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A volumetric study of aqueous solution of poly (vinyl alcohol) over temperature range 298.15-328.15 K.

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Abstract

The densities of aqueous solution of poly (vinyl alcohol)with molecular weight (125000 g.mol^{-1}) have been determined up to a weight molality of 0.0487 over temperature range 298.15-328.15 K. From these data, the apparent specific volume of the solute and the partial specific volume of the solute and solvent were calculated. The specific excess volume of the solution and the coefficients of the virial expansion of the excess property were evaluated and interpreted in terms of solute-solute and solute-solvent interaction.

الخلاصة

تم في هذه الدراسة قياس الكثافة للمحلول المائي لبوليمر الكحول الفينايلي ذو الوزن الجزيئي (125000غم.مول$^{-1}$) على مدى درجات الحراره 298.15-328.15 كلفن. ومن هذه القيم تم حساب الحجم النوعي الظاهري للمذاب والحجم النوعي الجزيئي للمذاب والمذيب. الحجم الفائض النوعي للمحلول وكذلك معاملات التمدد الفيرالية للخاصية الفائضة تم حسابها في هذه الدراسة وفسرت النتائج على اساس التأثيرات المتبادلةبين مذاب-مذاب ومذاب-مذيب.

Introduction

The volumetric properties of aqueous solutions containing a macromolecular non-electrolyte as solute are important for understanding solute-solvent and solute-solute interactions, since they may give us an indirect insight into the conformational features of the polymer molecule in solution [1]. Volumetric properties of binary liquid mixtures have been extensively studied , as they 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 specific excess volume of the solution where only solute-solute and solute-solvent interactions are present [2,3]. Poly(vinyl alcohol) (PVA;-(CH_2-CHOH)$_n$-) is a polymer which is soluble in water to alarge degree but considerably less so in most organic solvents. Many of its applications are determined by its hydrophilicity (researchers have, for example, worried about the water content of PVA films as early as 1946) [4]. Among them are the use as hydrogel former and as material for separation membranes where research is still very active [5,6]. It is often used in pervaporation systems for the removal of water (minority component) from liquid mixtures.

In the present study, we systematically investigated the effect of the concentration and temperature range 298.15-328.15 K on the volumetric properties of aqueous solution of poly(vinyl alcohol). To obtain a deeper insight on solute-solute and solute-solvent interactions, we extended the concentration range of solute up to a weight molality of 0.0487.

Experimental

a) Materials

Deionized and doubly distilled water was used . Its specific conductivity was<$1x10^{-6}$ $S.cm^{-1}$.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.

(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 ± 0.001K. 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 $2x10^{-6}g.cm^{-3}$.

Results and Discussion

The density data of the system investigated as a function of weight molality, w(g solute / g of water) [7], at the temperature range studied is presented in Table (1). It can be seen from these, that the density of the solution increases in an almost linear manner with solute concentration and decreases with increases temperature. From the density data, the apparent specific volume, $\upsilon_{2\phi}$, was calculated by the equation below [8]:

$$\upsilon_{2\phi} = \frac{1}{d}\left[1 + \left(\frac{d_\circ - d}{wd_\circ}\right)\right] \qquad \text{……….(1)}$$

where d and d_0 are the densities of solution and water. At calculation of the apparent specific volume the density of pure water, d_0 at the temperature range studied was used from the literature [9]. From Eq. (1) it can be seen that the accuracy of the apparent specific volume determination depends on the precision of the density ,∂d , and concentration measurements , ∂w . The uncertainties in the apparent specific volume determination ,$\partial \upsilon_{2\phi}$,were calculated from the equation

$$\left(\partial \upsilon_{2\phi}\right)^2 = \left(\frac{w+1}{d^2 w}\right)^2 \left(\partial d\right)^2 + \left(\frac{d - d_\circ}{dd_\circ w^2}\right)^2 \left(\partial w\right)^2 \quad \text{...(2)}$$

The calculated values of $\upsilon_{2\phi}$ as a function of solute concentration are given in Table (1). From the data presented in this table a regular decrease in the apparent specific volumes with increasing concentration of solute can be observed. Furthermor, from Table (1) it can be seen that $\upsilon_{2\phi}$ also increases with increasing temperature.

The calculated values of $\upsilon_{2\phi}$ were fitted to the following equation:

$$\upsilon_{2\phi} = \upsilon_{2\phi}^{\infty} + b_v w + b_{vv} w^2 \qquad \text{……….(3)}$$

where $\upsilon_{2\phi}^{\infty}$ is the apparent specific volume of solute at infinite dilution, b_v and b_{vv} are empirical parameters which depend on solute, solvent and temperature. The values of the parameters in Eq.(3) were calculated by a weighted regression method [10]. As a weighting factor the reciprocal value of the square of the apparent specific volume error, i.e., $1/\left(\partial \upsilon_{2\phi}\right)^2$ was used. The parameters obtained from Eq.(3) are given in Table (2). The maximal standard error of $\upsilon_{2\phi}^{\infty}$ is $2\times10^{-4}cm^3.g^{-1}$, while for the parameters b_v and b_{vv} it is $1\times10^{-3}cm^3.g^{-1}$. From Table (2), it can also be seen that the values of $\upsilon_{2\phi}^{\infty}$ increase with increasing temperature and decrease with increasing viscosity average molecular weight of solute, what was also observed by others [11-14].

The partial specific volume of the solute, $\overline{\upsilon}_2$, was calculated from the equation [8]

$$\overline{\upsilon}_2 = \upsilon_{2\phi} + w\left(\frac{\partial \upsilon_{2\phi}}{\partial w}\right)_{T,P} \quad \text{……….(4)}$$

and considering Eq.(3) as

$$\overline{\upsilon}_2 = \upsilon_{2\phi}^{\infty} + 2b_v w + 3b_{vv}w^2 \quad \text{………(5)}$$

On the other hand, the partial specific volume of solvent, $\overline{\upsilon}_1$,can be obtained from

$$\overline{\upsilon}_1 = \overline{\upsilon}_1^{\infty} - b_v w^2 - 2b_{vv}w^3 \quad \text{………(6)}$$

From Eqs.(5) and (6) it follows that $\overline{\upsilon}_2^{\infty} = \upsilon_{2\phi}^{\infty}$ and $\overline{\upsilon}_1^{\infty} = 1/d_{\circ}$, respectively. The calculated values of $\overline{\upsilon}_2$ and $\overline{\upsilon}_1$ are given in Table (1). From this table it can be seen that $\overline{\upsilon}_2$ values decrease gradually with increasing concentration of solute,and temperature. In contrast, the $\overline{\upsilon}_1$ values increase very slightly with increasing solute concentration and temperature. The variation of the partial specific volume of water may be attributed to the formation of a structurally ordered polymer solution in the low concentration region, while at higher concentration this structure is disturbed[15].

According to the McMillan-Mayer theory of solutions [16], which proposes a formal separation of the excess thermodynamic functions into contribution arising from the pairs, triplets, etc., of solute particles, the volumetric results were analysed by the relation

$$\upsilon_{1,2}^{ex} = \upsilon_{1,2} - \overline{\upsilon}_1^{\infty} - \overline{\upsilon}_2^{\infty}w = a_{22}w^2 + a_{222}w^3 \quad \text{……….(7)}$$

where $\upsilon_{1,2}^{ex}\left(cm^3.g^{-1}\right)$ is the specific excess volume of the solution, $\upsilon_{1,2}\left(cm^3.g^{-1}\right)$ is the volume of the solution containing 1.0g of solvent and w grams of solute, calculated from

$$\upsilon_{1,2} = \frac{1.0+w}{d} \quad \text{………………..(8)}$$

and $a_{22}\left(cm^3.g^{-1}\right)$ and $a_{222}\left(cm^3.g^{-1}\right)$ are the specific virial coefficients. From the results given in Table (1),it can be seen that the specific excess volume for the solution investigated here is negative and decrease with increasing concentration of solute and with increasing temperature. The values of the specific virial coefficients a_{22} and a_{222} in Eq.(7) were determined by the method of least squares and collected in Table (2). The standarad error of a_{22} and a_{222} are $2\times10^{-3}cm^3.g^{-1}$ and $4\times10^{-3}cm^3.g^{-1}$, respectively. It can be seen from Table (2) the coefficients a_{22} are negative while the coefficients a_{222} are positive.

The specific virial coefficients a_{22} and a_{222} are extended to obtain the molar virial coefficients $\upsilon_{22}\left(cm^3.kg.mol^{-2}\right)$ and $\upsilon_{222}\left(cm^3.kg^2.mol^{-3}\right)$ [16,17], by the simple equations

$$\upsilon_{22} = a_{22}\left(\overline{M}_{2,\eta}.10^{-3}\right)^2 \quad \text{…………..(9)}$$

$$\upsilon_{222} = a_{222}\left(\overline{M}_{2,\eta}.10^{-3}\right)^2 \quad \text{………(10)}$$

where $\left(\overline{M}_{2,\eta}\right)$, is the viscosity average molecular weigh of solute.

In terms of the solvation model proposed by Wurzburger et al.[17], the υ_{22} values represent the volume changes of hydrated molecules with increasing solute concentration. This process can be assumed as a consequence of the overlap of the hydration co-spheres of the solute pair. Thus, the overlap of the solvated co-spheres of solvated molecules gives rise to a negative volume change when solvent is released from the co-sphere, which is more structured than the bulk of the solvent. Thus, from the negative values of υ_{22} it follows that the solvent molecules are more structured in the co-sphere than in the bulk of the solvent. From these results it may be concluded that this system behave rather non-ideally and that the solvation process as well as the structural changes of the solvent depend primarily on the average molecular weight of the solute molecule [18].

Table(1) Density, apparent specific volume, parial specific volumes of solute and solvent and excess volume of aqueous solution of PVA at temperature range 298.15-328.15 K.

w	$d\left(g.cm^{-3}\right)$	$\upsilon_{2\phi}\left(cm^{3}.g^{-1}\right)$	$\overline{\upsilon}_{2}\left(cm^{3}.g^{-1}\right)$	$\overline{\upsilon}_{1}\left(cm^{3}.g^{-1}\right)$	$\upsilon_{1,2}^{ex}\left(cm^{3}.g^{-1}\right)$
298.15 K					
0.0000	0.99707	1.0029	1.0058	1.0029	0.0000
0.0040	0.99790	1.0021	1.0041	1.0029	-0.0008
0.0061	0.99820	1.0018	1.0033	1.0029	-0.0011
0.0081	0.99862	1.0014	1.0024	1.0030	-0.0016
0.0121	0.99960	1.0004	1.0007	1.0030	-0.0026
0.0161	1.00048	0.9995	0.9990	1.0030	-0.0035
0.0182	1.00108	0.9989	0.9981	1.0030	-0.0041
0.0203	1.00144	0.9986	0.9972	1.0030	-0.0045
0.0243	1.00238	0.9976	0.9954	1.0031	-0.0054
0.0283	1.00324	0.9968	0.9936	1.0031	-0.0063
0.0325	1.00423	0.9958	0.9917	1.0032	-0.0074
0.0344	1.00468	0.9953	0.9909	1.0032	-0.0079
0.0364	1.00514	0.9949	0.9900	1.0032	-0.0083
0.0403	1.00591	0.9941	0.9882	1.0033	-0.0092
0.0487	1.00793	0.9921	0.9842	1.0035	-0.0113
308.15 K					
0.0000	0.99406	1.0060	1.0030	1.0060	0.0000
0.0040	0.99519	1.0048	1.0013	1.0060	-0.0011
0.0061	0.99569	1.0043	1.0004	1.0060	-0.0017
0.0081	0.99591	1.0041	0.9995	1.0060	-0.0019
0.0121	0.99668	1.0033	0.9977	1.0060	-0.0027
0.0161	0.99752	1.0025	0.9959	1.0060	-0.0035
0.0182	0.99804	1.0020	0.9950	1.0060	-0.0041
0.0203	0.99847	1.0015	0.9940	1.0061	-0.0045
0.0243	0.99930	1.0007	0.9922	1.0061	-0.0054
0.0283	1.00032	0.9997	0.9904	1.0061	-0.0065
0.0325	1.00120	0.9988	0.9885	1.0062	-0.0074
0.0344	1.00144	0.9986	0.9876	1.0062	-0.0077
0.0364	1.00172	0.9983	0.9867	1.0063	-0.0080
0.0403	1.00305	0.9970	0.9849	1.0063	-0.0094
0.0487	1.00476	0.9953	0.9810	1.0065	-0.0112
318.15 K					
0.0000	0.99025	1.0098	1.0147	1.0098	0.0000
0.0040	0.99113	1.0089	1.0128	1.0099	-0.0009
0.0061	0.99160	1.0085	1.0118	1.0099	-0.0014
0.0081	0.99216	1.0079	1.0109	1.0099	-0.0020
0.0121	0.99312	1.0069	1.0090	1.0099	-0.0030
0.0161	0.99425	1.0058	1.0072	1.0099	-0.0041

0.0182	0.99479	1.0052	1.0062	1.0099	-0.0047
0.0203	0.99523	1.0048	1.0052	1.0099	-0.0052
0.0243	0.99563	1.0044	1.0033	1.0100	-0.0056
0.0283	0.99704	1.0030	1.0014	1.0100	-0.0071
0.0325	0.99777	1.0022	0.9994	1.0101	-0.0079
0.0344	0.99853	1.0015	0.9985	1.0101	-0.0087
0.0364	0.99887	1.0011	0.9976	1.0101	-0.0090
0.0403	0.99954	1.0005	0.9958	1.0102	-0.0098
0.0487	1.00116	0.9988	0.9918	1.0103	-0.0115
328.15 K					
0.0000	0.98573	1.0145	1.0100	1.0145	0.0000
0.0040	0.98630	1.0139	1.0079	1.0145	-0.0006
0.0061	0.98663	1.0136	1.0068	1.0145	-0.0009
0.0081	0.98743	1.0127	1.0058	1.0145	-0.0018
0.0121	0.98832	1.0118	1.0039	1.0145	-0.0027
0.0161	0.98921	1.0109	1.0020	1.0145	-0.0036
0.0182	0.98979	1.0103	1.0010	1.0146	-0.0042
0.0203	0.99010	1.0100	1.0001	1.0146	-0.0046
0.0243	0.99087	1.0092	0.9984	1.0146	-0.0054
0.0283	0.99209	1.0080	0.9967	1.0147	-0.0067
0.0325	0.99306	1.0070	0.9950	1.0147	-0.0077
0.0344	0.99347	1.0066	0.9943	1.0148	-0.0082
0.0364	0.99394	1.0061	0.9935	1.0148	-0.0087
0.0403	0.99471	1.0053	0.9921	1.0149	-0.0095
0.0487	0.99671	1.0033	0.9892	1.0150	-0.0117

Table(2) Apparent specific volume at infinite dilution $\upsilon_{2\phi}^{\infty}$, the regression coefficients of Eqs.(3) and (7) with standard error of the estimate, s , for investigated system at the temperature range studied.

$T(K)$	$\upsilon_{2\phi}^{\infty}$ $\left(cm^3.g^{-1}\right)$	b_v $\left(cm^3.g^{-1}\right)$	b_{vv} $\left(cm^3.g^{-1}\right)$	$s(Eq.(3))$	a_{22} $\left(cm^3.g^{-1}\right)$	a_{222} $\left(cm^3.g^{-1}\right)$	$s(Eq.(7))$
298.15	1.0030	-0.219	-0.108	0.00084	-13.184	178.721	0.00088
308.15	1.0058	-0.205	-0.218	0.00080	-13.291	181.931	0.00085
318.15	1.0100	-0.265	-0.709	0.00087	-15.199	291.028	0.00091
328.15	1.0147	-0.234	-0.017	0.00088	-13.655	184.881	0.00092

List of Symbols :-

a_{22}, a_{222}	Specific virial coefficients in Eq.(7) $\left(cm^3.g^{-1}\right)$
b_v, b_{vv}	Empirical parameters from Eq.(3) $\left(cm^3.g^{-1}\right)$
d	Density of solution $\left(g.cm^{-3}\right)$
$d_\circ$	Density of water $\left(g.cm^{-3}\right)$
$\overline{M}_{2,\eta}$	Viscosity average molecular weight of the solute $\left(g.mol^{-1}\right)$
s	Standard error of the estimate by Eqs.(3) and (7)
$\overline{\upsilon}_1$	Partial specific volume of the solvent $\left(cm^3.g^{-1}\right)$
$\overline{\upsilon}_2$	Partial specific volume of the solute $\left(cm^3.g^{-1}\right)$
$\overline{\upsilon}_2^{\infty}$	Partial specific volume of the solute at infinite dilution $\left(cm^3.g^{-1}\right)$

$\upsilon_{1,2}$	Volume of the solution containing 1.0 g of solvent and w grams of solute $\left(cm^3.g^{-1}\right)$
$\upsilon_{1,2}^{ex}$	Specific excess volume of the solution $\left(cm^3.g^{-1}\right)$
$\upsilon_{22}, \upsilon_{222}$	Molar virial coefficients in Eq.(9) $\left(cm^3.kg.mol^{-2}\right)$and Eq.(10) $\left(cm^3.kg^2.mol^{-3}\right)$
$\upsilon_{2\phi}$	Apparent specific volume of the solute $\left(cm^3.g^{-1}\right)$
$\upsilon_{2\phi}^{\infty}$	Apparent specific volume of the solute at infinite dilution $\left(cm^3.g^{-1}\right)$
w	Weight molality
$\partial w, \partial d, \partial \upsilon_{2\phi}$	Uncertainty in the determination of $w, d, \upsilon_{2\phi}$

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