

Volumetric and Viscometric Properties of N-Acetylcysteine in Dimethylformamide Containing Binary and Ternary Mixtures

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



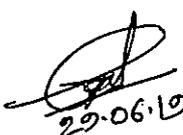
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Dedicated
To
The oppressed people all over the World

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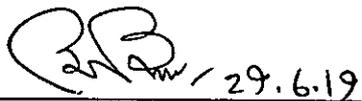
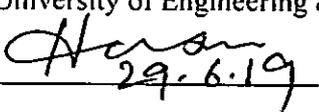
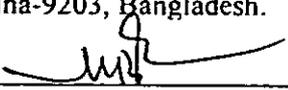
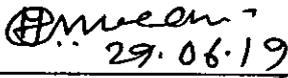
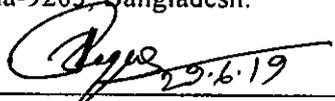

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Abstract

The density and viscosity of NAC (~ 0.10 to ~ 1.00) mol.L⁻¹ in H₂O, DMF and DMF–H₂O mixed solutions were measured and studied over the entire molarity range with in the temperature range of 298.15 to 318.15 K at 5 K interval. The apparent molar volumes, φ_v , were determined from density values experimented by Density and Sound Velocity Meter (DSA 5000M) Anton Paar, Austria. In the NAC–H₂O and NAC in [1:4] and [2:3] [DMF–H₂O] solvent systems the apparent molar volumes of NAC were found to be increased, whereas in the NAC–DMF and NAC in [4:1] and [3:2] [DMF–H₂O] solvent systems apparent molar volumes of NAC were found to be decreased. Apparent molar volume at infinite dilution, φ_v^0 and S_v values were also computed according to the experimented density values. The apparent molar volume at infinite dilution provided an idea about the presence of solute–solvent interactions of the investigated systems. S_v , the experimental slopes which provided an idea about the prevailing solute–solute interactions in the mixtures. Both φ_v^0 and S_v values indicated that there both solute-solute and solute-solvent interactions present in the binary as well as in ternary solutions.

The investigated systems showed hasty increase of viscosity values with the increased NAC concentration but the values of viscosity decreased with the increase of temperature. In binary and ternary systems showed the similar trend viscosity changes but in different order of magnitude. The order for binary and ternary systems are: NAC–DMF > NAC–H₂O and NAC in [3:2] [DMF–H₂O] > NAC in [4:1] [DMF–H₂O] > NAC in [2:3] [DMF–H₂O] > NAC in [1:4] [DMF–H₂O] > NAC–DMF > NAC–H₂O, respectively. The viscosity values were employed to determine the viscosity coefficients i.e., A and B-coefficients; change of free energy, ΔG^* ; change of enthalpy, ΔH^* as well as change of entropy, ΔS^* . Negative values of A and positive values of B co-efficients suggesting that weak solute-solute but strong solute-solvent interaction present in the binary and ternary solution, respectively. From these thermodynamic parameters state of the spontaneity of the investigated systems were known. On the basis of this data, the predominant molecular interactions occurring between NAC–H₂O and NAC in [1:4] and [2:3] [DMF–H₂O] solvent systems were found to be solute-solute interaction, where as in NAC–DMF and NAC in [4:1] and [3:2] [DMF–H₂O] solvent systems solute-solvent interaction were predominant.

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List of the Symbols and Abbreviations

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_v^0	Apparent molar volume at infinite dilution
ΔG^*	Free energy
ΔH^*	Change of Enthalpy
ΔS^*	Change of Entropy
g	Acceleration due to gravity
NAC	N-Acetylcysteine
DMF	Dimethylformamide
IUPAC	The International Union of Pure and Applied Chemistry

CHAPTER I

Introduction

1.1 General

As fundamental and important properties of solution, viscosity and volume could provide a lot of information on the structures and molecular interactions of liquid mixtures. Viscosity and volume are different types of properties of one solution and there is a certain relationship between them. So by measuring and studying them together, relatively more realistic and comprehensive information could be expected to be gained. The relationship between them could also be studied.

Although there are many works on either volume measurements or viscosity measurements of liquid mixtures, there are much fewer investigations on them together. So studies on the relationship between them are scarce. Much more attention to this aspect has been paid here. On this aspect the achievements were first made by Singh p. p. [1] and Singh *et al.* [2]. Relatively, viscometric properties could provide more and deeper information on molecular interactions.

1.2 The phenomena of solute-solvent interaction

Revelation of the nature of ion-solvent interaction [3–4] 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 [3–4] 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 force 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 [5].

(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 [6]. Potassium iodide is less soluble than sodium iodide in methanol or water [7], but in dimethylsulfoxide or DMF 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.

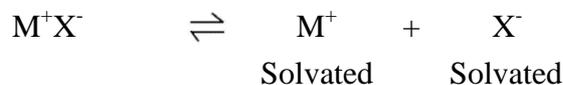
The solubility of halides in various solvents generally follows the order:

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 [8]. 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 [9].



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 [3]. Fuoss *et al.* [10] 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 [11] but have low K_d values which have been attributed to the loss of the solvent molecules from the ion-pairs [11]. 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 [12]. 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 [12], 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 [13] used the relation between viscosity η_l , 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 dimethylamide 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 law and is given by

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

Where η (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, ϕ , or $\phi = \frac{1}{\eta}$

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's equation [14]. If a liquid with a coefficient of viscosity (η) flows with a uniform velocity, at a rate of v cm³ 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 [14]:

$$\eta = \frac{\pi Pr^4 t}{8lv} \dots\dots\dots (1.1.1)$$

This equation known as Poiseuille 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⁻¹sec⁻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 10 μ Pa.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 glass 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 Dimethylformamide

Dimethylformamide is an organic compound with the formula $(\text{CH}_3)_2\text{NC}(\text{O})\text{H}$. It is a colorless liquid miscible with water and the majority of organic liquids. DMF is a common solvent for chemical reactions. Density of DMF is 0.95 g cm^{-3} at 20°C similar to that of water. DMF is a well-known material that is used as selective solvents in extraction or extractive distillation processes. N,N'-Dimethylformamide (DMF) has a large dipole moment and a high dielectric constant [15]; therefore, it may work as an aprotic protophilic solvent used in the synthesis of pharmaceuticals, in agricultural chemistry, and as a solvent for polymers [16]. It is used to a great extent as a substitute for traditional organic solvents in electrochemistry, chemical reactions, catalysis, separations, heat transfer, lubrication, and analysis. Some of its benefits, as solvents, are its high thermal stability, excellent dissolution properties for most organic and inorganic compounds, and non-flammability [17–18].

DMF is an important industrial liquid that has found various applications in different areas [19]. It is an interesting molecule, hydrophobic methyl groups can disturb the water structure. Besides, “cross” hydrogen bonds are expected to form between molecules belonging to two different species. Computer modelling studies can be classified according to the details of the force fields describing the internal structure of the DMF molecule. Specifically, one set of models with either five or six force centers (in each of models the methyl group has been considered as a single site) was explored in [20–23]. The primary use of DMF is as a solvent with low evaporation rate. DMF is used in the production of acrylic fiber and plastics. It is also used as a solvent in peptide coupling for pharmaceuticals, in the development and production of pesticides, and in the manufacture of adhesives, synthetic leathers, fibers, films, and surface coatings [24]. DMF is effective at separating and suspending carbon nanotubes, and is recommended by the NIST for use in near infrared spectroscopy of such [25].

Table 1.1: Some properties of Dimethylformamide

Property	Data
Chemical Name	Dimethylformamide
Chemical formula	$(\text{CH}_3)_2 \text{NC(O)H}$
Appearance	Colorless liquid
Molecular mass	$73.095 \text{ g}\cdot\text{mol}^{-1}$
Melting point	$-60.5 \text{ }^\circ\text{C}$
Boiling point	152 to 154 $^\circ\text{C}$
Density	0.948 g mL^{-1}
Viscosity	0.92 mPa.S (at 20 $^\circ\text{C}$)
Dipole moment	3.86 D
Solubility	Soluble in water

1.5 Properties of Water

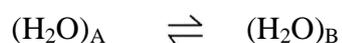
Water has a very simple atomic structure. The nature of the atomic structure of water causes its molecules to have unique electrochemical properties. The hydrogen side of the water molecule has a slight positive charge. On the other side of the molecule a negative charge exists. This molecular polarity 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.

1.5.1 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 [26]. The deviations from regularity indicate some kind of association of water molecules. The notable unique

physical properties exhibited by liquid water are [27] : 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 cases 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 [28, 29] 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 [30, 31 and 32] 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 [33], later developed by Nemethy and Scheraga [28], 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 tetrahedrally hydrogen bonded clusters, referred to as bulky water (H₂O)_A, are in dynamic equilibrium with the monomers, referred to as dense water, (H₂O)_B as represented by [30].



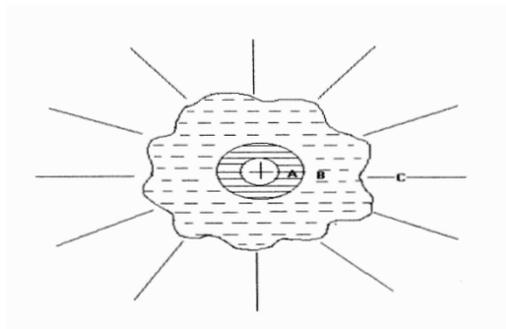


Figure 1.1: Frank and Wen model for the structure modification produced by an ion

The hydrogen bonding in the clusters is postulated [34] to be a cooperative phenomenon. So when one bond forms several others also come into existence. The properties of a solution can be accounted for in terms of solvent-solvent, solvent-solute and solute-solute interactions. 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 those brought about by temperature or pressure. The solute that shifts the equilibrium to the left and increases the average half-life of the clusters is termed a structure maker, whereas that which has an effect in the opposite direction is called a 'structure breaker'. The experimental results on various macroscopic properties provide useful information for a proper understanding of specific interactions between the components and the structure of the solution. Thermodynamic and transport properties are sensitive to solute-solvent, solute-solute, and solvent-solvent interactions. In solution systems these three types of interaction are possible, but solute-solute interactions 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.

1.5.2 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 [35].

1.5.3 Hydrophobic hydration

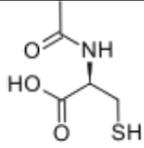
The hydrophobic effect refers to the combined phenomena of low solubility and the entropy dominated character of the solvation energy of non-polar substances in aqueous media [36]. It is also reflected by anomalous behavior in other thermodynamic properties, such as the partial molar enthalpies, heat 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 [37]. The tendency of relatively nonpolar molecules to “stick together” in aqueous solution is denoted as the hydrophobic interaction [38]. 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 adsorb, 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.

1.6 Properties of N-Acetylcysteine

N-Acetyl-L-Cysteine (NAC), the preacetylated 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 dissolves 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; non-hygroscopic (oxidizes in moist air). The pH of NAC is 2 to 2.75 (1 in 100 ml) and dissociation constants $pK_a=3.24$ (carboxylic acid moiety) and Spectral Properties is Specific optical rotation: +5 °C at 20 °C (concentration = 3 g/100 mL). NAC is not found naturally in food sources; however cysteine is present in most high protein foods. NAC converts into cysteine.

Table 1.2: Some properties of N-Acetylcysteine

Property	Data
Chemical Name	N-Acetylcysteine
Chemical formula	$C_5H_9NO_3S$
Chemical structure	 <p>The chemical structure of N-Acetylcysteine is shown as a skeletal structure. It features a central chiral carbon atom bonded to a hydrogen atom (not explicitly shown), a carboxylic acid group (-COOH), an acetyl group (-NH-C(=O)-CH₃), and a thiol group (-CH₂-SH).</p>
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

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 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.

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 N-acetylcysteine in ethanol and ethanol-water systems were

performed [39]. From the results it was seen that NAC showed more interaction in ethanol-water mixture than those for individual solvents. So this research is devoted to solution properties of NAC which may have enormous medicinal and biological applications. The solution behavior of NAC has been investigated in versatile solvent, water and common organic solvent dimethylformamide. The investigation has also been carried out in water + dimethylformamide mixed solvents and to the best of my knowledge that hadn't been done before.

Theoretical Background

1.7 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 enable 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 [40].

(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.

1.8 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,

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

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

The unit of molarity is mol/L

1.9 Molar volume of Mixtures

The volume in mL occupied by 1 mole of any substance is called the molar volume. On the other hand, if ρ 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,

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

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

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

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

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

$$\text{Molar volume, (V}_m) = \frac{M}{\rho} \text{ mL mol}^{-1} \dots\dots\dots (1.2.4)$$

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.

1.10 Apparent molar volume

The apparent molar volume of a solute in solution, generally denoted by ϕ_v [41]

$$\phi_v = \frac{V - n_1 \bar{V}_1^0}{n_2} \dots\dots\dots (1.2.5)$$

Where, V is the volume of solution containing n_1 moles of solvent and n_2 moles of solute and \bar{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 [42],

$$\phi_v = \frac{1}{n_2} \left[\frac{n_1 M_1 + n_2 M_2}{\rho} - n_1 \bar{V}_1^0 \right] \dots\dots\dots (1.2.6)$$

Where, $V = \frac{n_1 M_1 + n_2 M_2}{\rho}$ 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 [42,43],

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

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

where, ρ_0 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 [44]:

$$\phi_v = \left[\frac{M_2}{\rho_0} - \frac{1000(\rho - \rho_0)}{C\rho_0} \right] \dots\dots\dots (1.2.8)$$

Where, the relation,

$$C = \frac{m \cdot \phi_v \cdot 1000}{1000 + \phi_v \cdot m \cdot \rho_0}$$

[37]. 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:

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

Similarly for component 2,

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

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,

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

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

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

At infinite dilution, (m or $c \rightarrow 0$), 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 [45], the Redlich-Mayer equation [47] and Owen-Brinkley equation [46]. Masson [45] found that the apparent molar volume of the electrolytes vary with the square root of the molar concentration as,

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

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

Redlich and Rosenfeld [40] 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,

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

Where, the terms K and W are given by

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

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

where, β is the compressibility of the solvent, γ_i is the number of ions of the species i of valency Z_i formed by one molecule of the electrolyte and the other symbols have their usual significance [47]. For dilute solutions the limiting law for the concentration dependence of the apparent molar volume of electrolytes is given by the equation,

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

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

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

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

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

