

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 $(14) \text{kg.mol}^{-1}$ 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: $-(\text{CH}_2-\text{CHOH})_n-$) 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 $(14) \text{kg.mol}^{-1}$. 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:

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

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

(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 ($3cm^3$) 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 $\rho_{1,2} (kg.m^{-3})$ and absolute viscosity $\eta_{1,2} (kg.m^{-1}.s^{-1})$, 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, $\Delta G_{1,2} (J.mol^{-1})$ 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 $V_{1,2} (m^3.mol^{-1})$ is the volume of one mole of solution.

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

where $m (mol.kg^{-1})$ 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

been studied in details. Three major reviews of the subject are available in the literature [13-15]. Jones and Dole [16] have reported a semi-empirical formula to describe the concentration dependence of aqueous solutions of electrolytes at constant temperature.

$$\eta_r = \frac{\eta_{1,2}}{\eta_1^0} = 1 + A\sqrt{C} + Bc \dots(6)$$

where η_1^0 is the absolute viscosity of pure solvent, A and B are empirical coefficients and C is the molar concentration of solution. The coefficient A is the ion-ion interaction parameter, which can be calculated from Debye-Huckel theory [17] if the dielectric constants and viscosities of solvents and the limiting ionic conductivities are known. The coefficient A is always positive while the B coefficient can either be positive or negative depending on the nature of interaction between the solvent molecules and solute ions. These interactions persist at infinite dilution, this tends to be obscured by the fact that as

$C \rightarrow 0$. The importance of the B coefficient can be illustrated by re-writing equation(6) in the form :

$$\left[\left(\eta_{1,2} / \eta_1^0 \right) - 1 \right] / \sqrt{C} = A + B\sqrt{C} \dots(7)$$

Plotting the left part of equation (7) versus \sqrt{C} should produce a straight line of slope B (positive or negative). If equation (6) is modified by ignoring the term $A\sqrt{C}$ and replacing the molarity by the molality at low concentration (up to 0.05%) [18]

$$\dots \text{molality} = \frac{\text{molarity}(\text{solute})}{M.W(\text{solute})} \times \frac{1000}{\text{molarity}(\text{solvent})} \dots(8)$$

Jones -Dole equation takes the form [19] :

$$\eta_{1,2} / \eta_1^0 = 1 + B_c m \dots(9)$$

where m is the molality and B_c is the corrected B coefficient.

The validity of Jones -Dole equation (equation(9)) was tested.

$\eta_{1,2} / \eta_1^0$ values were plotted versus m at four different Utilizing the method of least-Squares curve fitting temperatures giving a straight line at low molality $0 < m < 2 \times 10^{-3}$ and a curvature line at high molality $2 \times 10^{-3} < m < 3.5 \times 10^{-3}$ with positive B_c coefficient 952, 899, 832 and 777 at 298.15, 308.15, 318.15, and 328.15 K respectively in figures (1-4) Generally, the B_c values were found decrease with increases the absolute temperature as given in figure (5) suggesting a linear relationship having a form ($B_c = a + bT$) where a and b are constants.

Table(1)Densities of PVA in Aqueous Solution in the Molality and Temperature Range Studied.

$m \times 10^3$ (mol.kg ⁻¹)	$\rho_{12} \times 10^3$ (kg.m ⁻³)			
	298.15 K	308.15 K	318.15 K	328.15 K
0.0000	0.99707	0.99406	0.99025	0.98573
0.2900	0.99745	0.99495	0.99154	0.98598
0.4350	0.99804	0.99541	0.99193	0.98633
0.5794	0.99859	0.99581	0.99238	0.98690
0.8761	0.99963	0.99674	0.99327	0.98768
1.1642	1.00072	0.99783	0.99453	0.98881
1.3034	1.00102	0.99811	0.99473	0.98919
1.4554	1.00170	0.99872	0.99519	0.98972
1.7415	1.00259	0.99957	0.99559	0.99078
2.0147	1.00363	1.00055	0.99671	0.99183
2.3262	1.00464	1.00135	0.99745	0.99285
2.4653	1.00515	1.00175	0.99848	0.99333
2.5931	1.00566	1.00225	0.99873	0.99382
2.8751	1.00645	1.00244	0.99916	0.99451
3.4781	1.00867	1.00444	1.00089	0.99649

Table(2) Absolute Viscosities of PVA in Aqueous Solution in the Molality and Temperature Range Studied.

$m \times 10^{-3}$ (mol. kg ⁻¹)	$\eta_{1,2} \times 10^4$ (kg.m ⁻¹ .s ⁻¹)			
	298.15 K	308.15 K	318.15 K	328.15 K
0.0000	0.8901	0.7190	0.5972	0.5042
0.2900	1.0286	0.9243	0.7897	0.6798
0.4350	1.2000	0.9836	0.8165	0.7181
0.5794	1.2824	1.0491	0.8868	0.7612
0.8761	1.4937	1.2108	1.0650	0.8596
1.1642	1.7219	1.3811	1.1353	0.9593
1.3034	1.8114	1.4600	1.1967	1.0082
1.4554	2.0108	1.6005	1.3037	1.0879
1.7475	2.3317	1.8210	1.4621	1.2163
2.0147	2.7634	2.1006	1.8501	1.5451
2.1262	3.3105	2.4625	2.3148	2.0321
2.4653	3.6669	2.6410	2.5035	2.1399
2.5931	3.9467	2.7490	2.8289	2.3607
2.8751	4.6139	3.5649	3.4141	2.8484
3.4781	6.7834	5.5285	5.1476	4.3499

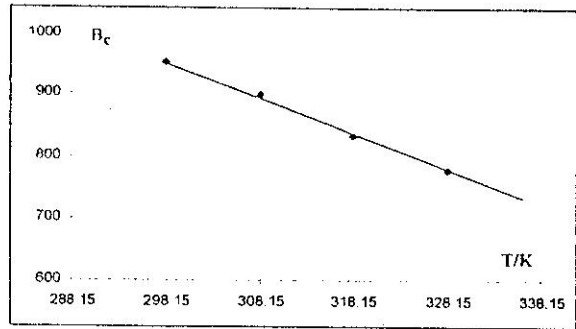


Figure (2) the relation between viscosity coefficient B_c and absolute temperature T .

Table (3) Molar Gibbs Free Energies of Activation for Viscous Flow of PVA in Aqueous Solution in the Molality and Temperature Range Studied.

$M \times 10^{-3}$ (mol. kg ⁻¹)	$\Delta G_{1,2}$ (J.mol ⁻¹)			
	298.15 K	308.15 K	318.15 K	328.15 K
0.0000	43404	44313	45259	46220
0.2900	43932	44969	46021	47074
0.4350	44139	45127	46172	47223
0.5794	44312	45291	46326	47380
0.8761	44688	45656	46654	47710
1.1642	45037	45990	46973	48006
1.3034	45189	46132	47112	48140
1.4554	45419	46366	47337	48347
1.7475	45784	46694	47640	48648
2.0147	46201	47058	48259	49298
2.1262	46665	47461	48873	50043
2.4653	46900	47641	49054	50182
2.5931	47081	47743	49177	50439
2.8751	47477	48408	49873	50950
3.4781	48416	49527	50955	52104

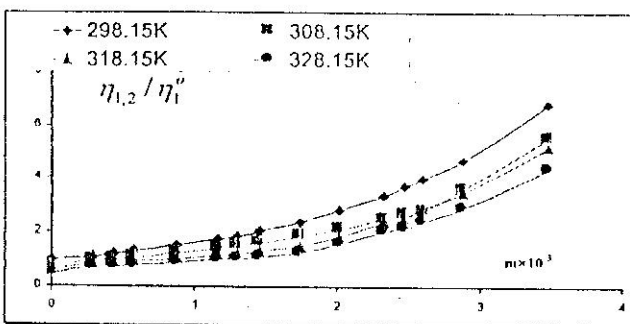


Figure (1). Concentration dependence of relative viscosity of PVA in aqueous solution at 298.15, 308.15, 318.15 and 328.15k.

REFERENCES

1. Yamakawa, H.,1971, "Modern Theory of Polymer Solutions", Harper and Row, New York.
2. Kamider, K.,1992," Thermodynamics of Polymer Solutions", Elsevier, Amsterdam.
3. Creutz, E. and Wilson,R., 1946 ,J.Chem.Phys., Vol. 14,P. 725.
4. Muller-Plathe, F.,1998," Microscopic Dynamics in Water-Swollen Poly(vinyl alcohol)",J. Chem.Phys., Vol. 108,P.8252.
5. Muller-Plathe, F.,1998, "Diffusion of Water in Swollen Poly(vinyl alcohol) Membranes Studied by Molecular Dynamics Simulation",J. Membrane Sci.,Vol.141,P.147.
6. Norio, N.,Akihiro, K.,and Kunihiko, O.,1996,"Dynamic Light Scattering and Dynamic Viscoelasticity of Poly(vinyl alcohol) in Aqueous Borax Solutions 2.Polymer Concentration and Molecular Weight Effects", Macromolecules, Vol.29,P. 1445.
7. Muller-Plathe,F.,andWilfred, F., 1997,"Solvation of Poly(vinyl alcohol) in Water,Ethanol and an

- Equimolar Water-Ethanol Mixture :Structure and Dynamics Studied by Molecular Dynamics Simulation ", *Polym.*, Vol. 38, P. 2259 .
8. Cheng R., Shao Y., Liu M., and Lu R ., 1998, "Effect of Adsorption on the Viscosity of Dilute Polmer Solution ". *Chinese J. Polm. Sci.*, Vol. 16, P. 1
 9. Akihiko, T., Miki N., Akihiro K., and Norio N., 1998, "Dynamic Light Scattering and Dynamic Viscoelasticity of Poly(vinyl alcohol) in Aqueous Borax Solutions . 4. Further Investigation on Polymer Concentration and Molecular Weight Dependencies ", *Macromolecules*, Vol. 31, P. 436 .
 10. Kazuki, K., Akihiko T., and Norio N., 1999, "Dynamic Light Scattering and Dynamic Viscoelasticity of Poly(vinyl alcohol) in Aqueous Borax Solutions. 5. Temperature Effects", *Macromolecules*, Vol. 32, P. 8872 .
 11. Rongshi, C., Yu Y., and Xiaohu, Y ., 1999, "The Wall Effect on Viscosity Measurement of Dilute Aqueous Solution of Poly(ethylene glycol) and Poly(vinyl alcohol) Using a Paraffin-Coated Capillary Viscometer". *Polym.*, Vol. 40, P. 3773 .
 12. Glasstone, S., Laidler K., and Eyring H., 1941, "The Theory of Rate Processes", 1st edn ., McGraw Hill, New York .
 13. Stokes , R., and Mills, R., 1971 , "Viscosity of Electrolytes and Related Properties ", Pergamon Press New York chap. 7 .
 14. Partington, J., 1951, "Treatise of Physical Chemistry", Vol. 2, Longmans Green and Co., New York .
 15. Harrap, B., and Heymann E., 1951, *Chem. Rev.*, Vol. 48, P. 46 .
 16. Feakins, D., 1967, "Physico-Chemical Process in Mixed Aqueous Solvents", ed. Franks F. (Heiner mann, London) .
 17. Harned, H.S., and Owen B.B., 1958, "The Physical Chemistry of Electrolytic Solutions ", (Reinhold, New York) 3rd edn .
 18. Isa , S.A., 1998, "Concentration and Temperature Dependence of Viscosity of Potassium Iodide in Methanol-Water Solutions", *J. Coll .Educ. for Women, Univ. Baghdad*, Vol. 9, P. 189 .
 19. Stokes , R., and Mills, R., 1971 , "Viscosity of Electrolytes and Related Properties", Pergamon Press New York chap. 4 .

دراسة بعض الخواص الفيزيائية للمحاليل المائية لبوليمر الكحول الفيينايلي عند اربع درجات حرارية

*ايمان طالب كريم *تقي الدين عبد الهادي حمدان

*قسم الكيمياء-كلية التربية (ابن الهيثم)-جامعة بغداد

الخلاصة

تتضمن هذه الدراسة قياسا للكثافة و اللزوجة للمحاليل المائية لبوليمر الكحول الفيينايلي ذو الوزن الجزيئي (٤١٤ كغم .مول⁻¹) في المدى من درجات الحرارة (١٥ , ٢٩٨ الى ١٥ , ٣٢٨ كلفن) .بالاعتماد على نظريه ايرنك لسرعه العمليات تم حساب طاقة تنشيط كبس الحره لهذه المحاليل بالاضافه الى ذلك تم حساب معامل اللزوجه لمعادله جونز - دول . كما تمت دراسه تاثير درجة الحرارة على هذه المعاملات .