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VISCOMETRIC STUDY OF NONIONIC SURFACTANTS NON-IONIC SURFACTANT TRITON-X114 IN PRESENCE OF POLYELECTROLYTE POLYVINYLSULPHONIC ACID AT DIFFERENT TEMPERATURES IN AQUEOUS MEDIUM

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ABSTRACT

Intrinsic viscosity of aqueous solutions of nonionic surfactants TritonX-114 at T = 298K, 303K, 308K and 313K in presence and in absence of polyelectrolyte polyvinyl sulphonic acid are determined. The intrinsic viscosities [η] presumably so named because it is an intrinsic function of the dissolved or dispersed macromolecules. The η_{sp} is directly proportional to the concentration (c) of solution. Intrinsic viscosity values have been used to discuss structural alteration and molecular interactions. Intrinsic viscosity of polyelectrolyte-surfactant solution was determined in presence of various amounts of surfactants TritonX-114, it was observed that values increase as the temperature of the system increases, indicating increase in solvent power and solubility of PVSA.

KEYWORDS: Polysorbates, TritonX-114 (TX-114), Polyvinylsulphonic acid (PVSA), Intrinsic viscosity, solvent power.

INTRODUCTION

The viscosity of a liquid is a measure of its resistance to flow. Viscosity is a unique property of liquids (Fluids). When a fluid flows through a tube then a layer in contact with the wall of the tube remains stationary. As a result of this, velocity of different layers increases continuously with the distance from the wall of the tube and the fluid in the center of the tube has the maximum velocity because of the friction which retards the flow of liquid is known as viscosity.

The viscosity of a liquid is a measure of its resistance to flow. The chemists tend to regard viscosity as a specific property of fluids (both liquids and gases) but for physicist viscosity is rather a coefficient used in the equations of flow.[1-2] The dimensions of viscosity are poise in C. G. S. unit (dyne.cm^{-2}.s) or Pascal.second in S.I. units (N.m^{-2}.s). The accurate knowledge of viscosity is essential for detailed design and modeling of equipment like piping, pumps, heat exchangers.[3]

The force F (friction) acting between two layers can be given by equation 1

$$F = \eta F \frac{du}{dx} \qquad \text{--------------- 1}$$

Where, A is the area of contact (m^2), du is the difference in the velocities of two layers (ms^{-1}), dx is the distance between two layers (m) and η is the coefficient of viscosity. The coefficient of viscosity, η can be defined as the force per unit area required to maintain unit difference of viscosity between two parallel layers in the liquid, unit distance apart. The common unit of η is 'poise'. The viscosity of the liquid is said to be one poise when a force of one dyne maintains a velocity difference of one centimeter apart and have an area of contact one square centimeter.

According to Poiseuille, the viscosity of a liquid on the basis of its flow through capillary tube given by equation 2

$$\eta = \frac{\pi r^4 t P}{8 Vl} \qquad \text{--------------- (2)}$$

Where, r is the radius of capillary, t is the time in seconds required for the volume V (ml) of the liquid to flow through the length *l* (cm) and P is the hydrostatic pressure on the liquid.

For same volume of two liquids and with the use of same viscometer their viscosity coefficient can be represented by equations 3 and 4

$$\eta = \frac{\pi r^4 t P}{8 Vl} \qquad \text{--------------- (3)}$$

$$\eta_0 = \frac{\pi r^4 t_0 \ P_0}{8 Vl} \qquad \text{--------------- (4)}$$

From equations 3 and 4

$$\therefore \frac{\eta}{\eta_0} = \frac{t \times p}{t_0 \times p_0} \qquad \text{-----------------} (5)$$

Since the pressure is directly proportional to the density of liquid, then equation 5 becomes

$$\therefore \frac{\eta}{\eta_0} = \frac{d \times t}{d_0 \times t_0} = \frac{\eta_{Solution}}{\eta_{Solvent}} = \eta_r \qquad \text{-----------------} (6)$$

Where d and d_0 are the densities of solution and solvent respectively, t and t_0 are the time flow for solution and solvent. The ratio η/η_0 or $\eta_{soln.}/\ \eta_{solv}$ is known as relative viscosity. It is denoted by 'η_r'.

The specific viscosity is given by the relation

$$\eta_{sp} = \eta_r - 1 = \frac{\eta}{\eta_0} - 1 \qquad \text{--------------}(7)$$

The η_{sp} is directly proportional to the concentration (c) of solution. Hence plot of □$_{sp}$/C against C or 2.303/C log η/η_o against C gives a straight line. The intercept of this line on Y-axis i.e. at zero concentration gives intrinsic viscosity [η] which is defined by the equation 8.

$$\lim_{c \to 0} \frac{\eta_{sp}}{C} = \lim_{c \to 0} \frac{2.303}{C} log \frac{\eta}{\eta_0} \qquad \text{-----------------} (8)$$

The viscosity of polyelectrolyte solutions is a very important and fundamental property. It is essential in many end products such as shampoos, detergents and paint contain polyelectrolyte + surfactant mixtures.

Triton X-114 is one of the polysorbate which is non-ionic surfactant used for cell lysis, nuclei isolation and cell fractionation, also widely used in cosmetics and some pharmaceutical preparation.[4]

The polyelectrolyte is charged polyelectrolyte[5] and their every repeating unit is capable of bearing electronic charge. The polyelectrolyte are macromolecules, as the polyelectrolytes that contain net negative or net positive charge are called as anionic or cationic polyelectrolytes respectively. Poly (vinylsulfonic acid, sodium salt) (PVSA) has negatively chargeable sulfonate groups and it is a blood compatible material. Many researchers have reported that the incorporation of sulfonate groups into the substrates reduces protein adsorption or platelet adhesion, due to the negatively charged character of these groups in aqueous solutions.[6]

Water soluble polyelectrolytes are often interacting strongly with surfactants in aqueous solutions; this gives a very rich pattern of behaviour of properties such as surface tension and other bulk properties. Water soluble polyelectrolytes are widely used to control the rheological properties of an extensive range of aqueous based formulations.

The intrinsic viscosities [η] presumably so named because it is an intrinsic function of the dissolved or dispersed macromolecules. The intrinsic viscosity [η] is not a new parameter which is used by Einstein[7] for the suspension of spherical particles. The classical review of its measurement and application for the protein studied.[8] theory for linear macromolecules studied[9] and for linear polyelectrolytes studied.[10] The intrinsic viscosity [η] is not a true viscosity. It is essentially measure of two internal frictions or resistance to displacement of high polyelectrolyteic molecule in solution is of a great technical and scientific interest. It has reciprocal concentration units and expressed in $dl.g^{-1}$ but nowadays C. G. S. unit of $ml.g^{-1}$ is used in Physical Biochemistry.

The various solution was prepared twenty-four hours before taking any measurements in distilled water for computation of relative viscosity (η_{rel}), specific viscosity (η_{sp}), reduced viscosity (η_{sp}/C) and intrinsic viscosities [η] by using following equations.

$$\text{Relative viscosity } (\eta_{rel}) = \frac{\eta}{\eta_0} \qquad \text{-----------------} (9)$$

$$\text{Specific viscosity } (\eta_{sp}) = \eta_{rel} - 1 \qquad \text{-----------------} (10)$$

or

$$\text{Specific viscosity } (\eta_{sp}) = \frac{\eta - \eta_0}{\eta_0} = \frac{t - t_0}{t_0} \qquad \text{-----------------} (11)$$

$$\text{Reduced viscosity } (\eta_{red}) = \frac{\eta_{sp}}{C} \qquad \text{-----------------} (12)$$

$$\text{Intrinsic viscosities } [\eta] = \left(\frac{\eta_{sp}}{C}\right)_{c=0} \qquad \text{-----------------} (13)$$

Where, η and η_0 are viscosities of solution (polyelectrolyte solution or mixture of polyelectrolyte and surfactant solution) and pure solvent distilled water respectively, t and t_0

are the flow times of solution (polyelectrolyte solution or mixture of polyelectrolyte and surfactant solution) and pure solvent distilled water respectively, C is concentration of aqueous polyelectrolyte solution in $dl.g^{-1}$.

A plot of η_{sp}/C Vs. concentration can be used to obtain value of intrinsic viscosities [η] as an intercept on Y axis of the plot.

The Relative viscosity (η_{rel}) can be measured by three ways[11] viz 1) Using capillary viscometer such as Ostwald viscometer[12] or Ubbelhode viscometer[13] 2) Using plate viscometer such as Cone and plate or parallel plate or cub and bob[14] and 3) Using pressure-imbalance differential method.[15]

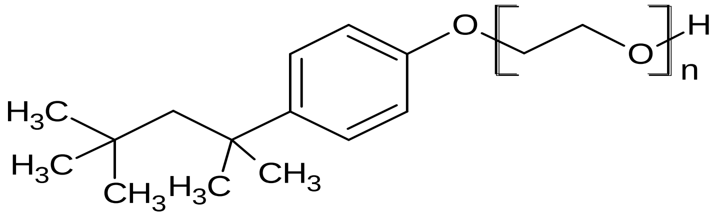
The Relative viscosity (η_{rel}) is self-explanatory while specific viscosity (η_{sp}) expresses the incremental viscosity due to presence of polyelectrolyte solution. Normalizing η_{sp} to concentration gives η_{sp}/C which expresses the capacity of polyelectrolyte to cause the solution viscosity to increase incremental viscosity per unit concentration of polyelectrolyte. The extrapolated value of η_{sp}/C at zero concentration is nothing but the η_{sp}/C which can be used to measure the molecular weight of the polyelectrolyte.

In the present investigation, the P-S interaction of PVSA with Polysorbates TritonX-114 and Tween-80 in solution by Viscometric method has been studied. The P-S interaction by viscometric method has been studied due to their importance of system containing both products in many applications like paints, pharmaceuticals[16] oil recovery[17] etc.

MATERIALS AND METHODS

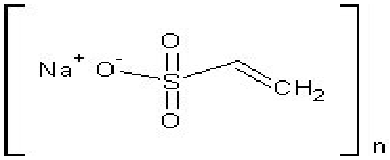
The nonionic surfactant Tween 40 (M.W. 682) is the product of E-Merck (Germany), another nonionic surfactant Tween 80 (M.Wt. 1310) is the product of SIGMA-ALDRICH, USA and the water-soluble polyelectrolytes used for the present study are polyvinylsulphonic acid 25% aqueous sodium salt solution (MW 5000) is the product of Sigma-Aldrich (USA). Brij-56, Tween 80 and polyvinylsulphonic acid were used as received.

The Molecular structures of TritonX-114 and additive PVSA are given in Figure 1 as follows



n = 7-8

Structure of TritonX-114



Additive: PVSA

Fig. 1: Molecular structures of Polysorbates (Tweens) and additive.

Doubly distilled water with Specific Conductance 2- 4 μ S cm^{-1} at 303.15 K was used in the preparation of all solutions of different concentrations.

In the present work, the various solution was prepared twenty-four hours before taking any measurements in distilled water for computation of relative viscosity (η_{rel}), specific viscosity (η_{sp}), reduced viscosity (η_{sp}/C) and intrinsic viscosities [η]. The intrinsic viscosity [η] of water-soluble polyelectrolyte (PVSA) solution in presence and in absence of non-ionic surfactants TritonX-114 and Tween-80 was computed at different temperatures viz. 298, 303, 308 and 313K as per method described elsewhere[18-22] using capillary Ubbelhode viscometer suspended which is mounted vertically in glass walled transparent thermostat having accuracy of $\pm 0.01^{0}$C.

The Ubbelhode Viscometer was calibrated separately at each temperature i.e. 298, 303, 308, 313 K with exactly same volume of liquid having known viscosity and density, usually water, the density and viscosity of which are taken from the literature.[23] Since all the time flows of water were greater than 150 seconds hence the kinetic energy correction was not applied.

RESULT AND DISCUSSION

The computed intrinsic viscosity [η] of water-soluble polyelectrolyte PVSA solution in presence and in absence of non-ionic surfactants TritonX-114 reported in the Table 1.

Table No. 1: Intrinsic Viscosity [η] (dl/g) of Poly vinyl sulphonic acid (PVSA) in presence of TritonX-114 at different temperatures.

[TritonX-114] Weight %	[η] (dl/g)			
	298K	303K	308K	313K
0.000	0.094	0.103	0.078	0.095
0.025	0.017	0.025	0.014	0.027
0.050	0.019	0.042	0.029	0.057
1.0	0.059	0.095	0.079	0.111

The representative plot η_{sp}/C Vs. Concentration for water soluble polyelectrolyte PVSA and non-ionic surfactant TritonX-114 mixed system at 298, 303, 308 and 313K temperatures are depicted in the Figure No. 2 respectively.

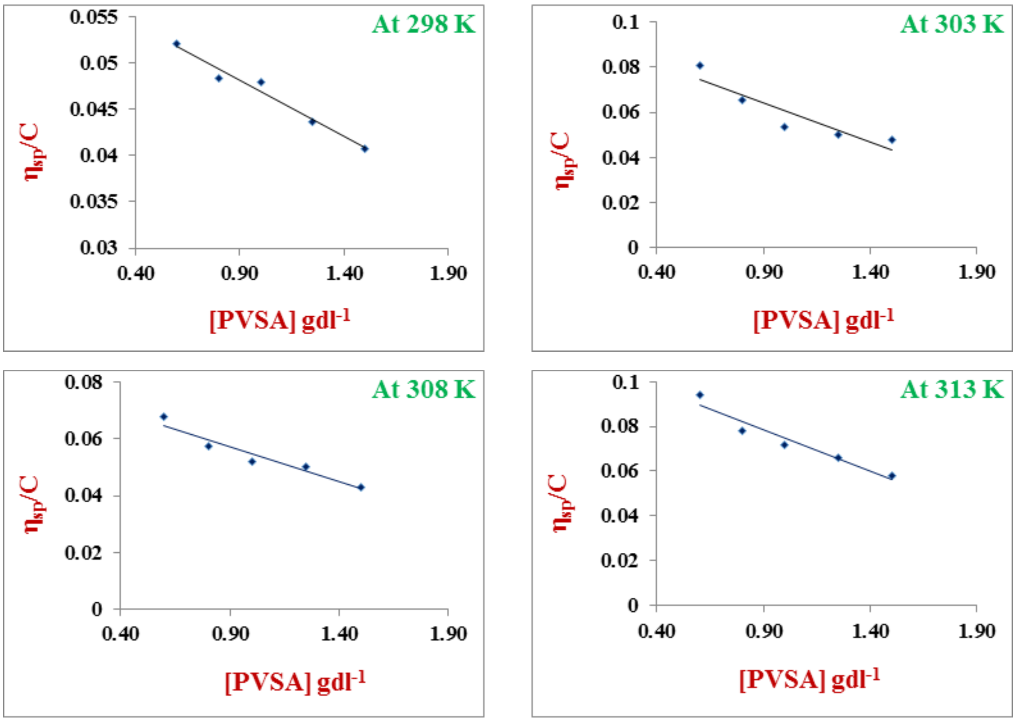


Figure No. 2: Representative plot η_{sp}/C Vs. Concentration for PVSA/1.0 % TritonX-114 at 298, 303, 308 and 313 K temperatures.

It was observed that, the intrinsic viscosity [η] of all the P-S mixed systems increases as concentration of non-ionic surfactant increases. A. Rangraj and A. K. Rakshit.[21] discuss the effect of temperature on the intrinsic viscosity [η] as, the solubility of polyelectrolyte increases due to increase in solvent power so that uncoiling of polyelectrolyte chain occur which increases the interactions and as a consequence of this the intrinsic viscosity [η] increases. But as temperature further rises kinetic energy help in lowering of rotational barrier about skeletal bond allowing molecular chain to assume more compact coiled configuration, causes the decrease of the intrinsic viscosity [η] with increase in temperature. The surfactants help to decrease enlargement of polyelectrolyte chains causes a smother flow.[24]

The configuration of polyelectrolyte molecule in a dilute solution may be greatly expanded by electrostatic repulsion between its charged group's causes the effect on configuration manifests itself in a large intrinsic viscosity.[25]

The accurate knowledge of viscosity is applied for detailed design and modeling of equipment such as piping, pumps and heat exchangers, mixer drive sizing, mixer selection, extruder performance prediction, product formulation. e.g. paint, cosmetics, confectionary, quality control, material science investigations, etc. Therefore Polymer-Surfactant interaction in solution has been studied due to their importance of system in both products as well as many applications like paints, Pharmaceuticals.

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