

Research Article

Volumetric Properties of Aqueous Solutions of Ethylene Glycols in the Temperature Range of 293.15–318.15 K

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Densities of aqueous solutions of Ethylene glycol (EG), diethylene glycol (DEG), and triethylene glycol (TEG) were measured at temperatures from 293.15 to 318.15 K and molalities ranging from 0.0488 to 0.5288 mol·kg⁻¹. Volumes of all investigated solutions at a definite temperature were linearly dependent on the solute molality; from this dependence the partial molar volumes at infinite dilution were determined for all solutes. It was found that the partial molar volumes at infinite dilution ($\bar{V}_{2,0}$) were concentration independent and slightly increase with increasing temperature. The partial molar volumes at infinite dilution ($\bar{V}_{2,0}$) or the limiting apparent molar volumes of ethylene glycols were fitted to a linear equation with the number of oxyethylene groups (n) in the solute molecule. From this equation a constant contribution of the terminal (OH) and the (CH₂CH₂O) groups to the volumetric properties was obtained. The thermal expansion coefficient ($\alpha_{1,2}$) for all investigated solutions was calculated at temperatures from 293.15 to 318.15 K. The thermal expansion coefficients for all solutes increase with increasing temperature and molality. Values of ($\alpha_{1,2}$) were higher than the value of the thermal expansion coefficient of the pure water.

1. Introduction

Mixing effects for thousands of chemical compounds and their mixtures used in industry are rather difficult to be known; hence, knowledge of thermodynamic properties such as densities, as well as excess molar volumes, V^E , partial molar volumes, and apparent molar volumes of organic mixtures at various temperatures, is of great importance. Solvation of a solute in certain solvent and different types of interactions, solute-solvent and solvent-solvent interactions, are of great importance in physical chemistry [1].

Analysis of multicomponent liquid mixtures in terms of mole fraction or molality and their thermodynamic and volumetric properties are important for the design of industrial processes. These properties are also important in the search of models capable of correlating the molecular structure and macroscopic properties of liquids [2]. During the liquid

mixture formation the changes of molecule interactions occur, and difference in the components packing becomes apparent. When there is developed hydrogen bond network in, at least, one of the solvents then the mixture properties change in a special way [3].

The physical properties of liquid mixtures are very important in understanding the nature of molecular interactions between the molecules of liquid mixtures. Such properties of liquid mixtures are useful in designing various transport and process equipments in the chemical industry [4].

An amphiphilic molecule possesses at the same time a polar and nonpolar group. In aqueous solutions, these molecules can self-associate into aggregates called micelles [5], where contact between water and hydrocarbon is greatly reduced while the polar groups maintain their hydration. In this process the main contributions to the free energy are the elimination of unfavorable hydrocarbon-water contacts,

TABLE 1: Physical properties of pure component liquids at 298.15 K^a.

Material	Molar mass (g·mol ⁻¹)	Purity %	ρ (g·cm ⁻³)			n_D		
			Exp.	Lit.	Reference	Exp.	Lit.	Reference
EG	62.07	>99	1.1063	1.1061	[19]	1.4303	1.4304	[20]
DEG	106.12	>99	1.1128	1.1129	[12]	1.4472	1.4467	[20]
TEG	150.18	>99	1.1195	1.1195	[21]	1.4562	1.4561	[22]

^aStandard uncertainties u are $u(T) = 0.01$ K, $u(\rho) = 2.0 \times 10^{-5}$ g·cm⁻³, and $u(n_D) = 2.0 \times 10^{-4}$.

the head-group interactions, and the interaggregate interactions [6, 7].

Hydration properties of solutes, that is, organic molecules and biomolecules in water mixtures, in general, reflect in a complex manner the combined effect of different heterogeneous interactions around the solute. The hydrophilic and hydrophobic hydration and interaction are the central topics in liquid state chemistry and physics. The interface of hydrophilic and hydrophobic effects with each other leads to destructive or, under certain conditions, the cooperative interaction [8].

Ethylene glycols are very interesting solvents owing to the presence of the oxy and hydroxyl groups in the same molecule. Due to this the formation of intra- and intermolecular hydrogen bonds between the -O- and -OH groups of the same or different molecules of ethylene glycols has been observed [9]. Despite their interesting characteristics and industrial importance, thermodynamic properties of mixtures containing ethylene glycols have not been studied extensively enough [10].

In the present work, we report the density of binary mixtures containing ethylene glycol (EG), diethylene glycol (DEG), and triethylene glycol (TEG) with water at temperatures ranging between 298.15 and 318.15 K. Values of densities are correlated with temperature and molality. The experimental data have been used to calculate the partial molar volumes and thermal expansion coefficients.

2. Experimental

2.1. Chemicals. All the solvents used were of analytical grade and purchased from Fluka AG. Densities and refractive indices of the pure liquids were measured and the results are listed in Table 1 together with the literature data for comparison. These liquids were kept over freshly activated molecular sieves of type 4.A (Union Carbide) for several days before use to reduce the water content. Table 1 reported some chemical and physical properties of all chemicals used in this study.

2.2. Preparation of Solutions. All solutions were prepared by dissolving the appropriate amount (by mass) of each solute in deionized distilled water. Solutions of different molalities ranging from 0.0466 to 0.5297 mol·kg⁻¹ for each solute were prepared in a 25 cm³ volumetric flask, using digital balance (Sartorius BL210 S) accurate to within ± 0.0001 g. All solutions were left at least 24 hrs before measurements to attain equilibrium. Densities, ρ , and refractive indices, n_D ,

of the pure liquids are compared with the published data (Table 1).

2.3. Density Measurements. An Anton Paar digital densimeter (model DMA 60/601) was employed for the determination of the densities of pure component liquids and the binary mixtures. The density measurements are based on the variation of the natural frequency of a tube oscillator filled with sample liquid with respect to the air. The measuring cell is embodied in its separate housing, complete with oscillator counter mass and thermostat connectors. The oscillator or sample tube, made of borosilicate glass, is fused into a dual-wall glass cylinder, thus allowing temperature control to be carried out by water circulation from a constant temperature path. The temperature of the water path was kept constant to within 0.01 K with Haake digital thermostat. The precision of density measurements is estimated to be better than 10⁻⁴ (g·cm⁻³).

3. Results and Discussion

3.1. Density. The experimental measured densities of binary mixtures of (water + ethylene glycols) at 293.15, 298.15, 303.15, 308.15, 313.15, and 318.15 K are listed in Table 2. The obtained results of the densities of all binary mixtures are plotted as a function of the molality of solution (m/mol·kg⁻¹), (Figure 1). Density values at different temperatures for the aqueous solutions of ethylene glycols are in a good agreement with those published by Sun and Teja [11] and Müller and Rasmussen [12].

Experimental densities for the various binary mixtures in the molality ranges studied obey equation of the type [13]

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

The a , b , and c coefficients for the (ρ) versus (m) plots are shown in Table 3 together with the standard deviation, σ , defined by

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

where (ρ_{obs}) and (ρ_{cal}) are the observed and calculated density values, respectively, N is the number of experimental points and P is the number of coefficients in (1). Fitted values of the constant (a) in (1) compare well with the average density of water for the various density determinations of water obtained during the set of experiments performed for each solute at each temperature.

TABLE 2: Experimental densities ρ ($\text{g}\cdot\text{cm}^{-3}$) for all aqueous binary mixtures at different temperatures.

m (mol/kg)	293.15 K	298.15 K	ρ ($\text{g}\cdot\text{cm}^{-3}$) 303.15 K	308.1 K	313.15 K	318.15 K
EG						
0.0000	0.99823	0.99708	0.99561	0.99400	0.99222	0.99022
0.0488	0.99838	0.99716	0.99577	0.99419	0.99240	0.99033
0.0982	0.99890	0.99760	0.99601	0.99451	0.99278	0.99090
0.1561	0.99923	0.99780	0.99640	0.99497	0.99312	0.99114
0.2365	0.99965	0.99840	0.99698	0.99541	0.99361	0.99138
0.2726	0.99989	0.99876	0.99730	0.99575	0.99399	0.99186
0.3143	1.00031	0.99906	0.99752	0.99601	0.99425	0.99228
0.3796	1.00075	0.99945	0.99798	0.99640	0.99473	0.99260
0.4268	1.00103	0.99977	0.99830	0.99676	0.99495	0.99302
0.5201	1.00163	1.00041	0.99894	0.99740	0.99553	0.99351
DEG						
0.0000	0.99823	0.99708	0.99561	0.99400	0.99222	0.99022
0.0517	0.99893	0.99764	0.99604	0.99481	0.99294	0.99075
0.1112	0.99998	0.99885	0.99736	0.99559	0.99366	0.99159
0.1505	1.00050	0.99939	0.99805	0.99638	0.99435	0.99294
0.1965	1.00110	0.99979	0.99843	0.99660	0.99521	0.99340
0.2618	1.00199	1.00080	0.99929	0.99730	0.99577	0.99399
0.3103	1.00247	1.00160	0.99981	0.99799	0.99612	0.99441
0.3472	1.00295	1.00184	1.00012	0.99843	0.99658	0.99477
0.4235	1.00410	1.00293	1.00128	0.99992	0.99774	0.99579
0.4602	1.00484	1.00353	1.00221	1.00060	0.99893	0.99666
0.5017	1.00550	1.00432	1.00285	1.00128	0.99941	0.99732
TEG						
0.0000	0.99823	0.99717	0.99587	0.99392	0.99187	0.99002
0.0538	0.99943	0.99828	0.99697	0.99496	0.99269	0.99108
0.0994	1.00069	0.99971	0.99824	0.99645	0.99452	0.99271
0.1543	1.00158	1.00077	0.99935	0.99742	0.99549	0.99396
0.2001	1.00272	1.00140	1.00005	0.99834	0.99653	0.99416
0.2552	1.00403	1.00283	1.00128	0.99945	0.99764	0.99585
0.3192	1.00494	1.00389	1.00285	1.00092	0.99913	0.99752
0.3686	1.00564	1.00512	1.00341	1.00178	0.99977	0.99818
0.4366	1.00743	1.00630	1.00498	1.00319	1.00128	0.99915
0.4804	1.00878	1.00743	1.00586	1.00401	1.00192	0.99993
0.5288	1.00942	1.00801	1.00667	1.00484	1.00293	1.00092

^aStandard uncertainties u are: $u(T) = 0.01$ K, $u(\rho) = 2.0 \times 10^{-5}$ $\text{g}\cdot\text{cm}^{-3}$.

3.2. Partial Molar Volumes. The volumes of the investigated solutions, $V_{1,2}$ (cm^3), containing m moles of solute per kilogram of solvent, were calculated from [14]

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

where M_2 ($\text{g} \cdot \text{mol}^{-1}$) is the solute molecular weight and (ρ) is the density of solution. The values of $(V_{1,2})$ for investigated solutions are increased with increasing concentration. Figure 2 shows the plots of $(V_{1,2})$ versus (m) for all investigated solutes. We can reasonably assume that a “substitutional” mixing occurs for water + EGs systems,

which transform gradually to an “interstitial” accommodation due to the possible cavity occupation by the hydrocarbon chain, the polar character of the second (OH) group getting progressively less important. Reinforcement of the water structure becomes more and more important from water + EG to water + TEG systems.

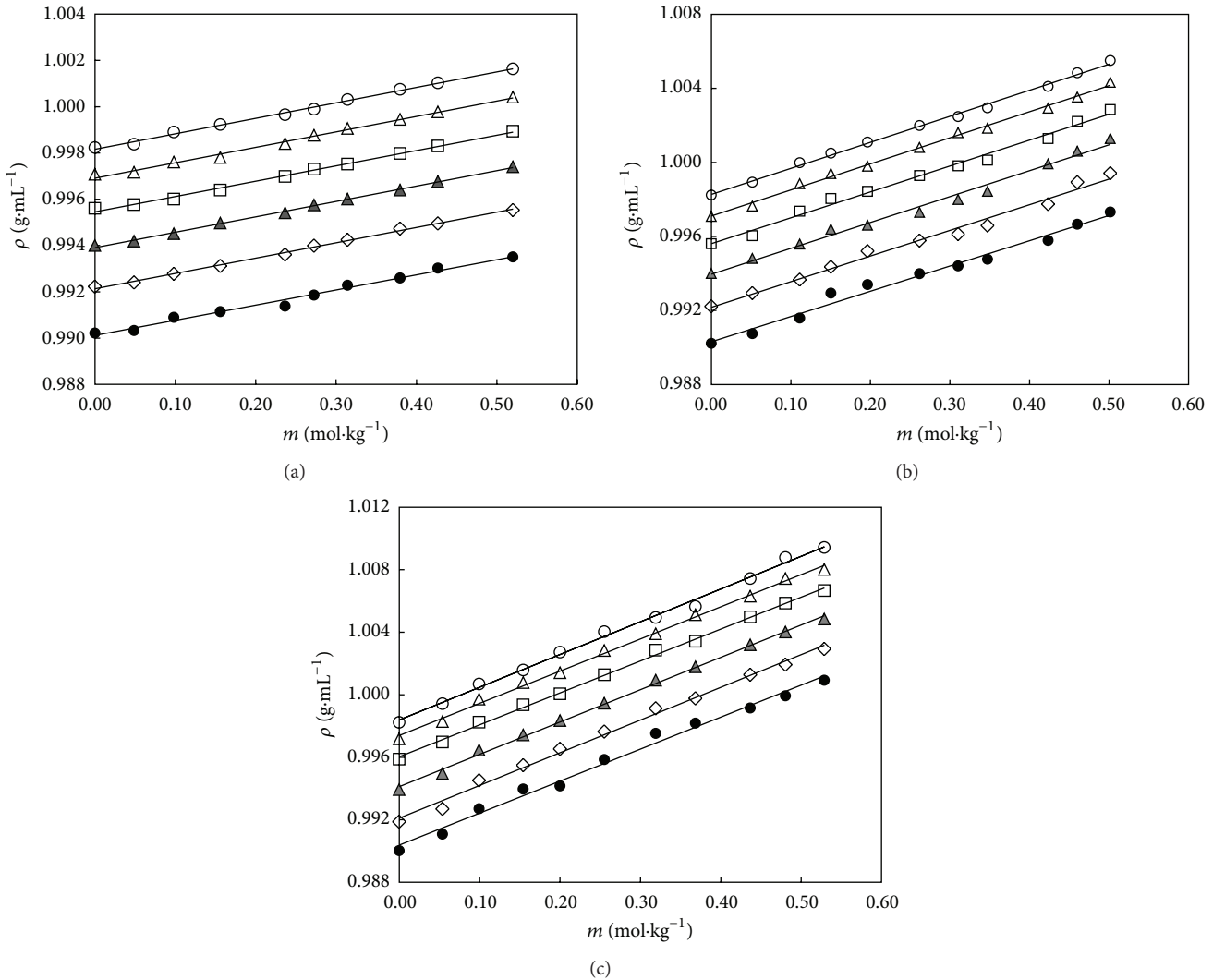
The concentration dependence of $V_{1,2}$ can be described by [15]

$$V_{1,2} = V_S^0 + \bar{V}_{2,0}m + \nu_{22}m^2 + \nu_{222}m^3 + \dots, \quad (4)$$

where $(V_S^0 = 1000/\rho_1^\phi)$, ρ_1^ϕ ($\text{g}\cdot\text{cm}^{-3}$) is the density of the pure solvent, $\bar{V}_{2,0}$ ($\text{cm}^3\cdot\text{mol}^{-1}$) is the partial molar volume of solute at infinite dilution, and ν_{22} , ν_{222} , and so forth are the virial

TABLE 3: Parameters in (1), $a/(\text{g}\cdot\text{cm}^{-3})$, $b/(\text{g}\cdot\text{cm}^{-3}\cdot\text{mol}^{-1}\cdot\text{kg})$, and $c/(\text{g}\cdot\text{cm}^{-3}\cdot\text{mol}^{-2}\cdot\text{kg}^2)$ for all solutes together with (σ) values.

Temperature	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
EG						
a	0.99820	0.99705	0.99558	0.99397	0.99214	0.99016
b	0.0060	0.0037	0.0042	0.0055	0.0065	0.0061
c	0.0017	0.0087	0.0070	0.0034	0.0001	0.0008
σ	0.0001	0.0004	0.0003	0.0002	0.0001	0.0001
DEG						
a	0.99832	0.99708	0.99565	0.99423	0.99236	0.99022
b	0.0134	0.0143	0.0134	0.0105	0.0115	0.0148
c	0.0013	-0.0004	0.0012	0.0067	0.0047	-0.0024
σ	0.0001	0.0002	0.0003	0.0002	0.0003	0.0003
TEG						
a	0.99836	0.99721	0.99589	0.99391	0.99176	0.99009
b	0.0213	0.0228	0.0223	0.0234	0.0253	0.0257
c	-0.0006	-0.0042	-0.0034	-0.0051	-0.0083	-0.0098
σ	0.0003	0.0002	0.0002	0.0001	0.0003	0.0003

FIGURE 1: Density-concentration curves for aqueous solutions of (a) EG, (b) DEG, and (c) TEG, at temperatures, $T/K = 293.15$, \circ ; $T/K = 298.15$, \triangle ; $T/K = 303.15$, \square ; $T/K = 308.15$, \blacktriangle ; $T/K = 313.15$, \diamond ; $T/K = 318.15$ K, \bullet .

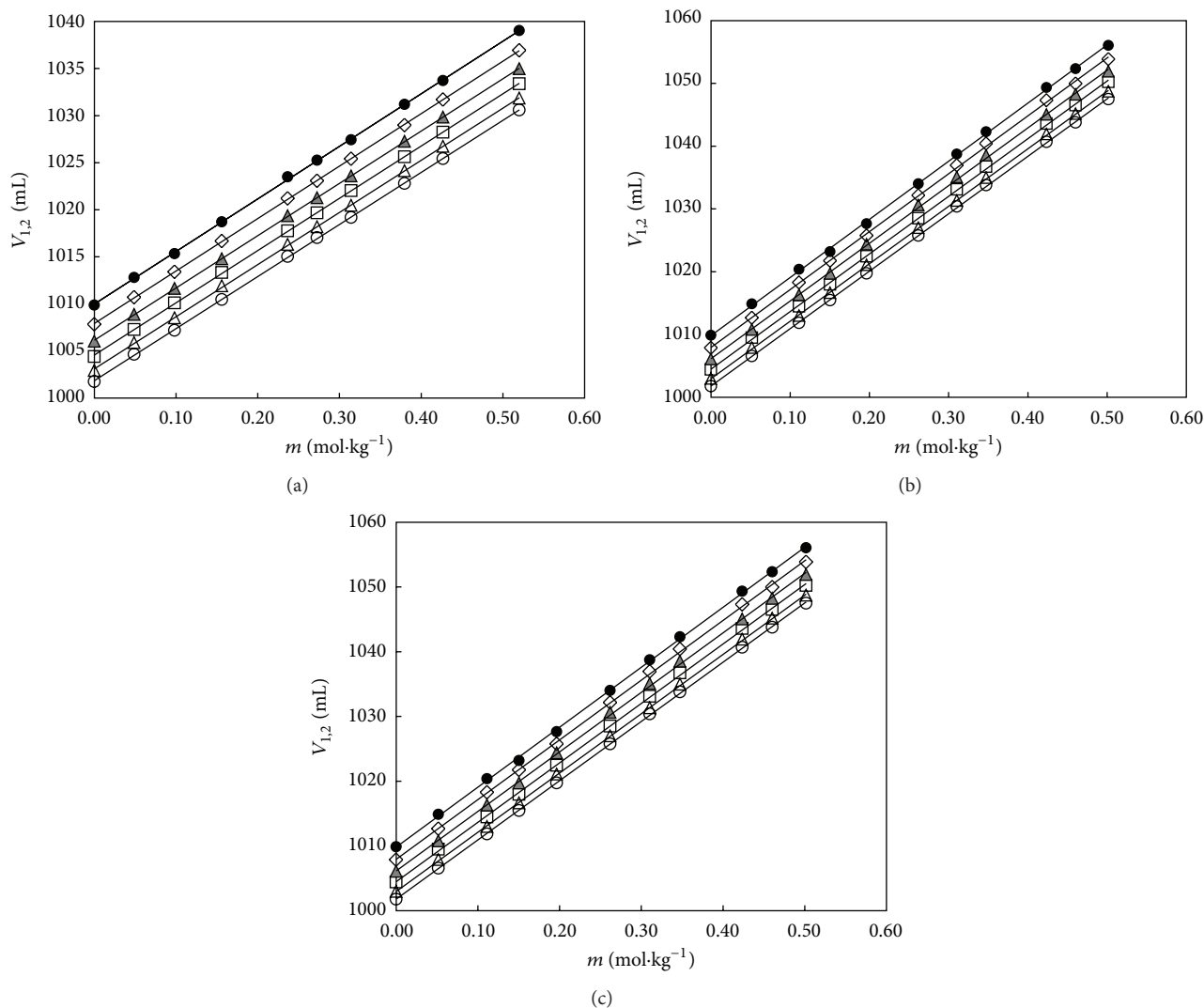


FIGURE 2: Volumes of aqueous solutions containing m mole of solute per kg of solvent: (a) EG, (b) DEG, and (c) TEG, at temperatures, $T/K = 293.15$, \circ ; $T/K = 298.15$, \triangle ; $T/K = 303.15$, \square ; $T/K = 308.15$, \diamond ; $T/K = 313.15$, \blacktriangle ; $T/K = 318.15$ K, \bullet .

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 solutions, it was found that the volumes of solution at a definite temperature for each solute are linearly dependent on the concentration of solute; that is, the relation (4) is reduced to

$$V_{1,2} = V_S^0 + \bar{V}_{2,0}m. \quad (5)$$

From this relation the partial molar volume at infinite dilution ($\bar{V}_{2,0}$) for each solute at a definite temperature can be determined from the plots of ($V_{1,2}$) as a function of molality (m) (Figure 2). The values of ($\bar{V}_{2,0}$) together with the standard errors are given in Table 4. The values of ($\bar{V}_{2,0}$) are concentration independent and slightly increase with increasing temperature.

The partial molar volumes at infinite dilution or the limiting apparent molar volumes of EG oligomers can be fitted by the linear equations:

$$\begin{aligned} \bar{V}_{2,0} &= 36.34n + 18.92 & (293.15 \text{ K}), \\ \bar{V}_{2,0} &= 36.52n + 18.76 & (298.15 \text{ K}), \\ \bar{V}_{2,0} &= 36.55n + 18.86 & (303.15 \text{ K}), \\ \bar{V}_{2,0} &= 36.62n + 18.85 & (308.15 \text{ K}), \\ \bar{V}_{2,0} &= 36.67n + 18.96 & (313.15 \text{ K}), \\ \bar{V}_{2,0} &= 36.87n + 18.92 & (318.15 \text{ K}), \\ & & (1 \leq n \leq 3), \end{aligned} \quad (6)$$

where n is the number of oxyethylene ($\text{CH}_2\text{CH}_2\text{O}$) groups in the molecule. These equations outline a constant contribution

TABLE 4: Partial molar volumes at infinite dilution ($\bar{V}_{2,0}$) for all aqueous binary mixtures at different temperatures.

Temperature	$\bar{V}_{2,0} \text{ (cm}^3 \cdot \text{mol}^{-1}\text{)}$					
	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
EG	55.29 \pm 0.08	55.37 \pm 0.10	55.47 \pm 0.08	55.53 \pm 0.06	55.67 \pm 0.07	55.82 \pm 0.14
DEG	91.53 \pm 0.15	91.60 \pm 0.15	91.83 \pm 0.25	91.96 \pm 0.29	92.23 \pm 0.31	92.60 \pm 0.32
TEG	127.97 \pm 0.26	128.40 \pm 0.19	128.57 \pm 0.17	128.76 \pm 0.15	129.01 \pm 0.26	129.55 \pm 0.34

TABLE 5: Partial molecular volumes at infinite dilution $\bar{v}_{2,0}$, molecular volumes of pure solutes v_2^0 , excess partial molecular volumes at infinite dilution $\bar{v}_{2,0}^{\text{exc}}$, and the ratio ($\bar{v}_{2,0}/v_2^0$).

Temperature/K	293.15	298.15	303.15	308.15	313.15	318.15
EG						
$\bar{v}_{2,0} \times 10^{23} \text{ cm}^3 \cdot \text{molecule}^{-1}$	9.1813	9.1946	9.2112	9.2212	9.2444	9.2693
$v_2^0 \times 10^{23} \text{ cm}^3 \cdot \text{molecule}^{-1}$	9.3227	9.3168	9.3109	9.3051	9.2992	9.2933
$\bar{v}_{2,0}/v_2^0$	0.9848	0.9869	0.9893	0.9910	0.9941	0.9974
$\bar{v}_{2,0}^{\text{exc}} \times 10^{24} \text{ cm}^3 \cdot \text{molecule}^{-1}$	-0.1414	-0.1222	-0.0997	-0.0839	-0.0548	-0.0240
DEG						
$\bar{v}_{2,0} \times 10^{23} \text{ cm}^3 \cdot \text{molecule}^{-1}$	15.1993	15.2109	15.2491	15.2707	15.3155	15.3770
$v_2^0 \times 10^{23} \text{ cm}^3 \cdot \text{molecule}^{-1}$	15.8604	15.8500	15.8396	15.8292	15.8189	15.8085
$\bar{v}_{2,0}/v_2^0$	0.9583	0.9597	0.9627	0.9647	0.9682	0.9727
$\bar{v}_{2,0}^{\text{exc}} \times 10^{24} \text{ cm}^3 \cdot \text{molecule}^{-1}$	-0.6611	-0.6391	-0.5905	-0.5585	-0.5034	-0.4315
TEG						
$\bar{v}_{2,0} \times 10^{23} \text{ cm}^3 \cdot \text{molecule}^{-1}$	21.2504	21.3218	21.3500	21.3816	21.4231	21.5128
$v_2^0 \times 10^{23} \text{ cm}^3 \cdot \text{molecule}^{-1}$	22.2920	22.2765	22.2610	22.2455	22.2300	22.2146
$\bar{v}_{2,0}/v_2^0$	0.9533	0.9571	0.9591	0.9612	0.9637	0.9684
$\bar{v}_{2,0}^{\text{exc}} \times 10^{24} \text{ cm}^3 \cdot \text{molecule}^{-1}$	-1.0416	-0.9547	-0.9110	-0.8639	-0.8069	-0.7018

of the oxyethylene ($\text{CH}_2\text{CH}_2\text{O}$) group and the terminal (OH) group to the volumetric properties. The linearity of ($\bar{V}_{2,0}$) with n and then with the molecular weight, is typical for rod-like molecules, and, on the other hand, it is reasonable to hypothesize this shape for the first oligomer molecules. The volume contribution value for the ethoxyl group ranging from 36.34 to 36.87 $\text{cm}^3 \cdot \text{mol}^{-1}$ is in a good agreement with the value reported by Vergara et al. [17] (37.18 $\text{cm}^3 \cdot \text{mol}^{-1}$) or that reported by Kirinčić and Klofutar [18] (36.9 $\text{cm}^3 \cdot \text{mol}^{-1}$) or the value derived from group contribution theory (36.1 $\text{cm}^3 \cdot \text{mol}^{-1}$). Furthermore this value increases with increasing temperature which suggests that the contribution of the oxyethylene group increase with temperature. The average value of hydroxyl group contribution is 18.88 $\text{cm}^3 \cdot \text{mol}^{-1}$ which is a comparable amount with the literature value (17.54 $\text{cm}^3 \cdot \text{mol}^{-1}$) [17].

The partial molecular volumes at infinite dilution ($\text{cm}^3 \cdot \text{molecule}^{-1}$) for the investigated liquid solutes at 298.15 K were calculated from:

$$\bar{v}_{2,0} = \frac{\bar{V}_{2,0}}{N_A}, \quad (7)$$

where N_A is Avogadro's constant. The molecular volumes of the pure liquid solutes ($\text{cm}^3 \cdot \text{molecule}^{-1}$) at 298.15 K were calculated from

$$v_2^0 = \frac{M_2}{\rho_2^\phi N_A}, \quad (8)$$

where (ρ_2^ϕ) is the density of the pure solute. A comparison of the partial molecular volumes at infinite dilution ($\bar{v}_{2,0}$) for all solutes with their molecular volumes (v_2^0) shows that the former are smaller than the latter. Values of $\bar{v}_{2,0}$ and v_2^0 together with the values of their ratio ($\bar{v}_{2,0}/v_2^0$) are given in Table 5. The values of the partial excess molecular volumes were calculated from

$$\bar{v}_{2,0}^{\text{exc}} = \bar{v}_{2,0} - v_2^0. \quad (9)$$

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 increase in magnitude with increasing oxyethylene units, and decrease with increasing temperature.

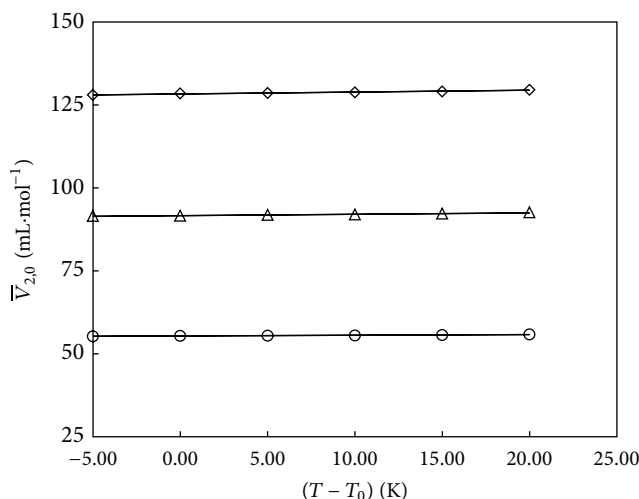


FIGURE 3: The temperature dependence of the partial molar volume at infinite dilution for aqueous solutions of (○ EG; △ DEG; ◇ TEG).

TABLE 6: Regression coefficients of (10) and the ratio (a_1/a_0) at the temperature range studied.

Solute	a_0	a_1	$(a_1/a_0) \times 10^4/\text{K}^{-1}$	R^2
EG	55.37	0.021	3.793	0.978
DEG	91.64	0.042	4.583	0.953
TEG	128.28	0.057	4.443	0.964

3.3. Thermal Expansion Coefficients. The partial molar volumes at infinite dilution for all investigated aqueous solutions, listed in Table 4, are slightly temperature dependent. From Figure 3 it can be seen that the plots of ($\bar{V}_{2,0}$) against ($T - T_0$) are linear, so it can be described by

$$\bar{V}_{2,0} = a_0 + a_1 (T - T_0), \quad (10)$$

where a_0 and a_1 are empirical constants and T is the absolute temperature; $T_0 = 298.15$ K. The coefficients a_0 and a_1 , determined by the method of least squares, are given in Table 6.

As the partial molar volumes of all investigated solutes in water are concentration independent and equal to their volumes at infinite dilution, so the values of the partial molar expansibility of the solute ($\bar{E}_2 = (\partial \bar{V}_2 / \partial T)_P$) ($\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) are also concentration independent and equal to their values 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 (10), and the thermal expansion coefficient of the solute at infinite dilution ($\alpha_{2,0}$) (K^{-1}) is defined as [14]

$$\alpha_{2,0} = \frac{1}{\bar{V}_{2,0}} \left(\frac{\partial \bar{V}_{2,0}}{\partial T} \right)_P = \frac{\bar{E}_{2,0}}{\bar{V}_{2,0}} \quad (11)$$

which is equal to the ratio a_1/a_0 . The values of ($\alpha_{2,0}$) calculated from (11) are given in Table 7. 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

$$\alpha_{1,2} = \frac{1}{V_{1,2}} \left(\frac{\partial V_{1,2}}{\partial T} \right)_P, \quad (12)$$

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 solutions is calculated from

$$\alpha_{1,2} = \frac{1}{V_{1,2}} \left(\frac{10^3}{\rho_1^\phi} \alpha_1^0 + m \bar{E}_{2,0} \right), \quad (13)$$

where α_1^0 is the thermal expansion coefficient of pure water.

The values of $\alpha_{1,2}$ for all investigated solutions are given in Table 8. The thermal expansion coefficients for all solutes increase with increasing temperature and molality. The dependence of ($\alpha_{1,2} - \alpha_1^0$) against the volume fraction of solute (Φ) is shown in Figure 4. 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

$$\Phi = \frac{m \bar{V}_{2,0}}{1000/\rho_1^\phi + m \bar{V}_{2,0}}. \quad (14)$$

From Figure 4, it can be seen that the dependence of ($\alpha_{1,2} - \alpha_1^0$) on (Φ) is linear. This dependence may be expressed in the form [14]

$$\alpha_{1,2} - \alpha_1^0 = (\alpha_{2,0} - \alpha_1^0) \Phi. \quad (15)$$

TABLE 7: Thermal expansion coefficients at infinite dilution ($\alpha_{2,0}$) at the temperature range studied.

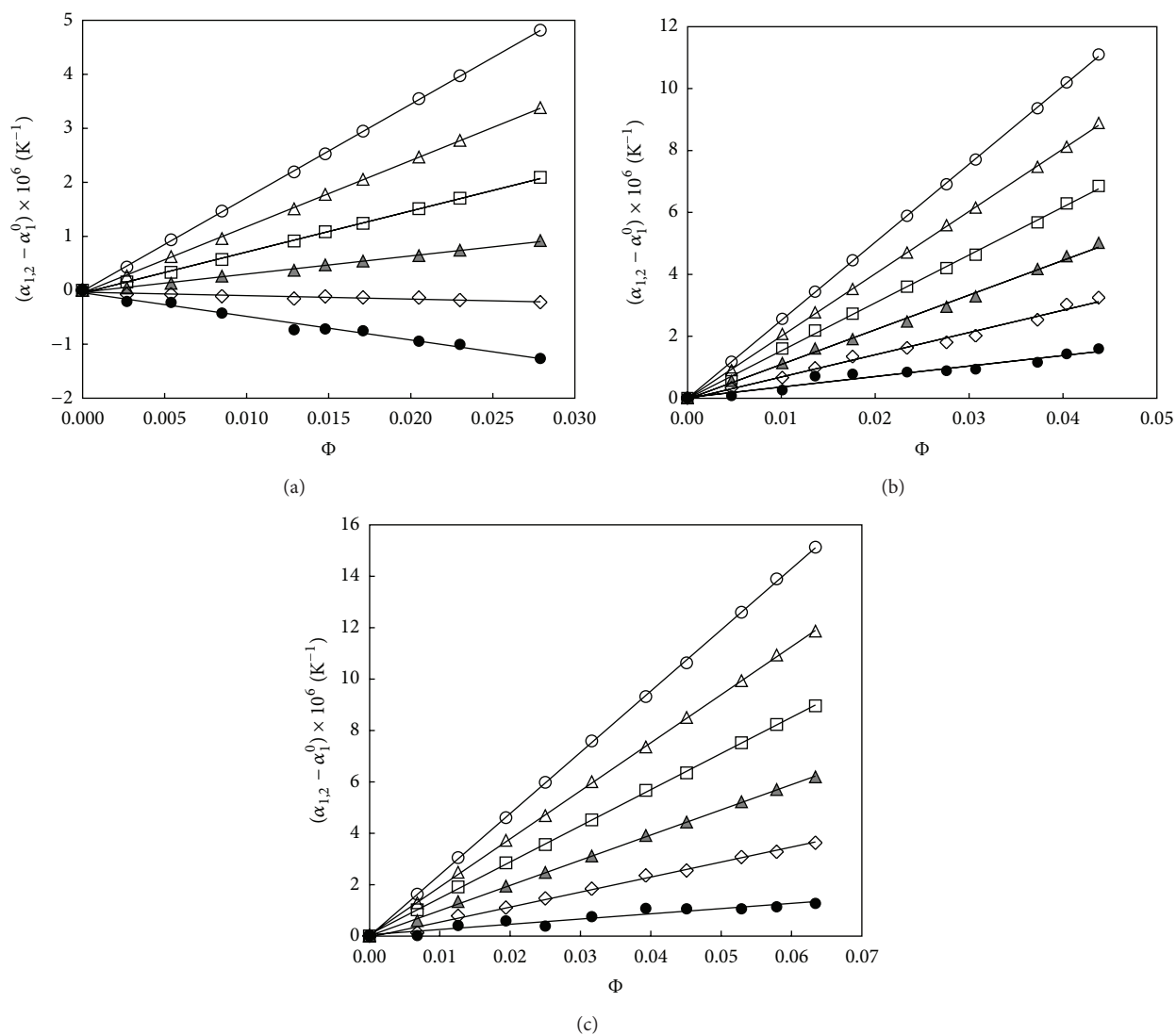
Solute	$\alpha_{2,0} \times 10^4 \text{ (K}^{-1}\text{)}$					
	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
EG	3.798	3.793	3.786	3.782	3.772	3.762
DEG	4.589	4.585	4.574	4.567	4.554	4.536
TEG	4.454	4.439	4.433	4.427	4.418	4.400

TABLE 8: Values of the thermal expansion coefficients $\alpha_{1,2} \times 10^4 \text{ (K}^{-1}\text{)}$ and the volume fraction (Φ) of the investigated solutions.

$m/(\text{mol}\cdot\text{kg}^{-1})$	Φ	$\alpha_{2,0} \times 10^4 \text{ (K}^{-1}\text{)}$					
		293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
EG							
0.0000	0.0000	2.0666	2.5690	3.0263	3.4464	3.8352	4.1974
0.0488	0.0027	2.0709	2.5716	3.0278	3.4468	3.8345	4.1953
0.0982	0.0054	2.0759	2.5752	3.0296	3.4477	3.8345	4.1951
0.1561	0.0085	2.0813	2.5786	3.0320	3.4490	3.8341	4.1931
0.2365	0.0129	2.0885	2.5840	3.0354	3.4501	3.8336	4.1901
0.2726	0.0148	2.0919	2.5867	3.0371	3.4511	3.8341	4.1902
0.3143	0.0171	2.0960	2.5895	3.0387	3.4518	3.8339	4.1899
0.3796	0.0205	2.1021	2.5937	3.0414	3.4528	3.8338	4.1879
0.4268	0.0230	2.1063	2.5967	3.0433	3.4538	3.8334	4.1873
0.5201	0.0279	2.1148	2.6028	3.0472	3.4556	3.8330	4.1847
DEG							
0.0000	0.0000	2.0666	2.5690	3.0263	3.4464	3.8352	4.1974
0.0517	0.0047	2.0783	2.5780	3.0326	3.4519	3.8385	4.1981
0.1112	0.0101	2.0922	2.5896	3.0423	3.4576	3.8418	4.2000
0.1505	0.0136	2.1010	2.5967	3.0481	3.4623	3.8449	4.2045
0.1965	0.0176	2.1111	2.6042	3.0536	3.4654	3.8486	4.2052
0.2618	0.0234	2.1255	2.6160	3.0623	3.4710	3.8514	4.2058
0.3103	0.0276	2.1357	2.6248	3.0683	3.4758	3.8532	4.2062
0.3472	0.0307	2.1436	2.6304	3.0726	3.4791	3.8553	4.2067
0.4235	0.0372	2.1603	2.6437	3.0831	3.4880	3.8605	4.2090
0.4602	0.0403	2.1686	2.6502	3.0892	3.4921	3.8654	4.2117
0.5017	0.0438	2.1776	2.6578	3.0948	3.4965	3.8677	4.2133
TEG							
0.0000	0.0000	2.0666	2.5690	3.0263	3.4464	3.8352	4.1974
0.0538	0.0068	2.0829	2.5818	3.0365	3.4522	3.8365	4.1975
0.0994	0.0126	2.0971	2.5937	3.0454	3.4597	3.8431	4.2015
0.1543	0.0194	2.1127	2.6061	3.0548	3.4657	3.8463	4.2033
0.2001	0.0250	2.1264	2.6157	3.0618	3.4710	3.8498	4.2012
0.2552	0.0316	2.1425	2.6289	3.0715	3.4774	3.8536	4.2049
0.3192	0.0393	2.1598	2.6425	3.0830	3.4854	3.8587	4.2081
0.3686	0.0451	2.1729	2.6540	3.0898	3.4906	3.8607	4.2079
0.4366	0.0529	2.1926	2.6682	3.1015	3.4985	3.8659	4.2080
0.4804	0.0579	2.2055	2.6783	3.1086	3.5033	3.8680	4.2087
0.5288	0.0634	2.2179	2.6876	3.1159	3.5082	3.8715	4.2101

TABLE 9: Values of $(\alpha_{2,0} - \alpha_1^0)$ for all investigated solutions together with correlation coefficients (r^2).

Solute	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
EG	173.20	122.48	76.06	33.61	-6.31	-43.62
r^2	1.000	1.000	0.999	0.997	0.949	0.994
DEG	252.17	201.55	154.80	112.05	72.00	33.94
r^2	1.000	1.000	1.000	0.999	0.997	0.984
TEG	238.440	188.028	142.244	98.288	57.440	21.432
r^2	1.000	1.000	1.000	1.000	0.998	0.976

FIGURE 4: Dependence of $(\alpha_{1,2} - \alpha_1^0)$ on volume fraction of solute (Φ) for: (a) EG, (b) DEG, and (c) TEG, at temperatures, $T/K = 293.15$, \circ ; $T/K = 298.15$, \triangle ; $T/K = 303.15$, \square ; $T/K = 308.15$, \blacktriangle ; $T/K = 313.15$, \diamond ; $T/K = 318.15$ K, \bullet .

The calculated values of $(\alpha_{1,2} - \alpha_1^0)$ are given in Table 9. From Figure 4 and Table 9 it can be seen that the values of the thermal expansion coefficient of the investigated solutions are higher than those of the pure solvent except in the case of ethylene glycol at higher temperatures (313.15 and 318.15 K) where the thermal expansion coefficient of the solution is lower than that of the pure solvent. The low values for TEG

may be indicative of the presence of entanglements of the chain in a coiled structure [17].

4. Conclusions

Density data and molar volumes as a function of temperature and molality are measured for aqueous solutions of ethylene

glycol, diethylene glycol, and triethylene glycol. These data were used to derive the partial molar volume at infinite dilution ($\bar{V}_{2,0}$). $\bar{V}_{2,0}$ values were found to be slightly increased with increasing temperature. These values are correlated with the number of oxyethylene ($\text{CH}_2\text{CH}_2\text{O}$) groups in the molecule (n). It was assumed that a constant contribution of the terminal (OH) group and ($\text{CH}_2\text{CH}_2\text{O}$) group to the volumetric properties of these mixtures. The values of the partial excess molecular volumes ($\bar{v}_{2,0}^{\text{exc}}$) were also calculated. These values are negative and increase in magnitude with increasing oxyethylene units and decreasing temperature.

The thermal expansion coefficients ($\alpha_{1,2}$) for all solutes increase with increasing temperature and molality. It was found that the values of the thermal expansion coefficient of the investigated solutions are higher than those of the pure solvent except in the case of ethylene glycol at higher temperatures (313.15 and 318.15 K) where the thermal expansion coefficient of the solution is lower than that of the pure solvent.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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