# Effect of Molecular Mass of Polyethylene oxide over its Aggregation Behavior

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**Summary**: Samples of polyethylene oxide having different molecular mass (35, 12, 6 Kg/mol) are investigated with reference to characteristic concentration (CC), critical aggregation concentration (CAC) and hydrodynamic radius ($R_H$), using surface tension, light scattering, viscosity and conductance measurement. It has been concluded that CC and CAC decrease with molecular mass of polymer. The intrinsic viscosity, $R_H$ and molecular mass relationship have also been established.

## Introduction

Polyethylene oxide is among the few polymers which are soluble in water as well as in organic solvents and possesses a number of novel and versatile properties due to its electrostatic nature in solution [1]. It has wide applications in high energy density batteries [2-6] and electronic devices [7-8]. There has been a lot of research interest over PEO/water system, due to great similarity with protein/water system showing similar basic interactions like hydrogen bonding and hydrophobic interactions. Further the PEO/water system is a simple model system (synthetic analogue) to study fundamental bimolecular interactions in which hydrogen bonding and hydrophobic interactions play an important role. Among all the unique properties of PEO solution, the clustering behavior of PEO in water is the most intriguing and has been extensively studied. However, the contradiction of the experimental results and the theory has raised several questions and need to be addressed properly [9-17]. Realizing this important aspect, quite a good number of scientists are working over such systems to get some experimental results and explain them in the light of existing theories [18-22], whereas others are trying to develop some theoretical background about such polymer systems and emphasizing over the role of charge density, solvent polarity and electrolytes added [23-24]. Keeping in view these facts we have investigated PEO with reference to their intermolecular association and role of molecular mass over these. For the purpose, various physical techniques like flow properties, surface tension, conductance were employed. The characteristic association concentration (CAC) and critical micelle concentration (CMC) of polyethylene oxide, RH and intrinsic viscosity were determined and discussed in detail.

## Results and Discussion

The results obtained for surface tension of PEO6, PEO12 and PEO35 solution in deionized water is plotted in Fig. 1. The figure shows that as the concentration of polymer increases the surface tension decreases very slowly up to a certain concentration. However, the further increase in concentration leads to a sharp decrease in surface tension. The concentration at which surface tension decreases sharply is named as characteristic concentration (CC). If the concentration of polymer is further increased the surface tension becomes constant and the concentration is known as critical aggregation concentration (CAC). The trend in variation of surface tension is according to others surfactants [20-22]. It means that the polymer behaves as surfactant irrespective of molecular mass of polymer. The results obtained for CC and CAC are plotted in Fig. 2. The figure shows that both the characteristic concentration (CC) and critical aggregation concentration (CAC) decrease as the molecular mass of the Polyethylene oxide increases. This can be explained by the fact that the polymer having longer chain length (high molecular mass) covers more surface area as compared to low molecular mass and hence fewer amounts will be needed to reach CC or CAC [20, 22-24]. The results conclude that a general relationship between CC or CAC and molecular mass can be:

$$CC/CAC = a + \ln M^{b} \quad (1)$$

Here a and b are constants and their values depends upon nature of polymer/ surfactant and the solvent. The values of these constants in our case are given below.

$$CC = 0.0119 + \ln M^{-0.0011} \quad (2)$$

$$CAC = 0.0109 + \ln M^{-0.0011} \quad (3)$$

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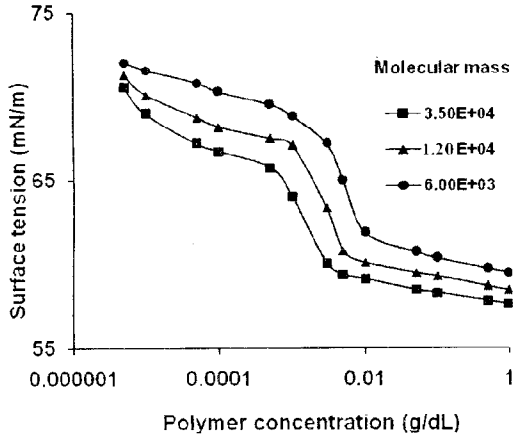


Fig. 1: Surface tension of polyethyleneoxide as it varies with its concentration and molecular mass.

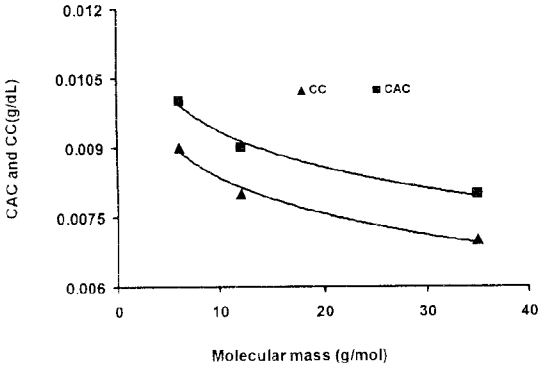


Fig. 2: Characteristic concentration (CC) and Critical aggregation concentration (CAC) of PEO as a function of its molecular mass.

The results obtained from dynamic light scattering, viscosity and conductance also provide the same values for CC and CAC. It is to be pointed out that the only surface tension and viscosity can give the results for CC very accurately and the results obtained by us using these techniques are the same, showing an accuracy of the techniques [25]. The hydrodynamic radius and intrinsic viscosities of PEO having different molecular mass were calculated and plotted versus the molecular mass of PEO in Fig. 3. This figure shows that hydrodynamic radius and intrinsic viscosity are also molecular mass dependent and increase as the molecular mass of the polymer which is according to our expectations. The exact

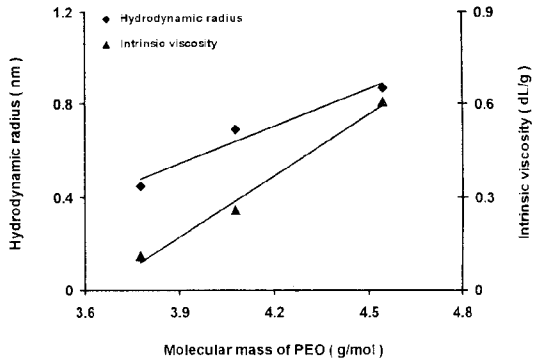


Fig. 3: Hydrodynamic radius and intrinsic viscosity of PEO as a function of its molecular mass.

relationship derived from the results between intrinsic viscosity and molecular mass is given by Mark- Houwink equation given below.

$$[\eta] = kM^{a} \qquad (4)$$

Where K and a are constants and equal to $3.9 \times 10^{-3}$ and 0.659 respectively. These results conclude that the polymer in water shows a random chain conformation. With the analogy of intrinsic viscosity, the $R_H$ values can be related to molecular mass as,

$$R_H = k_H M^{a_H} \qquad (5)$$

where $k_H$ and $a_H$ are constants having the values $2.9 \times 10^{-2}$ and 0.534 respectively. These results conclude that polymer behaves as coil like conformation and not associated at this concentration.

## Experimental

*Material*

Polyethylene oxide, PEO with different ($6.0 \times 10^3$, $12.0 \times 10^3$ and $35.0 \times 10^3$ g/mol) molecular masses was used for investigation. It was originally obtained from Shell Company and used as such.

The solvent used was de-ionized water whose conductance was ranged from 1.2-2.5μS/cm.

*Preparation of Solutions*

A stock solution of polyethylene oxide was prepared by dissolving a known amount of these

polymers in deionized water. The rest of solutions were prepared by dilution method. Solutions so prepared were subjected to surface tension, light scattering, viscosity and conductance measurements.

*Procedure*

*Surface Tension Measurement*

The surface tension of the solvent and solutions was measured by using stalagmometer at constant temperature. For the purpose, number of drops of fixed volume solution and water was counted and the surface tension was calculated.

*Dynamic Light Scattering*

Diffusion coefficient of the polymer was measured by dynamic Light scattering (DLS) technique and the $R_H$ value was calculated using the following equation

$$D = k T/6\pi\eta R_H$$

Where D is the diffusion coefficient, k is Boltzmann constant and $\eta$ is the viscosity of solvent. The instrument used for the measurement of dynamic light scattering was DAWN EOS/QELS supplied by Wyatt U.S.A.

*Viscosity Measurement*

The viscosity of all the polymer solutions and solvent was determined at constant temperature using Ostwald type viscometer; the viscosity bath used for the purpose was supplied by F.G.Bode and CO. Laboratory Equipment Humberg 90 Lunebergerstrass 2.

*Conductance Measurement*

The conductance of solvent and polymer solutions was determined by Inno Lab Conductometer, Italy. The measurements were made after carefully washing the electrode and the container.

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