Effect of N-Acetylcysteine on Volumetric and Viscometric Properties of Chitosan in Aqueous Acidic Solution

by

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A thesis submitted in partial fulfillment of the requirements for the degree of
M.Phil in Department of Chemistry

Khulna University of Engineering & Technology
Khulna-9203, Bangladesh.

December 31, 2017

Dedicated

To

My beloved late father Md. Abdur Rahim

Declaration

This is to certify that the thesis work entitled **"Effect of N-Acetylcysteine on Volumetric and Viscometric Properties of Chitosan in Aqueous Acidic Solution"** has been carried out by **Md. Abul Kashem** in the Department of Chemistry, Khulna University of Engineering & Technology, Khulna, Bangladesh. The above thesis work or any part of this work has not been submitted anywhere for the award of any degree or diploma.

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Approval

This is to certify that the thesis work submitted by Md. Abuk Kashem entitled **"Effect of N-acetylcysteine on Volumetric and Viscometric properties of chitosan in aqueous acidic solution"** has been approved by the board of examiners for the partial fulfillment of the requirements for the degree of Master of Philosophy in the Department of Chemistry, Khulna University of Engineering & Technology, Khulna, Bangladesh in 31 December, 2017.

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Acknowledgement

It is my pleasure to thanks to my honorable supervisor Prof. Dr. Mohammad Abu Yousuf for his sincere guidance and persisting effort throughout the research.

I wish to pay appreciations to Prof. Dr. Mohammad Hasan Morshed, Head of the Chemistry Department for necessary help and suggestions when needed.

I would like to express honor to all teachers of this department for their constant help and guidance regarding many issues throughout the research.

I would like to express countless respect and appreciation to the authority of my working place, Ideal College, Keshabpur, Jessore and also the colleagues present there.

Immeasurable respect and love to my family members, especially my late father Md. Abdul Rahim, whom I lost when I was working here.

I am also thankful to my all friends, seniors and juniors.

Md. Abul Kashem

Abstract

Volumetric and viscometric studies of Chitosan-H_2O-CH_3COOH and NAC (N-Acetylcysteine)-Chitosan-[H_2O-CH_3COOH] systems were investigated at 298.15 to 323.15 K at 5 K intervals. In all investigated systems concentrations of NAC were 0.10, 0.50 & 1.00 mol.L^{-1} and concentrations of chitosan were 0.003, 0.006 & 0.012 mol.L^{-1}. H_2O-CH_3COOH mixed solvent was used for the experiment and H_2O to CH_3COOH ratios 9:1, 7:3 and 3:2 were maintained.

Densities have been found to be increased with increasing concentration of both NAC and chitosan but decreased with increasing temperature. Densities were found to be increased with increasing the ratio of CH_3COOH in Chitosan-H_2O-CH_3COOH systems but this trend was not so significant is case of NAC-Chitosan-H_2O-CH_3COOH systems. Density Values of NAC-Chitosan-[H_2O-CH_3COOH] systems were remarkably higher than those Chitosan-H_2O-CH_3COOH systems.

The apparent molar volumes, φ_v of both Chitosan-H_2O-CH_3COOH and NAC-Chitosan-H_2O-CH_3COOH systems were determined from the experimental density values data at 298.15 to 323.15 K at 5 K intervals. The φ_v values were dependent upon concentration of NAC and chitosan in mixed solvents as well as the temperature. φ_v values have been found to be positive in all investigated systems. The φ_v values decreased throughout the whole concentration range for NAC and chitosan in their specific solvent systems. These results may be due to the solute–solvent, and solute–solute interaction through dipole-dipole interaction, ion-dipole interaction, hydrogen bond, hydrophilic or hydrophobic interaction among NAC, chitosan and aqueous acetic acid in the solutions. Besides, φ_v values were found to be increased with increasing temperature at any concentration of NAC and chitosan in solutions and this is may be due to increased thermal agitation at higher temperatures.

Apparent molar volume at infinite dilution, φ_v^0; apparent molar expansivity and S_v values were also determined. The φ_v^0 values of chitosan-[H_2O-CH_3COOH] systems decreased with increasing temperatures and increased with increasing the ratio of CH_3COOH in H_2O-CH_3COOH mixed solutions. At elevated temperatures cages in the investigated systems becomes less important hence the apparent molar volume at infinite dilution, φ_v^0 decreased with increasing temperature. In addition, incorporation of more acetic acid ratio in Chitosan-H_2O-CH_3COOH system hydrophobic-

hydrophobic repulsion predominant over hydrogen bonding or dipole-dipole interaction. The apparent molar volume at infinite dilution gives an idea about the presence of solute–solvent interactions. The expansivity values are positive at all the investigated temperatures. Positive values indicate that, on heating some NAC and chitosan molecules may be released from the solvation layer of ion. It may also be conferred that the positive φ_E^0 values may be originated from the hydrophobic character and steric effect of the NAC and chitosan in systems. As a whole there is a hydrophilic/hydrophobic balance among the solute and solvent molecules. S_v parameters contribute an idea about the prevailing solute–solute interactions in the mixtures. The negative and large in magnitude values of S_v in all investigated systems supports the weak solute-solute interaction present.

Both Chitosan-H_2O-CH_3COOH and NAC-Chitosan-H_2O-CH_3COOH systems showed rapid increase of viscosity values with the increase of chitosan and NAC concentrations but viscosities decreased with the increase of temperature. The increase of η values of with concentration of chitosan and NAC can be attributed to the increase in solute–solvent, and solute–solute interactions in solution. The small range of dissolution of chitosan and/or NAC in H_2O-CH_3COOH might have intriguing aspects which may be the consequence of the great ability of H_2O and CH_3COOH to make hydrogen bond and dipole-dipole, ion-dipole interaction. In all cases with the increase of temperature internal energy of the systems increased as a result solute-solute or solute-solvent interaction may be depleted and viscosity values decreased.

The viscosity data were employed to determine A and B-coefficients; change of free energy, ΔG^*; change of enthalpy, ΔH^* and change of entropy, ΔS^*. From these thermodynamic parameters state of the spontaneity of the investigated systems were known. Besides, negative A and positive B co-efficient suggesting that weak solute-solute but strong solute-solvent interaction present. The change of free energy values for viscous flow, ΔG^* were found to be positive indicate that work has to be done to overcome the energy barrier for the flow process. The positive ΔH values indicate that work has to be done for all the investigated systems. The ΔS^* values are negative for all the systems studied. This means that Chitosan-[H_2O-CH_3COOH] and NAC-Chitosan-[H_2O-CH_3COOH] systems are regular than those of the pure one. Here one point may be remarked that as $\Delta S < 0$ and $\Delta H > 0$, so the processes are never spontaneous but the reverse process is always spontaneous.

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Symbols/ Abbreviations	Explanation
K_d	Dissociation Constant
λ_i	Ionic conductance
η	Viscosity
λ_1^0	Limiting Ionic conductance
A	Area of contact between the two layers
f	Tangential force
ϕ	Fluidity
l	Length
Pa.S	Pascal-Second
cP	centipoise
mPa.S	Milli-Pascal-second
v	Velocity
r	Radius
P	Pressure
t	Flow time
ρ	Density of the liquid/solution
φ_v	Apparent molar volume
φ_E^0	Apparent molar expansivity at infinite dilution
ΔG^*	Free energy
ΔH^*	Change of Enthalpy and
ΔS^*	Entropy
h	Difference in height of the surface of the two reservoirs
g	Acceleration due to gravity
IUPAC	The International Union of Pure and Applied Chemistry

CHAPTER I

INTRODUCTION

CHAPTER I

Introduction

1.1 General

Viscometric and volumetric properties of solution provide a lot of information on the structures and molecular interactions of liquid mixtures. There is a certain relationship among viscometric and volumetric properties of solution as well as thermodynamic properties. So by determining and studying them together, relatively more realistic and comprehensive information of solution might be obtained.

In interpreting the composition, the structure of molecules and the molecular interaction in the binary and ternary systems, it is inevitable to find out the size and the shape of the molecules and the geometry of the arrangement of their constituent atoms. The measurement of bulk properties like, density, surface tension, viscosity etc. are also have gained increased importance during the recent years, because not only of their great usefulness in elucidating the composition and structure of molecules, but also the molecular interaction in binary and ternary systems. Viscometric and volumetric properties provide valuable tools in elucidating the composition and structure as well as interaction of solute and solvent in solution.

1.2 The phenomena of solute-solvent interaction

Revelation of the nature of ion-solvent interaction and interpretation of the thermodynamic and transport processes in terms of such parameters as effective size of the solvated ions in solutions have been two of the most difficult problems in the understanding of electrolytic solutions. This is because there is not satisfactory model to represent the various phenomena that occur in solution and the incompleteness in the understanding of the structure of the liquids in general. There are a number of evidences of solvation of ions [1–2] or solute molecules a number of studies have discussed the effect of solvation on the equilibrium properties of liquids.

The process of solvation and the process of dissolution are known to be closely related. When ionic crystal is added to a solvent, the electrostatic forces of attraction between the oppositely charged ions in the crystal have to overcome by interposing solvent layers around each of the ions. The ability of a solvent to dissolve a crystal is reflected by the following properties, its dielectric properties, polarity, degree of self-association and its ability to solvate. Studies on the phenomena of solvation have led to the conclusions that:

(i) The ionic compounds are moderately soluble in dipolar aprotic solvents of relatively high dielectric constant but are much more soluble in water and other hydroxylic solvents like methanol. A number of inorganic salts are dissociated in acetonitrile, which is otherwise known to solvate cations and anions rather poorly [3].

(ii) The dielectric constant alone is not an adequate measure of solvating ability and may even play a major role in determining the solvation of ionic species. Cations should be better solvated in solvents having atoms with an unshared electron pair like nitrogen and oxygen. The cations have been found to be strongly solvated in highly polar solvents with the negative charge localized on an oxygen atom, e.g. in sulphur dioxide, dimethylsulfoxide, phosphorus oxide, dimethylformamide [4]. Potassium iodide is less soluble than sodium iodide in methanol or water [5], but in dimethylsulfoxide or dimethylformamide the reverse is true, which could be due to differences of cation solvation.

The anions have been found to be solvated in two ways:

(i) Small ions are mostly solvated by hydrogen bonding which is superimposed upon solvation by ion-dipole interactions, and

(ii) Large ions are solvated by interaction due to mutual polarizability of the anions and the solvent superimposed upon solvation by dipole interactions. Thus while the anions are more strongly solvated in hydrogen bonding solvents than in dipolar aprotic solvents, the cations are better solvated in the latter type of solvents.

The solubility of halides in various solvents generally follows the order:

Iodides > bromides > chlorides > fluorides.

The alkaline halides are more soluble in hydroxylic solvents than in the dipolar aprotic solvents like acetonitrile and acetone. These are found to be more soluble in acetonitrile than in acetone [6]. Electrolytes may be divided into two categories: ionophores and ionogens. While the former are ionic in character in the crystalline state as well as in the fused state and in highly dilute solutions, the latter have molecular crystal lattice and ionize in solution only if suitable interaction occurs with the solvent molecules.

The ionophores may exist in solution as an equilibrium mixture containing ion-pairs and free ions [7].

$$M^+X^- \rightleftharpoons \underset{\text{Solvated}}{M^+} + \underset{\text{Solvated}}{X^-}$$

The ion-pairs are of oppositely charged ions having life terms sufficiently long to be recognized as kinetic entities in solution and in which only electrostatic forces are assumed [1]. Fuoss *et al.* [8] have studied intensely the dependence of the dissociation constant, K_d, on the dielectric constant, the temperature and the nature of the salt. It was found to be large for solvents having high dielectric constant. It has also been found to be dependent on the distance of closest approach of the ions in the ion pairs. For hydroxylic solvents, large ions have larger K_d values and lower conductance values than smaller ions, which doesn't hold for other solvents.

Interaction of the ions with the solvent molecules causes low conductance. Na^+ ion behaves as a large ion as the K_d of iodides of Bu_4N^+ and Na^+ are found to be of the same order. Small ions like Li^+, F^- have low conductance in acetone but have low K_d values which have been attributed to the loss of the solvent molecules from the ion-pairs [9]. Solute-solvent interactions have been studied in details by various methods; some important ones may be listed as follows:

(i) Study of the solute-solvent interactions through transference experiments.
(ii) The effect of solvation on the ionic conductance.
(iii) The experiments applying stoke's law and their relevance to the nature of solvation.
(iv) Polarographic measurements of solutions.
(v) The spectral results due to the presence of the ions in solutions.

A relationship between the values of the limiting equivalent ionic conductance, λ_i and the viscosity, η value was advocated and utilized by Walden and others to study the solute-solvent interactions [10]. In one approach which assumes the constancy of the product $\lambda_i\eta$ the effects of variation of temperature, viscosity and variation of the solvent were studied. For large organic ions [10], the temperature co-efficient was found to be nearly constant in water as well as other non-aqueous solvents, while for the other ions it showed variations. For changing solvents, the product was found to vary widely in the case of inorganic ions which have been interpreted to be due to differences in solvation numbers of the ion in the various solvents. In another approach to this study Pure and Sherrington [11] used the relation between viscosity η_i, and limiting ionic conductance λ_i^0, to measure the radii of interaction of solvent and solute, called stoke's law radii, r. They compared the crystallographic radii of some cations and anions with stoke's law radii in the case of diethylamide and dimethylsulphoxide solvents. They found the degree of solvation to decrease from lithium to cesium and to be less for silver and ammonium ions which have nearly comparable crystallographic radii. They postulated the anions to be unsolvated in dipolar aprotic solvents as the radii obtained are of the same order as that of the crystallographic radii, and that the negative end of the dipole in the solvent molecule is unshielded while the positive end is protected by two methyl groups, so that the cations, but not the anions are solvated by these solvents. Volumetric and viscometric measurement provides valuable tool for the determination of interaction among solutes and solvents.

1.3 Viscosity

Viscosity means viscous ability. Simply, viscosity of a material is resistance to flow. The internal friction which opposes the relative motion of the adjacent layers of a fluid causes for the resistance to flow. When a fluid is flowing through a cylindrical tube, this internal friction arises because of intermolecular friction. Molecules are a slower moving layer try to decrease the velocity of the molecules in a faster moving layer and vice versa.

Viscosity is really a frictional effect experienced by one layer of a liquid in moving past another in much the same way as an object experiences frictional resistance when dragged on a surface. The friction force, *f*, resisting the flow of one layer of fluid past the adjacent layer is proportional to the area, A, of the interface between the layers and to $\frac{du}{dr}$, the velocity gradient. This is Newton's lawand is given by

$$f = \eta A \frac{du}{dr}$$

Whereη (eta, a Greek letter), the constant of proportionality, is called the co-efficient of viscosity. When the velocity gradient is unity and the area is 1 sq-cm, η is equal to the force; or the co-efficient of viscosity,η may be defined as the force per 1 sq-cm required to maintain a difference of velocity of 1 cm per second between two parallel layers 1 cm apart. The reciprocal of the co-efficient of viscosity is known as the fluidity, ∅, or

$$\varnothing = \frac{1}{\eta}$$

Fluidity is a measure of the ease with which a liquid can flow. The connection between these quantities was first derived by J.L.M. Poiseuille in 1844, known as the Poiseuille equation [12]. If a liquid with a coefficient of viscosity (η) flows with a uniform velocity, at a rate of v cm^3 in t seconds through a narrow tube of radius r cm, and length 1 cm under a driving pressure of P dynes cm^{-2} then [12]:

$$\eta = \frac{\pi P r^4 t}{8 l v} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \text{(1.1.1)}$$

This equation known as Poiseuille's equation holds accurately for stream-line flow but not for the turbulent flow which sets as higher velocities; where, η is a proportionality constant, known as the coefficient of viscosity or simply viscosity of the liquid. The CGS unit of viscosity i.e., dynes sec cm^{-2} = g cm^{-1}sec^{-1} is called poise, in honor of J. L. M. Poiseuille who is the pioneer in the study of viscosity. The SI unit of viscosity is the Pascal-second (Pa.s). Since viscosity of liquid is usually very small, it is usually expressed in millipoise (mP) or centipoise (cP) or mPa.s.

1.3.1 Factors affecting viscosity

Viscosity is first and foremost function of material. Most ordinary liquids have viscosities on the order of 1 to 1000 mPa·s, while gases have viscosities on the order of 1 to 10μPa·s. Pastes, gels, emulsions, and other complex liquids are harder to summarize.

Some fats like butter or margarine are so viscous that they seem more like soft solids than like flowing liquids.

Temperature: The viscosity of a simple liquid decreases with increasing temperature (and vice versa). As temperature increases, the average speed of the molecules in a liquid increases and the amount of time they spend "in contact" with their nearest neighbors decreases. Thus, as temperature increases, the average intermolecular forces decrease. The exact manner in which the two quantities vary is nonlinear and changes abruptly when the liquid changes phase.

Pressure: Viscosity is normally independent of pressure, but liquids under extreme pressure often experience an increase in viscosity. Since liquids are normally incompressible, an increase in pressure doesn't really bring the molecules significantly closer together. Simple models of molecular interactions won't work to explain this behavior and, to my knowledge, there is no generally accepted more complex model that does. The liquid phase is probably the least well understood of all the phases of matter.

While liquids get runnier as they get hotter, gases get thicker. The viscosity of gases increases as temperature increases and is approximately proportional to the square root of temperature. This is due to the increase in the frequency of intermolecular collisions at higher temperatures. Since most of the time the molecules in a gas are flying freely through the void, anything that increases the number of times one molecule is in contact with another will decrease the ability of the molecules as a whole to engage in the coordinated movement. The more these molecules collide with one another, the more disorganized their motion becomes.

Cohesive forces: Cohesive forces are the intermolecular forces (such as those from hydrogen bonding and Van Der Waals forces) which cause a tendency in liquids to resist separation. These attractive forces exist between molecules of the same substance. For instance, rain falls in droplets, rather than a fine mist, because water has strong cohesion which pulls its molecules tightly together, forming droplets. This force tends to unite molecules of a liquid, gathering them into relatively large clusters due to the molecules' dislike for its surrounding. The materials having stronger cohesive forces normally exhibit lower viscosities and vice-versa.

Adhesive force: Adhesive forces are the attractive forces between unlike molecules. They are caused by forces acting between two substances, such as mechanical forces (sticking together) and electrostatic forces (attraction due to opposing charges). In the case of a liquid wetting agent, adhesion causes the liquid to cling to the surface on which it rests. When water is poured on clean glass, it tends to spread, forming a thin, uniform film over the glasses surface. This is because the adhesive forces between water and glass are strong enough to pull the water molecules out of their spherical formation and hold them against the surface of the glass, thus avoiding the repulsion between like molecules. The materials having stronger adhesive forces normally reveal higher viscosities and vice-versa.

1.4 Properties of Water

Water has a very simple atomic structure. The nature of the atomic structure of water causes its molecules to have unique electrochemical properties. The hydrogen side of the water molecule has a slight positive charge. On the other side of the molecule a negative charge exists. This molecular polarity causes water to be a powerful solvent and is responsible for its strong surface tension.

When the water molecule makes a physical phase change its molecules arrange themselves in distinctly different patterns. The molecular arrangement taken by ice (the solid form of the water molecule) leads to an increase in volume and a decrease in density. Expansion of the water molecule at freezing allows ice to float on top of liquid water.

1.4.1 Structure of water

It has been recognized that water is an 'anomalous' liquid many of its properties is differ essentially from normal liquids of simple structures [13]. The deviations from regularity indicate some kind of association of water molecules. The notable unique physical properties exhibited by liquid water are [14]: i) negative volume of melting ii) density maximum in normal liquid range (at 4 ∘C) iii) isothermal compressibility minimum in the normal liquid range at (46 ∘C) iv) numerous crystalline polymorphs v) high dielectric constant vi) abnormally high melting, boiling and critical temperatures for such a low molecular weight substance that is neither ionic nor metallic vii) increasing liquid fluidity with increasing pressure and viii) high mobility transport for H^+ and OH^- ions pure water has a unique molecular structure. The O-H bond length is 0.096 nm and the H-O-H angle 104.5°. For a very long time the physical and the chemists have pondered over the possible structural arrangements that may be responsible for imparting very unusual properties to water. To understand the solute water interaction the most fundamental problem in solution chemistry the knowledge of water structure is a prerequisite. The physico-chemical properties of aqueous solution in most of the cares are interpreted in terms of the structural change produced by solute molecules. It is recognized that an understating of the structural changes in the solvent may be crucial to study of the role of water in biological systems. Various structural models that have been developed to describe the properties of water may generally be grouped into two categories, namely the continuum model and the mixture models. The continuum models [15, 16] treat liquid water as a uniform dielectric medium, and when averaged over a large number of molecules the environment about a particular molecules is considered to be the same as about any other molecules that is the behavior of all the molecules is equivalent. The mixture model theories [17, 18 and 19] depict the water as being a mixture of short lived liquid clusters of varying extents consisting of highly hydrogen bonded molecules which are mixed with and which alternates role with non-bonded monomers. Among the mixture models, the flickering cluster of Frank and Wen [20], later developed by Nemethy and Scherage [15], is commonly adopted in solution chemistry. Properties of dilute aqueous solutions in terms of structural changes brought about by the solutes can be explained more satisfactorily using this model than any other model. According to this model the tetrahedraly hydrogen bonded clusters, referred to as bulky water $(H_2O)_A$, are in dynamic equilibrium with the monomers, referred to as dense water, $(H_2O)_B$ as represented by [19].

$$(H_2O)_A \rightleftharpoons (H_2O)_B$$

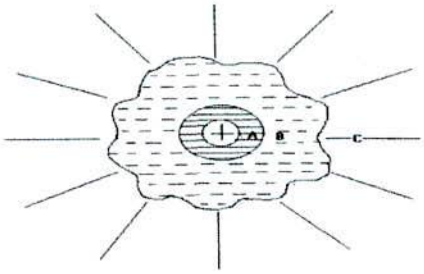


Figure 1.1: Frank and Wen model for the structure modification produce by an ion

The hydrogen bonding in the clusters is postulated [21] to be cooperative phenomenon. So when one bond forms several other also come into existence will be dissolved. The properties of solution can be accounted for in terms of solvent-solvent, solvent-solute and solute-solute interaction. In terms of thermodynamics, the concentration dependence of a given property extrapolated to the limit of infinite dilution provides a measure of solute-solvent interactions. Solute-water interaction or hydration phenomenon can be conveniently classified into three basic types:

i. Hydrophilic Hydration
ii. Ionic hydration
iii. Hydrophobic hydration

The introduction of a solute into liquid water produces changes in the properties of the solvent which are analogous to these brought about by temperature or pressure. The solute that shifts the equilibrium to the left and increase the average half-life of the clusters is termed as structure maker whereas that which has an effect in the opposite direction is called 'Structure breaker. The experimental result on various macroscopic properties provides useful information for proper understanding of specific interactions between the components and the structure of the solution. The thermodynamic and transport properties are sensitive to the solute-solvent, solute-solute, and solvent-solvent interaction. In solution systems these three types of interaction are possible but solute-solute interaction are negligible at dilute solutions. The concentration dependencies of the thermodynamic properties are a measure of solute-solute interaction and in the limit of infinite dilutions these parameters serve as a measure of solute-solvent interactions.

The solute induced changes in water structure also result in a change in solution viscosity.

1.4.2 Hydrophilic hydration

Solvation occurs as the consequences of solute-solvent interactions different from those between solvent molecules themselves. The solubilization of a solute molecule in water is characterized by changes in the water structure that depend on the nature of the solute. Dissolution of any solute will disrupt the arrangement of water molecules in the liquid state and create a hydration shell around the solute molecule. If the solute is an ionic species, then this hydration shell is characterized to extend from an inner layer where water molecules near the charge species are strongly polarized and oriented by the electrostatic field, through an intermediate region where water molecules are significantly polarized but not strongly oriented, to an outer solvent region of bulk water where the water molecules are only slightly polarized by the electric field of the ion [22].

1.4.3 Hydrophobic hydration

The hydrophobic effect refers to the combined phenomena of low solubility and the entropy dominated character of the solvation energy of non-polar substances in aqueous media [23]. It is also reflected by anomalous behavior in other thermodynamic properties, such as the partial molar enthalpies, heat capacities, and volumes of the nonpolar solutes in water. This effect originated from as much stronger attractive interaction energy between the nonpolar solutes merged in water than their van der Waals interaction in free space [24]. The tendency of relativity nonpolar molecules to "stick together" in aqueous solution is denoted as the hydrophobic interaction [25]. It results from hydrophobic hydration of a nonpolar molecule. Because hydrophobic hydration plays an important role in facilitating amphiphiles to aggregates in the aqueous bulk phase and to absorb, excessively, at the aqueous solution/air interface, it has been an ongoing objective of chemists working in these areas to seek a clear understanding of the molecular nature behind the subtle hydration phenomenon occurring between nonpolar solutes and water. A brief but detailed account of the general aspects of hydrophobic hydration, which is essential to the rationalization of the results obtained in this work, is given at this point.

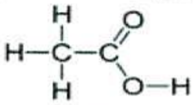
1.5 Properties of Acetic Acid

Acetic acid, also known as ethanoic acid or methane carboxylic acid, is a colorless liquid that has a strong and distinct pungent and sour smell. It is an organic chemical compound best recognized for giving vinegar. It is one of the simplest carboxylic acids (the second-simplest, after formic acid) and has the chemical formula CH_3COOH. Acetic acid is classified as a carboxylic acid. A carboxylic acid, shown as RCOOH, is a group of organic compounds that contain a carboxyl group. Here, the R group in the carboxylic acid structure may contain one or more carbon and/or hydrogen atoms.

It is produced by fermentation and synthesis methods. In both these methods, acetic acid must be separated from dilute aqueous solutions. Because the separation of acetic acid by a distillation process is quite difficult and expensive, the liquid–liquid extraction process can be used by means of an appropriate organic solvent. It is also well known for its ability to form dimers in the gas phase, whereas in the liquid phase or in a solution the point is not so clear. Infrared and Raman spectroscopic study of aqueous solutions of acetic acid, at low concentrations the acid is largely a hydrated monomer. As acid concentration increases, the hydrated monomer is gradually replaced by a hydrated linear dimer and then by the cyclic dimer. At higher concentrations, longer oligomers coexist with cyclic dimers. Presence of hydrogen bonds in acetic acid is the reason for its high boiling temperature, even though its dipole moment is less than 2 D. Indeed, it is known that acetic acid (and other acids) dimerize in the vapor phase, while the liquid phase may contain both dimers and higher oligomers.

Acetic acid is an excellent polar proteic solvent. It is frequently used as a solvent for recrystallization to purify organic compounds. Acetic acid is used as a solvent in the production of terephthalic acid, the raw material for polyethylene terephthalate. It is often used as a solvent for reactions involving carbocations, such as Friedel-Crafts alkylation. For example, one stage in the commercial manufacture of synthetic camphor involves a Wagner-Meerwein rearrangement of camphene to isobornyl acetate; here acetic acid acts both as a solvent and as a nucleophile to trap the rearranged carbocation. Glacial acetic acid is used in analytical chemistry for the estimation of weakly alkaline substances such as organic amides. Glacial acetic acid is a much weaker base than water, so the amide behaves as a strong base in this medium. It then can be titrated using a solution in glacial acetic acid of a very strong acid, such as perchloric acid. It is used in many industries such as the production of acetic ester and pharmaceuticals. It is an effective antiseptic when used as a 1% solution, with broad spectrum of activity against streptococci, staphylococci, pseudomonas, enterococci and others. It may be an option for skin infections caused by pseudomonas resistant to typical antibiotics. A brief description of properties of acetic acid is given in Table 1.1.

Table 1.1.: Properties of Acetic Acid

Chemical formula	$C_2H_4O_2$ or CH_3COOH
Molar mass	60.05 $g \cdot mol^{-1}$
Appearance	Colorless liquid
Structure	
Odor	Pungent/Vinegar-like
Density	1.049 $g\ cm^{-3}$
Melting point	16 to 17 °C; 61 to 62 °F; 289 to 290 K
Boiling point	118 to 119 °C; 244 to 246 °F; 391 to 392 K
Solubility in water	Miscible
Acidity (pK_a)	4.76
Basicity (pK_b)	9.24 (basicity of acetate ion)
Viscosity	1.22 mPa.s
Dipole moment	1.74 D

1.6 Chemistry and physical properties of chitosan

Chemically, chitosan is a high molecular weight, linear, polycationicheteropolysaccharide consisting of two monosaccharaides: N-acetyl-glucosamine and D-glucosamine. They are linked by β-(1→4) glycosidic bonds. The relative amount of these two monosaccharide in chitosan vary considerably, yielding chitosans of different degrees of deacetylation varying from 75% to 95%, molecular weight in the range of 50-2000, different viscosities and pKa values [26]. In addition, chitosan has three functional moieties on its backbone; the amino group on the C2, the primary and secondary hydroxyl groups on the C3 and C6 positions, respectively. These functional groups play important roles in different functionalities of chitosan. The amino group is the most important among the others, especially in acidic conditions, due to the protonation phenomenon, rendering it able to interact with negatively charged molecules (or sites). Additionally, chitosan polymer interacts with the metal cations through the amino groups, hydroxyl ions and coordination bonds. Most of the naturally occurring polysaccharides e.g., cellulose, dextrin, pectin, alginic acid, agar, agarose, and carragenas are natural and acidic in nature, whereas chitosan is highly basic polysaccharide. Their properties include solubility in various media, solution, viscosity, polyelectrolyte behavior, formation, ability to form films, metal chelations, optical and structural characteristics [27].

Chitosan undergoes the reactions typical of amines, of which *N*-acylation and Schiff reactions are the most important. Chitosan glucans are easily obtained under mild conditions but it is difficult to obtain cellulose glucans.

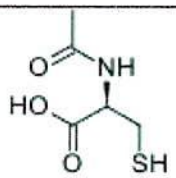
N-acylation with acid anhydrides or acyl halides introduces amido groups at the chitosan nitrogen. Linear aliphatic *N*-acyl groups higher than propionyl permit rapid acetylation of the hydroxyl groups in chitosan [28, 29]. Chitosan forms aldimines and ketimines with aldehydes and ketones, respectively, at room temperature. Reaction with ketoacids followed by reduction with sodium borohydride produces glucans carrying proteic and non-proteic amino acid groups. *N*-carboxy-methyl chitosan is obtained from glyoxylic acid. Examples of non-proteicamino acid glucans derived from chitosan are the *N*-carboxybenzyl chitosans obtained from *o*- and *p*-phthalaldehydicacids [30].

Chitosan and simple aldehydes produce *N*-alkyl chitosan upon hydrogenation. The presence of the more or less bulky substituent weakens the hydrogen bonds of chitosan; therefore, *N*-alkyl chitosans swell in water inspite of the hydrophobicity of alkyl chains. They retain the film forming property of chitosan [31, 32].

1.7 Properties of N-Acetylcysteine

N-Acetyl-L-Cysteine (NAC), the preacetylysed form of simple amino acid cysteine, a synthetic precursor of cysteine and reduced glutathione has been in clinical use for more than 40 years. It is a powerful intracellular antioxidant, antitoxin improves immunity. NAC is a thiol compound which is also called Acetylcysteine, is an amino acid with the molecular formula $C_5H_9NO_3S$, Molar mass of acid 163.195 g/mole. The melting point and boiling point of NAC are 106 °C and 407.7°C respectively. It is a white crystalline powder with a slightly acidic odor and characteristic sour tasting. It is a solid at room temperature, but melts easily with water, 4ml ALC; practically insoluble in chloroform and ether. The vapor pressure of NAC is estimated 1.1×10^{-5} mm Hg at 25 °C and stable of Stable in ordinary light; stable at temperature up to 120 °C; nonhygroscopic (oxidizes in moist air). The pH of NAC is 2 to 2.75 (1 in 100 mL) and dissociation constants pKa = 3.24 (carboxylic acid moiety) and Spectral Properties is Specific optical rotation: +5 °C at 20 °C (concentration = 3 g/100 mL).

Table 1.2: Some properties of N-Acetylcysteine

Property	Data
Chemical Name	N-Acetylcysteine
Chemical formula	$C_5H_9NO_3S$
Chemical structure	
Appearance	white crystalline powder
Molecular mass	163.195 g/mole
Melting point	109 to 110 °C
Boiling point	407.7 °C at 760 mmHg
pH	2 to 2.75 (1 in 100 ml)
Density	1.294 g/cm^3
Flash Point	200.4 °C

NAC is not found naturally in food sources; however cysteine is present in most high protein foods. NAC converts into cysteine. Cysteine is a nonessential amino acid produced by the body. Cysteine is primarily found in animal protein, along with the other ten essential amino acids. Meats such as pork, chicken, sausage, turkey and duck all contain the amino acid cysteine. Fish and lunch meats also contain cysteine. Dairy sources of cysteine include ricotta cheese, cottage cheese, yogurt and eggs. Cysteine can be found in some plant sources plant sources for vegetarians and vegans. Cysteine is found in granola and oat flakes. Vegetables like broccoli, red pepper and onion are significant sources of cysteine. Other plant sources include bananas, garlic, soy beans, linseed and wheat germ. Cysteine is important amino acid, but deficiency is relatively rare. Low levels of cysteine can cause slow growth in children and lowered immunity. Muscle loss, weakness, apathy and liver damage may also be a result of low cysteine in the diet.

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NAC is a therapeutic medicine frequently used as a mucolytic agent and for treating acetaminophen hepatotoxicity. It increases the cell reserves of free radicals and acts as an antioxidant. It also inhibits the replication of HIV and prevents apoptosis in neurons. NAC prevents endotoxin-induced degeneration of oligodendrocyte progenitors and hypomyelination in developing rat brain. NAC may have a direct chelating effect on lead as seen by lowered serum lead levels. It prevents lead toxicity and reduces oxidative sequel of lead exposure. NAC crosses cell membranes and is rapidly consumed in producing intracellular glutathione. By reducing extracellular cysteine to cysteine, it acts as a source of SH groups and it can stimulate glutathione synthesis enhance glutathione-

S-transferase activity promote detoxification and act directly on reactive oxidant radicals. NAC corrects the reduction in glutathione concentration and results in significant preservation of fluidity of membranes and of the activities of catalase, mitochondrial superoxide dismutase and different forms of glutathione peroxidase in biliary obstructed rats. NAC is a powerful scavenger of hypochlorous acid and is capable of reducing hydroxyl radicals and hydrogen peroxide. SH groups are essential for defense against reactive oxygen species. NAC can also prevent apoptosis caused by oxidative stress and promote cell survival by activating signal regulating pathways. Recently, volumetric and viscometric study of NAC ethanol-water and DMSO-water systems were performed [33-34]. From the results it was seen that NAC showed more interaction in ethanol-water mixture than those for individual solvents. Similar results were obtained in DMSO-water systems. So to get more information of NAC, this research is devoted to solution properties of NAC in acidic aqueous solution in presence of chitosan biopolymer. Mixed solutions were prepared by varying the ratio of ethanoic acid in water. Effect of addition of NAC in Chitosan-H_2O-CH_3COOH system has also been explored which hasn't been done before to the best of my knowledge.

1.8 Physical Properties and chemical constitutions

In interpreting the composition, the structure of molecules and the molecular interaction in the binary and ternary systems, it is inevitable to find out the size and the shape of the molecules and the geometry of the arrangement of their constituent atoms. For this purpose the important parameters are bond lengths or interatomic distance and bond angles. The type of atomic and other motions as well as the distribution of electrons around the nuclei must also be ascertained; even for a diatomic molecule a theoretical approach for such information would be complicated. However, the chemical analysis and molecular mass determination would reveal the composition of the molecules, and the study of its chemical properties would unable one to ascertain the group or sequence of atoms in a molecule. But this cannot help us to find out the structures of molecules, as bond length, bond angles, internal atomic and molecular motions, polarity etc. cannot be ascertained precisely.

For such information it is indispensable to study the typical physical properties, such as absorption or emission of radiations, refractivity, light scattering, electrical polarization, magnetic susceptibility, optical rotations etc. The measurement of bulk properties like, density, surface tension, viscosity etc. are also have gained increased importance during the recent years, because not only of their great usefulness in elucidating the composition and structure of molecules, but also the molecular interaction in binary and ternary systems.

The various physical properties based upon the measurement of density, viscosity, surface tension, refractive index, dielectric constant etc., have been found to fall into the following four categories [35].

(i) **Purely additive properties:** An additive property is one, which for a given system, is the sum of the corresponding properties of the constituents. The only strictly additive property is mass, for the mass of a molecule is exactly equal to the sum of the masses of its constituent atoms, and similarly the mass of a mixture is the sum of the separate masses of the constituent parts. There are other molecular properties like molar volume, radioactivity etc. are large additive in nature.

(ii) **Purely constitutive properties:** The property, which depends entirely upon the arrangement of the atoms in the molecule and not on their number is said to be a purely constitutive property. For example, the optical activity is the property of the asymmetry of the molecule and occurs in all compounds having an overall asymmetry.

(iii) **Constitutive and additive properties:** These are additive properties, but the additive character is modified by the way in which the atom or constituent parts of a system are linked together. Thus, atomic volume of oxygen in hydroxyl group (–OH) is 7.8 while in ketonic group (=CO) it is 12.2. The molar refraction, molecular viscosity etc. are the other examples of this type.

(iv) **Colligative properties:** A colligative property is one which depends primarily on the number of molecules concerned and not on their nature and magnitude. These properties are chiefly encountered in the study of dilute solutions. Lowering of vapor pressure, elevation of boiling point, depression of freezing point and osmotic pressure of dilute solutions on the addition of non-volatile solute molecules are such properties.

1.9 Molarity

Molarity, (C) is defined as the number of moles of solute per liter of solution. If n is number of moles of solute and V liters is the volume of the solution then,

$$Molarity(C) = \frac{Number\ of\ moles\ of\ solute}{Volume of solution}$$

$$or, C = \frac{n}{V} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1.2.1)$$

The unit of molarity is mol.L^{-1}.

1.10 Molar volume of Mixtures

The volume in mL occupied by 1 mole of any substance is called the molar volume. On the other hand, ifρ is the density and M be the molar mass, molality (m) of a solution is defined as the number of moles of the solute per 1000 g of solvent. Mathematically,

$$Molality\ (\mathrm{m}) = \frac{\text{Number of moles of solute}}{\text{Weight of solvent in gram}} \times 1000$$

$$\text{or, } \mathrm{m} = \frac{\frac{\mathrm{a}}{\mathrm{M_2}} \times 1000}{\text{Volume of solvent in mL.} \times \text{density of solvent in g cm}^{-3}}$$

$$\text{or, } \mathrm{m} = \frac{\mathrm{a}}{\mathrm{M_2}} \times \frac{1000}{\mathrm{V_1} \times \rho_0} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1.2.2)$$

Where, a = weight of solute in gram.

M_2 = molecular weight of solute in gram.

V_1 = volume of solvent in mL.

ρ_0 = density of solvent in g.cm^{-3}.

$$\text{Specific volume, (V)} = \frac{1}{\rho}\,\mathrm{mL}g^{-1} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.2.3)$$

$$\text{Molar volume, } (\mathrm{V_m}) = \frac{M}{\rho}\, m\ Lmol^{-1} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1.2.4)$$

When two components are mixed together, there may be either a positive or a negative deviation in volume. One of cause of positive deviation in volume i.e. volume expansion has been explained by the disruption of the mode of association through H–bonding of liquids. The negative deviation in molar volume i.e. volume contraction has been thought of by many observers, as arising from the

I. compound formation through association

II. decrease in the intermolecular distance between the interacting molecules

III. interstitial accommodation of smaller species in the structural network of the larger species and

IV. change in the bulk structure of either of the substance forming the mixture.

1.11 Apparent molar volume

The apparent molar volume of a solute in solution, generally denoted by φ_v[36]

$$\varphi_v = \frac{V - n_1\overline{V}_1^{\,0}}{n_2} \quad \ldots\ldots\ldots (1.2.5)$$

Where, V is the volume of solution containing n_1 moles of solvent and n_2 moles of solute and $\overline{V}_1^{\,0}$ is the molar volume of the pure solvent at specified temperature and pressure. For binary solution, the apparent molar volume φ_v of an electrolyte in an aqueous solution is given by [37],

$$\varphi_v = \frac{1}{n_2}\left[\frac{n_1M_1 + n_2M_2}{\rho} - n_1\overline{V}_1^{\,0}\right] \quad \ldots\ldots\ldots (1.2.6)$$

Where, $V = \frac{n_1M_1 + n_2M_2}{\rho}$ and

n_1 and n_2 are the number of moles, M_1 and M_2 are molar masses of the solvent and solute respectively and ρ is the density of the solution. For molar concentration, $n_2 = m$, the molality and n_1, the number of moles of solvent in 1000 g of solvent, the equation for apparent molar volume takes the form [37, 38],

$$\varphi_v = \frac{1}{m}\left[\frac{1000 + mM_2}{\rho} - \frac{1000}{\rho_0}\right]$$

$$\text{or, } \varphi_v = \left[\frac{M_2}{\rho} - \frac{1000(\rho - \rho_0)}{m\rho\rho_0}\right] \quad \ldots\ldots\ldots (1.2.7)$$

where, ρ_o and ρ are the densities of the solvent and solution.

If the concentration is expressed in molarity (C), the equation (1.2.7) takes the form [39]:

$$\varphi_v = \left[\frac{M_2}{\rho_0} - \frac{1000(\rho - \rho_0)}{C\rho_0}\right] \quad \ldots\ldots\ldots (1.2.8)$$

Where, the relation,

$C = \frac{m.\varphi_v.1000}{1000 + \varphi_v.m.\rho_0}$ is used for inter conversion of the concentration in the two scales [39].

The partial molar property of a solute is defined as the change in property when one mole of the solute is added to an infinite amount of solvent, at constant temperature and pressure, so that the concentration of the solution remains virtually unaltered. If 'Y' represents partial molar property of a binary solution at constant temperature and pressure, Y will then be a function of two independent variables n_1 and n_2, which represent the number of moles of the two components present. The partial molar property of component one is then defined by the relation:

$$\bar{Y}_1 = \left(\frac{\delta Y}{\delta n_1}\right)_{n_2,P,T} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1.2.9)$$

Similarly for component 2,

$$\bar{Y}_2 = \left(\frac{\delta Y}{\delta n_2}\right)_{n_1,P,T} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1.2.10)$$

The partial molar property is designated by a bar above the letter representing the property and by a subscript, which indicates the components to which the value refers. The usefulness of the concept of partial molar property lies in the fact that it may be shown mathematically as,

$$Y_{(n_1,n_2)} = n_1\bar{Y}_1 + n_2\bar{Y}_2 \text{ at constant T and P} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1.2.11)$$

In respect of the volume of solution, equation 1.2.4 gives directly

$$V = n_1\bar{V}_1 + n_2\bar{V}_2 \text{ at constant T and P} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1.2.12)$$

At infinite dilution, (m or c →0), the partial molar volume and the apparent molar volume are identical. To obtain reliable φ_v values, it is necessary to measure the density, ρ with great precision because errors in ρ contribute considerably to the uncertainties in φ_v.

The concentration dependence of the apparent molar volume of electrolytes have been described by the Masson equation [40], the Redlich-Mayer equation [42] and Owen-Brinkley equation [41]. Masson [40] found that the apparent molar volume of the electrolytes vary with the square root of the molar concentration as,

$$\varphi_v = \varphi_v^0 + S_v\sqrt{c} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1.2.13)$$

Where, S_v is the experimental slope depending on the nature of the electrolyte.

Redlich and Rosenfeld [42] predicated that a constant limiting law slope S_v, should be obtained for a given electrolyte charge type if the Debye-Huckel limiting law is obeyed. By differentiating the Debye-Huckel limiting law for activity coefficients with respect to pressure, the theoretical limiting law slope S_v, could be calculated using the equation,

$$S_v = KW^{3/2} \cdots\cdots\cdots\cdots\cdots\cdots (1.2.14)$$

Where, the terms K and W are given by

$$K = N^2 e^3 \left(\frac{8\pi}{100 D^3 RT} \right)^{1/2} \left\{ \left(\frac{\delta \ln D}{\delta p} \right) - \left(\frac{\beta}{3} \right) \right\} \cdots\cdots\cdots\cdots (1.2.15)$$

And, $W = 0.5 \sum \gamma_i Z_i^2 \cdots\cdots\cdots\cdots\cdots\cdots (1.2.16)$

where, β is the compressibility of the solvent, γ_i is the number of ions of the species i of valencyZ_i formed by one molecule of the electrolyte and the other symbols have their usual significance [42]. For dilute solutions the limiting law for the concentration dependence of the apparent molar volume of electrolytes is given by the equation,

$$\varphi_v = \varphi_v^0 + KW^{3/2} \sqrt{C} \cdots\cdots\cdots\cdots\cdots\cdots (1.2.17)$$

and for not too low concentrations, the concentration dependence can be represented as,

$$\varphi_v = \varphi_v^0 + S_v \sqrt{C} + b_v C \cdots\cdots\cdots\cdots\cdots\cdots (1.2.18)$$

Where, S_v is the theoretical limiting law slope and b_v an empirical constant.

1.12 Apparent Molar Expansivities

From the apparent molar volumes determined at different temperatures, it is possible to derive the apparent molar expansivities through the thermodynamic relation given by equation 1.2.18.

$$\varphi_E = \left(\frac{\delta \varphi_v}{\delta t} \right)_P \cdots\cdots\cdots\cdots\cdots\cdots (1.2.19)$$

Where, φ_E is the apparent molar expansivity, *t* is the temperature, and *P* is the pressure. The slope of φ_v versus *t* plot gave φ_E.The linearity of the φ_v versus *t* plot over a certain temperature range indicates that φ_E is constant over that range and given by the slope of the line. The apparent molar expansivity at infinite dilution, φ_{E}^{o} can be obtained if φ_{v}^{0} values are used for φ_{v} in this treatment.

1.13 Viscosity

Viscosity means viscous ability. The internal friction opposes the relative motion of adjacent layers of a fluid. When a fluid is flowing through a cylindrical tube, layers just touching the sides of the tubes are stationary and velocities of the adjacent layers increases towards the center of the tube, the layer in the center of the tube having the maximum velocity. There thus exists a velocity gradient. Molecules are a slower moving layer try to decrease the velocity of the molecules in a faster moving layer and vice versa, with a result that some tangential force is required to maintain uniform flow. This tangential force will depend upon two factors,

(i) Area of contact 'A' between the two layers and

(ii) Velocity gradient $\frac{dv}{dx}$

Thus, $f \propto A\frac{dv}{dx}$

Or $$f = \eta A\frac{dv}{dx} \quad \text{………………………………………………} \quad (1.2.20)$$

Where, η is a proportionality constant, known as the coefficient of viscosity or simply viscosity of the liquid. Thus, the coefficient of viscosity may be defined as the force per unit area required to maintain unit difference in velocity between two parallel layers of liquid unit distance apart.

The reciprocal of viscosity called the fluidity (ϕ) is given by the relation.

$$\phi = \frac{1}{\eta} \quad \text{……………………………………………………………………} \quad (1.2.21)$$

If a liquid with a coefficient of viscosity (η) flows with a uniform velocity, at a rate of V cm^3 in t seconds through a narrow tube of radius r cm, and length 1 cm under a driving pressure of p dynes cm^{-2} then according to J.L.M. Poiseuille[43]:

$$\eta = \frac{\pi \mathrm{Pr}^4 t}{8lv} \quad \text{……………………………………………………………} \quad (1.2.22)$$

This equation known as Poiseuille's holds accurately for stream-line flow but not for the turbulent flow which sets as higher velocities. After correction for kinetic energy, the equation becomes,

$$\eta = \frac{\pi \Pr^4 t}{8lv} - \frac{\rho V}{8\pi lt} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1.2.23)$$

Where, ρ represents the density of the liquid/solution. However, in practical purposes, the correction factor is generally ignored.

The driving pressure P=$h\rho g$, where h is the difference in height of the surface of the two reservoirs, since the external pressure is the same at the surface of both reservoirs, g = acceleration due to gravity and ρ= the density of liquid. Thus the equation (1.2.22) becomes,

$$\eta = \frac{\pi h \rho g r^4 t}{8vl} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1.2.24)$$

For a particular viscometer h, l, r and v are fixed, so the equation (1.2.24) becomes,

$$\eta = A\rho t \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1.2.25)$$

Where $A = \frac{\pi h g r^4}{8vl}$, called the calibration constant of the viscometer used.

Putting the values of $A, \rho$and to f the investigated liquid in equation (1.2.25), the coefficient of viscosity can be obtained for a liquid at a definite temperature.

The CGS Unit of viscosity is poise, in honor of J.L.M. Poiseuille. The SI unit of viscosity is the pascal-second (Pa·S). Since viscosity of liquid is usually very small, it is usually expressed in centipoise (cP) or mPa.s.

1.14 Viscosity and temperature

The viscosity of a liquid generally decreases with the increase of temperature. Evaluation of energy of activation for viscous flow can be stated by the Arrhenius equation as follows:

$$\eta = Ae^{-\epsilon_a/_{RT}} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1.2.26)$$

Where, A is Arrhenius constant and ε is energy of activation for viscous flow. The linear form of the equation 1.2.26 is as follows:

$$ln\eta = lnA - \frac{\epsilon_a}{RT} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1.2.27)$$

$ln\eta$against$\frac{1}{T}$ offer straight line. From the slope and intercept the energy of activationand Arrhenius constant can be determined.

1.15 Different thermodynamic parameters

Eyring and co-workers [44] using absolute reaction rate theory and partition functions corrected viscosity, η as follows:

$$\eta = \frac{hN}{V}.e^{\frac{\Delta G^*}{RT}} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1.2.28)$$

Where, ΔG^* is the change of free energy of activation per mole for viscous flow, V_m is the molar volume for liquids or solutions and h, N, R and T have usual meaning. The values of change of free energy of activation (ΔG^*) can be calculated by using the Nightingle and Benck equation [45],

$$\Delta G^* = \mathrm{RTln}(\frac{\eta V}{hN}) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1.2.29)$$

And values for the corresponding thermodynamic parameters, enthalpy of activation, ΔH^* and entropy of activation ΔS^* for per mole for viscous flow of the liquids or solutions have been calculated from the relationship (1.2.28) [45]

$$ln\frac{\eta V}{hN} = \frac{\Delta H^*}{RT} - \frac{\Delta S^*}{R} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1.2.30)$$

Assuming $\Delta H^*$and $\Delta S^*$to be almost independent in the temperature range studied, a plot of $\ln\frac{\eta V_m}{Nh}$ against $\frac{1}{T}$, will give a straight line. From the slope and intercept $\Delta H^*$and ΔS^* can be determined respectively.

1.16 Viscosity Coefficients A and B Measurement

The Jones-Dole coefficient, A, reflects the effect of solute-solute interaction and B, is a measure of structural modifications induced by the solute-solvent interaction. The co-efficients A and B for the electrolyte solutions can be measured by using the empirical equations of Jones-Dole [46].

$$\eta_r = 1 + A\sqrt{C} + BC \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1.2.31)$$

Where, $\eta_r$is the relative viscosity.

Relative viscosity, $\eta_r = \frac{\text{viscosity of solution, } \eta}{\text{viscosity of solvent, } \eta_0}$

The values of the coefficients *A* and *B* were obtained from the intercept and slope of the plot

$\frac{\eta_r - 1}{\sqrt{C}}$against$\sqrt{C}$ respectively.

CHAPTER II

LITERATURE REVIEW

Chapter II

Literature Review

2.1 Literature review

NAC a sulfhydryl substance is a derivative of amino acid L-cysteine widely used as medicine. Mucolytic activity of NAC was used for the first time in the treatment of some respiratory diseases (e.g. chronic bronchitis) over 40 years ago [47]. Detoxifying properties of NAC were discovered in the 1970s and since then NAC was being used as an antidote in aminophen intoxication [48]. Currently it is known mainly as an antioxidant displaying direct and indirect activities [49]. Oxidative stress, the imbalance between reactive oxygen species (ROS) and actions of the antioxidant network which takes part in pathogenesis of a broad spectrum of diseases including cancer, cardiovascular, arthritis, diabetes, influenza-like symptomatology as well as some lung disturbances namely pulmonary oxygen toxicity, adult respiratory distress syndrome, chronic obstructive pulmonary disease, idiopathic pulmonary fibrosis [50] and cystic fibrosis. Increasing number of publications confirm efficacy of using NAC in the above mention diseases [49-52]. Antioxidant properties of NAC come from its specific structure. NAC contains amino acid L-cysteine plus an acetyl (-$OCCH_3$) group attached to the amino (NH_2) group. All amino acids including L-cysteine with sulphur group are characterized by antioxidant properties. Since L-cysteine is a precursor of reduced glutathione (GSH), synthesis of NAC contributes to augmentation of the level of this major intracellular antioxidant [49]. Depleted pool of GSH is often caused by oxidative stress and inflammation. NAC can therefore normalize disturbed redox status of the cells and thus influence redox – sensitive cell signaling and transcription pathways. Sulfhydryl group (–SH) in the NAC molecule make possible also to directly scavenge ROS such as superoxide radical (O_2), hydrogen peroxide, regulation of protein phosphorylation and regulation of calcium level inside the cells as well as phagocytosis process [53, 54].

Diversity of applying NAC is the source of broad spectrum of used dosage and routes of administrations. Oral administration (tablet or inhalations) can range from 250 to 1800 mg/day and is used mainly in lung diseases [50]. Toxicological data shows that intakes of NAC per day orally could be consumed without causing significant adverse effects [55].

Application of NAC (7 mg/ml) diminished UV induced ROS in melanocyte cell line and protects these cells from UV – induced oxidative damage. NAC reduced formation of 8-oxoguanine in mice skin protecting melanocytes from UV induced melanoma [56-58]. Most of anticancer therapies are based on growth of ROS production in cancer cells leading to their apoptosis [59-63]. The efficiency of vitamin E and NAC as an antioxidant adjuvant therapy was shown in chemotherapy/radiotherapy course during acute lymphoblastic leukemia in 40 children study. Toxicity of chemo- and radiotherapy measured as a diminished level of malondialdehyde, as well as increased level of glutathione peroxidase and decreased occurrence of toxic hepatitis was significantly reduced [64-66].

NAC as a mucoactive, anti-inflammatory and antioxidant agent was expected to have a benefit therapeutic effect in Cystic fibrosis patients. In 4 weeks trial [67-69] NAC was administered orally to 18 Cystic fibrosis patients in a high doses (600-1000 mg) three times daily. Endometriosis is known as a common gynaecological disorder affecting about 10% of women in a reproductive age. It is characterized by presence of endometrial tissue outside of the uterine cavity, resulting in pelvic pain, infertility and dysmenorhea. Development of the disease is caused by implantation of endometrial cells in the peritoneal cavity and their proliferation leading to invade peritoneum and disease progression. Pathophysiology of endometriosis includes chronic inflammation within oxidative stress and pathological angiogenesis [70-71]. A cataract is a cloudiness or opacity in the normally transparent crystalline lens of the eye. This cloudiness can cause a decrease in vision acuity and sometimes may lead to hand movements behind the eye or blindness. The leading risk factor of cataract is aging. As glutathione is an important antioxidant in the lens it has been suggested that increasing GSH level NAC supplementation could be used to reduce cataract risk [72]. Diabetes elevates the risk of cataract formation. This form of cataract can result from sorbitol accumulation in the lens. Pathophysiology of early cataract development and the potential benefit of supplementation with vitamin B6 and NAC among the diabetic population were studied by Jain *et. al.* [73]. High-glucose concentrations can cause the oxidation and modification of proteins in the lens. Vitamin B6 (pyridoxine) and NAC supplementation may be helpful in slowing the oxidation of lens proteins. The study of Liebermann [74] raised the possibility that administration of NAC may reverse early cataracts. Zhang et al. [75] evaluated the effect of NAC and glutathione ethyl ester (GSH-EE) eye drops on the progression of diabetic cataract formation in rats. Author concluded that NAC and GSH-EE can slightly inhibit the progression of the diabetic cataract at the earlier stage. NAC, used as an ophthalmic drug is promising in the treatment of a range of ophthalmic disorders with oxidative stress component involved in pathogenesis including cataract, glaucoma, dry eye syndrome, vitreous floaters, inflammatory disorders, corneal, retinal and systemic diseases and its ophthalmic complications.

Chitosan nanoparticles were first described in 1994, when Ohya and coworkers [76] proposed the intravenous delivery of 5-fluorouracil, an anticancer drug, carried by chitosan nanoparticles obtained by emulsification and cross-linking. Since then, these systems have been extensively studied for drug delivery purposes and the original formulation was either used for other applications, such as the incorporation of active substances in toothpastes [77], or modified by the application of different preparation methods [79-80]. The modern era of chitosan research was heralded by publications in the 1990_s that described the antimicrobial potentials of chitosan and its derivatives, exhibiting a wide spectrum of activities against human pathogens and food-borne microorganisms [81-84]. The first study reporting antibacterial properties was reported by [85]. They reported that chitosan showed a broad range of activities and a high inactivation rate against both Gram-positive and Gram-negative bacteria [85]. However, although several studies have been published in this area, the exact mechanism of the antimicrobial activity of chitosan remains ambiguous.

Six major mechanisms have been proposed in the literature, as follows [81, 83-84]: (1) the interaction between the positively charged chitosan amine groups and the negatively charged microbial cell membranes, leading to the leakage of proteinaceous and other intracellular constituents; (2) the activation of several defense processes in the host tissue by the chitosan molecule acting as a water-binding agent and inhibiting various enzymes by blocking their active centers; (3) the action of chitosan as a chelating agent, selectively binding metals and then inhibiting the production of toxins and microbial growth; (4) the formation, generally by high molecular weight chitosan, of an impervious polymeric layer on the surface of the cell, thereby altering cell permeability and blocking the entry of nutrients into the cell; (5) the penetration of mainly low-molecular weight chitosan into the cystosol of the microorganism to bind DNA, resulting in interference with the synthesis of mRNA and proteins; and (6) the adsorption and flocculation of electronegative substances in the cell by chitosan, distributing the physiological activities of the microorganisms, causing their death. However, it is very important to mention that chitosan is soluble only in acidic media and therefore, the effect of pH on microorganisms must be considered together with the effect of chitosan. Thus, the synergetic effect of chitosan/pH together is probably the most evident explanation of the antimicrobial effect of chitosan.

Chitosan, a natural and linear biopolyaminosaccharide, has received much attention as a functional biopolymer with applications in pharmaceuticals, food, cosmetics and medicines. Water is universal solvent used in daily life. But chitosan is insoluble in water but soluble in acidic medium. So solution of chitosan in ethanoic and water mixed solvent might have potential application. On the other hand, NAC is widely used as medicine also a scavenging agent. So investigation of effect of NAC in chitosan+H_2O+CH_3COOH mixture could be quite interesting and might have medicinal application as well that has not been investigated earlier so far.

2.2 Aim of the research

NAC is a molecule of extremely fast medicinal career and wide therapeutic profile. To date, at least 12 distinct biological activities have been attributed to NAC. In view of the fact that NAC is one of the smallest drug molecules, with a total of 19 atoms, the above pharmacological versatility is undoubtedly unique, indicating that the background of its biological complexity must be sought at the sub-molecular level. NAC is an acetylated amino acid with antioxidant and mucolytic properties. NAC is the most widely used mucolytic agent worldwide. Further indications for its use include rheumatoid arthritis, plasma hyperlipoproteinaemia and adult respiratory distress syndrome. NAC has also been reported to support repair processes after cytotoxic and radioactive damages in cancer therapy to remove atherosclerotic plaques. Its mode of action has generally been assumed to be related to the thiol (or thiolate) site, as the key moiety of the molecule. The reported thiolate-involved mechanisms are free radical scavenging, rupture of disulfide bonds in cross-linked mucous proteins, metal complex formation. It is obvious that NAC has some crucial properties that govern its viability and activity in biological media. So its solution behavior and the related protonation state and medium-dependent physicochemical interaction and thermodynamic properties are the discussion point at this time.

Chitosan, a natural and linear biopolyaminosaccharide, has received much attention as a functional biopolymer with applications in pharmaceuticals, food, cosmetics and medicines. Water is universal solvent used in daily life. But chitosan is insoluble in water

but soluble in acidic medium. So solution of chitosan in ethanoic and water mixed solvent might have potential application. To the best of our knowledge, still there is no explicit data of rheological and volumetric properties of NAC in chitosan+H_2O+CH_3COOH are available. The purpose of this study was to evaluate the miscibility of NAC in chitosan+H_2O+CH_3COOH mixed solution systems. Physico-chemical study recognized useful tool in getting sound information about the structure of various solution system. The specific aims of this study are:

i) to be aware of the probable interaction between chitosan and H_2O+CH_3COOH solution; NAC in chitosan+H_2O+CH_3COOH solution;

ii) to explore the data on physico-chemical properties of the systems mentioned above;

iii) to explore the role of NAC in physico-chemical interactions of all the systems and

iv) to understand the change in thermodynamic properties of NAC in chitosan+H_2O+CH_3COOH mixture.

CHAPTER III

EXPERIMENTAL

CHAPTER III

Experimental

3.1 General

During the course of the present work a number of techniques were involved which were in general standard ones. Constant efforts for attaining the ideal conditions for the experiments were always attempted.

The thoroughly cleaned glass pieces were dried in electric oven. The smaller pieces of apparatus were dried in electric oven and stored in desiccators, while larger pieces of apparatus were used directly from the oven.

Cannon-Fenske Opaque Viscometers were used for measurement of viscosity. The inside wall of the viscometer was cleaned thoroughly with warm chromic acid so that there was no obstruction in the capillary and the liquid could run clearly without leaving any drop behind. It was then rinsed thoroughly with distilled water followed by rectified spirit and finally with acetone and dried.

3.2 Apparatus

Viscosities of various liquids were measured using Cannon-Fenske Opaque Viscometers. And the densities were measured by Density and Sound Velocity Meter (DSA 5000M) Anton Paar, Austria. Electronic balance (HR 200, made in Japan) with an accuracy of ± 0.0001g was used for weighing. The flow time of liquids were recorded by a stop-watch capable to read up to 0.01 seconds. The temperature was controlled by water thermostat (Fisher Scientific ET-150, HAKKE, Germany) with an accuracy of ± 0.05 °C. The experimental temperatures were 298.15 to 323.15K at 5K intervals. Viscometers were calibrated with doubled-distilled water at the studied temperature. Calibrated volumetric flask, pipette and burette were used for necessary volume measurement.

3.3 Preparation and Purification of Reagents

High quality analytical grade reagents were used in all the experiments and where necessary further purifications were done.

3.4 Distillation of water

First time water was distilled by water distillation apparatus. First time distilled water was further purified by a quick-fit glass made distillation apparatus. About 1.5 L water was taken in a round bottom reservoir of which the capacity was 2.0 L. Then it was distilled in presence of $KMnO_4$. Distilled water was collected at only 100 °C. Other liquids of which the temperatures were below and above the mentioned boiling point were discarded. In all the experiments double distilled water was used.

3.5 Chemicals

N-acetylcysteine and chitosan were collected from Sigma Aldrich, USA. Acetic acid, CH_3COOH (HPLC Grade) was collected from E-Merck, Germany. All chemicals and reagents were of analytical grade and were used without further purification.

3.6 Preparation of solution

Solutions were prepared by mixing appropriate amount of NAC and/or chitosan of in H_2O-CH_3COOH mixed solvents using measuring flask. NAC and/or chitosan were weighed by electronic balance (HR 200, made in Japan) with an accuracy of ± 0.0001g. The volume taken by using pipette was corrected up to 0.1 cm^3. The volume of each component used as taken converted into molar solution. Stopper of measuring flask was kept closed to prevent evaporation and introduction of moisture into the solution.

3.7 Density measurement

The densities were measured by Density and Sound Velocity Meter (DSA 5000M) Anton Paar, Austria. The densities of solvents and solutions were measured separately. For this solvent and solutions were poured into the Density and Sound Velocity Meter through injection by syringe. The investigated temperatures were selected manually and the experimental data of density values were recorded automatically in the machine. Then the results were collected from the data memory. Precautions were taken in every injection and after each ejection machine was cleaned properly by ethanol, acetone on the basis of inorganic and organic solvents used.

3.8 Viscosity measurement

Viscosity of water, acetic acid and several solutions were measured by using the Cannon-Fenske Opaque Viscometers. The interior of the viscometer was cleaned thoroughly with warm chromic acid and then with distilled water, so that there was no obstruction in the capillary and the liquid could run freely without leaving any drop behind. It was then rinsed with acetone and dried in an oven at about 85 °C. The viscometer was then clamped vertically in the thermostatic water bath such that the upper mark of the top bulb was well below the water level. 10.0 mL of doubled-distilled water was poured into the viscometer by a pipette. Then it was allowed to keep in the thermostatic bath for about 30 minutes to attain the bath temperature. With the help of pipette filler attached to the narrower limb of the viscometer, the water was sucked up above the upper mark of the bulb. The water of bulb was then allowed to fall into the capillary and the time of fall between the two marks was noted with the help of stop-watch capable of reading up to 0.01 second. The reading at each temperature was repeated three/four even more times, in order to check the reproducibility of the flow time, the temperature being maintained at the same value. Since the accurate viscosity and density of water at different temperatures are known (from literature) calibration constant A of the viscometer for different temperature were obtained by using equation,

$$\eta = A\rho t \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1.2.26)$$

Where, $A = \frac{\eta_{H_2O}}{\rho_{H_2O} . t_{H_2O}}$

Like water, the flow time of different solutions were determined. Then putting the values of the calibration constant, density and time of flow of the experimental solutions, the viscosities of the solutions were determined by using the equation 1.2.26.

3.9 Apparent Molar Volume measurement:

Apparent molar volumes were determined from measured densities of solvent and solution by using the following equation 1.2.8.

$$\boldsymbol{\varphi_v} = \left[\frac{1000(\rho_0 - \rho)}{C\rho_0}\right] + \frac{M_2}{\rho_0} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.2.8)$$

Where $\varphi_v$is the apparent molar volume, C is the molarity, M_2 is the molecular mass of the solute (NAC), and ρ_0 and ρ are the densities of the solvent and the solution respectively. In general, $\varphi_v$was found to vary linearly with concentration for the systems studied. Thus, $\varphi_v$data were fitted into equation1.2.13 and 1.2.18.

$$\varphi_v = \varphi_v^0 + S_v\sqrt{c} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (1.2.13)$$

$$\varphi_v = \varphi_v^0 + S_v\sqrt{C} + b_v C \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (1.2.18)$$

Where $\boldsymbol{\varphi_v}$is the apparent molar volume at infinite dilution and $\boldsymbol{b_v}$ is an experimentally determined parameter.

3.10 Determination of Apparent Molar Expansivity

From the apparent molar volumes determined at different temperatures, it is possible to derive the apparent molar expansivities through the thermodynamic relation given by equation 1.2.19.

$$\varphi_E = \left(\frac{\delta\varphi_v}{\delta t}\right)_P \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.2.19)$$

Where φ_E is the apparent molar expansivity, t is the temperature, and P is the pressure. The slope of φ_v versus t plot gave φ_E. The linearity of the $\varphi_v$versus t plot over a certain temperature range indicates that φ_E is constant over that range and given by the slope of the line. The apparent molar expansivity at infinite dilution, φ_{E}^0, can be obtained if φ_v^0 values are used for φ_v in this treatment.

3.11 Determination of Thermodynamic Parameters

The activation energy for viscous flow is determined from logarithmic form of Eyring equation as:

$$ln\eta = lnA - \frac{\epsilon_a}{RT} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.2.27)$$

The slope and intercept of the straight line of plot of $ln\eta$ vs $\frac{1}{T}$ presented the values of activation energy for viscous flow and Arrhenius constant respectively.

Values of enthalpy of activation, ΔH^* and entropy of activation, ΔS^* for per mole for viscous flow of solutions have been calculated from the relationship (1.2.30)

$$ln\frac{\eta V}{hN} = \frac{\Delta H^*}{RT} - \frac{\Delta S^*}{R} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.2.30)$$

CHAPTER-IV

RESULTS AND DISCUSSION

CHAPTER-IV

Results and Discussion

4.1 Investigated Systems

The whole research work has been planned into the following eighteen investigated systems to identify the change of interaction in various concentrations of NAC in Chitosan-H_2O-CH_3COOH which will provide the change of information in volumetric, viscometric and thermodynamic properties of solutions to determine the molecular interactions among NAC, Chitosan and Aqueous Acetic Acid. The investigated systems are:

i.) 0.003 M Chitosan + [9:1] [H_2O-CH_3COOH]
ii.) 0.006 M Chitosan + [9:1] [H_2O-CH_3COOH]
iii.) 0.012 M Chitosan + [9:1] [H_2O-CH_3COOH]
iv.) 0.003 M Chitosan + [7:3] [H_2O-CH_3COOH]
v.) 0.006 M Chitosan + [7:3] [H_2O-CH_3COOH]
vi.) 0.012 M Chitosan + [7:3] [H_2O-CH_3COOH]
vii.) 0.003 M Chitosan + [3:2] [H_2O-CH_3COOH]
viii.) 0.006 M Chitosan + [3:2] [H_2O-CH_3COOH]
ix.) 0.012 M Chitosan + [3:2] [H_2O-CH_3COOH]
x.) NAC in 0.003 M Chitosan + [9:1] [H_2O-CH_3COOH]
xi.) NAC in 0.006 M Chitosan + [9:1] [H_2O-CH_3COOH]
xii.) NAC in 0.012 M Chitosan + [9:1] [H_2O-CH_3COOH]
xiii.) NAC in 0.003 M Chitosan + [7:3] [H_2O-CH_3COOH]
xiv.) NAC in 0.006 M Chitosan + [7:3] [H_2O-CH_3COOH]
xv.) NAC in 0.012 M Chitosan + [7:3] [H_2O-CH_3COOH]
xvi.) NAC in 0.003 M Chitosan + [3:2] [H_2O-CH_3COOH]
xvii.) NAC in 0.006 M Chitosan + [3:2] [H_2O-CH_3COOH]
xviii.) NAC in 0.012 M Chitosan + [3:2] [H_2O-CH_3COOH]

4.2 Volumetric Properties

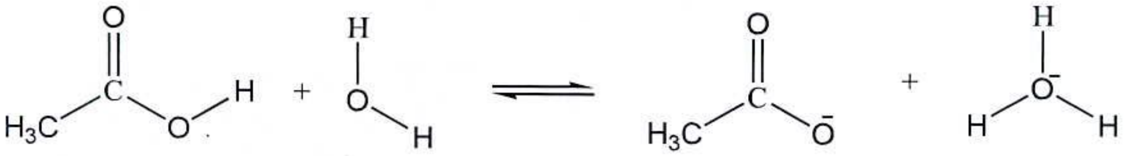
4.2.1 Density of Mixed Solvent

The density at different temperatures of the mixed pure solvents; water and Acetic Acid have been tabulated in Table 4.1. Here it is to be mentioned that the determined density values are reproducible. From Table the density values increased with the decreasing ratio of water in the H_2O-CH_3COOH mixed solvents system. It is also seen that densities of the solvents decreased remarkably with the increasing temperature.

Table 4.1: Densities, ρ of H_2O-CH_3COOH mixed solvent systems at 298.15 to 318.15 K at 5 K interval

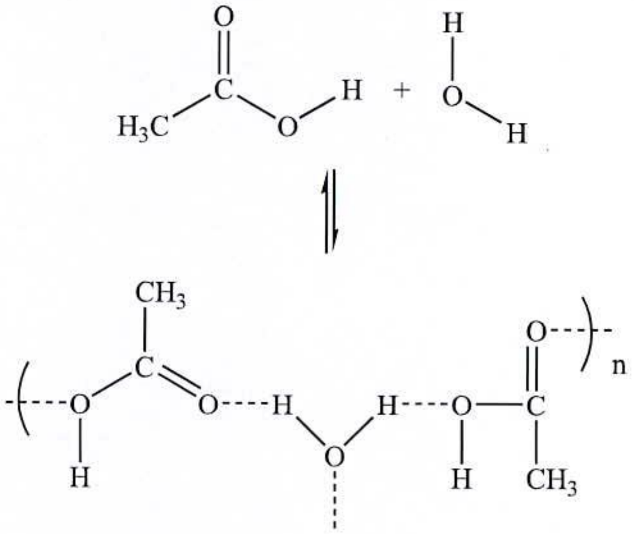
Name of the system	Density, ρ ($g.cm^{-3}$)				
	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
[9:1] [H_2O-CH_3COOH]	1.0114	1.0093	1.0072	1.0048	1.0023
[7:3] [H_2O-CH_3COOH]	1.0359	1.0327	1.0294	1.0260	1.0225
[3:2] [H_2O-CH_3COOH]	1.0456	1.0419	1.0382	1.0343	1.0304

When acetic acid is added to water, due to electronegativity differences of oxygen and hydrogen in -OH group of acetic acid and dipole interaction with water molecule, the acetic acid is transformed into acetate ion and H^+ ion which further combines with water to form hydronium ion. The reaction is-



Ionization of ethanoic acid in water

Smaller carboxylic (up to C4) acids dissolves in water in all proportions but after this solubility rapidly reduces. They dissolve because of the hydrogen bond formation to the water molecules as shown in the mechanism below:



Hydrogen bonding between water and ethanoic acid

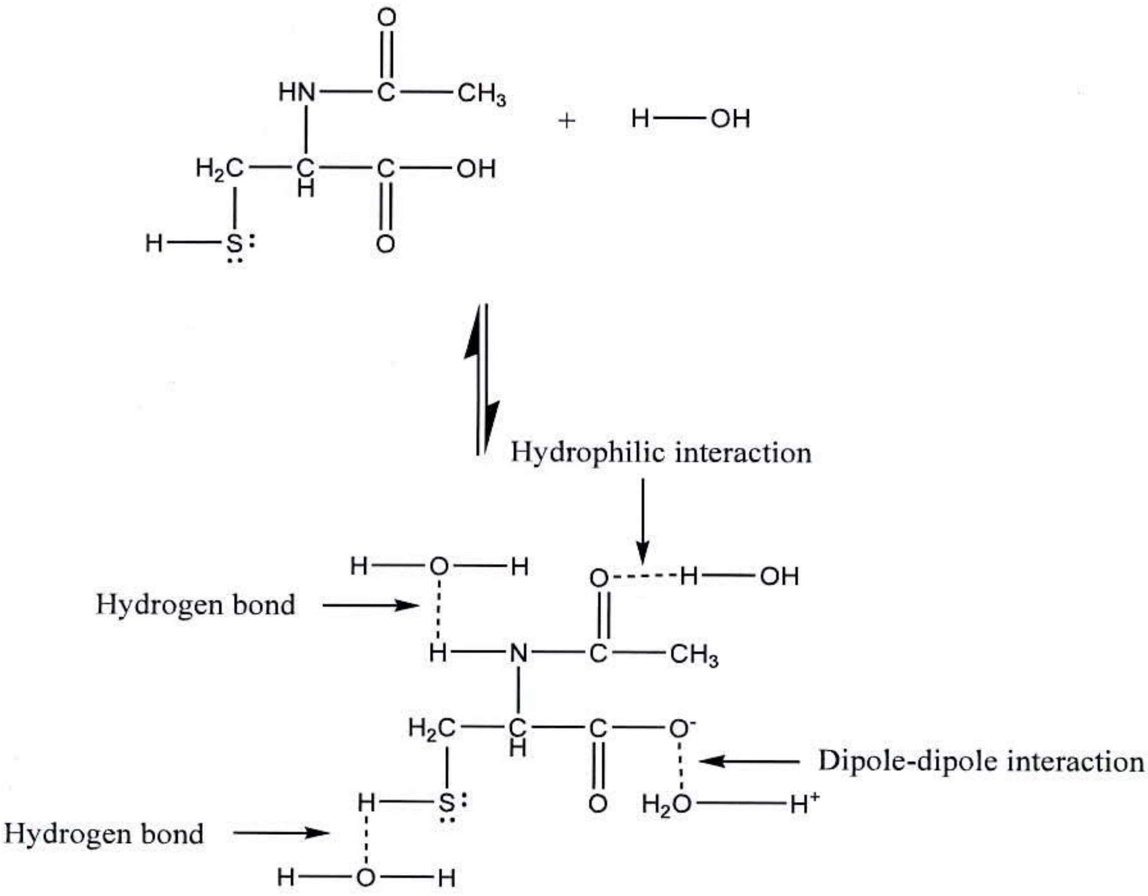
Before discussing Chitosan-H_2O-CH_3COOH & NAC-Chitosan-H_2O-CH_3COOH Systems; the investigated systems of this thesis; it is better to be discussed here the volumetric and viscometric properties NAC-H_2O system for effervescent understanding done by Hasan, M. and Yousuf, M. A. [34]. Densities of NAC–H_2O systems increased with increasing concentration within the investigated composition (~0.10 to ~1.00) M of NAC in water and decreased with temperature. Density values of NAC in water increased linearly with the concentration of the NAC within the temperature range of 298.15 K to 318.15 K at 5 K interval. This increase in density in NAC–H_2O system may be due to solute-solvent interaction through strong hydrogen bond, dipole-dipole as well as acid-base interaction between NAC and water. With increasing temperature as well as the internal energy solute–solvent interaction may be weaken and the volume is increased; the resultant is the lessen of densities.

The apparent molar volume values vary linearly with square root of concentration of NAC solution. The increase of apparent molar volume values of NAC with concentrations may be attributed to the increase in solvent-solvent, solute-solvent and the solute-solute interactions. In the case of solvent-solvent interaction: in H_2O–H_2O there are H-bond and dipole-dipole interaction might be present. When the concentration of NAC is increased in NAC–H_2O system it is assumed that in addition to solute-solvent interactions NAC molecules may interact through S···S linkage that link two molecules together, commonly termed as solute–solute interaction. Every S···S linkage is made between two molecules of NAC serves as a "staple" holding them in a more steady position.

The viscosities, η of NAC–H_2O system have been studied at 298.15, 303.15, 308.15, 313.15, and 318.15 K temperature over a concentration range of (~0.10 to ~1.00) M of NAC. The viscosity values in NAC–H_2O system increased with the increase of concentration and decreased with temperature at any specified temperature. The increase of η values of NAC with concentration can be attributed to the increase in both solute–solvent, solvent–solvent and solute–solute interactions in solution.

Possible interactions which occurred when NAC is dissolved in aqueous solution can be described as below:

The possible interactions between NAC and Water



NAC molecules in aqueous solution behave as weak acid because of its –COOH functional group that releases proton and exhibits negative charge and producing H_3O^+ ion in solution.

$$\underset{\text{NAC}}{C_5H_9NO_3S} + H_2O \rightleftharpoons \underset{[\text{NAC}]^-}{C_5H_8NO_3S^-} + H_3O^+$$

The amide and thiol group of NAC may form H–bond as well as dipole-dipole interaction with water. The solvation system has shown above. The apparent molar volume of different concentration (~0.10 to ~1.00) M of NAC in water solution is dependent upon the concentration of NAC as well as on temperature.

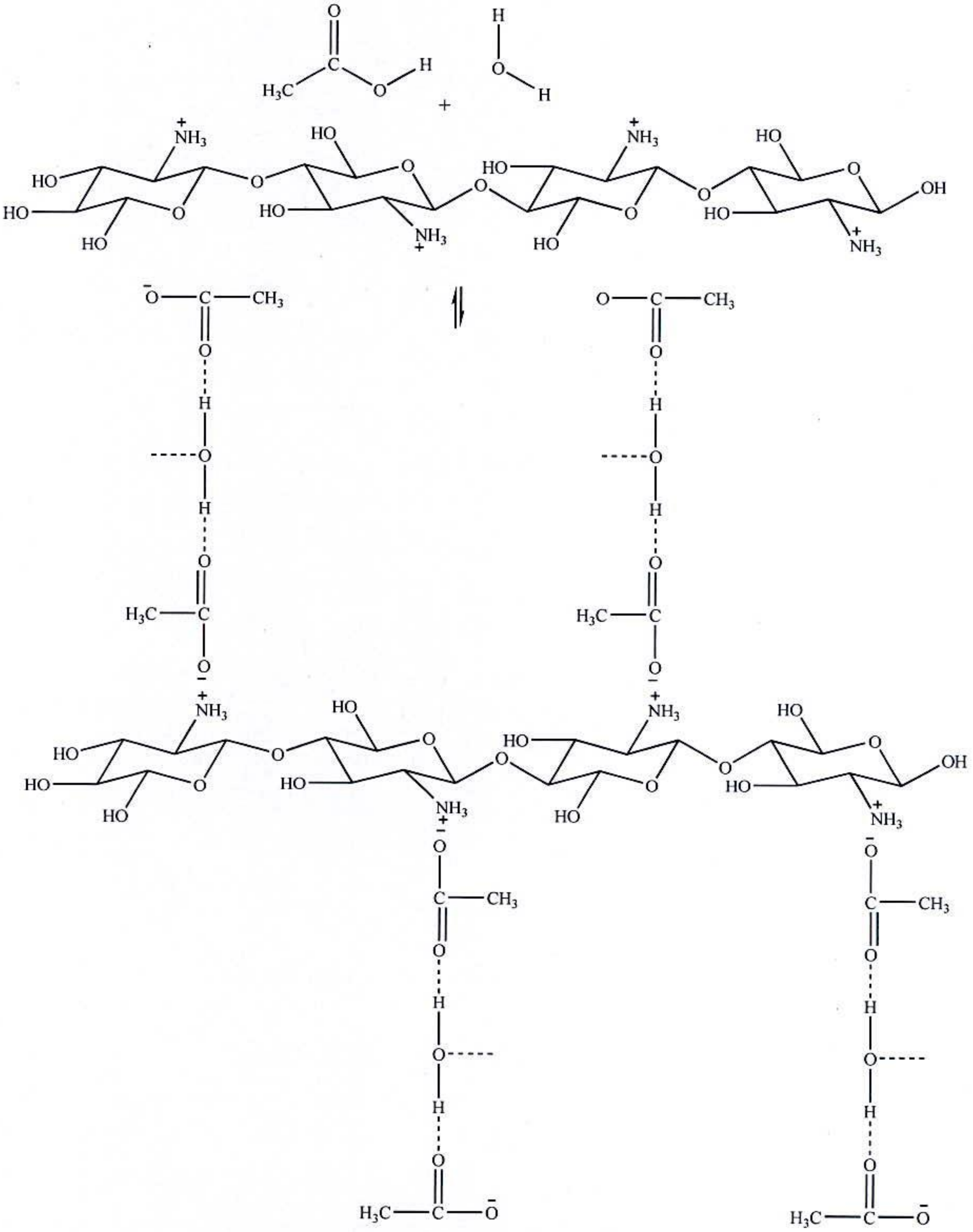
4.2.2 Density of Chitosan-H_2O-CH_3COOH System

The density values, ρ of different concentration of chitosan (0.003, 0.006 and 0.012) M in [9:1], [7:3] and [3:2] in [H_2O-CH_3COOH] mixed solvents have been investigated at 298.15, 303.15, 308.15, 313.15 and 318.15 K temperatures. The density values are shown in Table 4.2-4.4. In all systems density values increased with the increasing concentration of chitosan. Density values decreased with the increasing ratio of water in H_2O-CH_3COOH. Density values of the Chitosan-H_2O-CH_3COOH systems have fitted in Figure 4.1-4.3. From the Figure 4.1-4.3 it is seen that density values of chitosan in H_2O-CH_3COOH increased almost linearly with the concentration of the chitosan within the temperature range of 298.15 K to 318.15 K at 5 K interval. This increase in density in chitosan-H_2O-CH_3COOH systems may be due to solute-solvent interaction through strong dipole-dipole interaction, hydrogen bond, hydrophilic interaction between chitosan and aqueous acetic acid. It is also seen that density values of the investigated systems decreased with increasing temperature at a specific concentration. With increasing temperature internal energy of the molecules present in the systems is increased. As we know from the first law of thermodynamics, if energy of a system is increased then work is done on the system and changed it mode of dimension blindly, *e.g.,* increase in volume, plus some heat is absorbed. In other words, heat and work are equivalent ways of changing a system's internal energy [86]. So with increasing temperature as well as the internal energy solute–solvent interaction may be weaken and the volume is increased; the resultant is the lessen of densities.

In Chitosan-H_2O-CH_3COOH systems the order of density maxima is:

Chitosan in [3:2] [H_2O-CH_3COOH] > Chitosan in [7:3] [H_2O-CH_3COOH] > Chitosan in [9:1] [H_2O-CH_3COOH]

Possible interaction mechanism of Chitosan in Aqueous Acetic Acid system



Possible interaction among water, ethanoic acid and chitosan

Table 4.2: Densities, ρ of chitosan in [9:1] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol dm^{-3})	Density, ρ (g.cm^{-3})				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Chitosan in [9:1] [H_2O-CH_3COOH]	0.003	1.0130	1.0122	1.0115	1.0098	1.0072
	0.006	1.0142	1.0137	1.0131	1.0117	1.0094
	0.012	1.0167	1.0166	1.0164	1.0156	1.0141

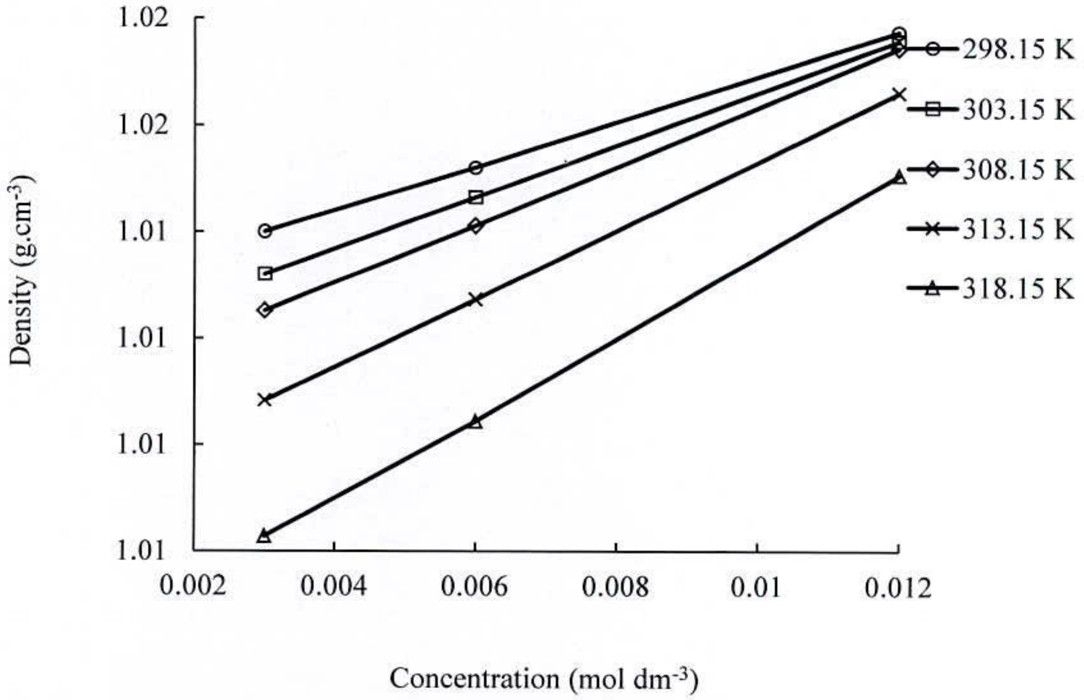


Figure 4.1: Densities, ρ vs concentration of chitosan in [9:1] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Table 4.3: Densities, ρ of chitosan in [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol dm^{-3})	Density, ρ ($g.cm^{-3}$)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Chitosan in [7:3] [H_2O-CH_3COOH]	0.003	1.0350	1.0339	1.0308	1.0276	1.0242
	0.006	1.0362	1.0351	1.0323	1.0292	1.0259
	0.012	1.0385	1.0379	1.0354	1.0325	1.0297

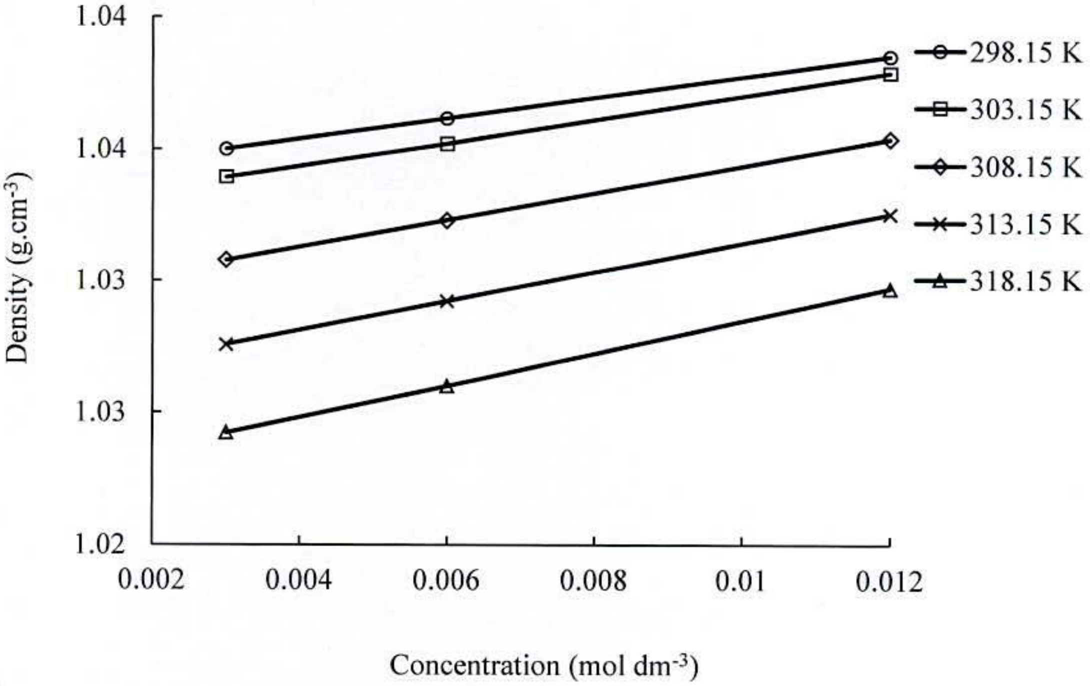


Figure 4.2: Densities, ρ vs concentration of chitosan in [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Table 4.4: Densities, ρ of chitosan in [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol dm^{-3})	Density, ρ ($g.cm^{-3}$)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Chitosan in [3:2] [H_2O-CH_3COOH]	0.003	1.0463	1.0429	1.0394	1.0357	1.0319
	0.006	1.0472	1.0440	1.0407	1.0372	1.0335
	0.012	1.0491	1.0463	1.0436	1.0403	1.0367

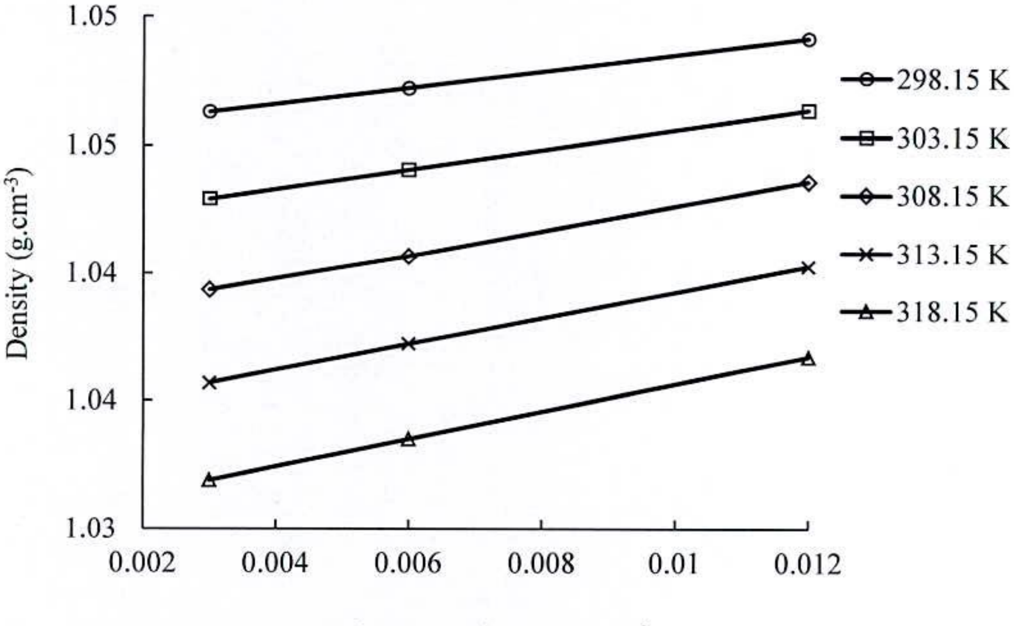


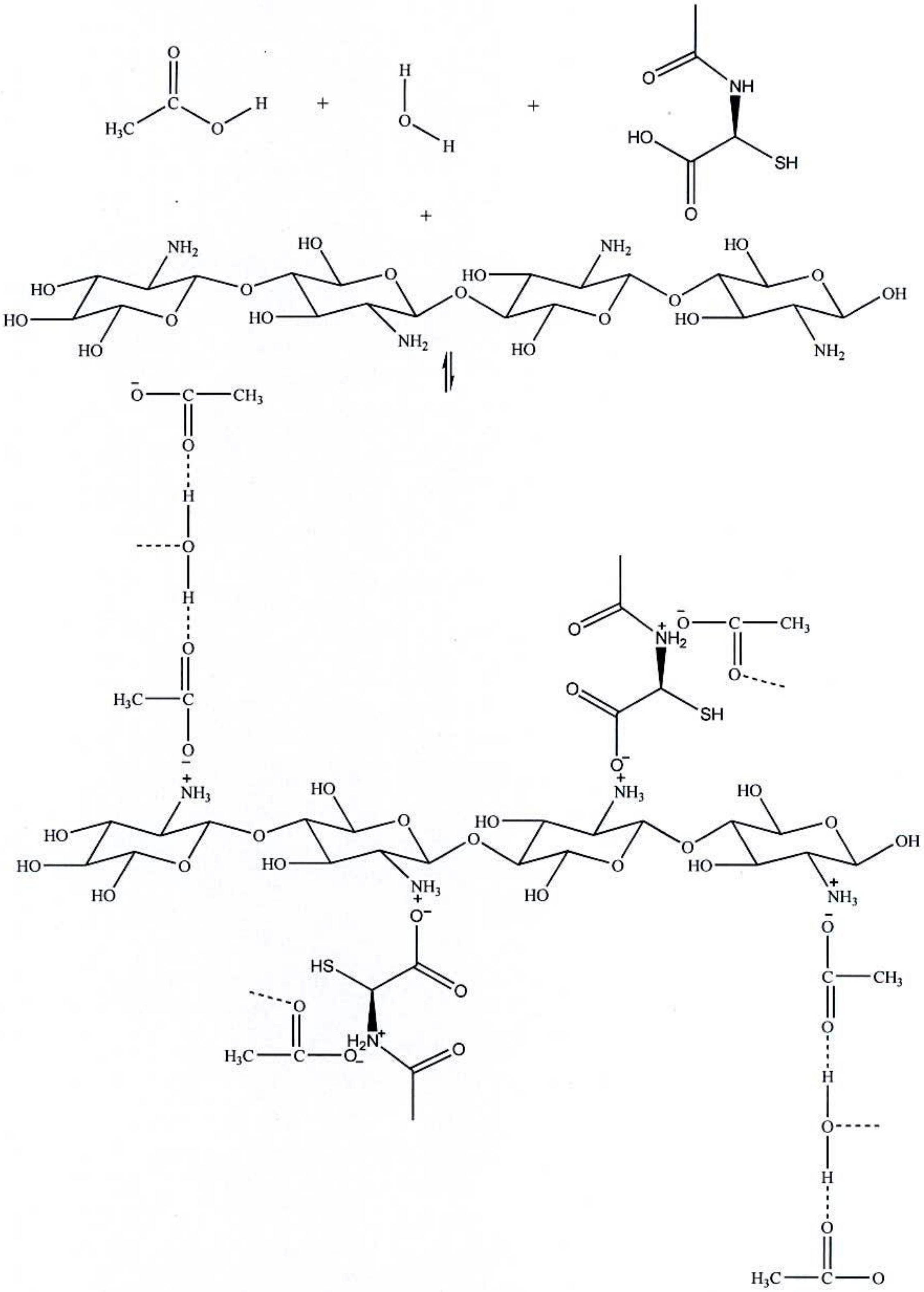
Figure 4.3: Densities, ρ vs concentration of chitosan in [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

4.2.3 Density of NAC in Chitosan-H_2O-CH_3COOH Systems

The densities, ρ of different concentration of NAC (0.10, 0.50 and 1.00 M) in Chitosan-H_2O-CH_3COOH systems at 298.15K to 318.15 K at 5K interval have been investigated. The density values are shown in Table 4.5-4.13. In all NAC-Chitosan-H_2O-CH_3COOH systems densities increased with the increasing concentration of NAC as well as chitosan and ratio of CH_3COOH.

Density values of the NAC-Chitosan-H_2O-CH_3COOH systems have fitted in Figure 4.4-4.12. From the Figure 4.4-4.12 it is seen that density values of NAC-Chitosan-H_2O-CH_3COOH systems increased almost linearly with the concentration of the NAC within the temperature range of 298.15 K to 318.15 K at 5 K interval. This increase in density of NAC-Chitosan-H_2O-CH_3COOH systems may be due to solute-solute, solute-solvent interaction through strong dipole-dipole bond, hydrogen bond, hydrophilic or hydrophobic interaction among NAC, chitosan and aqueous acetic acid. It is also seen that density values of the investigated this systems decreased with increasing temperature at a specific concentration. So with increasing temperature as well as the internal energy solute–solvent interaction may be weaken and the volume is increased; the resultant is the lessen of densities and the reason has been discussed in the earlier section 4.2.2.

Possible interaction mechanism of NAC in Chitosan & H_2O-CH_3COOH system



Possible interaction among water, ethanoic acid, chitosan and N-acetylcysteine

Table 4.5: Densities, ρ of NAC in 0.003 M chitosan and [9:1] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Density, ρ (g.cm^{-3})				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.003 M chitosan and [9:1] [H_2O-CH_3COOH]	0.10	1.0149	1.0138	1.0129	1.0111	1.0083
	0.50	1.0261	1.0243	1.0225	1.0194	1.0157
	1.00	1.0431	1.0410	1.0387	1.0361	1.0325

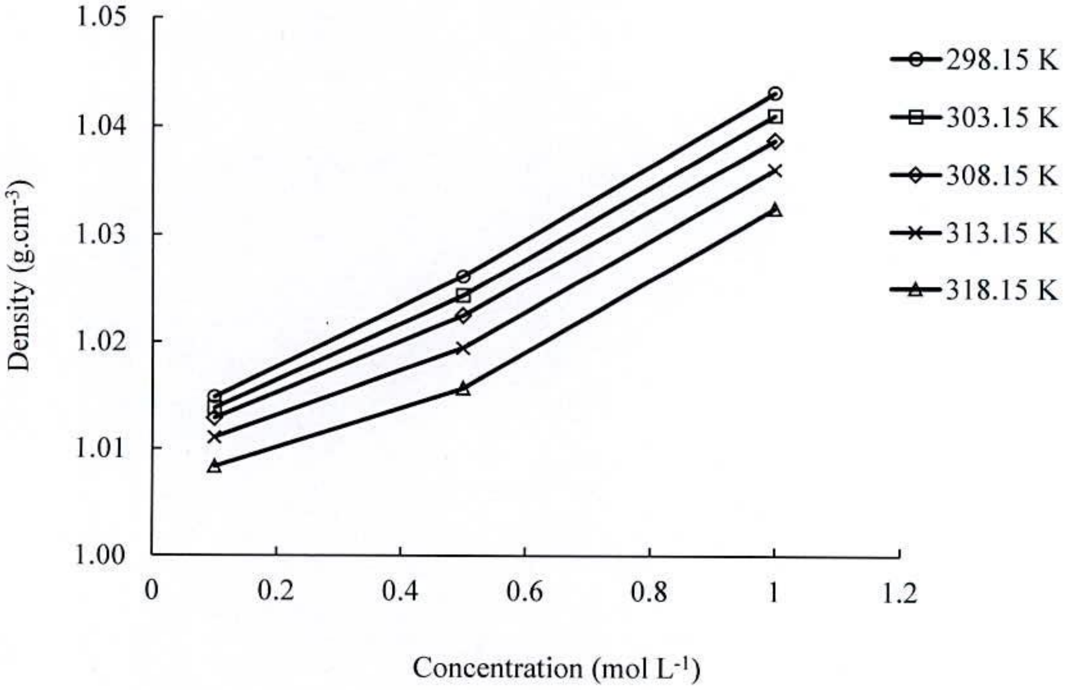


Figure 4.4: Densities, ρ vs concentration of NAC in 0.003 M chitosan and [9:1] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Table 4.6: Densities, ρ of NAC in 0.006 M chitosan and [9:1] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Density, ρ ($g.cm^{-3}$)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.006 M chitosan and [9:1] [H_2O-CH_3COOH]	0.10	1.0149	1.0142	1.0135	1.0120	1.0096
	0.50	1.0263	1.0246	1.0228	1.0202	1.0164
	1.00	1.0435	1.0409	1.0395	1.0369	1.0338

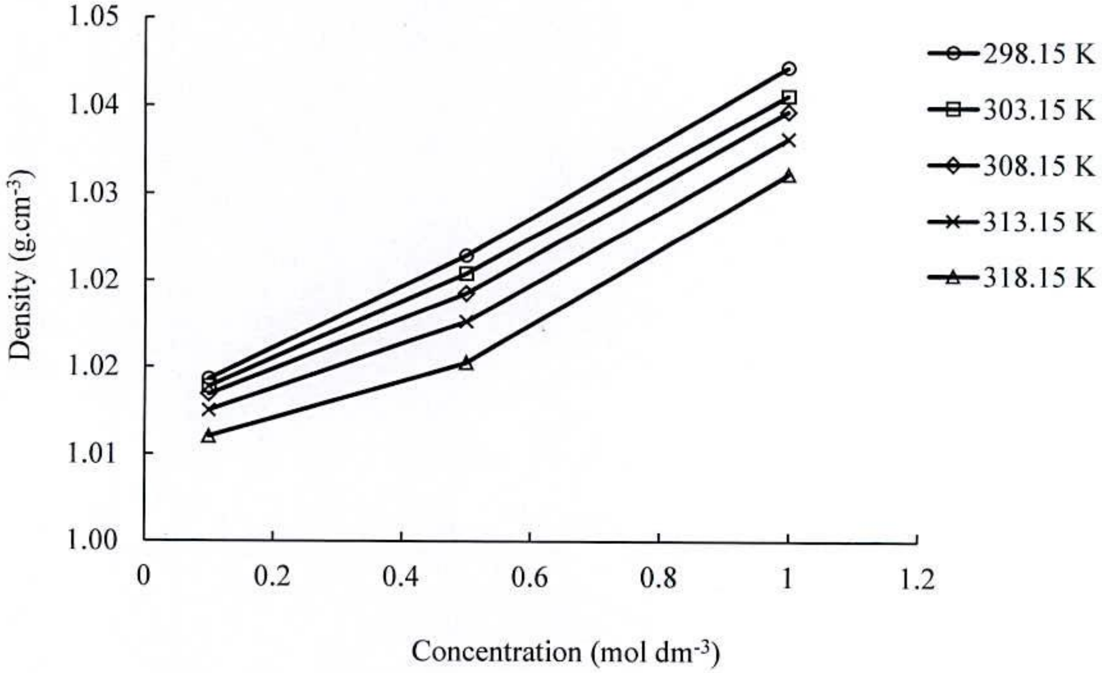


Figure 4.5: Densities, ρ vs concentration (M) of NAC in 0.006 M chitosan and [9:1] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Table 4.7: Densities, ρ of NAC in 0.012 M chitosan and [9:1] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Density, ρ ($g.cm^{-3}$)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.012 M chitosan and [9:1] [H_2O-CH_3COOH]	0.10	1.0173	1.0164	1.0158	1.0141	1.0114
	0.50	1.0272	1.0257	1.0245	1.0218	1.0177
	1.00	1.0444	1.0421	1.0403	1.0378	1.0348

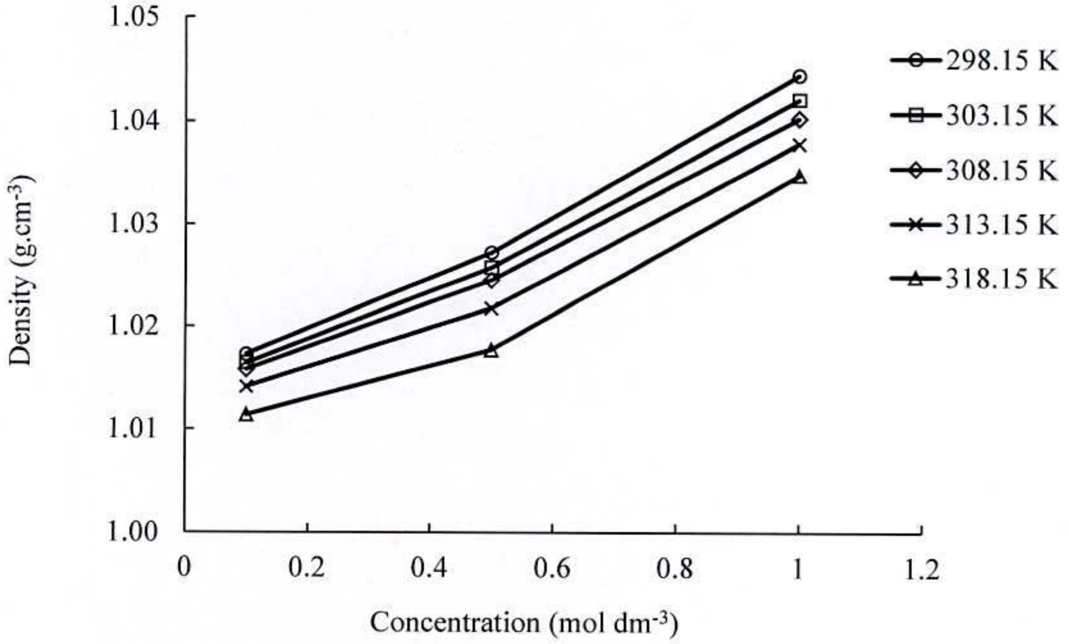


Figure 4.6: Densities, ρ vs concentration of NAC in 0.012 M chitosan and [9:1] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Table 4.8: Densities, ρ of NAC in 0.003 M chitosan and [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Density, ρ (g.cm^{-3})				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.003 M chitosan and [7:3] [H_2O-CH_3COOH]	0.10	1.0360	1.0349	1.0317	1.0283	1.0249
	0.50	1.0374	1.0361	1.0326	1.0292	1.0257
	1.00	1.0408	1.0393	1.0357	1.0321	1.0284

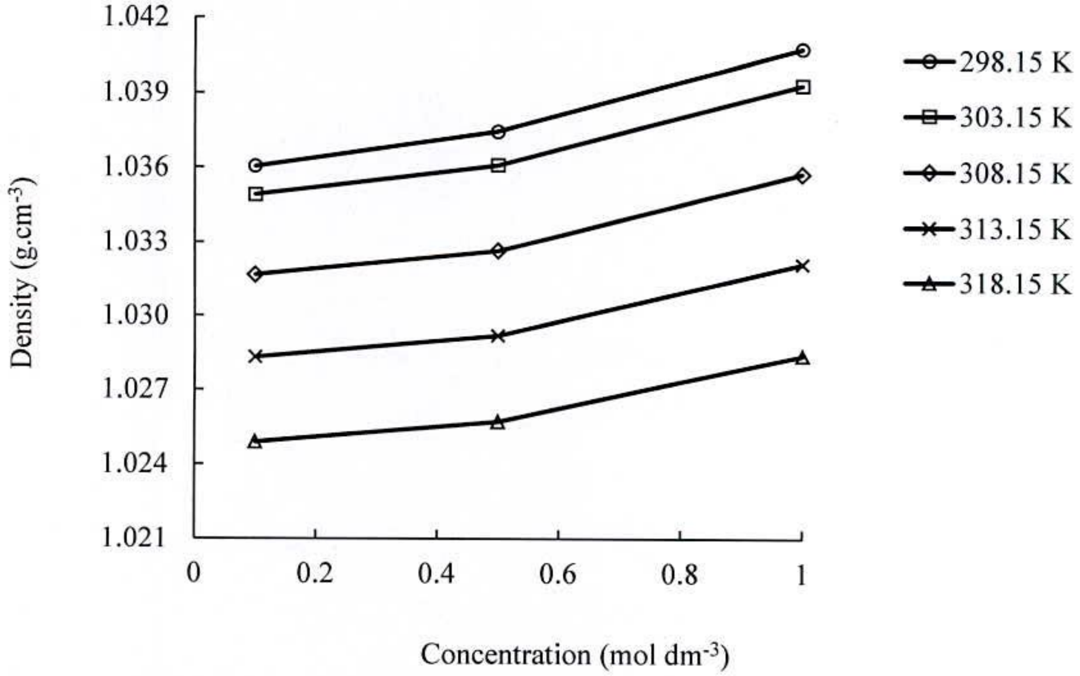


Figure 4.7: Densities, ρ vs concentration of NAC in 0.003 M chitosan and [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Table 4.9: Densities, ρ of NAC in 0.006 M chitosan and [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Density, ρ ($g.cm^{-3}$)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.006 M chitosan and [7:3] [H_2O-CH_3COOH]	0.10	1.0374	1.0363	1.0333	1.0302	1.0268
	0.50	1.0387	1.0376	1.0345	1.0313	1.0279
	1.00	1.0419	1.0403	1.0372	1.0339	1.0303

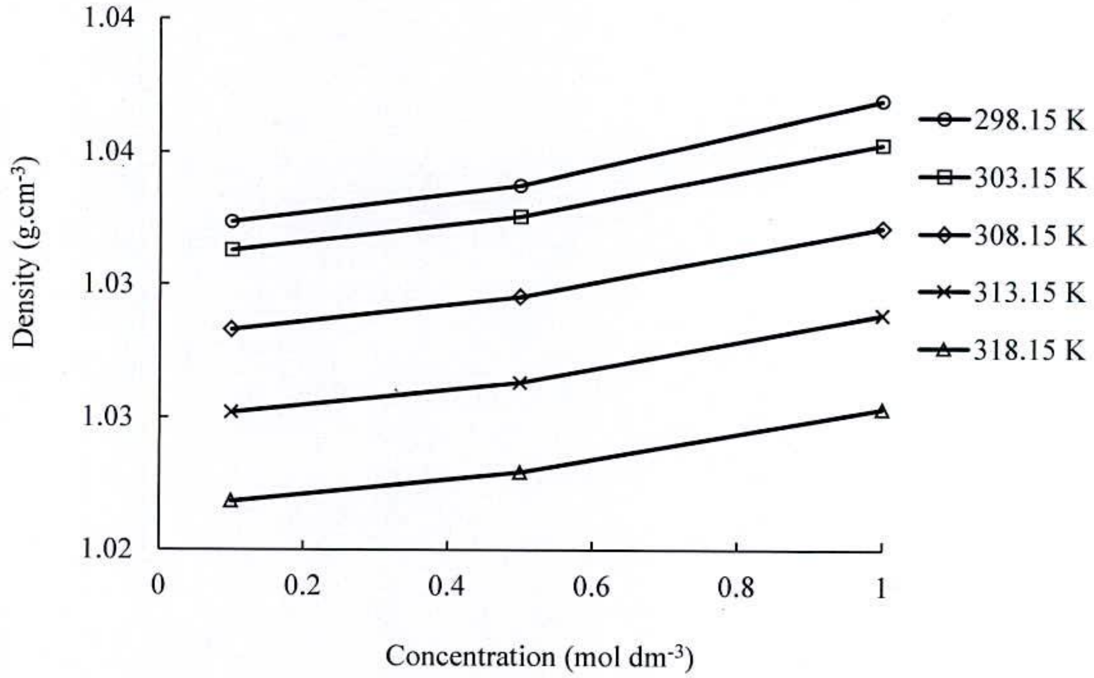


Figure 4.8: Densities, ρ vs concentration of NAC in 0.006 M chitosan and [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Table 4.10: Densities, ρ of NAC in 0.012 M chitosan and [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Density, ρ (g.cm^{-3})				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.012 M chitosan and [7:3] [H_2O-CH_3COOH]	0.10	1.0392	1.0385	1.0359	1.0330	1.0301
	0.50	1.0403	1.0396	1.0369	1.0340	1.0310
	1.00	1.0428	1.0418	1.0392	1.0362	1.0331

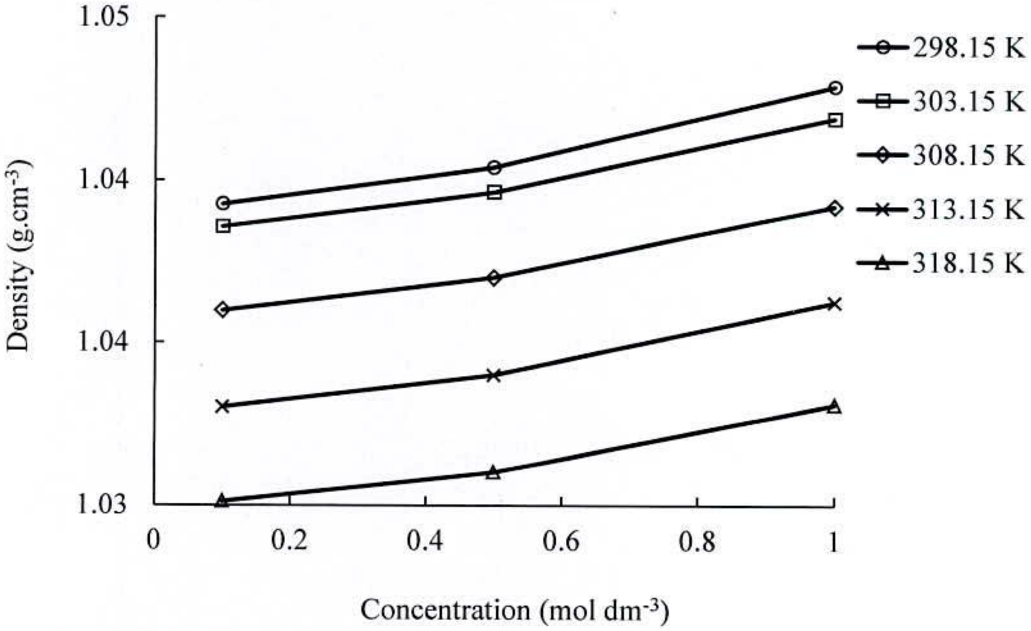


Figure 4.9: Densities, ρ vs concentration of NAC in 0.012 M chitosan and [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Table 4.11: Densities, ρ of NAC in 0.003 M chitosan and [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Density, ρ (g.cm^{-3})				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.003 M chitosan and [3:2] [H_2O-CH_3COOH]	0.10	1.0481	1.0444	1.0407	1.0369	1.0330
	0.50	1.0578	1.0529	1.0487	1.0446	1.0407
	1.00	1.0707	1.0668	1.0629	1.0589	1.0549

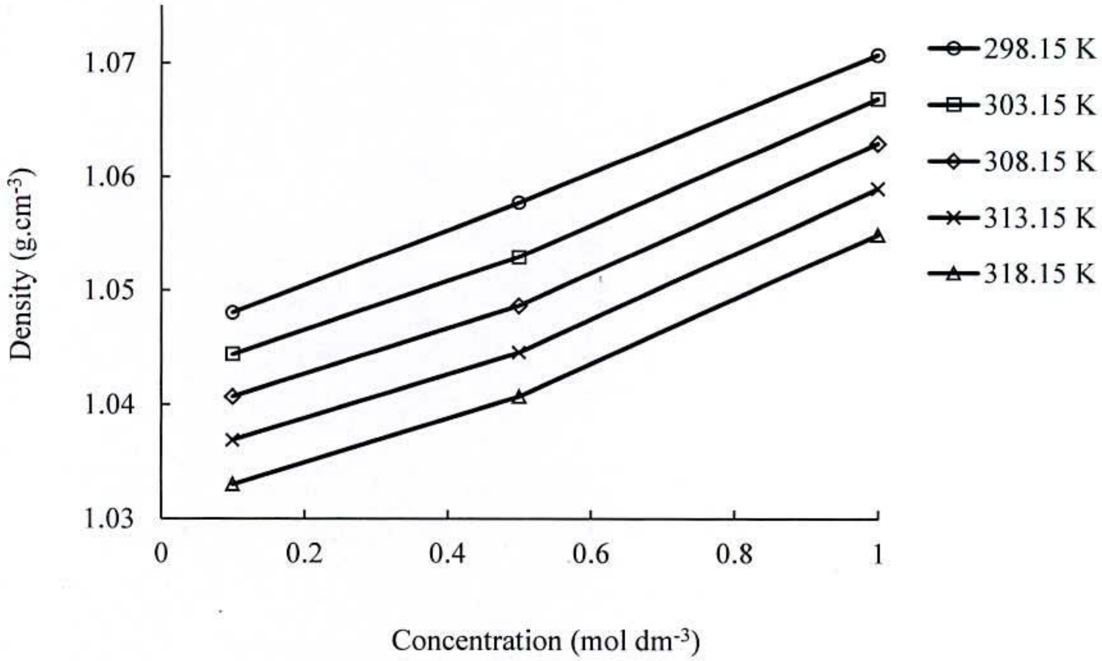


Figure 4.10: Densities, ρ vs concentration of NAC in 0.003 M chitosan and [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Table 4.12: Densities, ρ of NAC in 0.006 M chitosan and [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Density, ρ ($g.cm^{-3}$)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.006 M chitosan and [3:2] [H_2O-CH_3COOH]	0.10	1.0487	1.0455	1.0421	1.0386	1.0349
	0.50	1.0549	1.0518	1.0482	1.0448	1.0412
	1.00	1.0634	1.0604	1.0567	1.0534	1.0500

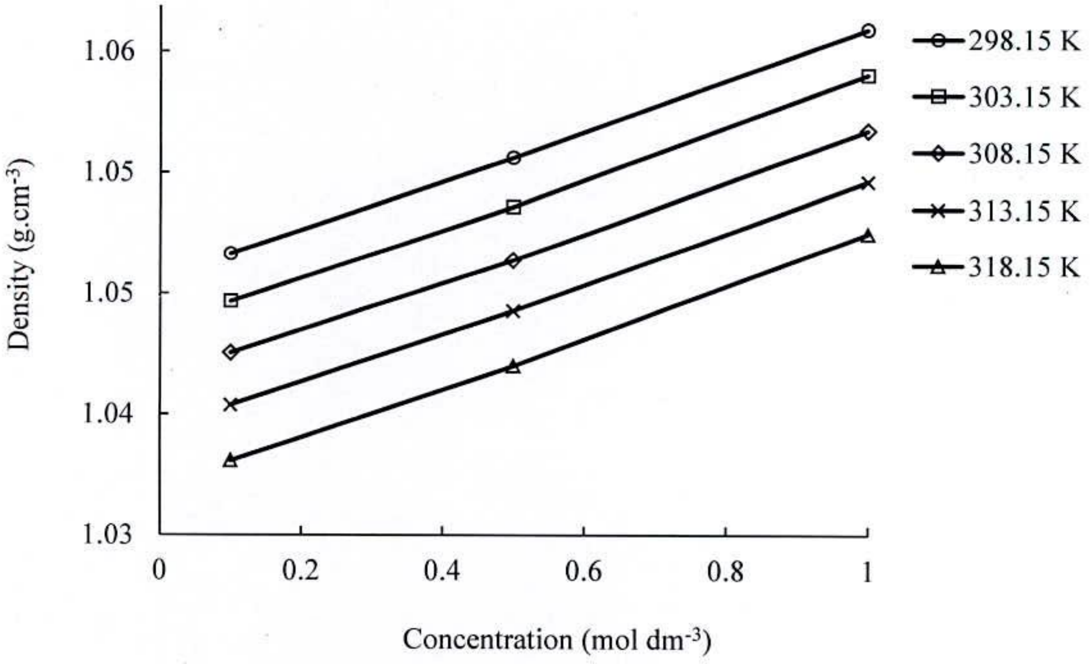


Figure 4.11: Densities, ρ vs concentration of NAC in 0.006 M chitosan and [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Table 4.13: Densities, ρ of NAC in 0.012 M chitosan and [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Density, ρ ($g.cm^{-3}$)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.012 M chitosan and [3:2] [H_2O-CH_3COOH]	0.10	1.0501	1.0472	1.0444	1.0411	1.0375
	0.50	1.0559	1.0531	1.0502	1.0468	1.0432
	1.00	1.0657	1.0626	1.0594	1.0559	1.0522

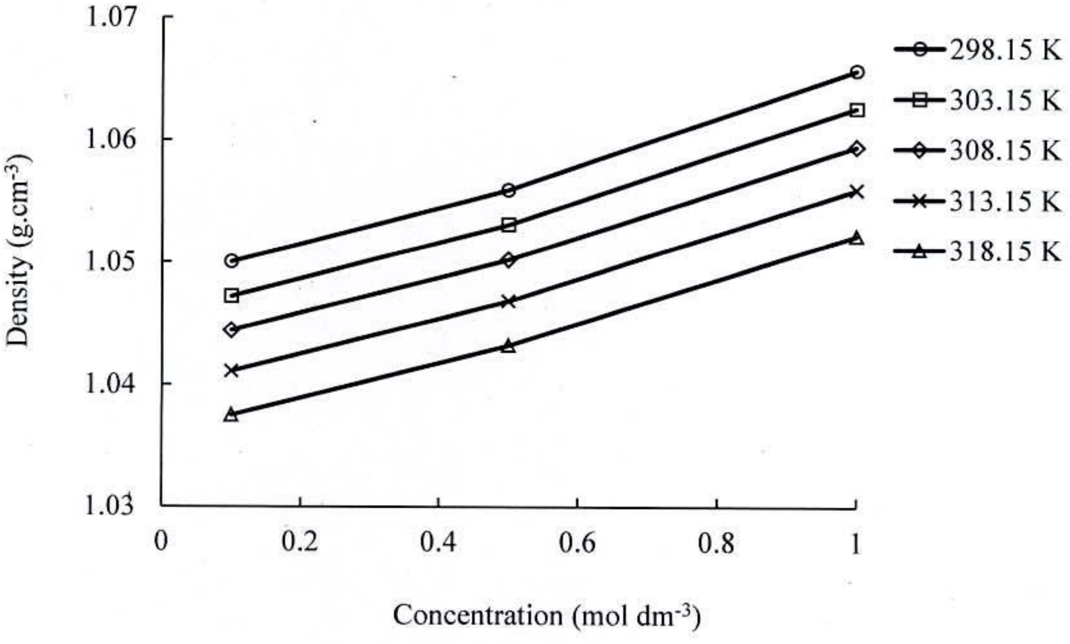


Figure 4.12: Densities, ρ vs concentration of NAC in 0.012 M chitosan and [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

4.3 Apparent Molar Volume

NAC may affect the volumetric properties of chitosan mixed H_2O-CH_3COOH solution which may provide useful information in elucidating the interactions occur in chitosan-H_2O-CH_3COOH system as well as their applications in various field. NAC possess both polar functional groups, viz., –COOH, CH3CONH–, –SH and non-polar groups, functional groups, viz., $-CH_3$, $-CH-CH_2-$ which have potential effects on the structure or molar volume of water, acetic acid and H_2O-CH_3COOH. Hydrophobic interactions between the organic parts of NAC and acetic acid may play an important role in the stability in the mixture even when water is added to it. On the other hand hydrophilic interactions between polar organic parts, e.g.., –COOH,–SH of NAC and water may play an important role in the solubility and stability in the mixture even when acetic acid is added to it and vice-versa. From a theoretical point of view, the most useful quantities are the limiting values of the apparent molar volume since these values depend only on the intrinsic size of the ion and on ion-solvent interaction. Moreover, the interactions of solutes with water may influence their accession to, and binding with, receptor sites, thus influencing their internal properties. In order to investigate the nature of the solute-solute and solute–solvent interactions of NAC in chitosan and H_2O-CH_3COOH solution, the apparent molar volume and apparent molar volume at infinite dilution were determined.

4.3.1 Apparent Molar Volume of Chitosan-H_2O-CH_3COOH systems

The apparent molar volumes, φ_v of different molarities (0.003, 0.006 & 0.012 M) of chitosan in aqueous acetic acid solution have been determined at 298.15 to 318.15 K temperature at 5 K interval by using equation 1.2.8. The values of apparent molar volumes of chitosan in H_2O-CH_3COOH have been shown in the Table 4.14-4.16. The graphical representation of the φ_v values of Chitosan-H_2O-CH_3COOH systems have been shown in Figure 4.13-4.15. The apparent molar volume values varied almost linearly with square root of concentration of chitosan in mixed solutions.

It is seen that apparent molar volume is dependent upon the concentration of chitosan as well as on temperature. The values have been found to be positive throughout the whole concentration range for chitosan in aqueous acetic acid medium. The apparent molar volumes of Chitosan-H_2O-CH_3COOH systems were found to be decreased with the increase of concentration of chitosan at any specified temperature. The decrease in magnitude of φ_v values with an increase in molarities of chitosan indicates solute-solvent interaction which can be explained by the structure-promoter behavior of amine and –OH groups in the same way as do non-polar fatty acid anion [87-88]. The decrease of apparent molar volume values with concentrations of chitosan may also be attributed to the decrease in solvent-solvent and solute-solvent interactions. However, the φ_v values of chitosan-H_2O-CH_3COOH decreased with a rise in temperature in the system this may be due to higher degree of association occurred among solute and mixed solvent molecules in an organized manner.

Table 4.14: Apparent molar volume, φ_v of chitosan in [9:1] [H_2O-CH_3COOH] systems at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol dm^{-3})	Apparent molar volume, φ_v (cm^3.mol^{-1})				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Chitosan in [9:1] [H_2O-CH_3COOH]	0.003	115.81	107.43	98.94	87.20	81.79
	0.006	113.72	104.85	97.70	85.86	78.17
	0.012	111.66	103.40	95.98	84.56	73.23

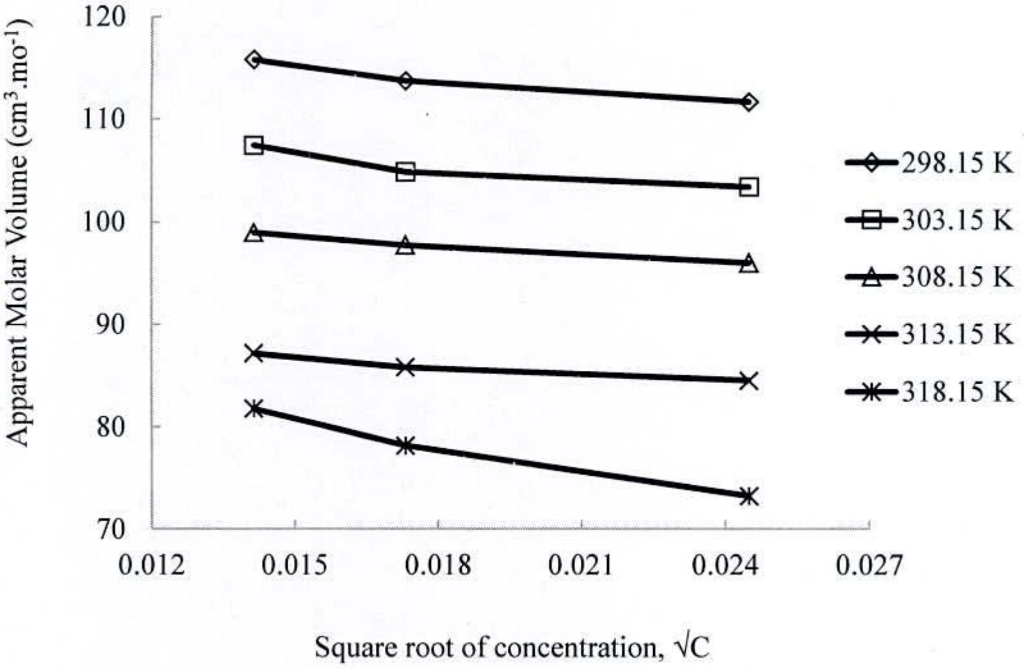


Figure 4.13: Apparent molar volume, φ_v vs square root of concentration, √C of Chitosan in [9:1] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Table 4.15: Apparent molar volume, φ_v of Chitosan in [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol dm^{-3})	Apparent molar volume, φ_v ($cm^3.mol^{-1}$)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Chitosan in [7:3] [H_2O-CH_3COOH]	0.003	120.55	109.92	103.98	97.46	91.11
	0.006	116.00	108.78	101.24	95.06	89.93
	0.012	113.30	106.49	99.06	93.85	87.58

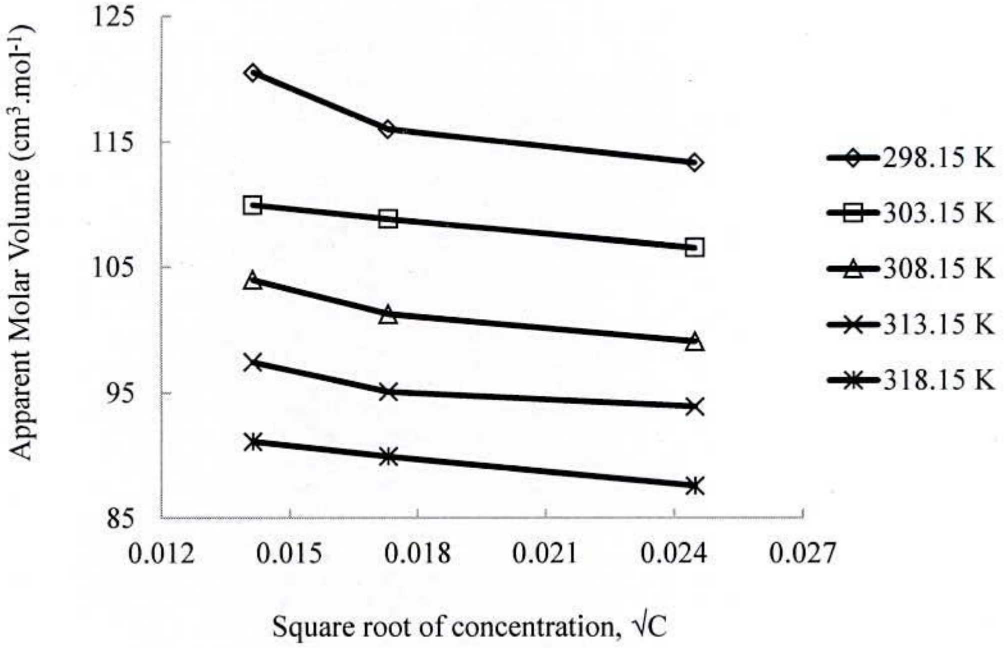


Figure 4.14: Apparent molar volume, φ_v vs square root of concentration, √C of chitosan in [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Table 4.16: Apparent molar volume, φ_v of chitosan in [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol dm^{-3})	Apparent molar volume, φ_v ($cm^3.mol^{-1}$)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Chitosan in [3:2] [H_2O-CH_3COOH]	0.003	130.75	119.27	111.07	104.82	99.66
	0.006	124.89	115.15	107.74	100.53	97.01
	0.012	121.17	112.77	103.57	98.83	95.75

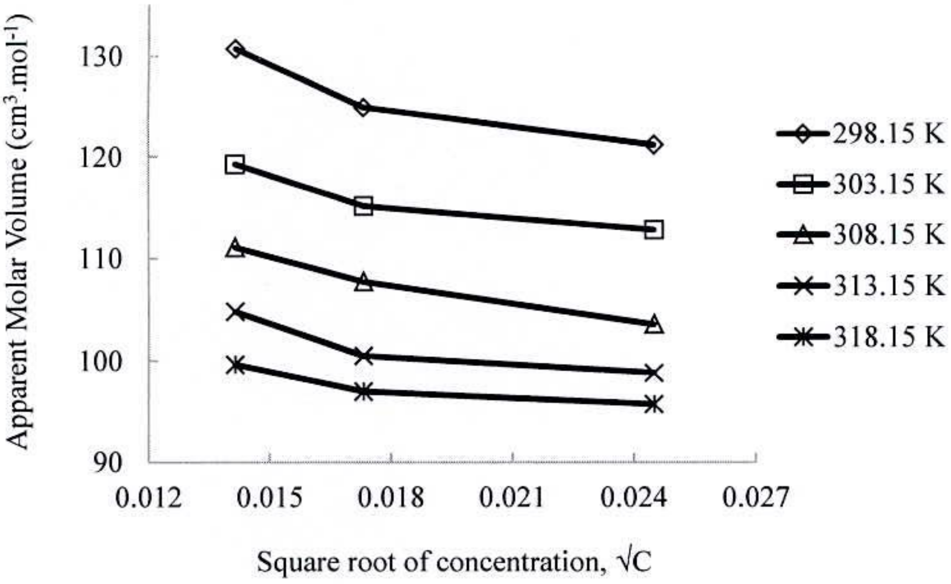


Figure 4.15: Apparent molar volume, φ_v vs square root of concentration, √C of chitosan in [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

4.3.2 Apparent Molar Volume of NAC in Chitosan-H_2O-CH_3COOH Systems

The apparent molar volume of NAC in Chitosan-H_2O-CH_3COOH systems have been determined at various concentrations (0.10, 0.50 and 1.00 M) of NAC from 298.15 to 318.15 K temperature at 5 K interval. Equation 1.2.8 has been used in calculating apparent molar volumes of NAC-Chitosan-H_2O-CH_3COOH systems. The values of apparent molar volume of the NAC-Chitosan-H_2O-CH_3COOH systems have been shown in the Table 4.17-4.25. It is seen that apparent molar volume is dependent upon the concentration of NAC as well as on temperature like Chitosan-H_2O-CH_3COOH systems as described in section 4.2. The values were found positive throughout the whole concentration range for NAC in all solutions. The apparent molar volume of NAC in Chitosan-H_2O-CH_3COOH systems has found to be decreased with increasing the concentration of NAC which suggested that in additional interaction among NAC and the constituent components of Chitosan-H_2O-CH_3COOH solutions though dipole-dipole interaction, hydrogen bond, hydrophilic and hydrophilic interaction might be supplemented there solute-solvent interaction present in NAC-Chitosan-H_2O-CH_3COOH systems [87-88]. On the other hand apparent molar volumes were found be increased with increasing temperature at any specified concentration of NAC in the solution Chitosan-H_2O-CH_3COOH but this results are opposite than those of Chitosan-H_2O-CH_3COOH systems. Anyway it can be said that with increasing temperature internal energy of the molecules present in the systems is increased. As we know from the first law of thermodynamics, if energy of a system is increased as heat then work is done on the system and changed it mode of dimension blindly, *e.g.,* increase in volume plus some internal energy is increased [86]. So with increasing temperature as well as the internal energy solute–solvent interaction may be weaken and the resultant is apparent molar volume is increased. At the same time it can also be assumed that with the addition of NAC in Chitosan-H_2O-CH_3COOH the systems become relatively giant; the steric effect become dominant and organized manner in these systems has ruined as was seen in the Chitosan-H_2O-CH_3COOH systems. The graphical representation of the φ_v values of NAC-Chitosan-H_2O-CH_3COOH systems has been shown in Figure 4.16-4.24. Results of apparent molar volumes, φ_v versus square root concentration of NAC in Chitosan-H_2O-CH_3COOH solutions have been plotted in Figure 4.16-4.24. From the figures it is seen that φ_v values decreased against concentration of NAC in all cases.

Table 4.17: Apparent molar volume, φ_v of NAC in 0.003 M chitosan and [9:1] [H_2O-CH_3COOH] systems at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Apparent molar volume, φ_v ($cm^3.mol^{-1}$)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.003 M chitosan and [9:1] [H_2O-CH_3COOH]	0.10	140.82	143.03	145.75	147.39	149.69
	0.50	133.18	135.27	137.63	140.55	143.32
	1.00	129.36	130.75	132.42	133.61	135.00

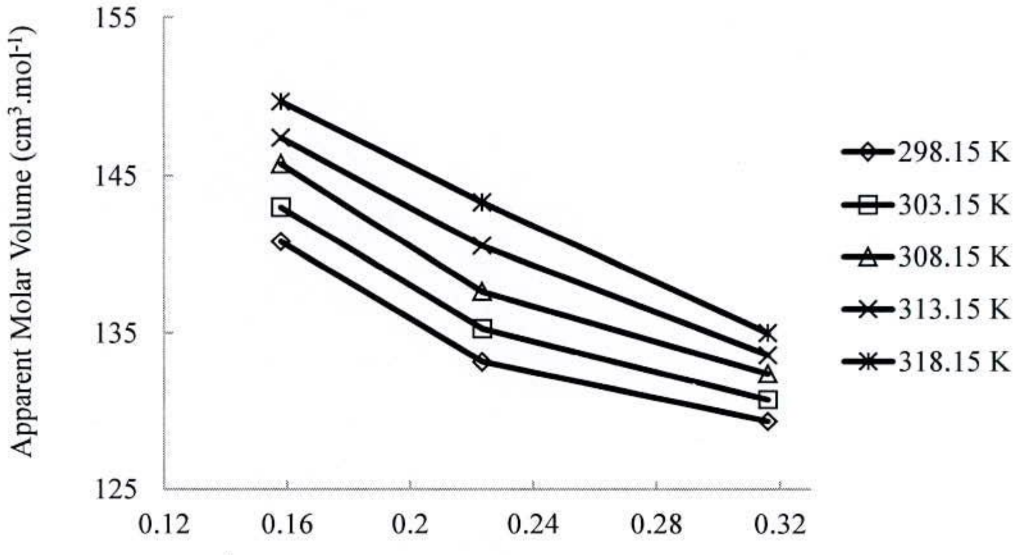


Figure 4.16: Apparent molar volume, φ_v vs square root of concentration, √C of NAC in 0.003 M chitosan and [9:1] [H_2O-CH_3COOH] systems at 298.15 to 318.15 K at 5 K interval

Table 4.18: Apparent molar volume, φ_v of NAC in 0.006 M chitosan and [9:1] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Apparent molar volume, φ_v ($cm^3.mol^{-1}$)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.006 M chitosan and [9:1] [H_2O-CH_3COOH]	0.10	151.87	153.34	155.04	156.39	157.84
	0.50	135.09	137.32	139.95	142.57	145.86
	1.00	130.05	132.12	133.05	134.34	135.54

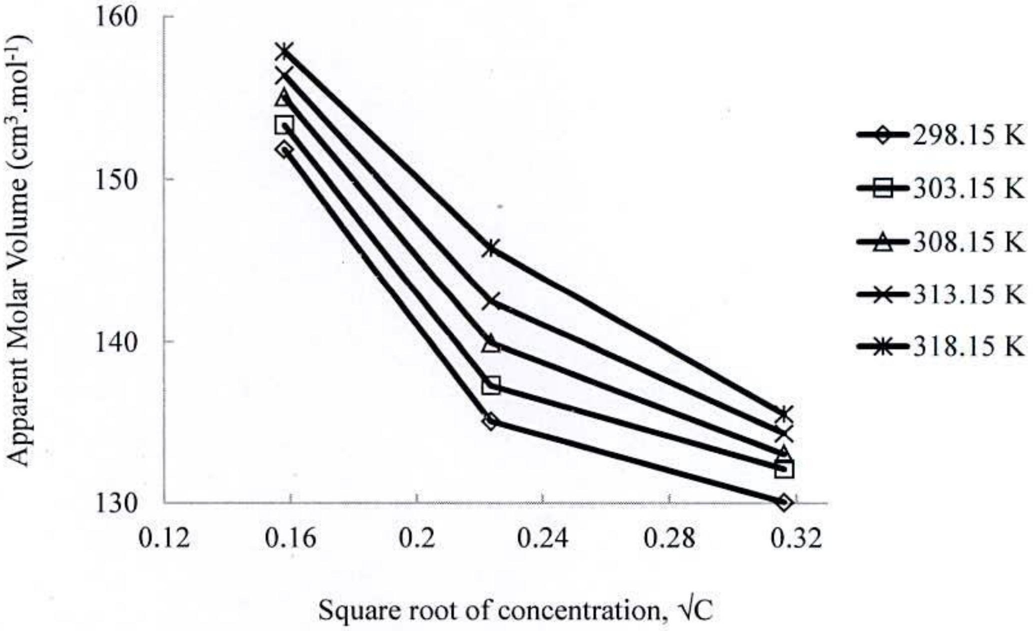


Figure 4.17: Apparent molar volume, φ_v vs square root of concentration, √C of NAC in 0.006 M chitosan and [9:1] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Table 4.19: Apparent molar volume, φ_v of NAC in 0.012 M chitosan and [9:1] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Apparent molar volume, φ_v ($cm^3.mol^{-1}$)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.012 M chitosan and [9:1] [H_2O-CH_3COOH]	0.10	152.93	154.86	156.88	157.76	159.11
	0.50	137.87	139.54	141.15	143.62	146.78
	1.00	131.27	133.00	134.42	135.45	136.20

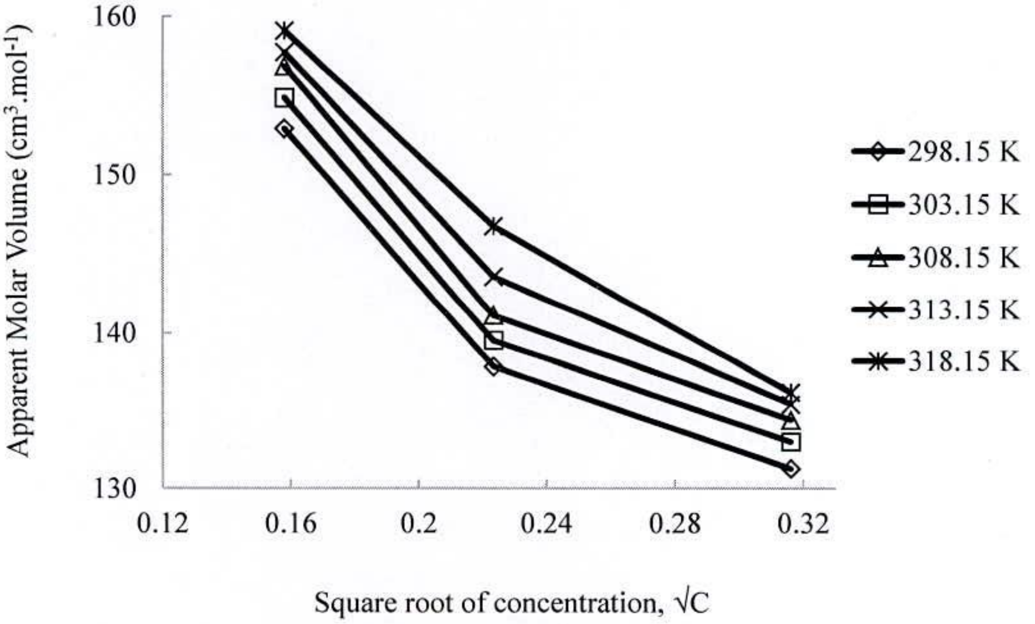


Figure 4.18: Apparent molar volume, φ_v vs square root of concentration, √C of NAC in 0.012 M chitosan and [9:1] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Table 4.20: Apparent molar volume, φ_v of NAC in 0.003 M chitosan and [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Apparent molar volume, φ_v (cm^3.mol^{-1})				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.003 M chitosan and [7:3] [H_2O-CH_3COOH]	0.10	117.88	121.12	125.22	129.54	133.52
	0.50	111.17	116.64	122.60	127.36	130.28
	1.00	102.22	106.30	110.65	114.92	118.96

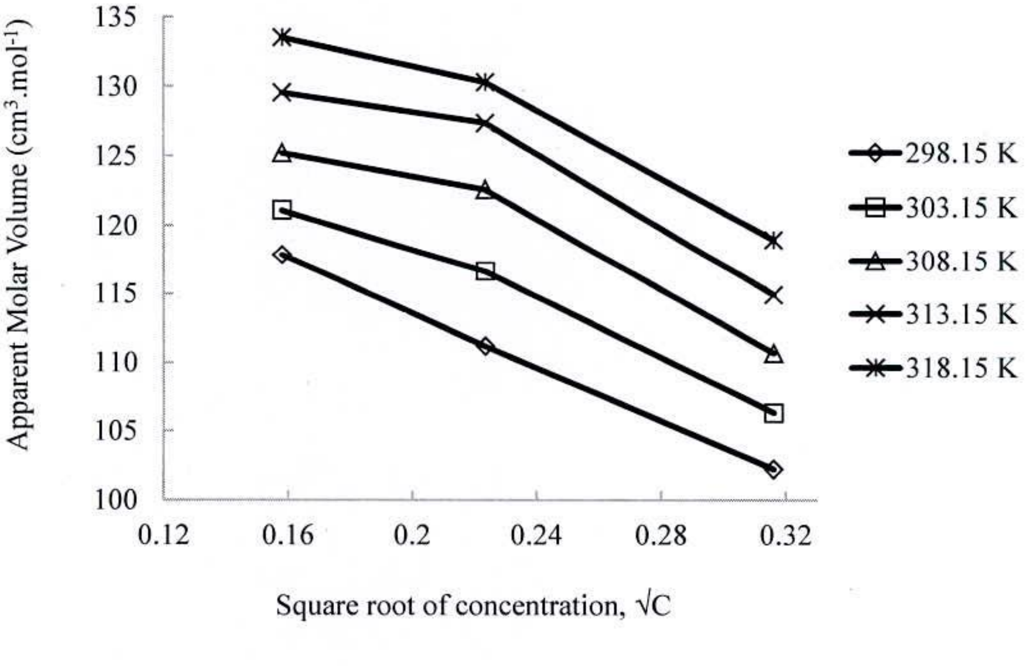


Figure 4.19: Apparent molar volume, φ_v vs square root of concentration, √C of NAC in 0.003 M chitosan and [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Table 4.21: Apparent molar volume, φ_v of NAC in 0.006 M chitosan and [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Apparent molar volume, φ_v ($cm^3.mol^{-1}$)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.006 M chitosan and [7:3] [H_2O-CH_3COOH]	0.10	110.48	114.56	119.46	121.33	126.19
	0.50	107.86	111.88	114.94	118.32	121.34
	1.00	101.88	108.61	111.11	113.61	116.86

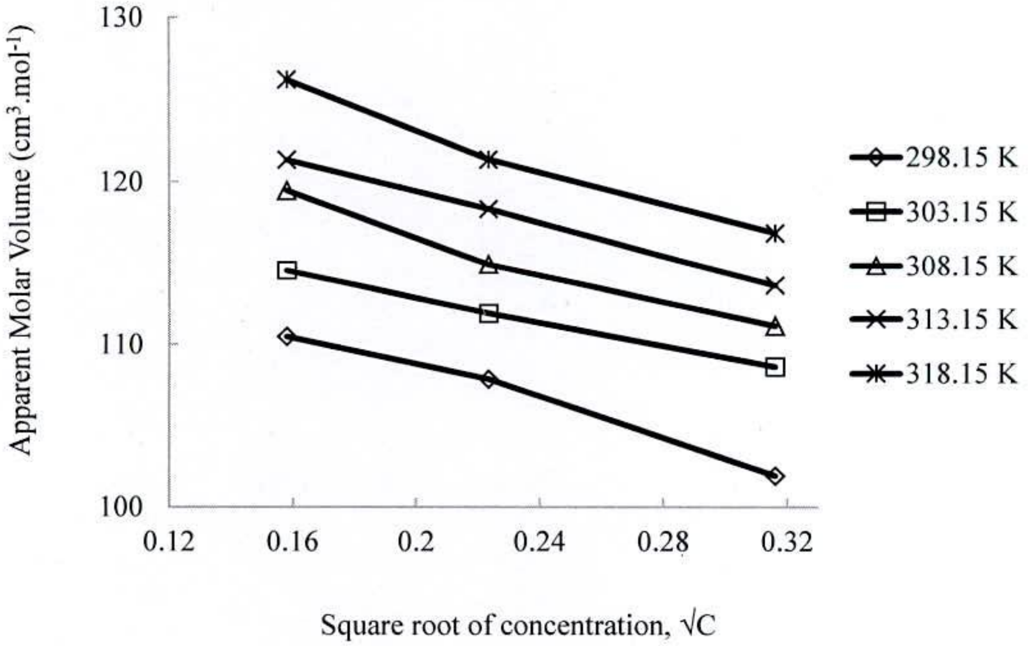


Figure 4.20: Apparent molar volume, φ_v vs square root of concentration, √C of NAC in 0.006 M chitosan and [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Table 4.22: Apparent molar volume, φ_v of NAC in 0.012 M chitosan and [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC ($mol.L^{-1}$)	Apparent molar volume, φ_v ($cm^3.mol^{-1}$)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.012 M chitosan and [7:3] [H_2O-CH_3COOH]	0.10	127.33	130.93	133.98	138.65	141.94
	0.50	120.88	123.43	126.37	129.45	132.38
	1.00	115.18	118.78	120.69	122.08	125.31

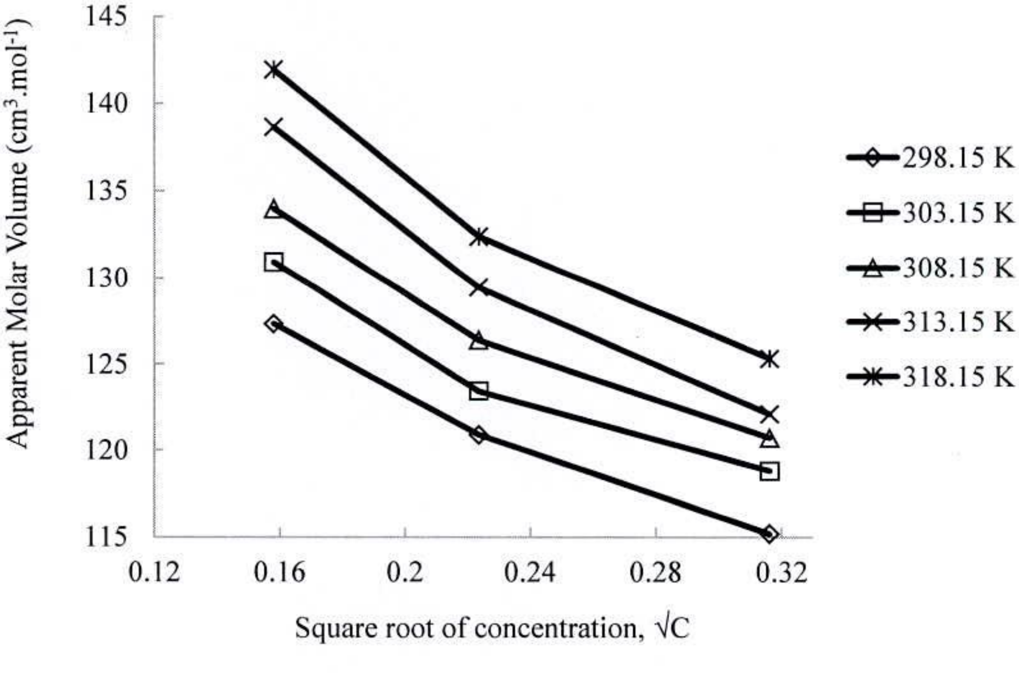


Figure 4.21: Apparent molar volume, φ_v vs square root of concentration, √C of NAC in 0.012 M chitosan and [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Table 4.23: Apparent molar volume, φ_v of NAC in 0.003 M chitosan and [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC ($mol.L^{-1}$)	Apparent molar volume, φ_v ($cm^3.mol^{-1}$)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.003 M chitosan and [3:2] [H_2O-CH_3COOH]	0.10	139.22	142.06	144.23	145.91	147.33
	0.50	134.08	137.20	139.14	140.41	141.05
	1.00	132.68	133.53	134.31	135.07	135.80

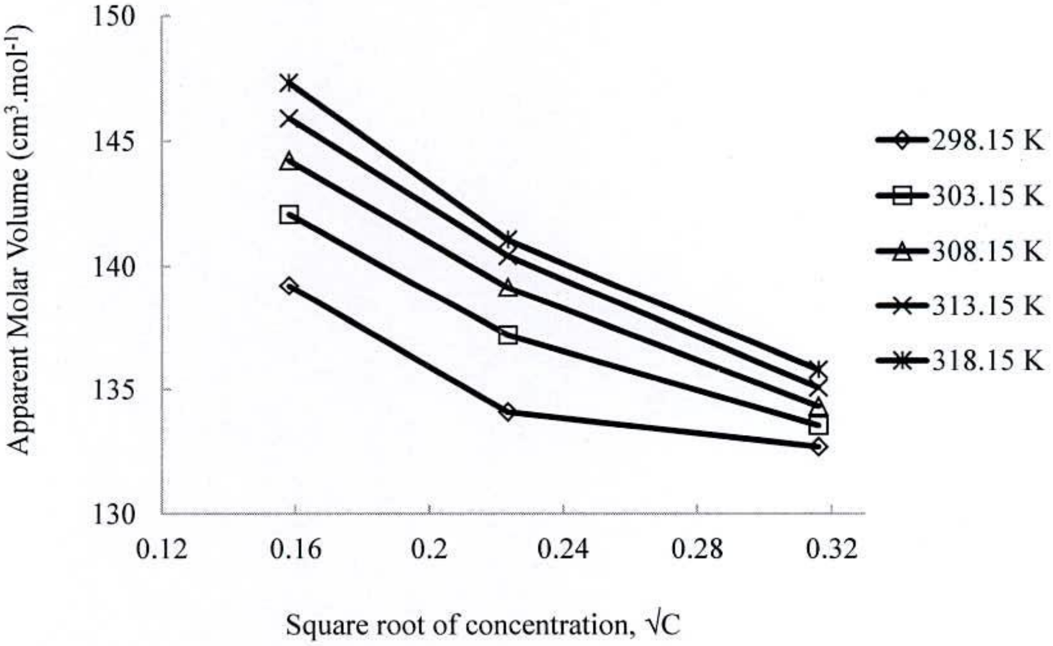


Figure 4.22: Apparent molar volume, $\varphi_v$vs square root of concentration, √C of NAC in 0.003 M chitosan and [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Table 4.24: Apparent molar volume, φ_v of NAC in 0.006 M chitosan and [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC ($mol.L^{-1}$)	Apparent molar volume, φ_v ($cm^3.mol^{-1}$)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.006 M chitosan and [3:2] [H_2O-CH_3COOH]	0.10	142.06	142.67	143.64	144.14	144.39
	0.50	141.02	141.52	142.32	142.67	143.07
	1.00	140.36	140.63	141.39	141.75	141.94

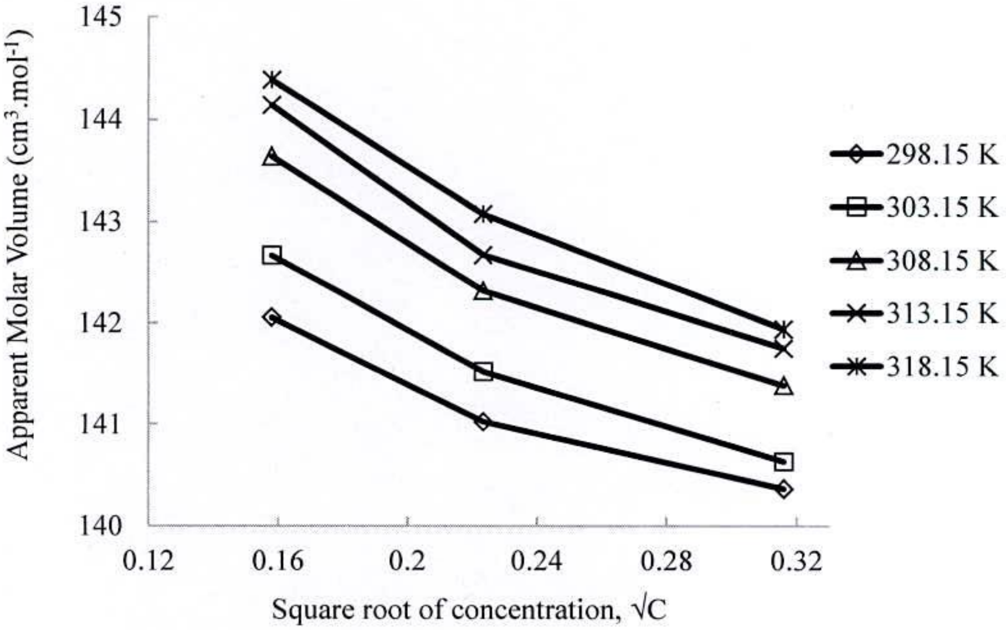


Figure 4.23: Apparent molar volume, φ_v vs square root of concentration, √C of NAC in 0.006 M chitosan and [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Table 4.25: Apparent molar volume, φ_v of NAC in 0.012 M chitosan and [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC ($mol.L^{-1}$)	Apparent molar volume, φ_v ($cm^3.mol^{-1}$)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.012 M chitosan and [3:2] [H_2O-CH_3COOH]	0.10	146.78	147.58	148.28	148.81	149.43
	0.50	142.57	143.04	143.66	144.22	144.86
	1.00	139.79	140.44	141.18	141.77	142.44

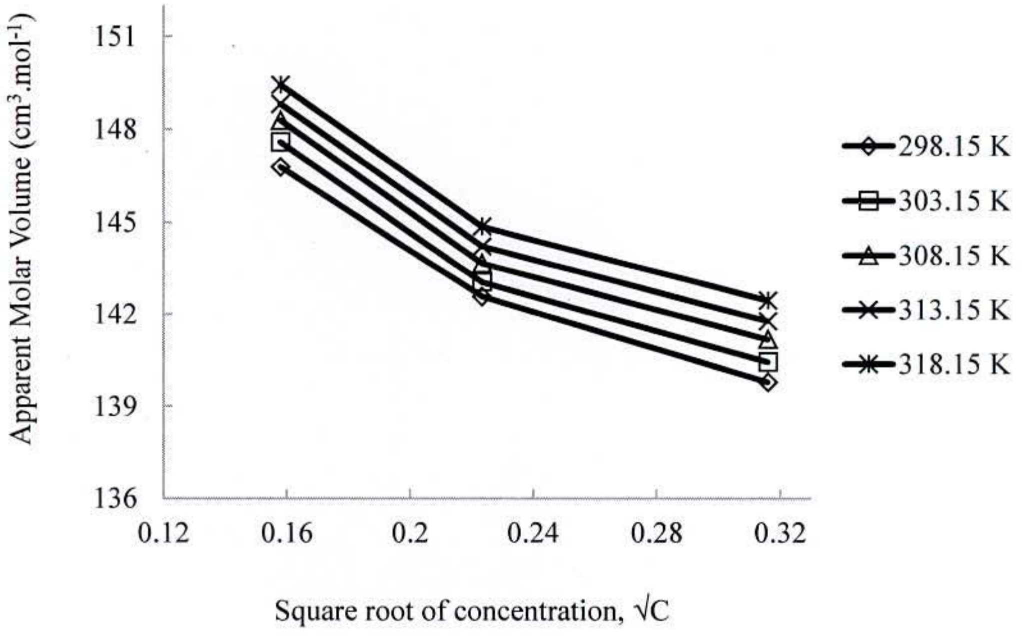


Figure 4.24: Apparent molar volume, φ_v vs square root of concentration, √C of NAC in 0.012 M chitosan and [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

4.4 Apparent molar volume at infinite dilution

Apparent molar volume at infinite dilution, φ_V^0 varies with the molarity of NAC as represented by the following Masson equation 1.2.13. Intercept of graph between φ_V and $C^{1/2}$ gives us apparent molar volume at infinite dilution, φ_V^0 and gives an idea about the presence of solute–solvent interactions. While S_v is the experimental slopes which give an idea about the prevailing solute–solute interactions in the mixtures. The apparent molar volumes at infinite dilution, φ_V^0 values of NAC in chitosan and aqueous acetic acid mixtures have been tabulated in Table 4.26-4.29. The results can be revealed as a function of both temperature and the structure of NAC. The φ_V^0 values of NAC reflect the true value of NAC at the specified temperatures. Apparent molar volumes at infinite dilution were computed from intercept of the plot between φ_V and $C^{1/2}$ as per following Masson equation 1.2.13.

$$\varphi_v = \varphi_v^0 + S_v\sqrt{c} \text{ ....1.2.13}$$

The apparent molar volumes, φ_V and square root of concentration, $C^{1/2}$ have been computed formerly to evaluate the value of apparent molar volume at infinite dilution which is the experimental intercept of graph between φ_V and $C^{1/2}$ and is a function of solute–solvent interactions. It is seen from Table 4.26 φ_V^0 values of chitosan in [9:1], [7:3] and [3:2] [H_2O-CH_3COOH] systems decreased with increasing temperatures and increased with increasing the ratio of CH_3COOH in H_2O-CH_3COOH mixed solutions. Chitosan in H_2O-CH_3COOH mixed solvent might have strong hydrogen bonding plus hydrophobic interactions among the organic parts of chitosan and acetic acid provide organized structure, leading to a decrease of the volume. In addition, one might accomplish that at increased temperature cage in the investigated systems becomes less important apparent molar volume at infinite dilution, φ_V^0 decreased with increasing temperature [89]. But incorporation of more acetic acid ratio in Chitosan-H_2O-CH_3COOH system hydrophobic-hydrophobic repulsion predominant over hydrogen bonding or dipole-dipole interaction of the investigated systems and apparent molar volume at infinite dilution, φ_V^0 increased.

It is seen from Table 4.27 φ_V^0 values of NAC-chitosan-[9:1] [H_2O-CH_3COOH] systems increased with increasing temperatures and concentration of NAC in Chitosan-H_2O-CH_3COOH solutions. Trend of the represents the large values of apparent molar volumes at infinite dilution supports the oversize molecules of chitosan as well as NAC in H_2O-CH_3COOH. The positive and large values of φ_V^0 indicate the ion−dipole interactions occurred. In case of NAC-chitosan-[H_2O-CH_3COOH] systems φ_V^0 values increase with a rise in temperature which suggests that at higher temperature significant solute−solvent interactions are present in the mixtures [87]. The increase in φ_V^0 values with an increase in NAC molarity represents the volume expansion [97] due to less hydrophobic interactions. Similar results regarding apparent molar volumes at infinite dilution for other NAC-Chitosan-H_2O-CH_3COOH systems were observed with miniature irregularities or deviations.

Table 4.26: Apparent molar volume, φ_V^0 at infinite dilution of chitosan in [9:1], [7:3] and [3:2] [H_2O-CH_3COOH] systems at 298.15 to 318.15 K at 5 K interval

Temperature (K)	Apparent molar volume at infinite dilution, φ_V^0 ($cm^3.mol^{-1}$)		
	Chitosan in [9:1] [H_2O-CH_3COOH]	Chitosan in [7:3] [H_2O-CH_3COOH]	Chitosan in [3:2] [H_2O-CH_3COOH]
298.15	119.76	127.04	139.38
303.15	110.99	113.49	125.06
308.15	101.89	108.54	118.47
313.15	89.73	100.62	109.90
318.15	90.31	94.78	103.06

Table 4.27: Apparent molar volume, φ_V^0 at infinite dilution of (0.10, 0.50, 1.00) M NAC in (0.003, 0.006, 0.012) M chitosan and [9:1] [H_2O-CH_3COOH] systems at 298.15 to 318.15 K at 5 K interval

Temperature (K)	Apparent molar volume at infinite dilution, φ_V^0 ($cm^3.mol^{-1}$)		
	NAC in 0.003 M chitosan and [9:1] [H_2O-CH_3COOH]	NAC in 0.006 M chitosan and [9:1] [H_2O-CH_3COOH]	NAC in 0.012 M chitosan and [9:1] [H_2O-CH_3COOH]
298.15	145.86	160.92	162.30
303.15	148.53	162.22	164.29
308.15	151.79	164.60	166.58
313.15	154.00	166.29	167.75
318.15	156.98	168.33	169.89

Table 4.28: Apparent molar volume, φ_V^0 at infinite dilution of (0.10, 0.50, 1.00) M NAC in (0.003, 0.006, 0.012) M chitosan and [7:3] [H_2O-CH_3COOH] systems at 298.15 to 318.15 K at 5 K interval

Temperature (K)	Apparent molar volume at infinite dilution, φ_V^0 ($cm^3.mol^{-1}$)		
	NAC in 0.003 M chitosan and [7:3] [H_2O-CH_3COOH]	NAC in 0.006 M chitosan and [7:3] [H_2O-CH_3COOH]	NAC in 0.012 M chitosan and [7:3] [H_2O-CH_3COOH]
298.15	133.43	119.55	138.78
303.15	136.78	120.40	141.85
308.15	141.49	127.28	146.21
313.15	146.11	129.14	154.04
318.15	149.47	135.04	157.23

Table 4.29: Apparent molar volume, φ_V^0 at infinite dilution of (0.10, 0.50, 1.00) M NAC in (0.003, 0.006, 0.012) M chitosan and [3:2] [H_2O-CH_3COOH] systems at 298.15 to 318.15 K at 5 K interval

Temperature (K)	Apparent molar volume at infinite dilution, φ_V^0 ($cm^3.mol^{-1}$)		
	NAC in 0.003 M chitosan and [3:2] [H_2O-CH_3COOH]	NAC in 0.006 M chitosan and [3:2] [H_2O-CH_3COOH]	NAC in 0.012 M chitosan and [3:2] [H_2O-CH_3COOH]
298.15	141.91	142.83	149.97
303.15	146.01	143.62	150.78
308.15	148.95	144.67	151.43
313.15	151.09	145.22	151.94
318.15	152.74	145.54	152.52

4.5 S_v parameter

The S_v parameter is the resultant of experimental slope of graph between φ_v and $C^{1/2}$ and is a function of ion–ion interactions. Sign of S_v gives information about the structural influence of solute on solvent system that is, whether solute acts as a structure promoting or structure breaker [90] of solvent or solvent mixture. Positive sign of S_v value indicate the weak solute-solvent interaction while those for negative value indicate the strong solute-solvent interaction present in the systems. The Sv values of investigated Chitosan--H_2O-CH_3COOH and NAC included Chitosan--H_2O-CH_3COOH have been represented in Table 4.30-4.33. The negative and large in magnitude values of S_v in all investigated systems supports the strong solute-solvent interaction present [91].

Table 4.30: S_v parameter of chitosan in [9:1], [7:3] and [3:2] [H_2O-CH_3COOH] systems at 298.15 to 318.15 K at 5 K interval

Temperature (K)	S_v parameter		
	Chitosan in [9:1] [H_2O-CH_3COOH]	Chitosan in [7:3] [H_2O-CH_3COOH]	Chitosan in [3:2] [H_2O-CH_3COOH]
298.15	-25.93	-44.79	-59.21
303.15	-24.82	-21.90	-40.13
308.15	-18.71	-30.58	-47.29
313.15	-16.56	-22.17	-36.58
318.15	-54.05	-22.53	-24.01

Table 4.31: S_v parameter of (0.10, 0.50 and 1.00 M) NAC in (0.003, 0.006 and 0.012 M) chitosan and [9:1] [H_2O-CH_3COOH] systems at 298.15 to 318.15 K at 5 K interval

Temperature (K)	S_v parameter		
	NAC in 0.003 M chitosan and [9:1] [H_2O-CH_3COOH]	NAC in 0.006 M chitosan and [9:1] [H_2O-CH_3COOH]	NAC in 0.012 M chitosan and [9:1] [H_2O-CH_3COOH]
298.15	-16.91	-32.50	-32.05
303.15	-18.06	-31.57	-32.35
308.15	-19.57	-32.50	-33.26
313.15	-20.00	-32.42	-32.83
318.15	-21.21	-32.49	-33.405

Table 4.32: S_v parameter of (0.10, 0.50 and 1.00 M) NAC in (0.003, 0.006 and 0.012 M) chitosan and [7:3] [H_2O-CH_3COOH] systems at 298.15 to 318.15 K at 5 K interval

Temperature (K)	S_v parameter		
	NAC in 0.003 M chitosan and [7:3] [H_2O-CH_3COOH]	NAC in 0.006 M chitosan and [7:3] [H_2O-CH_3COOH]	NAC in 0.012 M chitosan and [7:3] [H_2O-CH_3COOH]
298.15	-98.90	-55.06	-75.84
303.15	-94.96	-37.48	-75.08
308.15	-94.60	-52.06	-82.54
313.15	-95.29	-48.92	-103.08
318.15	-94.07	-58.35	-103.24

Table 4.33: S_v parameter of (0.10, 0.50 and 1.00 M) NAC in (0.003, 0.006 and 0.012 M) chitosan and [3:2] [H_2O-CH_3COOH] systems at 298.15 to 318.15 K at 5 K interval

Temperature (K)	S_v parameter		
	NAC in 0.003 M chitosan and [3:2] [H_2O-CH_3COOH]	NAC in 0.006 M chitosan and [3:2] [H_2O-CH_3COOH]	NAC in 0.012 M chitosan and [3:2] [H_2O-CH_3COOH]
298.15	-9.76	-2.49	-10.26
303.15	-12.47	-2.98	-10.52
308.15	-14.42	-3.28	-10.47
313.15	-15.76	-3.50	-10.38
318.15	-16.82	-3.57	-10.30

4.6 Apparent molar expansivity

The parameter that measures the variation of volume with temperature is the apparent molar expansivity, φ_E^0 which was defined by the equation 1.2.19. These values of apparent molar expansivities at infinite dilution φ_E^0 are shown in Table 4.34-4.37. The expansivity values are positive at all the investigated temperatures. Positive values indicate that, on heating some NAC and chitosan molecules may be released from the solvation layer of ion. It may also be conferred that the positive φ_E^0 values may be Chitosan-H_2O-CH_3COOH and NAC-Chitosan-H_2O-CH_3COOH systems. As a whole there is a hydrophilic/hydrophobic balance among the solute and solvent molecules.

The φ_E^0 values are found to be positive at all temperatures and concentrations of NAC and chitosan. The positive values of φ_E^0 as reported in Table 4.34-4.37 suggests the presence of solute-solvent interactions in these systems, as already indicated by apparent molar volume data [92].

Table 4.34: Apparent molar expansivity at infinite dilution φ_E^0 values of chitosan in [9:1], [7:3] and [3:2] [H_2O-CH_3COOH] systems at 298.15 to 318.15 K at 5 K interval

Name of the system	Apparent molar expansivity at infinite dilution, φ_E^0 ($cm^3.mol^{-1}.K^{-1}$)		
	[9:1] [H_2O-CH_3COOH]	[7:3] [H_2O-CH_3COOH]	[3:2] [H_2O-CH_3COOH]
0.003 M chitosan	1.7653	1.4270	1.5326
0.006 M chitosan	1.8014	1.3171	1.4079
0.012 M chitosan	1.9141	1.2815	1.2958

Table 4.35: Apparent molar expansivity at infinite dilution φ_E^0 values of (0.10, 0.50 and 1.00 M) NAC in (0.003, 0.006 and 0.012 M) chitosan and [9:1] [H_2O-CH_3COOH] systems at 298.15 to 318.15 K at 5 K interval

Name of the system	Apparent molar expansivity at infinite dilution, φ_E^0 ($cm^3.mol^{-1}.K^{-1}$)		
	0.003 M chitosan in [9:1] [H_2O-CH_3COOH]	0.006 M chitosan in [9:1] [H_2O-CH_3COOH]	0.012 M chitosan in [9:1] [H_2O-CH_3COOH]
0.10 M NAC	0.4421	0.2998	0.3052
0.50 M NAC	0.5111	0.5356	0.4383
1.00 M NAC	0.2828	0.2639	0.2457

Table 4.36: Apparent molar expansivity at infinite dilution φ_E^0 values of (0.10, 0.50 and 1.00 M) NAC in (0.003, 0.006 and 0.012 M) chitosan and [7:3] [H_2O-CH_3COOH] systems at 298.15 to 318.15 K at 5 K interval

Name of the system	Apparent molar expansivity at infinite dilution, φ_E^0 ($cm^3.mol^{-1}.K^{-1}$)		
	0.003 M chitosan in [7:3] [H_2O-CH_3COOH]	0.006 M chitosan in [7:3] [H_2O-CH_3COOH]	0.012 M chitosan in [7:3] [H_2O-CH_3COOH]
0.10 M NAC	0.7938	0.7639	0.7386
0.50 M NAC	0.9788	0.6682	0.5804
1.00 M NAC	0.8421	0.6991	0.4714

Table 4.37: Apparent molar expansivity at infinite dilution φ_E^0 values of (0.10, 0.50 and 1.00 M) NAC in (0.003, 0.006 and 0.012 M) chitosan and [3:2] [H_2O-CH_3COOH] systems at 298.15 to 318.15 K at 5 K interval

Name of the system	Apparent molar expansivity at infinite dilution, φ_E^0 ($cm^3.mol^{-1}.K^{-1}$)		
	0.003 M chitosan in [3:2] [H_2O-CH_3COOH]	0.006 M chitosan in [3:2] [H_2O-CH_3COOH]	0.012 M chitosan in [3:2] [H_2O-CH_3COOH]
0.10 M NAC	0.4016	0.1226	0.1305
0.50 M NAC	0.3429	0.1049	0.1150
1.00 M NAC	0.1557	0.0855	0.1329

4.7 Viscometric Properties

NAC and Chitosan has huge medicinal and biological applications in human body. The viscometric of study chitosan in H_2O-CH_3COOH mixed solvents and at the same time exploration of effect of NAC on Chitosan-H_2O-CH_3COOH systems might be applicable and interesting. Aqueous acetic acid mixtures are very important systems exhibiting properties that are of great interest in physics, chemistry and biology. Due to this reason viscometric behaviors of NAC in chitosan and H_2O-CH_3COOH mixture systems have been discussed.

4.7.1 Viscosity of Solvent System

The viscosity at different temperatures of the mixed pure solvents; H_2O-CH_3COOH have been tabulated in Table 4.38. The viscosity values increases with the increasing ratio of water in the water and acetic acid mixed solvents system. From the table it is also seen that densities of the solvents decreased with the increasing temperature.

Table 4.38: Viscosity values, η of H_2O-CH_3COOH system at 298.15 to 318.15 K at 5 K interval

Name of the system	Viscosity, η (mPa.s)				
	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
[9:1] [H_2O-CH_3COOH]	1.0947	0.9796	0.8713	0.7988	0.7186
[7:3] [H_2O-CH_3COOH]	1.4859	1.3169	1.1674	1.0475	0.9515
[3:2] [H_2O-CH_3COOH]	1.6669	1.4861	1.3078	1.1744	1.0654

4.7.2 Viscosity of Chitosan-H_2O-CH_3COOH Systems

The viscosities, η of chitosan in H_2O-CH_3COOH systems have been studied at 298.15, 303.15, 308.15, 313.15, and 318.15 K temperature over a concentration range of (0.003, 0.006 and 0.012 M) of chitosan. The experimented results are tabulated in Table 4.39-4.41. The viscosities in chitosan in H_2O-CH_3COOH systems increased with the increase of concentration as expected and the graphical presentation has been shown here in Figure 4.25-4.27. The increase of η values of chitosan with concentration can be attributed to the increase in solute–solvent, and solute–solute interactions in solution. The small range of dissolution of chitosan in H_2O-CH_3COOH might have intriguing aspects which may be the consequence of the great ability of H_2O and CH_3COOH to make dipole-dipole, ion-dipole and hydrogen bonds with chitosan. At the same time it is seen that the viscosity values decrease considerably with the rise in temperature at a constant molarity. In both cases with the increase of temperature in Chitosan-H_2O-CH_3COOH systems the internal energy of the system increased and as because of this the solute-solute or solute-solvent interaction may be depleted.

Table 4.39: Viscosity values, η of chitosan in [9:1] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol dm^{-3})	Viscosity, η (mPa.s)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Chitosan in [9:1] [H_2O-CH_3COOH]	0.003	1.4635	1.2339	1.0175	0.8832	0.7655
	0.006	1.7596	1.4837	1.2664	1.0422	0.8954
	0.012	2.2719	2.0306	1.7885	1.5346	1.3588

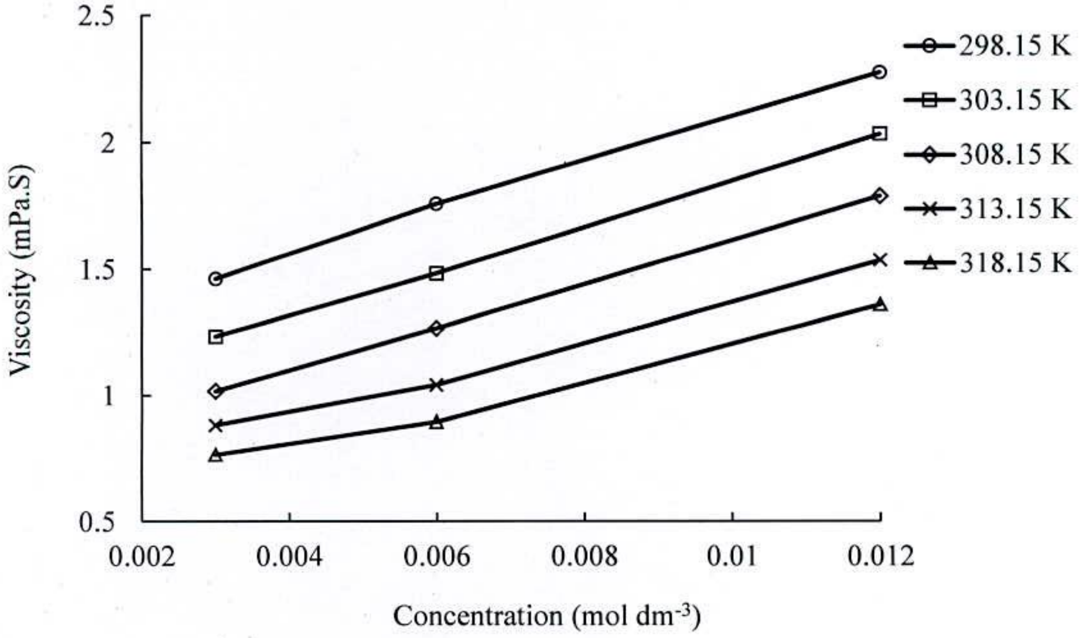


Figure 4.25: Viscosities, η vs concentration (M) of chitosan in [9:1] [H_2O-CH_3COOH] systems at 298.15 to 318.15 K at 5 K interval

Table 4.40: Viscosities, η of chitosan in [7:3] [H_2O-CH_3COOH] systems at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol dm^{-3})	Viscosity, η (mPa.s)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Chitosan in [7:3] [H_2O-CH_3COOH]	0.003	1.9516	1.6708	1.3642	1.1993	1.0336
	0.006	2.4189	1.9393	1.6739	1.4418	1.2648
	0.012	3.1301	2.6822	2.2963	1.9778	1.7207

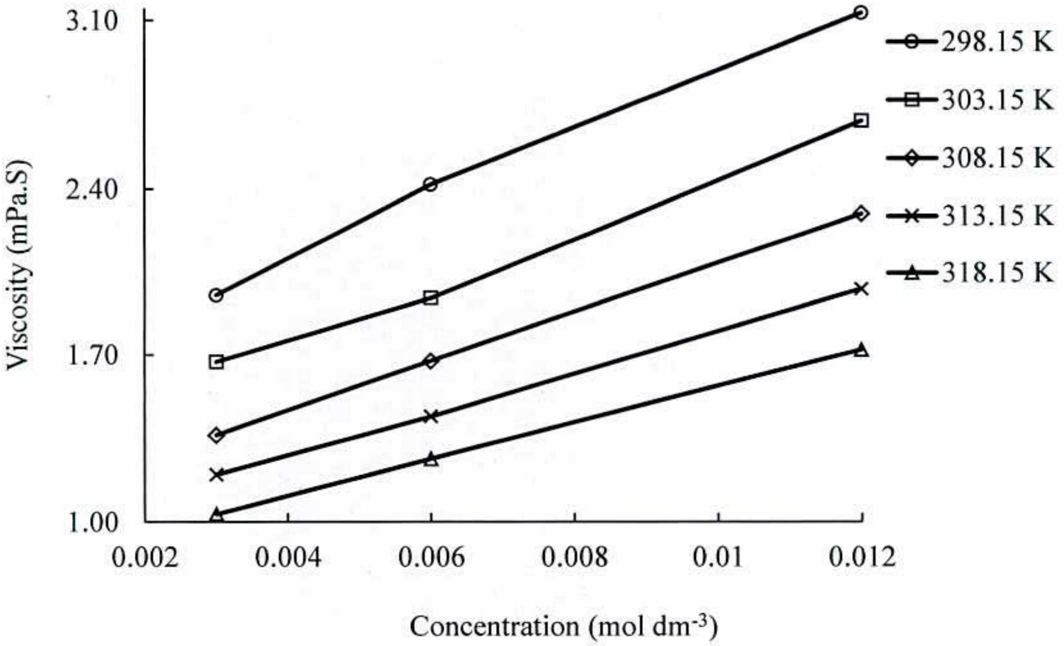


Figure 4.26: Viscosities, η vs concentration (M) of Chitosan in [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Table 4.41: Viscosity values, η of chitosan in [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol dm^{-3})	Viscosity, η (mPa.s)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Chitosan in [3:2] [H_2O-CH_3COOH]	0.003	2.4266	1.9465	1.5975	1.2589	1.0746
	0.006	2.9192	2.4824	2.0135	1.6080	1.4012
	0.012	3.6708	3.0999	2.6472	2.2803	1.9683

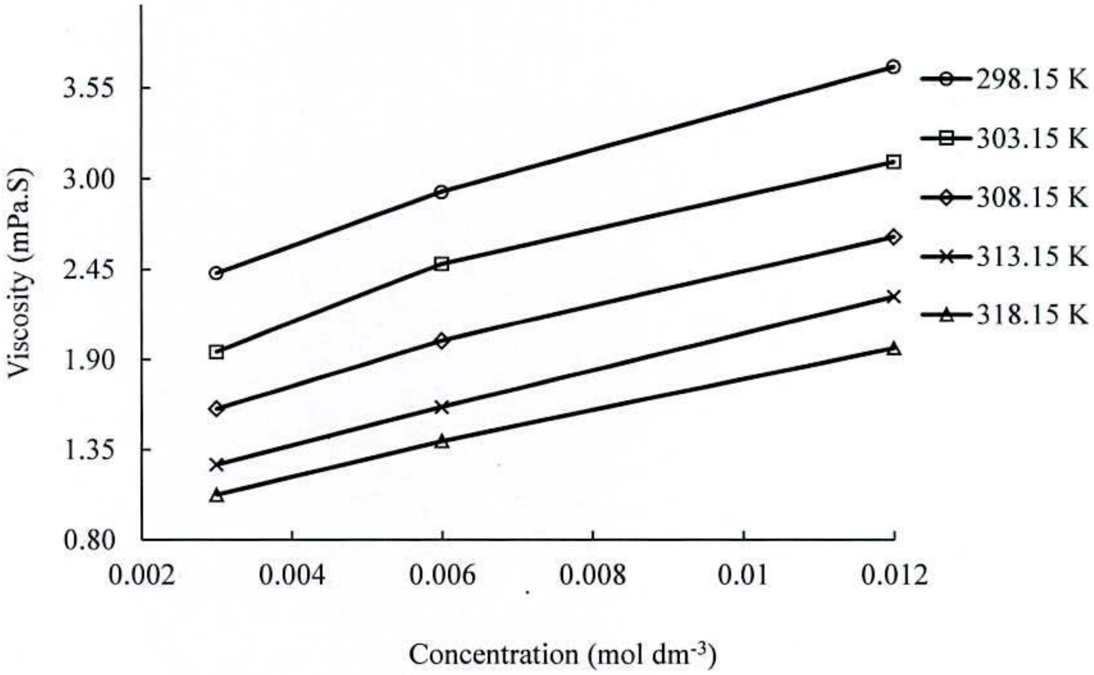


Figure 4.27: Viscosities, η vs concentration (M) of chitosan in [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

4.7.3 Viscosity of NAC-Chitosan-H_2O-CH_3COOH systems

The viscosities, η of NAC in Chitosan-H_2O-CH_3COOH systems have been described at 298.15, 303.15, 308.15, 313.15, and 318.15 K temperature over a concentration range of (0.10, 0.50 and 1.00 M). The values of the viscosity of NAC-Chitosan-H_2O-CH_3COOH systems have been tabulated in Table 4.42-4.50. The results are also presented graphically in Figure 4.28, 4.29, 4.30, 4.31, 4.32, 4.33, 4.34, 4.35 and 4.36. From the table we can see that the viscosity values are positive in all NAC-Chitosan-H_2O-CH_3COOH systems and are greater than Chitosan-H_2O-CH_3COOH systems as shown in Table 4.39-4.41 and even those of the solvents (Table 4.38). Stronger solute-solute or solute-solvent interactions present in the systems than the others. Viscosity values increased significantly with the increase in concentration of NAC. At the same time it is seen that the viscosity values decreased considerably with temperature at a constant molarity as expected. The reason is been discussed earlier in the section 4.7.2. The reason of more interactions in NAC-Chitosan-H_2O-CH_3COOH systems may be due to the fact that chitosan-H_2O-CH_3COOH systems can be stabilized by additional solute-solvent, solute-solute interactions through hydrogen-bond, ion-dipole, dipole-dipole interactions. As we know that chitosan consists of hydroxyl group and NAC which provide hydrophilic interaction with hydroxyl, thiol and amino group of NAC, Chitosan and Acetic Acid. Thus the solubility of NAC-Chitosan-H_2O-CH_3COOH solution systems is therefore become facile or make available more of the interactions and offer more organized structures.

Table 4.42: Viscosity values, η of NAC in 0.003 M chitosan and [9:1] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Viscosity, η (mPa.s)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.003 M chitosan and [9:1] [H_2O-CH_3COOH]	0.10	1.4110	1.2593	1.0795	0.9626	0.8885
	0.50	1.5274	1.3184	1.1598	1.0295	0.9135
	1.00	1.7650	1.5233	1.3289	1.1693	1.0335

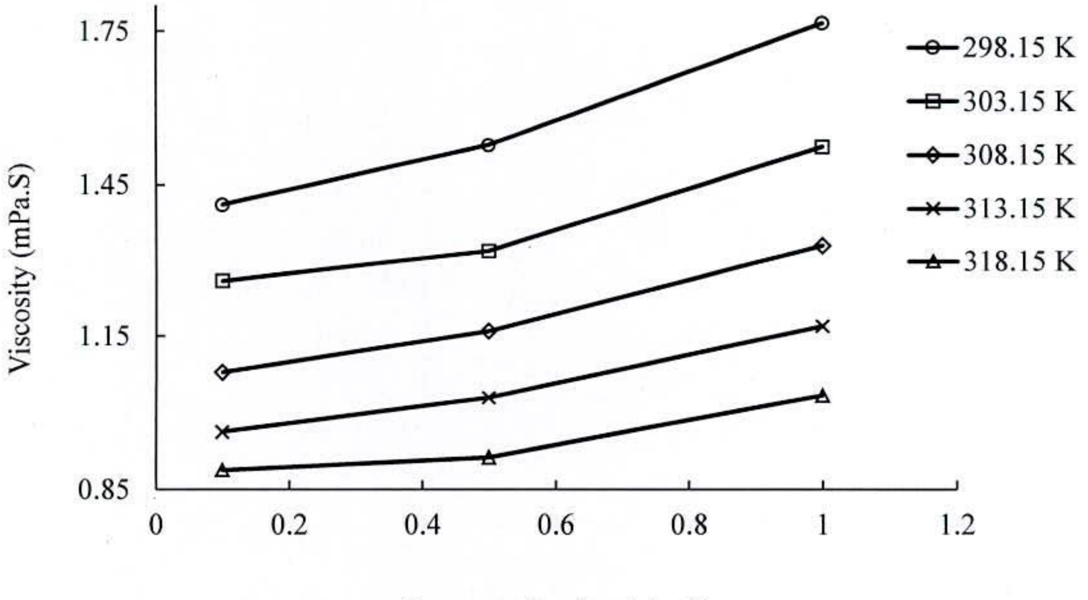


Figure 4.28: Viscosities, η vs concentration (M) of NAC in 0.003 M chitosan and [9:1] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Table 4.43: Viscosity values, η of NAC in 0.006 M chitosan and [9:1] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Viscosity, η (mPa.s)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.006 M chitosan and [9:1] [H_2O-CH_3COOH]	0.10	2.1825	1.6907	1.4455	1.2116	1.1185
	0.50	2.2867	1.7584	1.5193	1.2829	1.1499
	1.00	2.4307	1.9818	1.7565	1.3956	1.2038

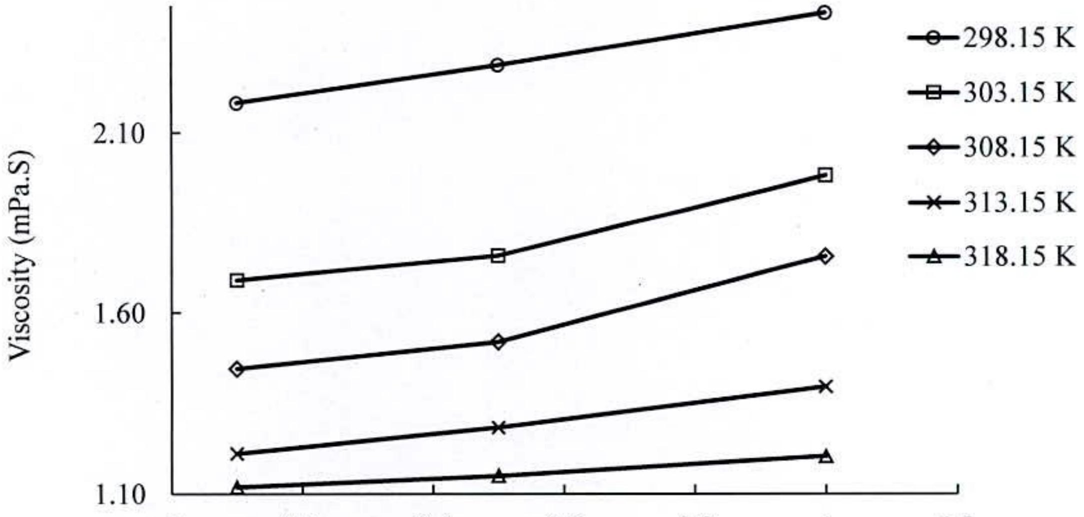


Figure 4.29: Viscosities, η vs concentration (M) of NAC in 0.006 M chitosan and [9:1] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Table 4.44: Viscosity values, η of NAC in 0.012 M chitosan and [9:1] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Viscosity, η (mPa.s)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.012 M chitosan and [9:1] [H_2O-CH_3COOH]	0.10	2.3831	2.0211	1.7598	1.5366	1.3499
	0.50	2.9020	2.4628	2.1215	1.8176	1.6018
	1.00	3.4664	2.9369	2.4996	2.2481	1.8651

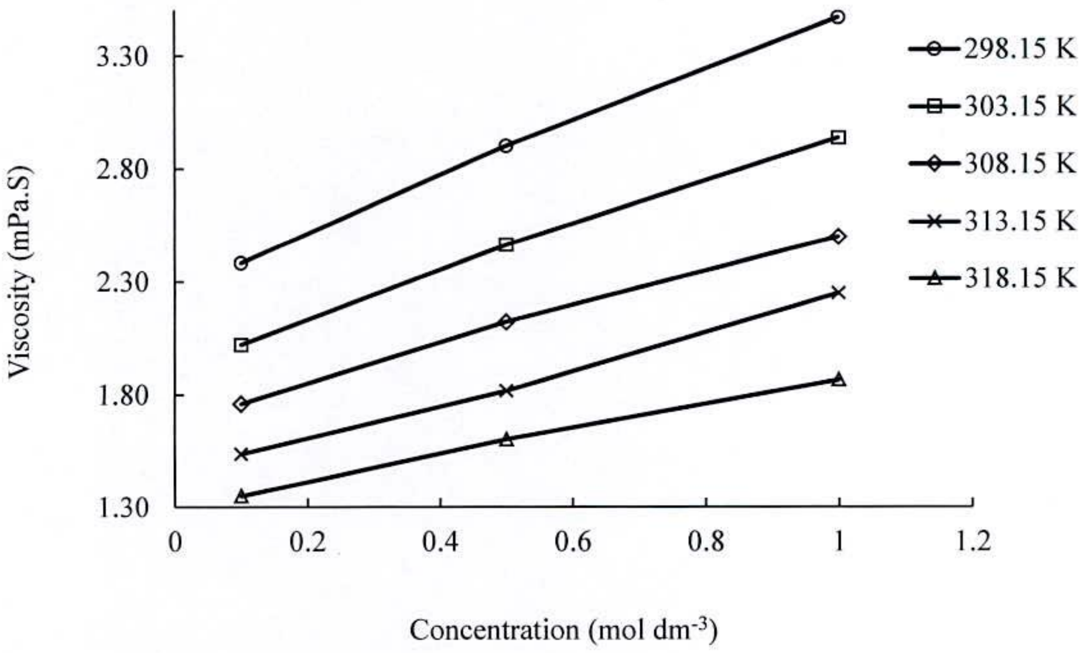


Figure 4.30: Viscosities, η vs concentration (M) of NAC in 0.012 M chitosan and [9:1] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Table 4.45: Viscosity values, η of NAC in 0.003 M chitosan and [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Viscosity, η (mPa.s)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.003 M chitosan and [7:3] [H_2O-CH_3COOH]	0.10	2.5442	2.2356	1.9372	1.7156	1.5478
	0.50	2.6072	2.2963	2.0232	1.7913	1.5926
	1.00	2.9956	2.6096	2.2773	1.9855	1.7754

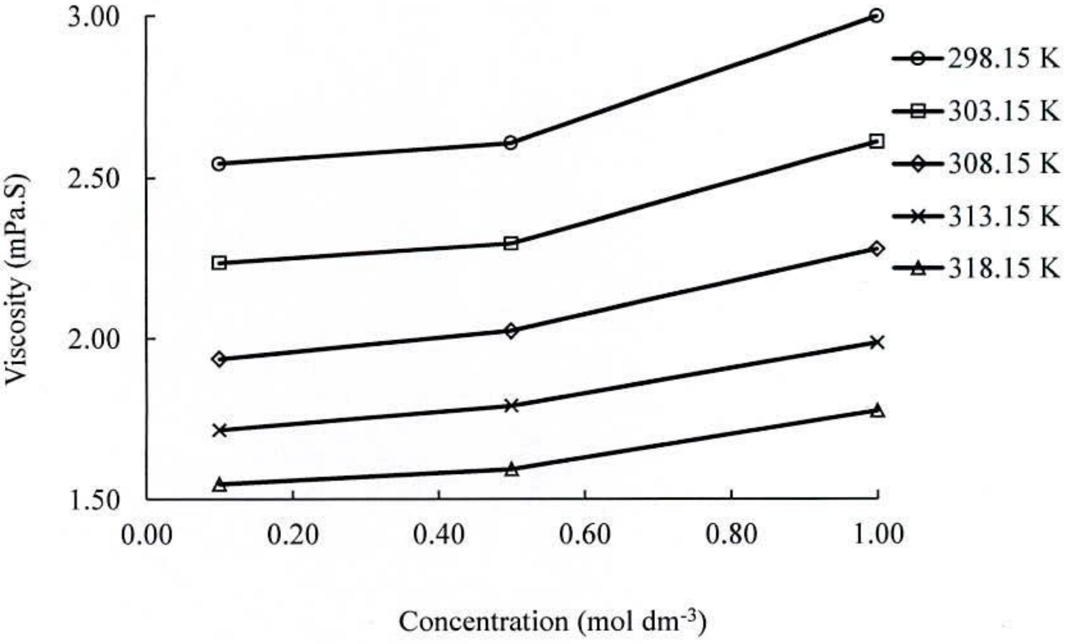


Figure 4.31: Viscosities, η vs concentration (M) of NAC in 0.003 M chitosan and [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Table 4.46: Viscosity values, η of NAC in 0.006 M chitosan and [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Viscosity, η (mPa.s)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.006 M chitosan and [7:3] [H_2O-CH_3COOH]	0.10	2.2898	1.9707	1.6925	1.4766	1.2883
	0.50	2.6511	2.2882	1.8872	1.6274	1.4888
	1.00	3.0399	2.5824	2.1049	1.8421	1.6988

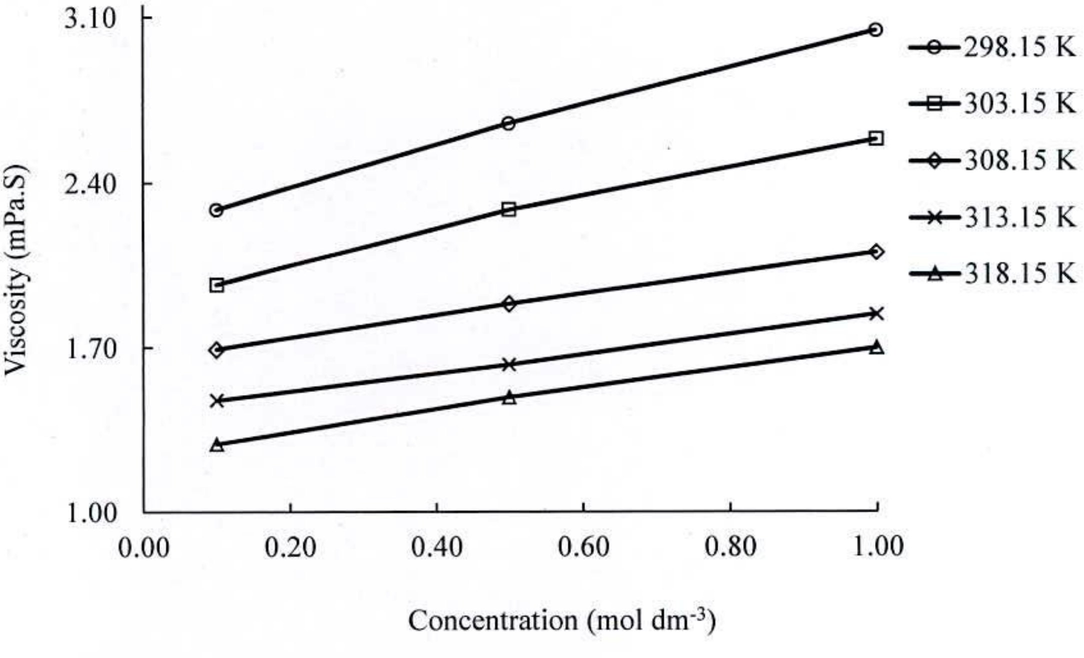


Figure 4.32: Viscosities, η vs concentration (M) of NAC in 0.006 M chitosan and [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Table 4.47: Viscosity values, η of NAC in 0.012 M chitosan and [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Viscosity, η (mPa.s)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.012 M chitosan and [7:3] [H_2O-CH_3COOH]	0.10	5.5019	4.7712	4.0853	3.5775	3.0989
	0.50	5.7970	4.9576	4.2017	3.7109	3.2097
	1.00	5.8572	5.0278	4.3388	3.7874	3.3019

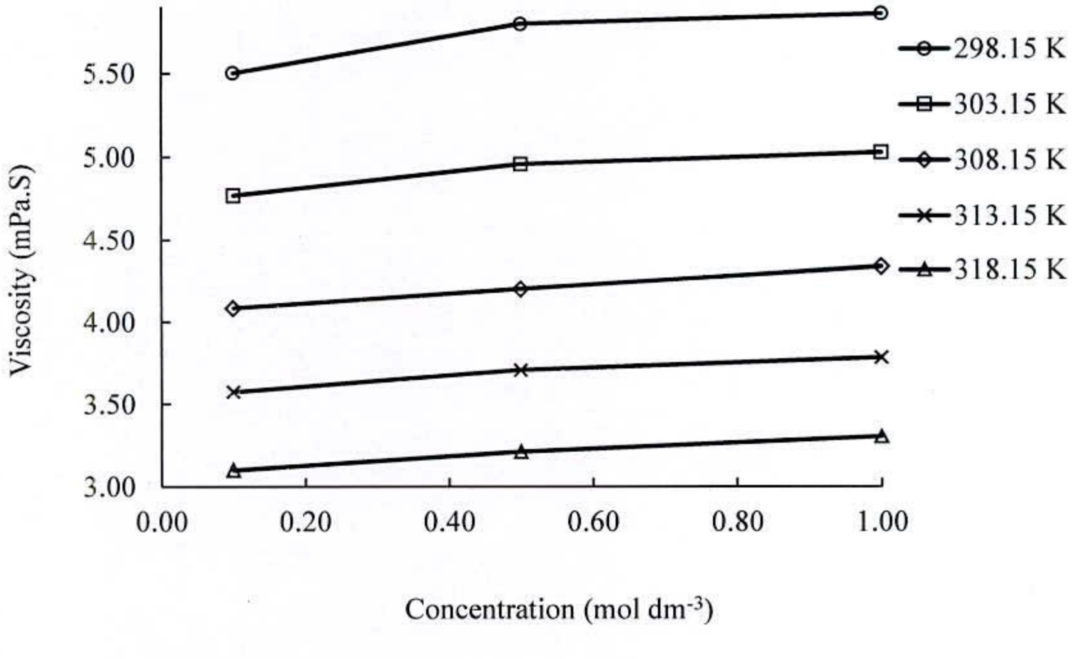


Figure 4.33: Viscosities, η vs concentration (M) of NAC in 0.012 M chitosan and [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Table 4.48: Viscosities, η of NAC in 0.003 M chitosan and [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Viscosity, η (mPa.s)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.003 M chitosan and [3:2] [H_2O-CH_3COOH]	0.10	1.0481	2.6381	2.3265	2.0534	1.8172
	0.50	1.0578	2.9318	2.5805	2.2435	1.97043
	1.00	1.0707	3.2677	2.8441	2.4812	2.1755

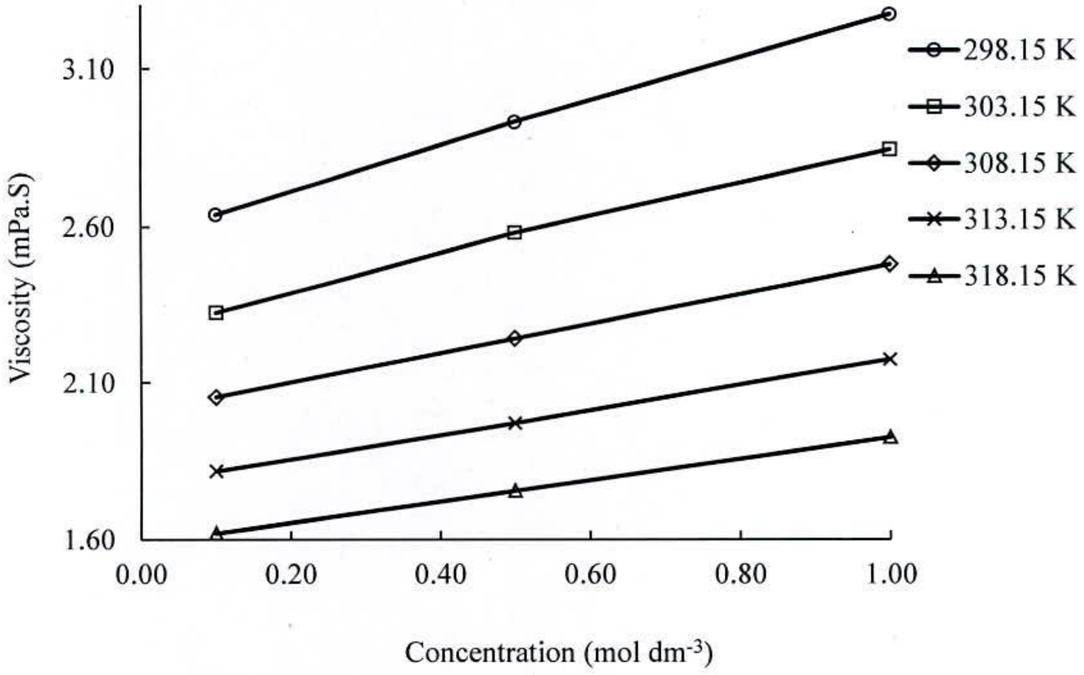


Figure 4.34: Viscosities, η vs concentration (M) of NAC in 0.003 M chitosan and [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Table 4.49: Viscosities, η of NAC in 0.006 M chitosan and [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Viscosity, η (mPa.s)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.006 M chitosan and [3:2] [H_2O-CH_3COOH]	0.10	2.4531	2.1389	1.8265	1.5935	1.3915
	0.50	2.7444	2.4511	2.1602	1.8850	1.5315
	1.00	3.0552	2.6324	2.3435	1.9636	1.7502

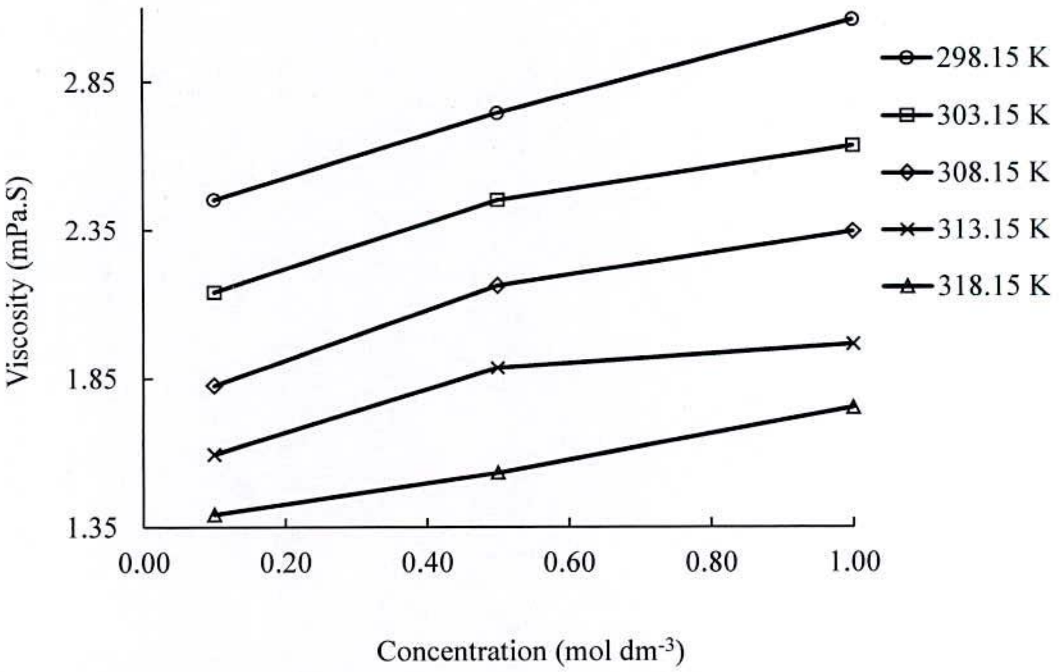


Figure 4.35: Viscosities, η vs concentration (M) of NAC in 0.006 M chitosan and [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Table 4.50: Viscosities, η of NAC in 0.012 M chitosan and [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Viscosity, η (mPa.s)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.012 M chitosan and [3:2] [H_2O-CH_3COOH]	0.10	5.6108	4.8531	4.1395	3.6451	3.1544
	0.50	5.8816	5.0435	4.2851	3.7814	3.2607
	1.00	5.9996	5.1146	4.4526	3.8807	3.4119

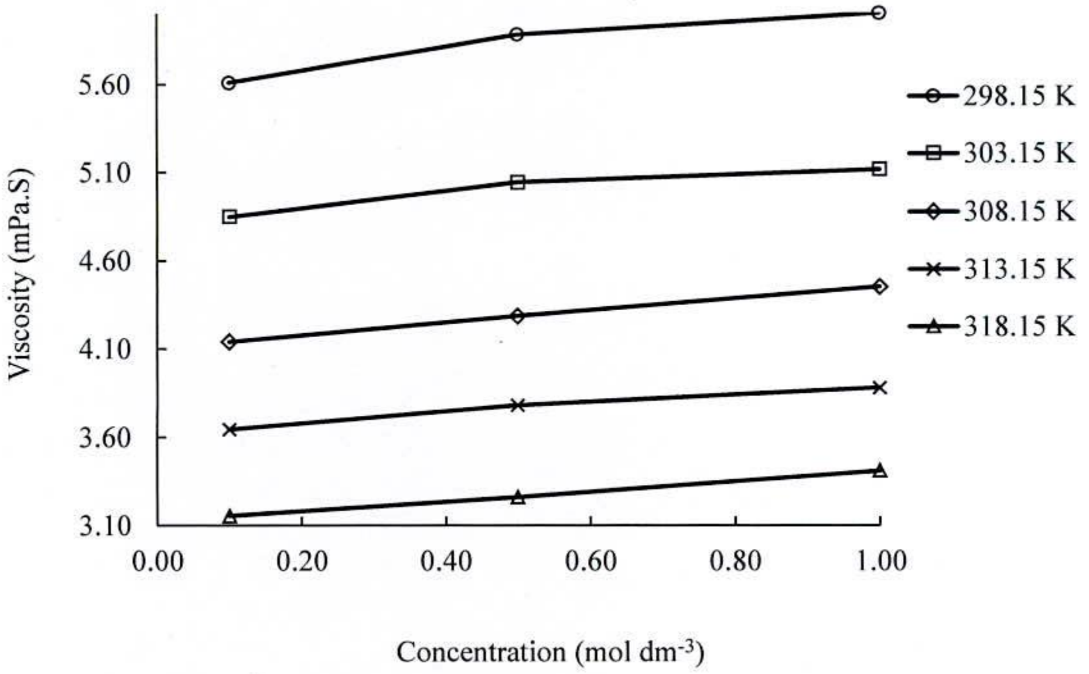


Figure 4.36: Viscosities, η vs concentration (M) of NAC in 0.012 M chitosan and [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

4.8 Jones-Dole co-efficient

The Jones-Dole co-efficient, A, reflects the effect of solute-solute interaction and B, is a measure of structural modifications induced by the solute-solvent interaction. The viscosity co-efficient A and B were obtained from the intercept and slope of the plots $(\eta_{rel} - 1)/C^{1/2}$ against $C^{1/2}$. The values of A and B are listed in Table 4.51-4.56 shows that in Chitosan-H_2O-CH_3COOH systems A and B co-efficient has positive and negative values respectively as well as in case of NAC-Chitosan-H_2O-CH_3COOH systems A and B co-efficient has negative and positive values respectively . Positive values of A co-efficient indicate the presence of strong solute-solute interactions and the negative values of B co-efficient point out the existence of weak ion-solvent interaction in the investigated systems at the all specific temperatures [93]. Negative values of A co-efficient indicate the presence of weak solute-solute interactions and the positive values of B co-efficient point out the existence of strong ion-solvent interaction in the investigated systems. Both values show variation with the increasing temperature.

A and B co-efficient support the behavior of φ_v, S_v and φ_v^0 which all suggest that solute-solvent interactions are predominant over solute-solute interaction in all experimented systems.

Table 4.51: Jones-Dole co-efficient for chitosan in [9:1] and [7:3] [H_2O-CH_3COOH] system

Temperature (K)	Chitosan in [9:1] [H_2O-CH_3COOH]		Chitosan in [7:3] [H_2O-CH_3COOH]	
	A co-efficient	B co-efficient	A co-efficient	B co-efficient
298.15	3.1764	-5.3622	0.5631	-9.4544
303.15	1.8791	-9.2316	0.0004	-10.1581
308.15	0.4457	-13.2396	0.9009	-12.5615
313.15	0.0827	-13.2408	0.9827	-11.9699
318.15	0.7589	-14.6066	1.4191	-12.6513

Table 4.52: Jones-Dole co-efficient for chitosan in [3:2] [H_2O-CH_3COOH] system and NAC in 0.003 M chitosan and [9:1] [H_2O-CH_3COOH] system

Temperature (K)	Chitosan in [3:2] [H_2O-CH_3COOH]		NAC in 0.003 M chitosan and [9:1] [H_2O-CH_3COOH]	
	A co-efficient	B co-efficient	A co-efficient	B co-efficient
298.15	2.0110	-5.7451	-0.2628	0.4661
303.15	0.6990	-9.0193	-0.0285	0.2384
308.15	0.3109	-11.4416	-0.1257	0.1578
313.15	1.9917	-15.8461	-0.2486	0.0477
318.15	2.4360	-16.4091	-0.5464	0.2511

Table 4.53: Jones-Dole co-efficient for NAC in (0.006 and 0.012 M) chitosan and [9:1] [H_2O-CH_3COOH] system

Temperature (K)	NAC in 0.006 M chitosan and [9:1] [H_2O-CH_3COOH]		NAC in 0.012 M chitosan and [9:1] [H_2O-CH_3COOH]	
	A co-efficient	B co-efficient	A co-efficient	B co-efficient
298.15	-0.5706	0.9066	-0.0108	0.5461
303.15	-0.1709	0.4615	-0.2156	0.6816
308.15	-0.1061	0.4437	-0.2442	0.6637
313.15	-0.2679	0.5739	-0.2107	0.6731
318.15	-0.6671	0.9614	-0.1909	0.5819

Table 4.54: Jones-Dole co-efficient for NAC in (0.003 and 0.006 M) chitosan and [7:3] [H_2O-CH_3COOH] system

Temperature (K)	NAC in 0.003 M chitosan and [7:3] [H_2O-CH_3COOH]		NAC in 0.006 M chitosan and [7:3] [H_2O-CH_3COOH]	
	A co-efficient	B co-efficient	A co-efficient	B co-efficient
298.15	-25.9201	15.2764	-1.3415	7.0611
303.15	-25.5866	14.8897	-0.6886	5.7623
308.15	-23.4324	13.9280	-0.5784	4.5692
313.15	-23.3069	13.5070	-0.5107	4.4972
318.15	-23.2181	13.2469	-0.7129	5.9228

Table 4.55: Jones-Dole co-efficient for NAC in 0.012 M chitosan and 0.003 M chitosan in [7:3] and [3:2] [H_2O-CH_3COOH] system respectively

Temperature (K)	NAC in 0.012 M chitosan and [7:3] [H_2O-CH_3COOH]		NAC in 0.003 M chitosan and [3:2] [H_2O-CH_3COOH]	
	A co-efficient	B co-efficient	A co-efficient	B co-efficient
298.15	-12.7860	6.7605	-0.1008	0.2375
303.15	-13.4932	6.9675	-0.2378	0.6733
308.15	-13.1306	6.8719	-0.5291	1.0326
313.15	-13.8624	7.2028	-1.0164	1.6621
318.15	-13.4439	7.0748	-1.2244	1.9224

Table 4.56: Jones-Dole co-efficient for NAC in (0.006 and 0.012 M) chitosan and [3:2] [H_2O-CH_3COOH] system

Temperature (K)	NAC in 0.006 M chitosan and [3:2] [H_2O-CH_3COOH]		NAC in 0.012 M chitosan and [3:2] [H_2O-CH_3COOH]	
	A co-efficient	B co-efficient	A co-efficient	B co-efficient
298.15	-0.7348	0.8211	-1.5477	2.0963
303.15	-0.6353	0.7468	-1.6997	2.2547
308.15	-0.4728	0.68793	-1.6484	2.2249
313.15	-0.1130	0.3831	-1.7804	2.3759
318.15	-0.1476	0.3961	-1.7569	2.3742

4.8 Thermodynamic Properties

Viscosity values were used to determine thermodynamic properties of the investigated systems, Thermodynamic parameters such as, change of free energy, ΔG*, change of enthalpy, ΔH*, change of entropy, ΔS* for viscous flow for Chitosan-[H_2O-CH_3COOH] and NAC-Chitosan-[H_2O-CH_3COOH] systems have been determined and discussed.

Thermodynamic properties, change of free energy, ΔG*, change of enthalpy, ΔH*, change of entropy, ΔS* for viscous flow have been calculated from viscometric data via Eyring equation. It is known that Gibbs free energy is a thermodynamic function and the energy of the system which is ready to work. The Gibbs free energy is used when considering processes that occur under constant pressure and temperature conditions. For a process that occurs at constant temperature and pressure, spontaneity can be determined using the change in Gibbs free energy, depends on the changes in enthalpy (ΔH) and entropy (ΔS), as well as on the absolute temperature (T).

In cases where ΔG [94] is-

- negative, the process is spontaneous and may proceed in the forward direction as written,
- positive, the process is non-spontaneous as written, but it may be proceed spontaneously in the reverse direction and
- zero, the process is at equilibrium, with no net change taking place over time.

The ΔG*, values are positive for all the studied systems Chitosan–Aqueous Acetic Acid and NAC–Chitosan–Aqueous Acetic Acid indicate that studied systems are non-spontaneous for the flow process as shown in Table 4.57 to 4.66 and it is spontaneous in the reverse direction. The positive free energy change, ΔG* for viscous flow may be interpreted by Furth model [95] which states that kinetic species involved in forming holes in the investigated solution systems may be stated by the work is required in forming the holes against surface tension of the solution. Positive ΔG* values also explain the interstitial incorporation, solute–solvent interaction that render the Chitosan-[H_2O-CH_3COOH] and NAC-Chitosan-[H_2O-CH_3COOH] systems are more structured.

Enthalpy is the thermodynamic quantity equivalent to the total heat content of a system. It is defined as the sum of internal energy of a system and the product of the pressure and volume of the system or pressure-volume work. Internal energy is the sum of translational energy, rotational energy, vibrational energy and the kinetic energy of a matter. The change in enthalpy is the sum of the change in the internal energy and the work done. Entropy is a measure of disorder or randomness of a system. In other words, it's a measurement of the degree of randomness of energy in a system. An ordered system has low entropy. A disordered system has high entropy.

The set of rules can be used to determine four distinct cases by examining the signs of the ΔS and ΔH [94].

- When $\Delta S > 0$ and $\Delta H < 0$, the process is always spontaneous as written.
- When $\Delta S < 0$ and $\Delta H > 0$, the process is never spontaneous, but the reverse process is always spontaneous.
- When $\Delta S > 0$ and $\Delta H > 0$, the process will be spontaneous at high temperatures and non-spontaneous at low temperatures.
- When $\Delta S < 0$ and $\Delta H < 0$, the process will be spontaneous at low temperatures and non-spontaneous at high temperatures.
- For the latter two cases, the temperature at which the spontaneity changes will be determined by the relative magnitudes of ΔS and ΔH.

The change enthalpy, ΔH^* values are positive for all the studied system as shown in Table 4.67-4.78. The positive ΔH values indicate that work has to be done for all the investigated systems. That is, the viscous flow is not thermodynamically favored for the systems studied. The change of entropy, ΔS^* of the investigated systems are shown in same Table 4.67-4.78. The ΔS^* values are negative for all the systems studied. This means that Chitosan-[H_2O-CH_3COOH] and NAC-Chitosan-[H_2O-CH_3COOH] systems are regular than those of the pure one. Here one point may be remarked that as $\Delta S < 0$ and $\Delta H > 0$, so the processes are never spontaneous but the reverse process is always spontaneous.

Table 4.57: Free energy, ΔG* of chitosan in [9:1] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol dm^{-3})	Free energy, ΔG* J.mol^{-1}				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Chitosan in [9:1] [H_2O-CH_3COOH]	0.003	15790.27	15625.00	15388.81	15269.93	15135.49
	0.006	16249.54	16092.23	15952.01	15703.51	15552.56
	0.012	16885.25	16885.42	16838.55	16713.23	16658.26

Table 4.58: Free energy, ΔG* of chitosan in [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol dm^{-3})	Free energy, ΔG* J.mol^{-1}				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Chitosan in [7:3] [H_2O-CH_3COOH]	0.003	16449.98	16337.57	16095.88	16030.26	15901.94
	0.006	16982.14	16713.17	16620.18	16509.68	16435.94
	0.012	17621.07	17530.57	17429.94	17332.14	17250.18

Table 4.59: Free energy, ΔG* of chitosan in [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol dm^{-3})	Free energy, ΔG* J.mol^{-1}				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Chitosan in [3:2] [H_2O-CH_3COOH]	0.003	16962.40	16700.22	16478.74	16135.65	15984.75
	0.006	17420.55	17313.09	17071.57	16772.79	16686.60
	0.012	17988.45	17873.03	17772.61	17682.26	17585.39

Table 4.60: Free energy, ΔG* of NAC in 0.003 M chitosan and [9:1] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. of NAC (mol dm^{-3})	Free energy, ΔG* J.mol^{-1}				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.003 M chitosan and [9:1] [H_2O-CH_3COOH]	0.10	15728.21	15707.44	15573.32	15532.15	15574.85
	0.50	15924.84	15822.85	15757.38	15706.90	15648.17
	1.00	16283.09	16186.98	16105.96	16038.53	15974.70

Table 4.61: Free energy, ΔG* of NAC in 0.006 M chitosan and [9:1] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. of NAC (mol dm^{-3})	Free energy, ΔG* J.mol^{-1}				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.006 M chitosan and [9:1] [H_2O-CH_3COOH]	0.10	16806.52	16446.23	16317.36	16126.14	16178.10
	0.50	16922.08	16545.07	16444.97	16275.11	16251.40
	1.00	17073.44	16846.50	16816.55	16494.26	16372.58

Table 4.62: Free energy, ΔG* of NAC in 0.012 M chitosan and [9:1] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. of NAC (mol dm^{-3})	Free energy, ΔG* J.mol^{-1}				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.012 M chitosan and [9:1] [H_2O-CH_3COOH]	0.10	17018.28	16890.09	16815.03	16738.93	16670.46
	0.50	17506.64	17388.19	17293.95	17176.19	17123.08
	1.00	17947.13	17831.98	17714.15	17729.60	17525.54

Table 4.63: Free energy, ΔG* of NAC in 0.003 M chitosan and [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. of NAC (mol dm^{-3})	Free energy, ΔG* J.mol^{-1}				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.003 M chitosan and [7:3] [H_2O-CH_3COOH]	0.10	17136.27	17097.73	17012.68	16972.36	16971.09
	0.50	17199.39	17167.88	17126.53	17087.49	17049.36
	1.00	17551.19	17497.80	17437.45	17363.40	17344.84

Table 4.64: Free energy, ΔG* of NAC in 0.006 M chitosan and [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. of NAC (mol dm^{-3})	Free energy, ΔG* J.mol^{-1}				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.006 M chitosan and [7:3] [H_2O-CH_3COOH]	0.10	16872.38	16779.37	16673.45	16596.54	16508.98
	0.50	17235.52	17155.87	16952.36	16849.56	16891.50
	1.00	17574.79	17460.73	17232.16	17172.19	17240.59

Table 4.65: Free energy, ΔG* of NAC in 0.012 M chitosan and [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. of NAC (mol dm^{-3})	Free energy, ΔG* J.mol^{-1}				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.012 M chitosan and [7:3] [H_2O-CH_3COOH]	0.10	19039.79	19001.40	18923.38	18891.99	18821.04
	0.50	19169.27	19098.03	18995.39	18987.35	18913.98
	1.00	19194.88	19133.47	19077.59	19040.47	18988.85

Table 4.66: Free energy, ΔG* of NAC in 0.003 M chitosan and [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. of NAC (mol dm^{-3})	Free energy, ΔG* J.mol^{-1}				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.003 M chitosan and [3:2] [H_2O-CH_3COOH]	0.10	17199.19	17179.05	17151.28	17120.64	17099.88
	0.50	17460.90	17440.17	17378.02	17331.26	17310.31
	1.00	17729.75	17685.30	17636.00	17589.12	17555.56

Table 4.67: Free energy, ΔG* of NAC in 0.006 M chitosan and [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. of NAC (mol dm^{-3})	Free energy, ΔG* J.mol^{-1}				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.006 M Chitosan and [3:2] [H_2O-CH_3COOH]	0.10	17016.81	16964.47	16847.94	16774.65	16693.51
	0.50	17295.01	17307.79	17277.86	17212.03	16947.07
	1.00	17560.88	17487.61	17486.46	17318.39	17300.10

Table 4.68: Free energy, ΔG* of NAC in 0.012 M chitosan and [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. of NAC (mol dm^{-3})	Free energy, ΔG* J.mol^{-1}				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
NAC in 0.012 M chitosan and [3:2] [H_2O-CH_3COOH]	0.10	19063.11	19023.82	18936.96	18921.35	18850.12
	0.50	19179.94	19120.83	19025.43	19016.93	18937.79
	1.00	19229.20	19156.13	19123.72	19084.40	19057.71

It is evident from Table 4.57-4.66 in all cases of Chitosan-H_2O-CH_3COOH and NAC–Chitosan–H_2O–CH_3COOH system, positive value of ΔG increases with the increase in solute concentration and the rise of temperature. This behavior of ΔG [96] suggests that the work is required for viscous flow. Lower values of ΔG at higher temperatures may be due to weaken solute–solvent and solvent–solvent interactions for greater thermal agitation. The positive value of ΔH increases with the increase of solute composition. This indicates that to overcome the energy barrier, some positive work has to be done. Thus the viscous flow is not favored for all the NAC molecules in solution systems. This might be due to the fact that the ground state of the Chitosan-H_2O-CH_3COOH and NAC-Chitosan-H_2O-CH_3COOH systems is more organized than the transition states.

It can also be here mentioned that the instrumental limitations during the experiments especially during determination of flow of time by Cannon-Fenske Opaque Viscometers may hamper of the data of investigated system in both Chitosan-H_2O-CH_3COOH and NAC-Chitosan-H_2O-CH_3COOH systems. So some irregularities as well as some ambiguity may be present in change enthalpy, ΔH* and change entropy, ΔS* values.

Table 4.69: Change of Enthalpy, ΔH* and Entropy, ΔS* of chitosan in [9:1] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration (mol dm^{-3})	Change of Enthalpy, ΔH* $J.K^{-1}mol^{-1}$	Change of Entropy, ΔS* $J.K^{-1}mol^{-1}$
Chitosan in [9:1] [H_2O-CH_3COOH]	0.003	25736.39	-33.41
	0.006	26877.09	-35.59
	0.012	20616.74	-12.39

Table 4.70: Change of Enthalpy, ΔH* and Entropy, ΔS*of chitosan in [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration (mol dm^{-3})	Change of Enthalpy, ΔH* J.K^{-1}mol^{-1}	Change of Entropy, ΔS* J.K^{-1}mol^{-1}
Chitosan in [7:3] [H_2O-CH_3COOH]	0.003	24840.67	-28.16
	0.006	24714.27	-26.16
	0.012	23231.21	-18.82

Table 4.71: Change of Enthalpy, ΔH* and Entropy, ΔS of chitosan in [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration (mol dm^{-3})	Change of Enthalpy, ΔH* J.K^{-1}mol^{-1}	Change of Entropy, ΔS* J.K^{-1}mol^{-1}
Chitosan in [3:2] [H_2O-CH_3COOH]	0.003	32001.57	-50.46
	0.006	29424.49	-40.15
	0.012	23933.73	-19.97

Table 4.72: Change of Enthalpy, ΔH* and Entropy, ΔS of NAC in 0.003 M chitosan and [9:1] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Change of Enthalpy, ΔH* J.K^{-1}mol^{-1}	Change of Entropy, ΔS* J.K^{-1}mol^{-1}
NAC in 0.003 M Chitosan and [9:1] [H_2O-CH_3COOH]	0.10	18636.58	-9.78
	0.50	19917.46	-13.45
	1.00	20849.61	-15.35

Table 4.73: Change of Enthalpy, ΔH* and Entropy, ΔS of NAC in 0.006 M chitosan and [9:1] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Change of Enthalpy, ΔH* $J.K^{-1}mol^{-1}$	Change of Entropy, ΔS* $J.K^{-1}mol^{-1}$
NAC in 0.006 M chitosan and [9:1] [H_2O-CH_3COOH]	0.10	26245.93	-32.03
	0.50	26546.38	-32.64
	1.00	27513.99	-35.03

Table 4.74: Change of Enthalpy, ΔH* and Entropy, ΔS of NAC in 0.012 M chitosan and [9:1] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Change of Enthalpy, ΔH* $J.K^{-1}mol^{-1}$	Change of Entropy, ΔS* $J.K^{-1}mol^{-1}$
NAC in 0.012 M chitosan and [9:1] [H_2O-CH_3COOH]	0.10	22069.23	-17.01
	0.50	23353.13	-19.65
	1.00	23569.56	-18.89

Table 4.75: Change of Enthalpy, ΔH* and Entropy, ΔS of NAC in 0.003 M chitosan and [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Change of Enthalpy, ΔH* $J.K^{-1}mol^{-1}$	Change of Entropy, ΔS* $J.K^{-1}mol^{-1}$
NAC in 0.003 M chitosan and [7:3] [H_2O-CH_3COOH]	0.10	19869.96	-9.19
	0.50	19468.48	-7.60
	1.00	20821.63	-10.97

Table 4.76: Change of Enthalpy, ΔH* and Entropy, ΔS of NAC in 0.006 M chitosan and [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Change of Enthalpy, ΔH* J.K^{-1}mol^{-1}	Change of Entropy, ΔS* J.K^{-1}mol^{-1}
NAC in 0.006 M chitosan and [7:3] [H_2O-CH_3COOH]	0.10	22300.18	-18.21
	0.50	23212.27	-20.10
	1.00	23339.01	-19.48

Table 4.77: Change of Enthalpy, ΔH* and Entropy, ΔS of NAC in 0.012 M chitosan and [7:3] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3}	Change of Enthalpy, ΔH* J.K^{-1}mol^{-1}	Change of Entropy, ΔS* J.K^{-1}mol^{-1}
NAC in 0.012 M chitosan and [7:3] [H_2O-CH_3COOH]	0.10	22302.33	-10.92
	0.50	22879.89	-12.48
	1.00	22207.45	-10.12

Table 4.78: Change of Enthalpy, ΔH* and Entropy, ΔS of NAC in 0.003 M chitosan and [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Change of Enthalpy, ΔH* J.K^{-1}mol^{-1}	Change of Entropy, ΔS* J.K^{-1}mol^{-1}
NAC in 0.003 M chitosan and [3:2] [H_2O-CH_3COOH]	0.10	18733.1596	-5.1376
	0.50	19914.2362	-8.2106
	1.00	20383.6709	-8.9064

Table 4.79: Change of Enthalpy, ΔH* and Entropy, ΔS of NAC in 0.006 M chitosan and [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Change of Enthalpy, ΔH* $J.K^{-1}mol^{-1}$	Change of Entropy, ΔS* $J.K^{-1}mol^{-1}$
NAC in 0.006 M chitosan and [3:2] [H_2O-CH_3COOH]	0.10	22011.21	-16.72
	0.50	21969.53	-15.45
	1.00	21676.12	-13.78

Table 4.80: Change of Enthalpy, ΔH* and Entropy, ΔS of NAC in 0.012 M chitosan and [3:2] [H_2O-CH_3COOH] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Concentration of NAC (mol dm^{-3})	Change of Enthalpy, ΔH* $J.K^{-1}mol^{-1}$	Change of Entropy, ΔS* $J.K^{-1}mol^{-1}$
NAC in 0.012 M chitosan and [3:2] [H_2O-CH_3COOH]	0.10	22217.36	-10.57
	0.50	22690.85	-11.79
	1.00	21703.46	-8.35

CHAPTER V

CONCLUSION

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Conclusion

Volumetric, viscometric and thermodynamic properties of Chitosan and NAC were studied in aqueous acetic acid solution. Some interesting solution properties among NAC, Chitosan and aqueous acetic acid in different systems were observed as follows:

(i) Volumetric, viscometric and thermodynamic properties are dependent upon the concentration of Chitosan and NAC as well as on the temperature.

(ii) In binary system the order of density maxima is:

Chitosan in [3:2] [H_2O-CH_3COOH] > Chitosan in [7:3] [H_2O-CH_3COOH] > Chitosan in [9:1] [H_2O-CH_3COOH]

(iii) The apparent molar volume, φ_v values decreased at all concentrations but increased with all specific temperatures indicate that solute-solvent interactions present in the systems.

(iv) The apparent molar volumes at infinite dilution φ_v^0 values of Chitosan-H_2O-CH_3COOH systems and NAC in Chitosan-H_2O-CH_3COOH ternary systems are positive and provide worthy understanding between solute–solvent interactions.

(v) The negative values of S_v indicate that in binary and ternary solution predicts there is a strong solute-solvent interaction present here.

(vi) The viscosity values, η increased with concentration but decreased with temperature for all systems.

(vii) The change of free energy, ΔG^* values for viscous flow are found to be positive for all the studied systems indicate that work has to be done to overcome the energy barrier for the flow process.

(viii) The positive ΔH values indicate that the viscous flow is not thermodynamically favored for the systems studied.

(ix) The ΔS^* values are negative for all the systems studied supports the presence of weak solute-solute interaction.

(x) In binary systems A co-efficients are positive whereas those of B co-efficients are negative, suggesting strong solute-solute and weak solute-solvent interaction present in the binary solution. But in case of ternary system A co-efficients are negative whereas those of B co-efficients are positive suggesting weak solute-solute and strong solute-solvent interaction present in the ternary solution.

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