

Some volumetric properties of aqueous solution of Polyvinyl alcohol over temperature range 298.15-328.15K.

بعض الخواص الحجمية للمحلول المائي لبوليمر الكحول الفينايولي لمدى من درجات الحرارة 298.15-328.15 كلفن .

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Abstract :-

The densities of aqueous solution of polyvinyl alcohol with molecular weight (14kg.mol^{-1}) have been determined over temperature range 298.15-328.15K. From these data, the volumes for the binary mixtures studied here were calculated. The volumes have been found linearly dependent on the solute molality (PVA), from this dependence, the partial molar volumes at infinite dilution ($\bar{V}_{2,0}$) were determined and it was found that the ($\bar{V}_{2,0}$) concentration independent and slightly increase with increasing temperature. The thermal expansion coefficient ($\alpha_{1,2}$) of aqueous solution of (PVA) at 298.15K was calculated and it was found that the values of ($\alpha_{1,2}$) were higher than the value (α_1°) of pure water .

الخلاصة :

تم في هذه الدراسة قياس الكثافة للمحلول المائي لبوليمر الكحول الفينايولي ذو الوزن الجزيئي (14kg.mol^{-1}) في مدى من درجات الحرارة 298.15-328.15 كلفن . ومن هذه القيم تم حساب الحجم لهذه المخاليط ثنائية المكون ووجد ان الحجم يعتمد خطياً على مولالية المذاب (PVA) ومن هذه الاعتمادية تم حساب الحجم المولاري الجزئي المحدد عند التخفيف الى ما لانهاية ($\bar{V}_{2,0}$) ولوحظ ان هذا الحجم لا يعتمد على تغير التركيز لكنه يزداد قليلاً بزيادة درجة الحرارة. تم حساب معامل التمدد الحراري ($\alpha_{1,2}$) في درجة حرارة 298.15 كلفن ولوحظ ان قيمة $\alpha_{1,2}$ () للمحلول المائي لبوليمر الكحول الفينايولي هي اكبر من قيمة (α_1°) للماء النقي .

Introduction

The calculation of physical properties using statistical theories is still not yet possible for complicated molecules such as long chain molecules, because of the range of different conformations, which can occur and the effect of these various structures on the intermolecular interactions [1] . Due to intermolecular hydrogen bonds molecular self-organization is one of the most important phenomenon, which determine the structure and properties of numerous liquids [2] . The physical properties of these liquids and their solutions differ essentially from those of non-associated ones.

In recent years, interest lies in exploring te extent to which analysis of the composition-dependence of the thermodynamic properties of non-ionic amphiphilic-water system can help us to understand the degree and nature of their self-aggregation [3] . Volumetric properties of binary liquid mixtures have been extensively studied, as the can contribute to clarification of the various intermolecular interactions existing between the different species found in solution. In particular much effort has gone into the determination of partial molar volumes at infinite dilution where only solvent-solvent and solute-solvent interactions are present [4] . 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 [5] . Among them are the use as hydrogel former and as material for separation membranes where research is still very active

[6,7] . 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 [8-13] .

Experimental:-

(a) Materials

Deionized and doubly distilled water was used . Its specific conductivity was $<1 \times 10^{-6} \text{ S.m}^{-1}$. 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.

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

Results and Discussion

The experimental measured densities of (PVA+water) at 298.15, 308.15, 318.15 and 328.15 K are given in Table (1). Experimental density for the binary mixture in the molality range studied obey equation of type [4] :

$$\rho = a + bm + cm^2 + \dots \dots \dots (1)$$

The a , b , and c coefficients for the equation (1) are listed in Table (2) together with the standard deviation σ , defined by :

$$\sigma = \left[\frac{\sum (\rho_{(obs)} - \rho_{(cal)})^2}{(N - P)^{1/2}} \right] \dots \dots \dots (2)$$

Where $\rho_{(obs)}$ and $\rho_{(cal)}$ are the observed and the calculated density values respectively, N is the number of experimental points and P is the number of coefficients in equation (1).

The volume of the binary solution, $V_{1,2} (\text{cm}^3)$, containing (m) moles of solute per kilogram of solvent was calculated from [14] :

$$V_{1,2} = \frac{(1000 + mM_2)}{\rho} \dots \dots \dots (3)$$

Where $M_2 (\text{g.mol}^{-1})$ is the solute molecular weight, and (ρ) is the density of solution. The values of $V_{1,2}$ for investigated solution are decreased with increasing concentration, Table (3).

The concentration dependence of $V_{1,2}$ can be described by [15] :

$$V_{1,2} = V_s^\circ + \bar{V}_{2,0}m + v_{22}m^2 + v_{222}m^3 + \dots \dots \dots (4)$$

Where $(V_s^\circ = 1000/\rho_1^\circ)$, $\rho_1^\circ (\text{g.cm}^{-3})$ is the density of the pure solvent, $\bar{V}_{2,0} (\text{cm}^3.\text{mol}^{-1})$ is the partial molar volume of solute at infinite dilution and v_{22}, v_{222} etc. are the virial coefficients according to McMillan-Mayer theory of solution [16], and present the contribution to the excess thermodynamic properties of pair, triplet and higher aggregates.

For the investigated solution, it was found that the volume of solution at a definite temperature are linearly dependent on the concentration of solute, i.e. the relation (4) is reduced to :

$$V_{1,2} = V_s^\circ + \bar{V}_{2,0}m \dots \dots \dots (5)$$

The values of $(\bar{V}_{2,0})$ are concentration independent and slightly increase with increasing temperature as shown in Table (4).

The partial molecular volume at infinite dilution, $\bar{v}_{2,0} (cm^3.molecule^{-1})$, for the investigated solution was calculated from :

$$\bar{v}_{2,0} = \bar{V}_{2,0} / N_A \dots\dots\dots(6)$$

Where N_A is the Avogadro's constant. The molecular volume of the pure liquid solute $v_2^\circ (cm^3.molecule^{-1})$, was calculated from :

$$v_2^\circ = M_2 / \rho_2^\circ N_A \dots\dots\dots(7)$$

Where ρ_2° is the density of the pure solute. A comparison of the partial molecular volume at infinite dilution $\bar{v}_{2,0}$ with molecular volume v_2° show that the former is smaller than the later. Values of $\bar{v}_{2,0}$ and v_2° together with the values of their $(\bar{v}_{2,0} / v_2^\circ)$ are given in Table(4). The partial excess molecular volume was calculated from :

$$\bar{V}_{2,0}^{exc} = \bar{v}_{2,0} - v_2^\circ \dots\dots\dots(8)$$

These values, which characterize the volume changes associated with the transfer of one molecule of solute from the pure solute to solution at infinite dilution, are negative and relatively high.

The partial molar volume at infinite dilution for investigated aqueous solution, listed in Table(4), is temperature dependent. From figure(1) it can be seen that the plots of $\bar{V}_{2,0}$ against $(T - T_0)$ are linear

$$\bar{V}_{2,0} = a_0 + a_1(T - T_0) \dots\dots\dots(9)$$

Where a_0 and a_1 are empirical constants and T is the absolute temperature, ($T_0 = 298.15K$). The coefficients a_0 and a_1 , determined by the method of least square, are (36.0126) and (0.0491) respectively. The ratio (a_1/a_0) at the temperature range studied was (0.1363×10^{-2}).

As the partial molar volume of investigated solution is concentration independent and equal to the volume at infinite dilution, so the value of the partial molar expansibility of the solute $\bar{E}_2 = (\partial \bar{V}_2 / \partial T)_p (cm^3.mol^{-1}.K^{-1})$ is also concentration independent and equal to that value at infinite dilution $[\bar{E}_2 = \bar{E}_{2,0}]$.

the partial molar expansibility of the solute at infinite dilution is equal to the regression coefficient a_1 of equation(9) and the thermal expansion coefficient of the solute at infinite dilution $\alpha_{2,0} (K^{-1})$ defined as [14] :

$$\alpha_{2,0} = \frac{1}{\bar{V}_{2,0}} \left(\frac{\partial \bar{V}_{2,0}}{\partial T} \right) = \frac{\bar{E}_{2,0}}{\bar{V}_{2,0}} \dots\dots\dots(10)$$

Which is equal to the ratio (a_1 / a_0) at 298.15K. The values of $\alpha_{2,0}$ calculated from equation(10) are given in Table(4). The values of $\alpha_{2,0}$ tend to decrease slightly with increasing temperature. On the other hand, the thermal expansion coefficient of solution $\alpha_{1,2} (K^{-1})$ is defined as :

$$\alpha_{1,2} = \frac{1}{V_{1,2}} \left(\frac{\partial V_{1,2}}{\partial T} \right) \dots\dots\dots(11)$$

Where $V_{1,2}$ is the volume of solution containing m mole of solute per kilogram of solvent. Thus, the thermal expansion coefficient of the investigated solution is calculated from :

$$\alpha_{1,2} = \frac{1}{V_{1,2}} \left(\frac{10^3}{\rho_1^\circ} \alpha_1^\circ + m \bar{E}_{2,0} \right) \dots\dots\dots(12)$$

Where α_1° is the thermal expansion coefficient of pure water ($2.1 \times 10^{-4} K^{-1}$) [17] .

The values of $\alpha_{1,2}$ for investigated solution at 298.15K are given in Table(4). The dependence of $(\alpha_{1,2} - \alpha_1^\circ)$ against the volume fraction of solute (ϕ) is shown in figure(2). The volume fraction was used instead of molality or mole fraction of solute to allow for the effects of size differences of solute and solvent molecules. The volume fraction of solute was calculated from :

$$\phi = \frac{m\bar{V}_{2,0}}{1000/\rho_1^\circ + m\bar{V}_{2,0}} \dots\dots\dots(13)$$

From figure(2), it can be seen that the dependence of $(\alpha_{1,2} - \alpha_1^\circ)$ on (ϕ) is linear. This dependence may be expressed in the form :

$$\alpha_{1,2} - \alpha_1^\circ = (\alpha_{1,2} - \alpha_{2,0}) + (\alpha_{2,0} - \alpha_1^\circ)\phi \dots\dots\dots(14)$$

The values $(\alpha_{2,0} - \alpha_1^\circ)$ and $(\alpha_{1,2} - \alpha_{2,0})$ for investigated solution at 298.15K are (8.6830×10^4) and (1.1432×10^4) respectively , it can be seen that the thermal expansion coefficient of the investigated solution is higher than that of the pure solvent .

Table(1)Experimental Densities for Aqueous PVA at the Temperature Range Studied.

$m \times 10^{-3}$ (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
0.2900	0.99745	0.99495	0.99154	0.98598
0.4350	0.99804	0.99541	0.99193	0.98633
0.5794	0.99859	0.99583	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)Parameters in the Equation(1), $a/(g.cm^{-3})$, $b/(g.cm^{-3}.mol^{-1}.Kg)$ and $c/(g.cm^{-3}.mol^{-2}.Kg^2)$ at the Temperature Range Studied.

Temperature	298.15 K	308.15 K	318.15 K	328.15 K
a	0.996740	0.993945	0.990427	0.990280
b	0.0003292	0.0003459	0.0003406	-0.0005905
c	0.000042	-0.000013	-0.000011	0.000094
σ	0.001038	0.001033	0.001021	0.001034

Table(3) Volume of Aqueous Solution, $V_{1,2}(cm^3)$ Containing (m) Moles of Solute per Kilogram of Solvent at the Temperature Range Studied.

$m \times 10^{-3}$ (mol .kg ⁻¹)	$V_{1,2} \times 10^{-5}(cm^3)$			
	298.15 K	308.15 K	318.15 K	328.15 K
0.0000	1.8068	1.8123	1.8193	1.8276
0.2900	1.8062	1.8107	1.8169	1.8272
0.4350	1.8051	1.8099	1.8162	1.8265
0.5794	1.8041	1.8091	1.8154	1.8255
0.8761	1.8022	1.8074	1.8138	1.8240
1.1642	1.8003	1.8055	1.8115	1.8219
1.3034	1.7997	1.8050	1.8111	1.8212
1.4554	1.7985	1.8039	1.8103	1.8203
1.7415	1.7969	1.8024	1.8096	1.8183
2.0147	1.7951	1.8006	1.8075	1.8164
2.3262	1.7933	1.7992	1.8062	1.8146
2.4653	1.7924	1.7985	1.8043	1.8137
2.5931	1.7915	1.7976	1.8039	1.8128
2.8751	1.7901	1.7972	1.8031	1.8115
3.4781	1.7861	1.7937	1.8000	1.8080

Table(4) Partial Molar Volume at Infinite Dilution $\bar{V}_{2,0}$, Partial Molecular Volume at Infinite Dilution $\bar{v}_{2,0}$, Molecular Volume of Pure Solute v_2° , the Ratio $(\bar{v}_{2,0} / v_2^\circ)$, Excess Partial molecular volume at infinite dilution $\bar{v}_{2,0}^{exc}$ and Thermal Expansion Coefficients at Infinite Dilution $\alpha_{2,0}$ at the Temperature Range Studied.

Temp.	$\bar{V}_{2,0}$ ($\text{cm}^3.\text{mol}^{-1}$)	$\bar{v}_{2,0} \times 10^{-23}$ ($\text{cm}^3.\text{molecule}^{-1}$)	$v_2^\circ \times 10^{-23}$ ($\text{cm}^3.\text{molecule}^{-1}$)	$(\bar{v}_{2,0} / v_2^\circ)$	$\bar{v}_{2,0}^{exc}$ ($\text{cm}^3.\text{molecule}^{-1}$)	$\alpha_{2,0} \times 10^{-2}$ (K^{-1})
298.15 K	36.0126	5.9802	20.1779	0.2964	-14.1977	0.1363
308.15 K	36.5521	6.0698	20.3258	0.2986	-14.2560	0.1343
318.15 K	37.0152	6.1467	20.4201	0.3010	-14.2734	0.1326
328.15 K	37.4959	6.2265	20.5523	0.3030	-14.3258	0.1309

Table(5) Values of the Thermal Expansion Coefficients ($\alpha_{1,2}$) and the Volume Fraction (ϕ) of the Investigated Solution at 298.15K .

$m \times 10^{-3} (\text{mol} .\text{kg}^{-1})$	(ϕ)	$(\alpha_{1,2})\text{K}^{-1}$ $\times 10^4$
0.0000	0.0000	1.1623
0.2900	0.0103	1.2415
0.4350	0.0154	1.2817
0.5794	0.0204	1.3217
0.8761	0.0305	1.4039
1.1642	0.0401	1.4840
1.3034	0.0447	1.5225
1.4554	0.0497	1.5650
1.7415	0.0589	1.6445
2.0147	0.0675	1.7209
2.3262	0.0771	1.8079
2.4653	0.0813	1.8469
2.5931	0.0852	1.8829
2.8751	0.0936	1.9617
3.4781	0.1110	2.1319

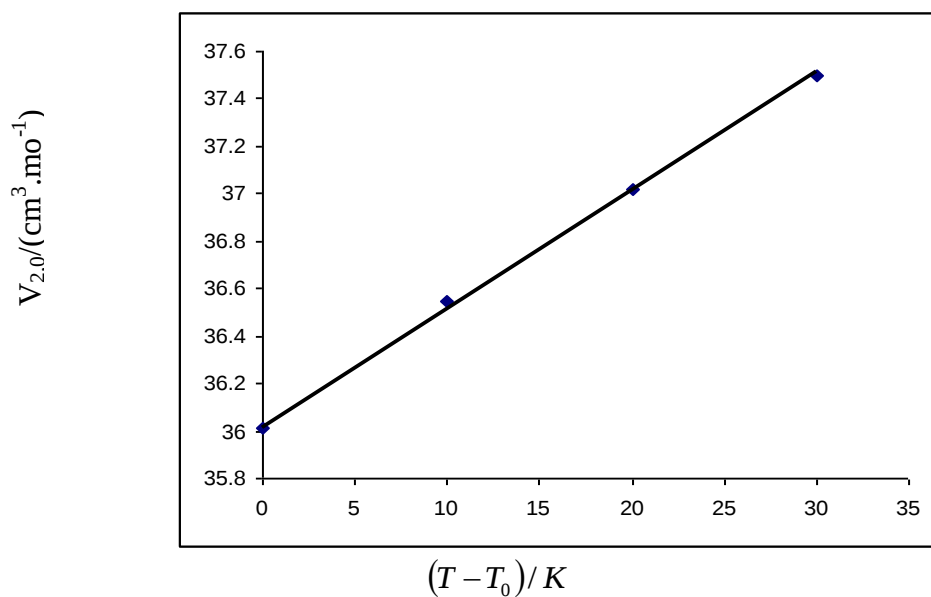


Figure (1) The temperature dependence of the partial molar volume of PVA

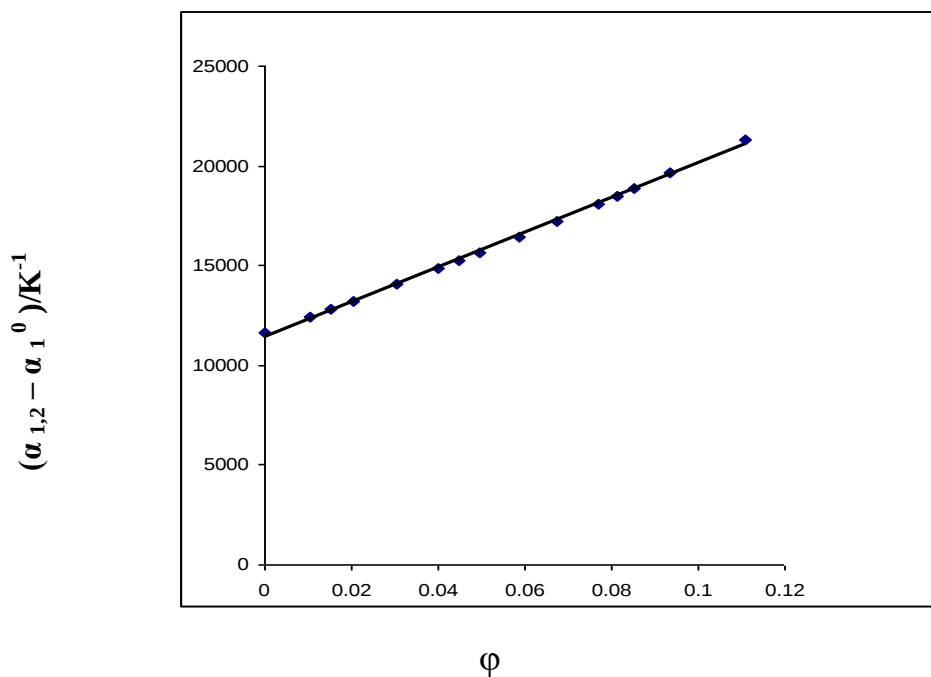


Figure (2) Dependence of $(\alpha_{1,2} - \alpha_1^0)$ on volume fraction of PVA at 298.15K .

References :-

1. O.E.A. Adam "Physical properties study of aqueous solutions of Glycols over temperature range 293.15-318.15K" Ph.D.Thesis, Baghdad University, (2004).
2. G.Douheret, M.I. Davis, I.J. Fjellandlanger, and H. Hoiland, J.Chem.Soc.,Faraday Trans., 93(10),1943(1997).
3. G.Czechowski, and J. Jadzyn, Z.Naturforsch,58a,321(2003).
4. E.F.G.Barbosa, S.M.C.Sousa, M.C.S.Santos, and I.M.S. Lampreia, Phs.Chem.Chem Phs., 3,556(2001).
5. E.Creutz and R.Wilson ,J.Chem.Phys.,Vol.14,P.725(1946) .
6. F.Muller-Plathe "Microscopic Dynamics in Water-Swollen Poly(vinyl alcohol)",J.Chem.Phys.,Vol.108,P.8252(1998) .
7. F.Muller-Plathe "Diffusion of Water in Swollen Poly(vinyl alcohol) Membranes Studied by Molecular Dynamics Simulation",J.Membrane Sci.,Vol.141,P.147(1998) .
8. N.Norio , K.Akihiro and O.Kunihiro "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(1996) .
9. F.Muller-Plathe and F.Wilfred "Solvation of Poly(vinyl alcohol) in Water,Ethanol and an Equimolar Water-Ethanol Mixture:Structure and Dynamics Studied by Molecular Dynamics Simulation",Polm.,Vol.38,P.2259(1997)
10. R.Cheng , Y.Shao , M.Liu and R.Lu "Effect of Adsorption on the Viscosity of Dilute Polmer Solution",Chinese J.Polm.Sci.,Vol.16,P.1(1998) .
11. T.Akihiko ,N. Miki ,K. Akihiro and N.Norio "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(1998) .
12. K.Kazuki , T.Akihiko and N.Norio "Dynamic Light Scattering and Dynamic Viscoelasticity of Poly(vinyl alcohol) in Aqueous Borax Solutions. 5.Temperature Effects",Macromolecules, Vol.32,P.8872(1999) .
13. C.Rongshi , Y.Yu and Y.Xiaohu "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(1999) .
14. C.Klofutar , S.Palijk and S.Golc-Teger , Thermochim.Acta, 196,401(1992).
15. S.Wurzbarger , R.Sartorio , G.Guarino and M.Nisi , J.Chem.Soc.,Faraday Trans.1, 84,2279(1988).
16. C.Dindar "High-Pressure viscosity and density of polymer solutions at the critical polymer concentration in near-critical and supercritical fluid" M.Sc. Thesis, Virginia Polytechnic Institute and State University,U.S.A.(2001).
17. P.W.Atkins , and J.de Paula , "Physical Chemistry",7th ed ,Oxford University Press, p.161-166,815(2008).