

Molar Gibbs Free Energy of Activation for Viscous Flow of Poly (Vinyl Alcohol) in Aqueous Solution at Four Different Temperatures.

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Abstract

The densities and viscosities of solutions of poly (vinyl alcohol)(PVA) molecular weight 125kg.mol⁻¹ in water up to 0.004% mol.kg⁻¹ at 298.15, 308.15, 318.15 and 328.15 K have been measured. On the base of Eyring's theory of rate processes, the molar Gibbs free energy of activation for viscous flow of solutions ΔG^{\ddagger} have been determined. Additionally, the viscosity coefficient B_0 in Jones-Dole equation is calculated. The influence of the temperatures on the above parameter is discussed.

Introduction

Dissolving a polymer in a low-molecular weight solvent is a very slow process occurs in two stages. First, the solvent molecules slowly diffuse into the polymer to produce a swollen gel. The second stage of solution can be take place when the gel gradually disintegrates into a true solution [1-3].

A knowledge of the behaviour of polymer in low molecular weight solvents is important academically and industrially.

Many industrial processes use polymers as polymer solutions and knowledge of the subject area is critical to the efficient utilization in artificial fibers, thin films, plasticizing, lacquers, adhesives, lubricating oils and hydraulic fluids [4]. Poly (vinyl alcohol) is one of the most important materials for the active separation layers of pervaporation membranes used for removing residual water from organic solvents. This is because (PVA) mixes easily with water, but does not mix with most organic compounds including hydrophilic solvents such as ethanol or acetic acid [5].

Experimental

Materials

Deionized and doubly distilled water was used. Its specific conductivity was $<1 \times 10^{-6}$ S.cm⁻¹. poly(vinyl alcohol) is available product of Aldrich Chemical Company (U.S.A) whose number average molecular weight 125kg.mol⁻¹. PVA used in this

study is solid (powder) material and completely soluble in water.

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 thermostated bath controlled to ± 0.001 K. The densimeter was calibrated with water, dehumidized air and several aqueous solutions of potassium chloride. The precision in the density values measured using this densimeter is estimated to be better than 2×10^{-6} g cm⁻³.

Viscosity Measurements

The viscosity of the investigated solutions was determined using an Ubbelohde viscometer. The capillary length of this viscometer of about (8cm) and the diameter about (0.36-0.63mm) and a flow volume of about (3cm³). The Ubbelohde viscometer

preferred to be used in this study among the other commercial ones such as Cannon Master viscometer, Cannon Penske viscometer and Ostwald viscometer because it minimize pressure corrections and surface tension effects. A constant temperature water bath (Schott-Gerate CT 1130) with a bath control unit was used. The temperature of the water bath was measured by a Hawlett-Packard, A quartz thermometer. The temperature fluctuations was limited to ± 0.01 K.

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

$m \times 10^{-4}$ (mol .kg ⁻¹)	$\rho_{1,2} \times 10^3$ (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
0.3224	0.99790	0.99519	0.99185	0.98610
0.4848	0.99820	0.99569	0.99197	0.98663
0.6450	0.99862	0.99621	0.99264	0.98713
0.9696	0.99960	0.99668	0.99312	0.98782
1.2913	1.00048	0.99757	0.99425	0.98871
1.4570	1.00108	0.99804	0.99479	0.98925
1.6234	1.00145	0.99847	0.99523	0.98976
1.9424	1.00258	0.99930	0.99563	0.99087
2.2650	1.00324	1.00032	0.99704	0.99209
2.5991	1.00423	1.00120	0.99777	0.99306
2.7523	1.00468	1.00144	0.99853	0.99347
2.9130	1.00511	1.00203	0.99887	0.99394
3.2275	1.00591	1.00310	0.99927	0.99471
3.8951	1.00793	1.00476	1.00116	0.99671

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

$m \times 10^{-4}$ (mol .kg ⁻¹)	$\eta_{1,2} \times 10^3$ (kg.m ⁻¹ .s ⁻¹)			
	298.15 K	308.15 K	318.15 K	328.15 K
0.0000	0.8903	0.7196	0.5972	0.5047
0.3224	1.3738	1.1027	0.9189	0.7913
0.4848	1.6483	1.3282	1.0449	0.9221
0.6450	1.9537	1.5094	1.2183	1.0247
0.9696	2.7710	2.1018	1.6570	1.3483
1.2913	3.9248	2.9166	2.2881	1.8269
1.4570	4.6698	3.4444	2.7727	2.1369
1.6234	5.6247	4.1257	3.1844	2.4854
1.9424	7.9433	5.8117	4.3905	3.3487
2.2650	10.9880	7.7573	5.8422	4.5250
2.5991	13.9728	10.6593	8.2224	6.3947
2.7523	17.0630	12.4600	9.5287	7.4916
2.9130	20.1596	14.5948	10.8107	8.6205
3.2275	26.6473	19.3812	14.3091	10.9983
3.8951	47.9013	34.5508	25.3201	19.3271

Results and Discussion

The experimental values of density $\rho_{1,2}$ (kg.m^{-3}) and absolute viscosity $\eta_{1,2}$ ($\text{kg.m}^{-1}\text{s}^{-1}$), which are given in Table (1) and (2), respectively. The theory of rate processes to viscous flow is applied [6]. Thereby, the molar Gibbs free energy of activation for viscous flow of a solution, $\Delta G_{1,2}$ (J.mol^{-1}) is calculated from

$$\Delta G_{1,2} = RT \ln \frac{V_{1,2} n_1}{n_1 V_A} \quad (1)$$

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

$$V_{1,2} = \frac{1000 + m.M_2}{n_1(n_1 + m)} \quad (2)$$

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 328.15 K. As can be seen from Table(3), the $\Delta G_{1,2}$ values of the investigated solutions are positive and show an increase with increasing temperature.

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 [7-9]. Jones and Dole [10-12] have reported a semi-empirical formula to describe the concentration dependence of aqueous solutions of electrolytes at constant temperature:

$$\eta = \frac{\eta_0}{\eta_0^*} = 1 + A\sqrt{C} + BC \quad (3)$$

Where η_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-Hückel theory [13] 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(3) in the form:

$$\left[\frac{\eta_{1,2}}{\eta_0^*} - 1 \right] / \sqrt{C} = A + B\sqrt{C} \quad (4)$$

Plotting the left part of equation (4) versus \sqrt{C} should produce a straight line of slope B (positive or negative), if equation (3) is modified

by ignoring the term $A\sqrt{C}$ and replacing the molality by the molality at low concentration, Jones-Dole equation takes the form:

$$\eta_{1,2} / \eta_0^* = 1 + B_c m \quad (5)$$

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

The validity of Jones-Dole equation (equation (5)) was tested. Utilizing the method of Least-Squares curve fitting, $\eta_{1,2} / \eta_0^*$ values were plotted versus m at four different temperatures giving a straight line at low molality ($0 < m < 2 \times 10^{-4}$) and a curvature line at high molality ($2 \times 10^{-4} < m < 4 \times 10^{-4}$) with positive B_c coefficient 47872, 32333, 27777 and 26315 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 curvature relationship between the coefficient and absolute temperature.

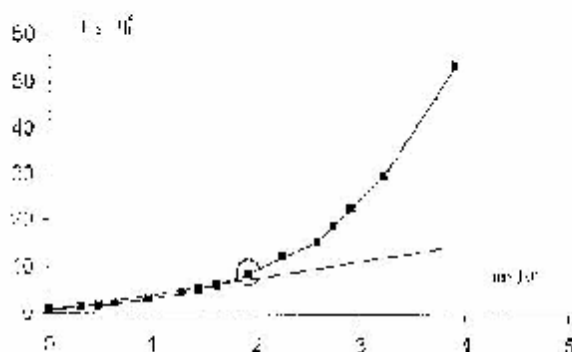


Figure (1) concentration dependence of relative viscosity of PVA in aqueous solution at 298.15K

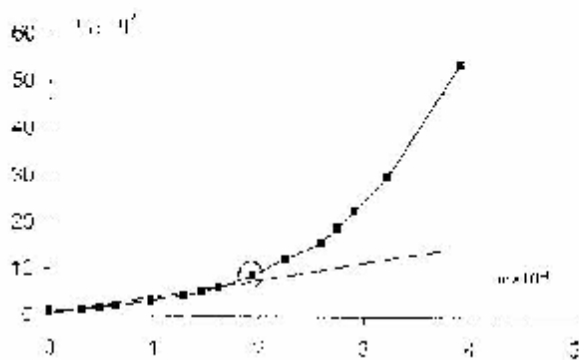


Figure (2) concentration dependence of relative viscosity of PVA in aqueous solution at 308.15K.

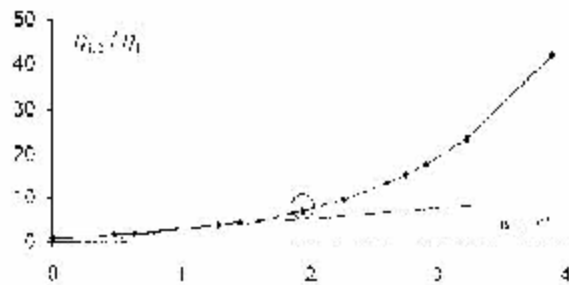


Figure (3) concentration dependence of relative viscosity of PVA in aqueous solution at 318.15K.

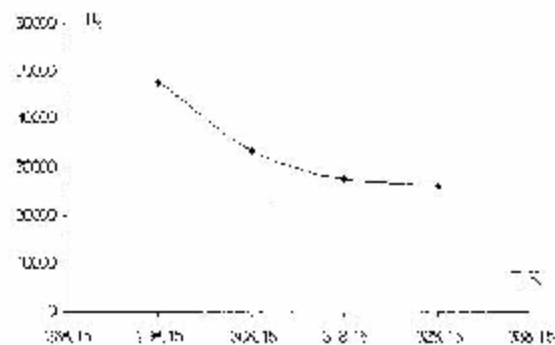


Figure (5) the relation between viscosity coefficient Bc and absolute temperature T.



Figure (4) concentration dependence of relative viscosity of PVA in aqueous solution at 328.15K.

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

m×10 ⁻⁴ (mol .kg ⁻¹)	ΔG [‡] (J.mol ⁻¹)			
	298.15 K	308.15 K	318.15 K	328.15 K
0.0000	43404	44313	45259	46220
0.3224	44185	45419	46421	47488
0.4848	44935	45895	46761	47904
0.6450	45353	46222	47165	48190
0.9696	46220	47065	47977	48937
1.2913	47080	47933	48828	49764
1.4570	47510	48331	49334	50190
1.6234	47970	48792	49674	50601
1.9424	48823	49668	50515	51410
2.2650	49525	50405	51300	52229
2.5991	50219	51217	52203	53170
2.7523	50713	51617	52534	53690
2.9130	51125	52020	52923	53982
3.2275	51815	52747	53663	54645
3.8951	53264	54221	55168	56177

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الخلاصة

تتضمن هذه الدراسة قياسا لكثافته والتزوجه لمحاليل المائيه لبوليمر الكحول الفينيلي ذوالوزن الجزيئي (125كغم مول) وعند اربع درجات حراريه (15، 298، 15، 308، 15، 318 و 328 كفن) .بالاحتماد على نظريه ايرنك لسرعه العمليات تم حساب طاقه تنشيط كيم الحره لهذه المحاليل بالاضافه الي ذلك تم حساب معامل التزوجه لمعادله جونز - دول . كما ونوقش في هذه الدراسه تأثير درجة الحراره على هذه المعاملات .