

# A Study the Effect of the Concentration and Temperature Range 298.15-328.15 K on the Volumetric Properties of Aqueous Solution of Ethylene Glycol .

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## Abstract

The densities of aqueous solution of ethylene glycol have been determined up to a weight molality of 0.4201 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 لثلاثين كلاكول على مدى درجات الحرارة 298.15-328.15 كلفن. ومن هذه القيم تم حساب الحجم النوعي الظاهري للمذاب والحجم النوعي الجزئي للمذاب والمذيب. الحجم الفائض النوعي للمحلول وكذلك معاملات التمدد الفيرالية للخاصية الفائضة تم حسابها في هذه الدراسة وفسرت النتائج على اساس التأثيرات المتبادلة بين مذاب-مذاب ومذاب-مذيب.

## Introduction

Recently, the study of molecular interactions in binary organic mixtures has been actively investigated (Aminabhavi *et al.*, 1993) . A great demand for the experimental data is due to the impetuous development of the computer simulation methods used for the elucidation and better understanding of the transport phenomena at the molecular level. The demand often concerns the viscosity data series of compounds of the same structure and polarity but of different length of the molecule (Jadzyn *et al.*, 2000) .

Water, is undoubtedly the most intensively studied solvent. In fact, it is difficult if not impossible to imagine another liquid that is suitable for complicated self-assembly and supramolecular organization to the extent and variation observed in water. The large number of unusual properties of water distinguishes it from normal liquids (Franks ,1982) . The molecule is small and interacts with other water molecules mainly by strong, directional hydrogen bonds, resulting in an unusually high boiling point for such a small molecule. However, the number of self-interactions; i.e. water-water interactions, is low. Aqueous chemistry often differs from non- aqueous chemistry because of these features. In particular hydrophobic effects distinguish water from other solvents(Vergara *et al.*, 2000) .

Ethylene glycol is a clear, colourless, odourless, and relatively non-volatile viscous liquid. It has a relatively low vapour pressure and a low Henry's constant. It is completely miscible with water, very hygroscopic and absorb up to 200% of its weight in water at 100% relative humidity. Ethylene glycol is used in the manufacturing of polyethylene tetraphthalate in natural gas processing, and as an antifreeze agent(Douheret *et al.*, 1993, Douheret *et al.*, 1994, Douheret *et al.*, 1996, and Yang *et al.*, 2003 ) .Glycols find a wide spread application in the automotive, aviation, explosives, textile, surface coatings, food, cosmetic, pharmaceutical, tobacco, petroleum, and other industries (Ottani *et al.*, 2002, Naidu *et al.*, 2002, Ottani *et al.*, 2004, Sun and Teja., 2003, and Rahbari-Sisakht *et al.*, 2003 ) .

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 ethylene glycol. 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 0.4201.

## Experimental

### (a) Materials

Deionized and doubly distilled water was used . Its specific conductivity was  $<1 \times 10^{-6}$  S.m<sup>-1</sup>. Ethylene glycol is available product by Fluka AG (Buchs , Switzerland) . Ethylene glycol was used without further purification , but kept over freshly activated molecular sieves of type 4A (Union Carbide) for several days before use to reduce the water content .

### (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 density data of the system investigated as a function of weight molality,  $w$  (g solute / g of water) (Eisenberg, 1976), 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,  $v_{2\phi}$ , was calculated by the equation (Durschlage, 1986)

$$v_{2\phi} = \frac{1}{d} \left[ 1 + \left( \frac{d_0 - d}{wd_0} \right) \right] \dots\dots\dots(1)$$

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 (Riddick and Bunger, 1986). From Eq. (1) it can be seen that the accuracy of the apparent specific volume determination depends on the precision of the density,  $\partial d$ , and concentration measurements,  $\partial w$ . The uncertainties in the apparent specific volume determination,  $\partial v_{2\phi}$ , were calculated from the equation

$$(\partial v_{2\phi})^2 = \left( \frac{w+1}{d^2 w} \right)^2 (\partial d)^2 + \left( \frac{d-d_0}{dd_0 w^2} \right)^2 (\partial w)^2 \dots\dots\dots(2)$$

The calculated values of  $v_{2\phi}$  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. Furthermore, from Table (1) it can be seen that  $v_{2\phi}$  also increases with increasing temperature.

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

$$v_{2\phi} = v_{2\phi}^\infty + b_v w + b_{vv} w^2 \dots\dots\dots(3)$$

where  $v_{2\phi}^\infty$  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 (Topping, 1972). As a weighting factor the reciprocal value of the square of the apparent specific volume error, i.e.,  $1/(\partial v_{2\phi})^2$  was used. The parameters obtained from Eq.(3) are given in Table (2). The maximal standard error of  $v_{2\phi}^\infty$  is  $2 \times 10^{-4} \text{ cm}^3 \cdot \text{g}^{-1}$ , while for the parameters  $b_v$  and  $b_{vv}$  it is  $1 \times 10^{-5} \text{ cm}^3 \cdot \text{g}^{-1}$ .

From Table (2), it can also be seen that the values of  $v_{2\phi}^\infty$  increase with increasing temperature and decrease with increasing viscosity average molecular weight of solute, what was also observed by others (Lepori and Mollica, 1978, Bahri and Guveli, 1988, Harada *et al.*, 1978, and Pal *et al.*, 1994)

The partial specific volume of the solute,  $\bar{v}_2$ , was calculated from the equation (Durschlage, 1986)

$$\bar{v}_2 = v_{2\phi} + w \left( \frac{\partial v_{2\phi}}{\partial w} \right)_{T,P} \dots\dots\dots(4)$$

and considering Eq.(3) as

$$\bar{v}_2 = v_{2\phi}^\infty + 2b_v w + 3b_{vv} w^2 \dots\dots\dots(5)$$

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

$$\bar{v}_1 = \bar{v}_1^\infty - b_v w^2 - 2b_{vv} w^3 \dots\dots\dots(6)$$

From Eqs.(5) and (6) it follows that  $\bar{v}_2^\infty = v_{2\phi}^\infty$  and  $\bar{v}_1^\infty = 1/d_s$ , respectively. The calculated values of  $\bar{v}_2$  and  $\bar{v}_1$  are given in Table (1). From this table it can be seen that  $\bar{v}_1$  values decrease gradually with increasing concentration of solute, and temperature. In contrast, the  $\bar{v}_2$  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 (Morenas and Douheret, 1978).

According to the McMillan-Mayer theory of solutions (McMillan and Mayer, 1945), 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

$$v_{1,2}^{ex} = v_{1,2} - \bar{v}_1^\infty - \bar{v}_2^\infty w = a_{22}w^2 + a_{222}w^3 \dots\dots\dots(7)$$

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

$$v_{1,2} = \frac{1.0 + w}{d} \dots\dots\dots(8)$$

and  $a_{22}(cm^3.g^{-1})$  and  $a_{222}(cm^3.g^{-1})$  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 standard error of  $a_{22}$  and  $a_{222}$  are  $2 \times 10^{-5} m^3.g^{-1}$  and  $4 \times 10^{-5} cm^3.g^{-1}$ , 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  $v_{22}(cm^3.kg.mol^{-2})$  and  $v_{222}(cm^3.kg^2.mol^{-3})$  (McMillan and Mayer, 1945, and, Wurzbürger *et al.*, 1988), by the simple equations

$$v_{22} = a_{22}(\bar{M}_{2,\eta}.10^{-3})^2 \dots\dots\dots(9)$$

$$v_{222} = a_{222}(\bar{M}_{2,\eta}.10^{-3})^3 \dots\dots\dots(10)$$

where  $(\bar{M}_{2,\eta})$ , is the viscosity average molecular weight of solute.

In terms of the solvation model proposed by (Wurzbürger *et al.*, 1988), the  $v_{22}$  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  $v_{22}$  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 behaves 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 (Ueberreiter, 1980).

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

w	$d(g.cm^{-3})$	$v_{2\phi}(cm^3.g^{-1})$	$\bar{v}_2(cm^3.g^{-1})$	$\bar{v}_1(cm^3.g^{-1})$	$v_{1,2}^{ex}(cm^3.g^{-1})$
<b>298.15 K</b>					
0.0000	0.99707	1.0029	0.9543	1.0029	0.0000
0.0016	1.02415	0.9593	0.9552	1.0015	0.0083
0.0035	1.03028	0.9561	0.9567	0.9954	0.0080
0.0059	1.03920	0.9553	0.9581	0.9797	0.0025
0.0086	1.04982	0.9467	0.9590	0.9482	-0.0626

0.0120	1.06000	0.9385	0.9626	0.8865	-0.1868
0.0164	1.06983	0.9306	0.9634	0.7623	-0.3842
0.0229	1.07877	0.9237	0.9658	0.4667	-0.6942
0.0328	1.08686	0.9176	0.9671	-0.3087	-1.1942
0.0477	1.09284	0.9132	0.9685	-2.4474	-1.9439
0.0757	1.10079	0.9072	1.0407	-10.9048	-3.5413
0.1147	1.10131	0.9072	1.2198	-36.6287	-5.3680
0.2086	1.10441	0.9050	2.0247	-205.0742	-10.2157
0.4201	1.10799	0.9023	5.7768	-1581.8001	-21.7081
<b>308.15 K</b>					
0.0000	0.99406	1.0060	0.9589	1.0060	0.0000
0.0016	1.01876	0.9659	0.9592	1.0046	0.0108
0.0035	1.02585	0.9658	0.9598	0.9985	0.0024
0.0059	1.03622	0.9581	0.9607	0.9829	-0.0050
0.0086	1.04603	0.9502	0.9634	0.9517	-0.0751
0.0120	1.05443	0.9436	0.9668	0.8904	-0.1843
0.0164	1.06362	0.9362	0.9691	0.7669	-0.3734
0.0229	1.06983	0.9316	0.9713	0.4729	-0.6253
0.0328	1.08122	0.9224	0.9736	-0.2992	-1.1972
0.0477	1.08492	0.9200	0.9740	-2.4307	-1.8574
0.0757	1.09291	0.9138	1.0465	-10.8674	-3.4161
0.1147	1.09544	0.9121	1.2261	-36.5462	-5.3750
0.2086	1.09916	0.9093	2.0321	-204.8119	-10.3434
0.4201	1.10161	0.9075	5.7868	-1580.7465	-21.5866
<b>318.15 K</b>					
0.0000	0.99025	1.0098	0.9635	1.0098	0.0000
0.0016	1.01549	0.9686	0.9649	1.0085	0.0078
0.0035	1.02161	0.9699	0.9663	1.0026	0.0050
0.0059	1.03047	0.9637	0.9679	0.9875	0.0009
0.0086	1.04072	0.9552	0.9691	0.9572	-0.0719
0.0120	1.04856	0.9490	0.9705	0.8974	-0.1747
0.0164	1.05736	0.9419	0.9724	0.7767	-0.3563
0.0229	1.06351	0.9372	0.9754	0.4883	-0.6024
0.0328	1.07406	0.9286	0.9788	-0.2716	-1.1445
0.0477	1.07901	0.9250	0.9807	-2.3768	-1.8363
0.0757	1.08553	0.9200	1.0545	-10.7374	-3.2933
0.1147	1.08752	0.9187	1.2358	-36.2524	-5.1406
0.2086	1.09166	0.9156	2.0459	-203.8484	-10.0027
0.4201	1.09504	0.9130	5.8099	-1576.8573	-21.2416
<b>328.15 K</b>					
0.0000	0.98573	1.0145	0.9688	1.0145	0.0000
0.0016	1.01008	0.9743	0.9693	1.0131	0.0085
0.0035	1.01638	0.9750	0.9709	1.0074	0.0061
0.0059	1.02564	0.9683	0.9725	0.9925	-0.0032
0.0086	1.03475	0.9608	0.9747	0.9626	-0.0686
0.0120	1.04283	0.9543	0.9789	0.9035	-0.1744
0.0164	1.05083	0.9478	0.9821	0.7841	-0.3450
0.0229	1.05800	0.9422	0.9846	0.4982	-0.6105
0.0328	1.06728	0.9346	0.9858	-0.2562	-1.1219
0.0477	1.07262	0.9306	0.9870	-2.3494	-1.8231
0.0757	1.07713	0.9273	1.0613	-10.6755	-3.1454
0.1147	1.07976	0.9254	1.2433	-36.1161	-4.9844
0.2086	1.08483	0.9214	2.0553	-203.4051	-9.8968
0.4201	1.08645	0.9202	5.8236	-1575.0832	-20.4175

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

$T(K)$	$v_{2\phi}^{\infty}$ ( $cm^3 \cdot g^{-1}$ )	$b_v$ ( $cm^3 \cdot g^{-1}$ )	$b_{vv}$ ( $cm^3 \cdot g^{-1}$ )	$s(Eq.(3))$	$a_{22}$ ( $cm^3 \cdot g^{-1}$ )	$a_{222}$ ( $cm^3 \cdot g^{-1}$ )	$s(Eq.(7))$
298.15	0.9540	-0.00056	0.00023	0.00289	-0.00039	0.00019	0.00060
308.15	0.9589	-0.00055	0.00027	0.00282	-0.00040	0.00017	0.00060
318.15	0.9635	-0.00053	0.00021	0.00274	-0.00038	0.00013	0.00059
328.15	0.9688	-0.00052	0.00022	0.00278	-0.00037	0.00011	0.00057

### List of Symbols

$a_{22}$ , $a_{222}$	Specific virial coefficients in Eq.(7) ( $cm^3.g^{-1}$ ).
$b_v$ , $b_{vv}$	Empirical parameters Eq.(3) ( $cm^3.g^{-1}$ ).
d	Density of solution ( $g.cm^{-3}$ ).
$d_0$	Density of water ( $g.cm^{-3}$ ).
$(\overline{M}_{2,n})$	Viscosity average molecular weight of the solute ( $g.mol^{-1}$ ).
s	Standard error of the estimate by Eqs.(3) and (7).
$\overline{v}_1$	Partial specific volume of the solvent ( $cm^3.g^{-1}$ ).
$\overline{v}_2$	Partial specific volume of the solute ( $cm^3.g^{-1}$ ).
$\overline{v}_2^\infty$	Partial specific volume of the solute at infinite dilution ( $cm^3.g^{-1}$ ).
$U_{1,2}$	Volume of the solution containing 1.0 g of the solvent and w grams of solute ( $cm^3.g^{-1}$ ).
$U_{1,2}^{ex}$	Specific excess volume of the solution ( $cm^3.g^{-1}$ ).
$U_{22}$ , $U_{222}$	Molar virial coefficients in Eq.(9) ( $cm^3.kg.mol^{-2}$ ) and Eq.(10) ( $cm^3.kg^2.mol^{-3}$ ).
$U_{2\phi}$	Apparent specific volume of the solute ( $cm^3.g^{-1}$ ).
$U_{2\phi}^\infty$	Apparent specific volume of the solute at infinite dilution ( $cm^3.g^{-1}$ ).
w	Weight molality .
$\partial w$ , $\partial d$ , $\partial U_{2\phi}$	Uncertainties in the determination of w , d , $U_{2\phi}$ .

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