater than (υ_w) by an amount associated void or empty volume (91) as given by the equation:

$$\bar{v}^0 = \frac{4}{3}\pi(r_w + \Delta)^3 \qquad \text{………… (4-5)}$$

Where:

r_w: the radius of Van der Waal's volume which is equal to $r_w = \left(\frac{3v_w}{4\pi}\right)^{1/3}$

Δ: is the thickness of spherical shell which is the empty volume ($\overline{\upsilon}^0$).

Terasawa et. al.(90) has reported the relation between (Φ^0_v) and (V_w) according to :

$$\Phi_v{}^0 = aV_w + b \qquad \text{………… (4-6)}$$

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

More information might be obtained from equation (4-7) which could be derived from equation (4-5) as follows:

$$\bar{v}^0 = \frac{4\pi}{3}(rw + \Delta)^3$$

$$\left(\bar{v}^0\right)^{1/3} = \left(\frac{4\pi}{3}\right)^{1/3}\left[\left(\frac{3v_w}{4\pi}\right)^{1/3} + \Delta\right]$$

$$\left(\bar{v}^0\right)^{1/3} = \left(\frac{4\pi}{3}\right)^{1/3}\left(\frac{3v_w}{4\pi}\right)^{1/3} + \left(\frac{4\pi}{3}\right)^{1/3}\Delta$$

$$\left(\frac{\bar{v}^0}{v_w}\right)^{1/3} = 1 + \frac{\left(4\pi/3\right)^{1/3}\Delta}{\left(v_w\right)^{1/3}}$$

$$\left(\frac{\overline{v}^{0}}{v_w}\right)^{1/3} = 1 + \frac{\Delta}{r_w} \qquad \text{………… (4-7)}$$

Experimental values of (Φ^0_v) at (298.15K), then calculated values of (v_w) by additivity and (r_w), have been introduced into equation (4-7), then (Δ) can be estimated for each amino acids. Then by introducing the values of (Δ) and (r_w) into equation (4-5), the theoretical value of (Φ^0_v) can be obtained. The obtained data of theoretical partial molal volumes with those corresponding experimental values have been listed in Tables (4-11 a, b).

It can be noticed that there is good agreement between the theoretical and experimental values of (Φ_v) which indicate strong solute-solvent interaction which coincide with other parameter for determination of molecular interaction.

Table (4-11a) Theoretical and experimental values for limited apparent molal volume Φ^0_v , Van der Waals volume v_w, Van der Waals radius r_w and Δ values for aqueous amino acids solutions

Amino cids	Φ^0_v Theoretical	Φ^0_v Experimental	r_w (cm)	v_w	Δ (cm)
DL-Valine	92.082	92.078	2.5714×10^{-8}	71.18	0.2304×10^{-8}
DL-Isolucine	110.409	110.409	2.6891×10^{-8}	82.29	0.2875×10^{-8}
DL-M ethionine	105.066	105.066	2.6987×10^{-8}	81.41	0.2290×10^{-8}
DL-Glutamine	106.555	106.555	2.6708×10^{-8}	102.45	0.2707×10^{-8}
L-Arginine	129.751	129.751	2.9032×10^{-8}	79.76	0.2379×10^{-8}
DL-Histidine	130.458	130.476	2.6393×10^{-8}	77.01	0.5071×10^{-8}

Table (4-11b) Theoretical and experimental values for limited apparent molal volume Φ^0_v , Van der Waals volume v_w, Van der Waals radius r_w and Δ values for acidic amino acids solutions

Amino cids	Φ^0_v Theoretical	Φ^0_v Experimental	r_w (cm)	v_w	Δ (cm)
DL-Valine	92.781	92.777	2.5714×10^{-8}	71.18	0.2870×10^{-8}
DL-Isolucine	114.392	114.392	2.6891×10^{-8}	82.29	0.3228×10^{-8}
DL-M ethionine	104.671	104.671	2.6987×10^{-8}	81.41	0.2253×10^{-8}
DL-Glutamine	143.559	143.559	2.6708×10^{-8}	102.45	0.5780×10^{-8}
L-Arginine	130.895	130.895	2.9032×10^{-8}	79.76	0.2471×10^{-8}
DL-Histidine	121.249	121.307	2.6393×10^{-8}	77.01	0.4316×10^{-8}

Chapter Five

Conclusions and Suggestions for Future Work

5

(5-1) Conclusions

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

From this work we can conclude that:

1. 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.
2. The apparent molal volume has it minimum value at 293.15K indicating an appreciable shrinkage at this temperature due to more incorporation taking place.
3. The extent of molecular interaction between solute and solvent depends largely on the structure of amino acids showed specific interaction with solvent (water). Methionine and Isolucine showed higher degree of interaction, while Histidine showed the lower degree of interaction.
4. Viscosity data reported for all amino acids solutions (studied here) indicate that the values of the viscosity coefficient (B) are negative (except acidic Isolucine) which means that these amino acids particles are structure breaking for solvent.

(5-2) Suggestions for Future Work

To obtain a complete picture of the molecular interaction of amino acids, We suggest the following topics for further research work

1. The study of the volumetric and viscometric behaviour of aqueous solutions of amino acids at moderate and high concentrations in terms of preferential solvation.
2. The study of physical properties (density, viscosity) of other amino acids with other solvents and different conditions, such studies may offer more information between amino acids and aqueous fluids in human body.

Supervisors Certification

We, certify that this thesis was prepared under our supervision at the Department of Chemistry, College of Science at Al-Nahrain University as partial requirements for the degree of Master of Science in Chemistry.

Signature:	Signature:
Name: **Dr. Wisal Abudul Aziz Isa**	Name: **Taghride Ali Salman**
(Supervisor)	**(Supervisor)**
Date: / / 2005	Date: / / 2005

In view of the available recommendations, I forward this thesis for debate by the Examining Committee.

Signature:

Name: **Dr. Shahbaz A. Maki**
Head of Department of Chemistry
College of Science, Al-Nahrain University

Date: / /2005

Examination Committee Certification

We, the examining committee certify that we read this thesis **“Study of Some Physical Properties for Amino Acids Solutions in Aqueous and Acidic Media Over Temperature Range (293.15-308.15)K”** and have examined the student **(Zeena Shukur Mahmoud)** in its contents and that our opinion, its adequate as a thesis for the degree of Master of Science in Chemistry with ***Excelant***

Signature:

Name:
Date: / /2005

(Chairman)

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Name:
Date: / /2005

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Name: **Taghried Ali Slaman**
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Approve by the council of the College of Science

Signature:

Name: **Laith Abdul Aziz Al-Ani**
Address: **Dean of the College of Science**
Date: / /2005

This humble work
is dedicated to my family and
especially my beloved parents
With lots of love

ACKNOWLEDGMENT

My first and deepest gratitude goes to ALLAH the Almighty, for this uncountable blessing, help and conciliation.

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My sincere appreciation also goes to my family who stood beside me all the time; I appreciate the moral support, patience encouragement during my work.

Finally special thanks to my dearest friends and all kind and lovely people who helped me directly and indirectly to complete this work.

Zeena

CONTENTS

Chapter One: *Solvent Solute Interaction and the Properties of Amino Acids*

Chapter Two: *Some Physical Properties of Solution*

Chapter Three: *Experimental*

Chapter Four: *Results and Discussion*

Chapter Five: *Conclusions and Suggestions for Future Work*

LIST OF SYMBOLES

Symbols	Definitions
$\bar{V}^0$	Partial Molal Volume.
Φ_v	Apparent Molal Volume.
Φ^0_v	The Apparent Molal Volume at infinite dilution.
ρ	Density of Liquid.
ρ_0	Density of Reference Liquid.
W	Weight of the Liquid.
V	Volume of the Liquid.
η	Viscosity of Liquid.
t	Flow time.
η_0	Viscosity of Reference Liquid.
η_r	Relative Viscosity.
υ	Kinematic Viscosity.
c	Viscometer Constant.
A	Electrostatic Constant Correspond the Interaction between Solute Particles.
B	Constant Correspond to the Interaction between Solvent Molecules and Solute Particles.
V_h	Effective Flow Volume.
Q	Particles Interaction Coefficient.
a	Shape Factor.
V_w	Van der Waal’s Volume
A	Pre-Exponential factor (Arrhenius Factor).
Ea	Activation Energy.
R	Gas Constant.
T	Temperature.
K	Kelvin.
C	The Molar Concentration.
Φ	Volume Fraction of Spherical Particles.
∂G	Partial Molal Gibbs Free Energy.
∂n	Partial Molal of Number of Moles.
S	Second
M	Molecular Mass.

SUMMARY

This thesis concerned with the study of solute-solvent interaction of amino acids: [DL-Valine, DL-Isolucine, DL-Methionine, DL-Glutamine, L-Arginine and DL-Histidine] 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.$^{-1}$) for DL-Valine, DL-Methionine and L-Arginine, and from (0.002-0.004 mol.L.$^{-1}$) for DL-Glutamine and DL-Histidine due to limited solubility for them, and from (0.055-0.27 mol.L.$^{-1}$) for DL-Isolucine at four temperatures in the range of (293.15-308.15)K. The resulting data have been utilized to veritfy 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 follow the order:

Isolucine ≈ Methionine > Valine > Arginine >Glutamine > Histidine

This study clarifies that each of B-Coefficient, Partial Molal Volume, Van der Waal's Volume and Effective Flow Volume can be considerd as parameters to account for solute-solvent interaction.