

A Study Some Physical Properties For Poly (vinyl alcohol)in Aqueous Solution at Four Temperatures.

Eman T.Kareem *

Takialdin A.Himdan **

Date of Acceptance 8/2/2005

Abstract

The densities and viscosities of solutions of poly (vinyl alcohol)(PVA) molecular weight (14)kg.mol⁻¹ in water up to 0.035% mol.kg⁻¹ at 298.15, 308.15, 318.15 and 328.15K have been measured. On the basis of Eyring's theory of rate processes, the molar Gibbs free energy of activation for viscous flow of solution $\Delta G_{1,2}$ have been determined. Additionally, the viscosity coefficient B_c in Jones-Dole equation is calculated. The influence of the temperature on the above parameter is discussed.

Introduction

The importance of solutions of polymers may not be readily apparent to the plastics engineer who is chiefly concerned with injection molding or extrusion, but it is of primary concern to the paint formulator. However, all polymers sooner or later are used in solution in one way or another [1,2]. Poly (vinyl alcohol) (PVA: $-(CH_2-CHOH)_n-$) is a polymer which is soluble in water to a large degree but considerably less so in most organic solvents. Many of its applications are determined by its hydrophilicity (researches have, for example, worried about the water content of PVA films as early as 1946 [3]. Among them are the use as hydrogel former and as material for separation membranes where research is still very active [4,5]. It is often used in pervaporation systems for the removal of water

(minority component) from liquid mixtures. More recently, polyelectrolytes such as aqueous PVA solutions attract attention in physical and biophysical chemistry [6-11].

Experimental

(a) Materials

Deionized and doubly distilled water was used. Its specific conductivity was $<1 \times 10^{-6}$ S.m-1. poly(vinyl alcohol) is available product of Aldrich Chemical Company (U.S.A) whose number average molecular weight (14)kg.mol⁻¹. PVA used in this study is solid (powder) material and completely soluble in water.

*Dr- Department of Chemistry- College of Education(Ibn Al -Haitham)-University of Baghdad

**Department of Chemistry- College of Education(Ibn Al -Haitham)- University of Baghdad

(b) Density Measurements.

The density of the investigated solutions was measured at the temperature range studied with an Anton Paar digital densimeter (DMA60/601) with a thermostatted bath controlled to $\pm 0.001\text{K}$. The densimeter was calibrated with water, dehumidized air and several aqueous solutions of potassium chloride. The density determination is based on the variation of the natural frequency of a tube oscillator filled with sample liquid. By measuring the period of oscillation (τ) of the vibrating

U-shaped sample tube, filled with the sample (air, water), and determining the densimeter constant (K_0) by using the standard values of the densities of water and air, and using the following equation :

$$K_0 = \frac{\rho_{H_2O} \tau_{air} - \rho_{air} \tau_{H_2O}}{\tau_{H_2O} - \tau_{air}} \quad (1)$$

Then the density of unknown liquid is determined from the measured oscillator period (δ) at fixed temperature and applying the following relation:

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

The precision in the density values measured using this densimeter is estimated to be better than $2 \times 10^{-6} \text{g.cm}^{-3}$.

(c) Viscosity Measurements

The viscosity of the investigated solutions was determined using an Ubblohde viscometer. The capillary length of this viscometer of about (8cm), the diameter about (0.36-0.63mm), a flow volume of about (3cm³) and the viscometer constant (0.0302). The Ubblohde viscometer preferred to be used in this study among the other commercial ones such as Cannon Master viscometer, Cannon Fenske viscometer

and Ostwald viscometer because it minimize pressure corrections and surface tension effects. A constant temperature water bath (Schott-Genate CT 1150) with a baric control unit was used. The temperature of the water bath was measured by a Hewlett-Packard A Quartz thermometer. The temperature fluctuation was limited to $\pm 0.01\text{K}$. The absolute viscosity $\eta_{1,2}$ was calculated from

$$\eta_{1,2} = \rho_{1,2} \cdot (\text{kinematic viscosity}) \quad (3)$$

Results and Discussion

The experimental values of density $\rho_{1,2} \text{ (kg.m}^{-3}\text{)}$ and absolute viscosity $\eta_{1,2} \text{ (kg.m}^{-1}\text{.s}^{-1}\text{)}$, which are given in Table (1) and (2), respectively. The theory of rate processes to viscous flow is applied [12]. Thereby, the molar Gibbs free energy of activation

for viscous flow of a solution, $\Delta G_{1,2} \text{ (J.mol}^{-1}\text{)}$ is calculated from

$$\Delta G_{1,2} = RT \ln \frac{V_{1,2} \eta_{1,2}}{h N_A} \quad (4)$$

where (R) is the gas constant, (T) is the absolute temperature, (h) is planck's constant, (N_A) is Avogadro's constant and $V_{1,2} \text{ (m}^3\text{.mol}^{-1}\text{)}$ is the volume of one mole of solution.

$$V_{1,2} = \frac{1000 + mM_2}{\rho_{1,2} (n_1 + m)} \quad (5)$$

where $m \text{ (mol.kg}^{-1}\text{)}$ is the molality of solution, n_1 is the number moles of solvent $n_1 = 1000/M_1$, M_1 and (M_2) are the molecular weights of solvent and solute, respectively. Table (3) represent the calculated values of molar Gibbs free energy of activation for viscous flow of solution at 298.15, 308.15, 318.15 and 328.15K. As can be seen from Table(3), the $\Delta G_{1,2}$ values of the investigated solutions are positive and show an increase with temperatures. By contrast, the viscosity of aqueous solutions of electrolytes has