Volumetric Properties of Mono-, Di-, Tri-, and Polyethylene Glycol Aqueous Solutions from (273.15 to 363.15) K: Experimental Measurements and Correlations

3 AUTHORS:

Waheed Afzal
University of Aberdeen
49 PUBLICATIONS   **366** CITATIONS

SEE PROFILE

Amir H. Mohammadi
550 PUBLICATIONS   **4,800** CITATIONS

SEE PROFILE

Dominique Richon
Aalto University
532 PUBLICATIONS   **6,591** CITATIONS

SEE PROFILE

Article

Volumetric Properties of Mono-, Di-, Tri-, and Polyethylene Glycol Aqueous Solutions from (273.15 to 363.15) K: Experimental Measurements and Correlations

Waheed Afzal, Amir H. Mohammadi, and Dominique Richon

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

Volumetric Properties of Mono-, Di-, Tri-, and Polyethylene Glycol Aqueous Solutions from (273.15 to 363.15) K: Experimental Measurements and Correlations

Waheed Afzal, Amir H. Mohammadi, and Dominique Richon*

MINES ParisTech, CEP/TEP, Centre Energétique et Procédés, 35 Rue Saint Honoré, 77305 Fontainebleau, France

Densities and excess molar volume data for various glycol (mono-, di-, tri-, and polyethylene glycol-400) aqueous solutions have been measured over wide ranges of compositions and temperatures generally from (273.15 to 363.15) K at atmospheric pressure. All the measurements were performed using a digital vibrating tube densimeter. Densities of mono-, di-, and triethylene glycol in pure form and those of polyethylene glycol (400) are correlated using the Daubert et al. correlation. Excess molar volumes of glycol aqueous solutions have been correlated with mole fraction polynomials. For all the studied systems, excess molar volumes are found to be negative, increasing from monoethylene glycol to polyethylene glycol-400.

Introduction

Glycols or *diol*s are chemical compounds containing two hydroxyl (−OH) groups. They can be derived from ethylene oxide and are described with the general formula HO-CH$_2$-CH$_2$-(O-CH$_2$-CH$_2$)$_n$-OH where n defines various glycols. For $n = 0$, it is monoethylene glycol (MEG) or simply ethylene glycol; for $n = 1$, it is diethylene glycol (DEG); for $n = 2$, it is triethylene glycol (TEG); and for $n = 3$, it is tetraethylene glycol (TTEG) and so on. The higher numbers for n describe a nontoxic polymer called polyethylene glycol (PEG) which is often specified by its average molar mass. Glycols are very important chemicals widely used in various industrial sectors, such as automotive, aviation, explosives, textiles, coatings, food, pharmaceuticals, cosmetics, natural gas processing, petroleum and petrochemicals, flue gas treatment, air conditioning systems, household, etc. Glycols are the most commonly used desiccants in gas dehydration for typical applications where dew point depressions are of the order of (30 to 70) K. They are completely soluble in liquid water, alcohols, and ethers due to hydrogen−oxygen bonds. Lower molar mass glycols are also used as inhibitors for gas hydrate (and ice) formation in gas pipelines and process equipment to avoid blockage and excessive pressure drop. The volumetric properties of the aqueous mixtures are scientifically important because of their link with the size and shape of the molecules, the intermolecular forces, geometrical packing, free volume, and fluid associations.[1−6]

The subject of densities of glycol aqueous solutions has attracted several authors.[1−19] Volumetric properties of glycol (MEG, DEG, TEG, and TTEG) aqueous solutions were studied by Morénas and Douhéret[1] at 298.15 K for all the glycol aqueous solutions except for MEG aqueous solution for which they reported the data from (288.15 to 308.15) K at three isotherms. Volumetric properties of glycol (MEG, DEG, TEG, TTEG, PEGs) aqueous solutions were further studied by Müller and Rasmussen;[2] however, their study is limited to four isotherms from (298.15 to 328.15) K over a wide concentration range. Obermeier et al.[3] and Bohne et al.[4] studied certain physical properties including density of glycol (MEG, DEG, and TEG) aqueous solutions over wide temperature and limited concentration ranges. However, they did not report the data in the form of any table. George and Sastry[5] presented density and some

other physical properties of glycol (MEG, DEG, and TEG) aqueous solutions from (298.15 to 348.15) K over wide concentration ranges. They provided only the mathematical and graphical representation of their data without any tabulated data. Sun and Teja[6] extended the temperature range of the density and some other physical property data from (290.15 to 450.15) K on nine isotherms for glycol (MEG, DEG, and TEG) aqueous solutions, but they worked only on three concentrations. There are also several studies on volumetric properties of single glycol aqueous solutions, most of them on limited temperatures and/or concentrations. Ray and Némethy[7] reported density and partial molar volumes of MEG aqueous solutions at (298.1 and 311.6) K in the mathematical and graphical forms. Hout et al.[8] presented a rather more detailed thermodynamic study of MEG aqueous solutions at (278.15, 298.15, and 318.15) K. They[8] did not report any tabulated density

Table 1. Chemical Information (Supplier, Purity, and CAS Registry Numbers)

chemical	supplier	purity %	CAS Registry no.
monoethylene glycol	Sigma-Aldrich	> 99	107-21-1
diethylene glycol	Sigma-Aldrich	99	111-46-6
triethylene glycol	Sigma-Aldrich	99	112-27-6
polyethylene glycol-400	BASF (Pluriol-E400)	> 99	25322-68-3

Table 2. Molar Distribution of Various Glycols Constituting PEG-400 Used in This Work[a]

constituents of PEG-400	$f(M_m)$/mole %
triethylene glycol	0.1
tetraethylene glycol	0.7
pentaethylene glycol	2.1
hexaethylene glycol	7.2
heptaethylene glycol	14.4
octaethylene glycol	19.1
nonaethylene glycol	19.2
decaethylene glycol	15.7
undecaethylene glycol	10.2
dodecaethylene glycol	5.9
tridecaethylene glycol	3.4
tetradecaethylene glycol	1.5
pentadecaethylene glycol	0.5
mean molar mass of PEG-400/g·mol^{-1}	414.5

[a] Source: Institut Français du Pétrole (IFP).

* Corresponding author. E-mail: dominique.richon@mines-paristech.fr. Tel.: +(33) 1 64 69 49 65. Fax: +(33) 1 64 69 49 68.

Table 3. Experimental and Literature Densities, ρ, at Various Temperatures, T, for the Glycols Studied in This Work

chemical	T/K	ρ/g·cm^{-3} density (this work)	density (lit.)	refs	chemical	T/K	ρ/g·cm^{-3} density (this work)	density (lit.)	refs
monoethylene glycol	273.16	1.12716			polyethylene glycol-400	283.16	1.13465		
	278.15	1.12371				285.65	1.13254		
	283.15	1.12023				288.15	1.13045		
	288.15	1.11676				290.65	1.12840		
	293.15	1.11327				293.15	1.12635		
	298.15	1.10977				295.65	1.12430		
	303.15	1.10625	1.10636	26		298.14	1.12224	1.12230	2
	308.15	1.10272	1.10282	26		300.65	1.12018		
	313.15	1.09917	1.09839	26		303.15	1.11813		
	318.15	1.09561	1.09572	26		305.65	1.11607		
	323.15	1.09202	1.09105	26		308.15	1.11402	1.11372	2
	328.14	1.08841				310.65	1.11197		
	333.15	1.08478				313.15	1.10992		
	338.15	1.08111				315.65	1.10788		
	343.15	1.07742				318.15	1.10583	1.10566	2
	348.14	1.07370				320.64	1.10379		
	353.15	1.06995				323.15	1.10175		
	358.14	1.06616				325.65	1.09971		
	363.14	1.06234				328.15	1.09767	1.09754	2
diethylene glycol	278.15	1.12704				330.65	1.09564		
	283.15	1.12352	1.12424	16		333.15	1.09360		
	288.15	1.11997				335.65	1.09157		
	293.15	1.11642	1.11705	16		338.15	1.08954		
	298.14	1.11285				340.65	1.08751		
	303.14	1.10928				343.15	1.08548		
	308.15	1.10569				345.64	1.08345		
	313.15	1.10209	1.10270	16		348.15	1.08142		
	318.15	1.09847				350.65	1.07939		
	323.15	1.09484				353.14	1.07737		
	328.15	1.09119				355.65	1.07534		
	333.15	1.08752	1.08830	16		358.15	1.07332		
	338.15	1.08382				360.64	1.07129		
	343.15	1.08011				363.14	1.06927		
	348.15	1.07638							
	353.14	1.07262	1.07374	16					
	358.14	1.06883							
	363.15	1.06501							
triethylene glycol	288.15	1.12760							
	298.15	1.11984	1.11979	2					
			1.11991	17					
	308.15	1.11207	1.11196	2					
			1.11209	17					
	318.15	1.10427							
	328.14	1.09645	1.09629	2					
			1.09646	17					
	338.15	1.08858							
	348.14	1.08066							
	358.15	1.07269							

data; similarly Lee et al.[9] reported density and excess volume data but for a limited temperature range from (283.15 to 303.15) K, at three isotherms. Tsierkezos and Molinou[10] studied density and some other physical properties of MEG aqueous solution from (283.15 to 313.15) K at four isotherms. Geyer et al.[11] measured volumetric properties of aqueous solutions of some *diols* including MEG from (278.15 to 318.15) K at four isotherms over a limited concentration range. Volumetric behavior and some of the other
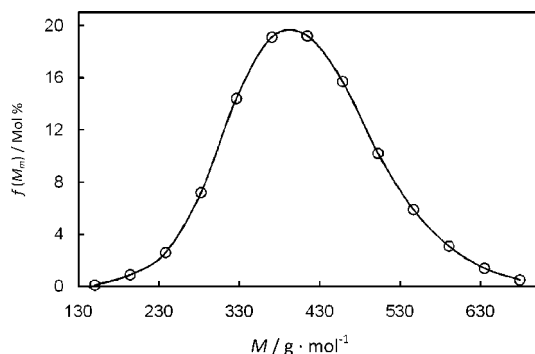

Figure 1. Molar distribution [$f(M_m)$] of various glycol fractions constituting polyethylene glycol-400 (PEG-400) used in this work. Symbols are based on information in Table 2, and the solid line is the tendency curve.

Table 4. Parameters of the Daubert et al.[21] Correlation Given in Equation 1 for Various Glycols Studied Here^a

chemical	$T_{C,i}$/K[22]	M_i[22]	A	B	C
monoethylene glycol	719.7	62.07	1.31506	0.25151	0.21621
diethylene glycol	744.6	106.12	0.83737	0.26149	0.24023
triethylene glycol	769.5	150.18	0.58301	0.25688	0.27195
polyethylene glycol 400	920.0^b	414.50	0.58650	0.42020	0.68657

^{a} M_i is the molar mass of the glycol, and $T_{C,i}$ represents the critical temperature in K. A, B, and C are the adjusted parameters. ^{b} Calculated by eq 2.

physical properties of MEG aqueous solutions were reported over broader temperature and concentration ranges by Yang et al.[12] Density data and partial molar volumes of dilute aqueous solutions of some polyhydric alcohols and MEG were studied by Hynčica et al.[13] over wide ranges of temperature and pressure. The study is devoted to a small part of the concentration range in the dilute region of glycol aqueous solutions. On the other hand, Kushare et al.[14] studied the density of MEG aqueous solution at only 298.15 K. There are few studies[15] on density and other physical properties of glycol aqueous solutions with salts at or near ambient temperatures. The volumetric behavior of DEG aqueous solutions has recently been reported by Bernal-García et al.[16] from (283.15 to 353.15) K and the whole concentration range. Densities of TEG aqueous solutions were reported by Valtz et al.[17] from (283.15 to

Table 5. Density, ρ, and Excess Molar Volume, v^E, Data of the (Monoethylene Glycol + Water) System at Various Temperatures, T, and Water Concentrations, x_{H2O}

x_{H2O}	ρ/g·cm^{-3}	v^E/cm^3·mol^{-1}	x_{H2O}	ρ/g·cm^{-3}	v^E/cm^3·mol^{-1}
	T = 273.16 K			T = 323.15 K	
0.8917	1.04455	−0.216	0.983443	0.99428	−0.020
0.8311	1.06242	−0.315	0.968368	0.99970	−0.040
0.7525	1.07956	−0.400	0.952169	1.00478	−0.053
0.6757	1.09148	−0.438	0.930925	1.01184	−0.088
			0.891684	1.02278	−0.136
	T = 283.15 K		0.831146	1.03658	−0.196
0.9834	1.00700	−0.025	0.752500	1.05021	−0.252
0.9684	1.01340	−0.051	0.675697	1.06003	−0.280
0.9522	1.01980	−0.077	0.572491	1.06970	−0.290
0.9309	1.02800	−0.119	0.432886	1.07849	−0.258
0.8917	1.04130	−0.188	0.302712	1.08408	−0.199
0.8311	1.05800	−0.276			
0.7525	1.07420	−0.354		T = 333.15 K	
0.6757	1.08560	−0.390	0.9834	0.98929	−0.020
0.5725	1.09650	−0.398	0.9684	0.99432	−0.034
0.4329	1.10610	−0.349	0.9522	0.99932	−0.048
0.3027	1.11200	−0.266	0.9309	1.00609	−0.079
			0.8917	1.01691	−0.128
	T = 293.15 K		0.8311	1.03026	−0.184
0.9834	1.00514	−0.023	0.7525	1.04349	−0.236
0.9684	1.01121	−0.047	0.6757	1.05308	−0.263
0.9522	1.01724	−0.070	0.5725	1.06256	−0.272
0.9309	1.02498	−0.107	0.4329	1.07125	−0.242
0.8917	1.03750	−0.168	0.3027	1.07681	−0.187
0.8311	1.05325	−0.248			
0.7525	1.06863	−0.319		T = 343.15 K	
0.6757	1.07952	−0.353	0.8917	1.01059	−0.121
0.5725	1.09001	−0.362	0.8311	1.02357	−0.174
0.4329	1.09937	−0.319	0.7525	1.03648	−0.222
0.3027	1.10518	−0.244	0.6757	1.04587	−0.247
			0.5725	1.05522	−0.256
	T = 303.15 K		0.4329	1.06385	−0.227
0.9834	1.00231	−0.022	0.3027	1.06940	−0.177
0.9684	1.00811	−0.044			
0.9522	1.01387	−0.065		T = 353.15 K	
0.9309	1.02122	−0.099	0.8917	1.00386	−0.114
0.8917	1.03311	−0.155	0.8311	1.01653	−0.164
0.8311	1.04808	−0.226	0.7525	1.02916	−0.209
0.7525	1.06277	−0.292	0.6757	1.03841	−0.232
0.6757	1.07324	−0.324	0.5725	1.04766	−0.241
0.5725	1.08341	−0.333	0.4329	1.05627	−0.216
0.4329	1.09253	−0.295	0.3027	1.06184	−0.167
0.3027	1.09824	−0.226			
				T = 363.15 K	
	T = 313.15 K		0.9834	0.97103	−0.017
0.9834	0.99865	−0.021	0.8917	0.99672	−0.108
0.9684	1.00424	−0.042	0.8311	1.00913	−0.154
0.9522	1.00977	−0.062	0.7525	1.02155	−0.196
0.9309	1.01682	−0.093	0.6757	1.03069	−0.218
0.8917	1.02819	−0.144	0.5725	1.03987	−0.226
0.8311	1.04252	−0.210	0.4329	1.04848	−0.203
0.7525	1.05663	−0.270	0.3027	1.05410	−0.158
0.6757	1.06675	−0.301			
0.5725	1.07664	−0.310			
0.4329	1.08558	−0.275			
0.3027	1.09121	−0.212			

353.15) K and over the whole concentration range. They[17] also reviewed some of the previous densimetric studies on TEG aqueous solutions, concluding the data over an extended temperature/concentration range are either reported in the forms of equations and graphs or are limited to near ambient temperatures. Aqueous solutions of PEGs were studied[18] at 298.15 K for molar masses from (300 to 35000) g·mol^{-1}. Recently, Han et al.[19] have published some excess properties and densities of PEG-400 aqueous solutions from (298.15 to 323.15) K at five isotherms.

Overall, it can be concluded that most of the volumetric properties of glycol aqueous solutions reported in the literature have not been provided in tabular form or are in limited temperature/concentration ranges. Most of the studies are at or near ambient temperatures with some exceptions: Yang et al.[12] for MEG aqueous solutions, Bernal-García et al.[16] for DEG aqueous solutions, and Valtz et al.[17] for TEG aqueous solutions; all of them worked in wide temperature and concentration ranges. Negative excess volumes over the whole range of compositions from low to moderately high temperatures for glycols were reported[16,17] except from Yang et al.[12] Surprisingly, they[12] found positive excess molar volumes of mixing for concentrated MEG aqueous solutions at elevated temperatures, generally above 310 K, which is contradictory to the expected behavior.[5,6] Negative excess volumes of mixing are normally expected for glycol aqueous solutions because of the miscibility and high degree of mutual affinity between the glycol and water. This can be explained by the occupation of the cavities of the water network by glycols. The aim of this work is to provide a comprehensive study of excess volumes of various glycol aqueous solutions. Densities of monoethylene glycol, diethylene glycol, triethylene glycol, and polyethylene glycol (with $n \cong 8$ and average molar mass of 400 g·mol^{-1}) and their aqueous solutions are reported generally from (273.15 to 363.15) K at atmospheric pressure, which have been measured using a digital vibrating tube densimeter. The density data are then used to calculate
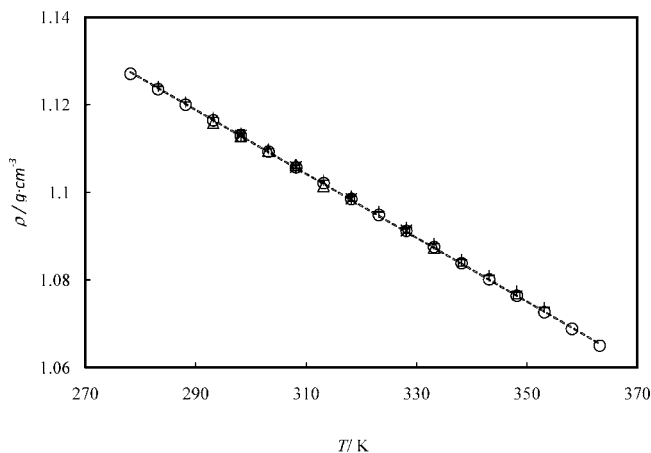
Figure 2. Comparisons of density, ρ, of pure diethylene glycol as a function of temperature, T, using literature values. Symbols: O, data from this work; +, data from Bernal-García et al.;[16] Δ, data from Bernal-García;[25] $\square$, data from George and Sastry;[5] *, data from Müller and Rasmussen;[2] dotted line is the tendency curve based on data from this work. All the data sets generally show good agreement.
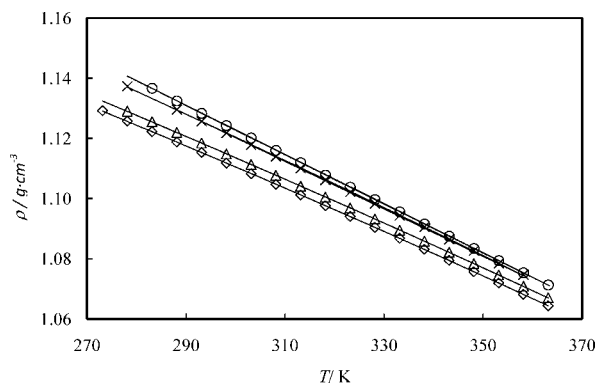

Figure 3. Density, ρ, of glycol as a function of temperature, T. Symbols: O, polyethylene glycol 400; ×, triethylene glycol; Δ, diethylene glycol; $\diamond$, monoethylene glycol. Solid lines: correlated values from eq 1 and parameters provided in Table 4.

excess molar volumes of glycol aqueous solutions. We demonstrate that the excess molar volumes for the glycol aqueous solutions studied in this work are negative in the temperature ranges of our study.

Experimental Section

Table 1 shows chemicals used in this work along with their purities and suppliers. All glycols were used after fresh degassing under warm conditions before making their aqueous solutions for the experimental measurements.

Polyethylene glycol-400 is a polymer with varying amounts of various glycols having an average or "approximately mean" molar mass of 400 g·mol^{-1}. The "exact mean" molecular mass of the PEG-400 used in this work was 414.5 g·mol^{-1}. The molar distribution of our PEG-400 is presented in Table 2. A graph between molar mass and its distribution is presented in Figure 1. PEG-400 was treated with the molecular sieve (UOP type 3A) before using it for experimental measurements. Special precautions were taken to minimize any possibility of contamination of glycols with water from air because of their hygroscopic nature.

Double-distilled and deionized pure water was prepared by Millipore Direct (Q5 model) for all solutions. An Anton Paar digital vibrating glass tube densimeter (DMA 5000 model) with a labeled precision of 10^{-5} g·cm^{-3} was used in this work. The maximum uncertainty on excess volumes reported here is less

than 0.005 cm^3·mol^{-1}. The experimental procedures used in this study were essentially similar to that of previous work.[17]

Results and Discussion

Densities of MEG, DEG, TEG, and PEG-400 (in the absence of water) were first measured. The density of water was taken from the literature[20] to allow calculating excess molar volumes of (water + glycol) solutions. The density data for MEG, DEG, TEG, and PEG-400 are presented in Table 3. Comparisons between our results and those obtained in the literature[2,16,17,26] are also made in Table 3 and Figure 2 to show the reliability of the work. A good agreement is observed between the data generated in this work and those already published.

Densities of MEG, DEG, TEG, and PEG-400 are correlated using the correlation of Daubert et al.,[21] given in eq 1

$$\rho_{i,\text{cor}} = \frac{A}{B^{\left[1+\left(1-\frac{T}{T_{C,i}}\right)^C\right]}} \cdot \frac{M_i}{1000} \tag{1}$$

where $\rho_{i,\text{cor}}$ is the correlated density of the glycol i; M_i is the molar mass of the glycol; and $T_{C,i}$ represents the critical temperature in Kelvin. A, B, and C are the adjusted parameters, which are reported in Table 4 along with M_i and $T_{C,i}$. These parameters were adjusted using the data reported in Table 3. The density data of glycols measured in this work are presented in Figure 3 along with the correlated values from eq 1 as a function of temperature.

The critical temperatures were taken from the Component Plus property package by ProSim[22,23] for all glycols (that uses Twu correlation[24] for critical properties based on normal boiling points and specific gravities), except for polyethylene glycol-400, which was not available in the package. It was found that the critical temperatures are linear functions of molar masses of MEG, DEG, TEG, and TTEG. This linear relationship is presented in eq 2

$$T_{C,i} = 0.5693 \cdot M_i + 684.24 \tag{2}$$

Behavior of PEG-400 for critical temperature was assumed similar to that of other glycols as presented by eq 2 to estimate its critical temperature. However, it should be mentioned that the usage of critical temperature, reported in this work for polyethylene glycol-400, should be restricted to density calculations in eq 1.

Densities and excess molar volumes of the binary glycol aqueous solutions along with mole faction of water in the solution and temperature are reported in Tables 5 to 8 for aqueous solutions of MEG, DEG, TEG, and PEG-400, respectively. Excess molar volumes were calculated using the following equation

$$v^E = \left[\frac{x_1 M_1 + x_2 M_2}{\rho}\right] - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \tag{3}$$

where v^E is the excess molar volume; M_1 and M_2 are the molar masses of glycol and water, respectively; ρ_1 is the density of glycol reported in Table 3; ρ_2 is the density of water reported by Bettin and Spieweck;[20] and x_1 and x_2 are the mole fractions of glycol and water, respectively.

The Redlich−Kister[23] correlation, eq 4, was then applied in the excess molar volume correlations for glycol aqueous solutions. The coefficients (A_i) were determined at each

Table 6. Density, ρ, and Excess Molar Volume, v^E, Data of the (Diethylene Glycol + Water) System at Various Temperatures, T, and Water Concentrations, x_{H2O}

x_{H2O}	ρ/g·cm^{-3}	v^E/cm^3·mol^{-1}	x_{H2O}	ρ/g·cm^{-3}	v^E/cm^3·mol^{-1}
	T = 278.15 K			T = 328.15 K	
0.9789	1.01705	−0.082	0.9789	0.99988	−0.067
0.9544	1.03456	−0.191	0.9544	1.01382	−0.146
0.9244	1.05237	−0.324	0.9244	1.02772	−0.237
0.8916	1.06774	−0.453	0.8916	1.03874	−0.300
0.8509	1.08218	−0.583	0.8509	1.05115	−0.416
0.7890	1.09700	−0.713	0.7890	1.06325	−0.513
0.7182	1.10650	−0.753	0.4878	1.08518	−0.542
0.4878	1.12154	−0.716	0.3310	1.08983	−0.497
0.3310	1.12589	−0.603	0.1763	1.09013	−0.231
0.1763	1.12614	−0.294			
				T = 338.15 K	
	T = 288.15 K		0.9789	0.99436	−0.064
0.9789	1.01532	−0.076	0.9544	1.00792	−0.120
0.9544	1.03178	−0.176	0.9244	1.02137	−0.226
0.9244	1.04849	−0.297	0.8916	1.03116	−0.262
0.8916	1.06292	−0.414	0.8509	1.04405	−0.395
0.8509	1.07656	−0.534	0.7890	1.05583	−0.486
0.7890	1.09066	−0.657	0.4878	1.07759	−0.517
0.4878	1.11445	−0.670	0.3310	1.08239	−0.485
0.1763	1.11906	−0.278	0.1763	1.08270	−0.222
	T = 298.15 K			T = 348.15 K	
0.9789	1.01260	−0.073	0.97893	0.98812	−0.058
0.9544	1.02824	−0.166	0.95440	1.00154	−0.134
0.9244	1.04404	−0.277	0.92439	1.01461	−0.216
0.8916	1.05768	−0.385	0.89165	1.02101	−0.166
0.8509	1.07064	−0.496	0.78901	1.04817	−0.460
0.7890	1.08413	−0.612	0.48775	1.06985	−0.492
0.4878	1.10727	−0.631	0.3310	1.07483	−0.474
0.3310	1.11167	−0.549	0.1763	1.07516	−0.212
0.1763	1.11192	−0.264			
				T = 358.15 K	
	T = 308.15 K		0.9544	0.99471	−0.128
0.9789	1.00906	−0.070	0.9244	1.00744	−0.205
0.9544	1.02403	−0.158	0.7890	1.04026	−0.436
0.9244	1.03908	−0.261	0.4878	1.06197	−0.469
0.8916	1.05201	−0.360	0.1763	1.06752	−0.203
0.8509	1.06444	−0.466			
0.7890	1.07739	−0.574			
0.4878	1.10001	−0.598			
0.3310	1.10446	−0.529			
0.1763	1.10473	−0.252			
	T = 318.15 K				
0.9789	1.00479	−0.069			
0.9544	1.01920	−0.151			
0.9244	1.03363	−0.248			
0.8916	1.04580	−0.335			
0.8509	1.05794	−0.440			
0.7890	1.07043	−0.542			
0.4878	1.09265	−0.568			
0.3310	1.09719	−0.512			
0.1763	1.09747	−0.241			

Table 7. Density, ρ, and Excess Molar Volume, v^E, Data of the (Triethylene Glycol + Water) System at Few Temperatures, T, and Water Concentrations, x_{H2O}[a]

x_{H2O}	ρ/g·cm^{-3}	v^E/cm^3·mol^{-1}
	T = 278.15 K	
0.9536	1.04949	−0.308
0.9065	1.08031	−0.585
0.7238	1.12115	−0.948
	T = 288.15 K	
0.9536	1.04577	−0.268
0.9065	1.07474	−0.524
0.7238	1.11374	−0.874
	T = 298.15 K	
0.9536	1.04145	−0.216
0.9065	1.06884	−0.454
	T = 308.15 K	
0.9536	1.03658	−0.150
0.9065	1.06264	−0.376

[a] A detailed study is reported elsewhere.[17]

studied temperature, which are presented in Table 9 for MEG aqueous solutions and in Table 10 for PEG-400 aqueous

solutions along with the standard deviation, σ, defined in eq 5 corresponding to each isothermal fit.

$$v^E = x_1 x_2 \sum_i A_i (x_1 - x_2)^i \qquad (4)$$

$$\sigma = \sqrt{\left[\sum \frac{(v^E - v^E_{cal})^2}{N_{exp} - P} \right]} \qquad (5)$$

where P represents the total number of A_i parameters; v^E_{cal} is the calculated excess molar volume; and N_{exp} is the number of experimental points. Volumetric studies of DEG or TEG aqueous solutions have been extensively studied elsewhere.[16,17]

Excess molar volumes for the (MEG + water) system, reported by Yang et al.[12] are presented in Figure 4 showing their data and correlation results. Excess molar volume data for the isothermal conditions are also presented in Figures 5 to 8 for the studied systems, namely, (MEG + water), (DEG +

Table 8. Density, ρ, and Excess Molar Volume, v^E, Data of the (Polyethylene Glycol-400 + Water) System at Various Temperatures, T, and Water Concentrations, x_{H2O}

x_{H2O}	ρ/g·cm^{-3}	v^E/cm^3·mol^{-1}	x_{H2O}	ρ/g·cm^{-3}	v^E/cm^3·mol^{-1}
T = 278.15 K			T = 328.15 K		
0.9963	1.01322	−0.070	0.9963	0.99656	−0.057
0.9928	1.02461	−0.142	0.9928	1.00573	−0.114
0.9876	1.03967	−0.255	0.9876	1.01760	−0.199
0.9822	1.05342	−0.379	0.9822	1.02822	−0.288
0.9768	1.06513	−0.500	0.9768	1.03718	−0.374
0.9627	1.08817	−0.788	0.9627	1.05471	−0.577
0.9571	1.09491	−0.886	0.9571	1.05989	−0.647
0.9472	1.10446	−1.038	0.9472	1.06730	−0.757
0.9007	1.12581	−1.436	0.9007	1.08494	−1.066
0.8536	1.13238	−1.553	0.8536	1.09111	−1.175
0.6867	1.13729	−1.465	0.6867	1.09619	−1.105
0.3411	1.13859	−0.963	0.1852	1.09760	−0.326
0.1852	1.13876	−0.716	0.3411	1.09747	−0.589
T = 288.15 K			T = 338.15 K		
0.9963	1.01167	−0.064	0.9963	0.99112	−0.056
0.9928	1.02242	−0.130	0.9928	1.00001	−0.110
0.9876	1.03659	−0.234	0.9876	1.01148	−0.192
0.9822	1.04947	−0.346	0.9822	1.02172	−0.277
0.9768	1.06044	−0.456	0.9768	1.03032	−0.358
0.9627	1.08206	−0.719	0.9627	1.04714	−0.550
0.9571	1.08841	−0.809	0.9571	1.05211	−0.616
0.9472	1.09743	−0.948	0.9472	1.05925	−0.719
0.9007	1.11786	−1.315	0.9007	1.07644	−1.014
0.8536	1.12431	−1.421	0.8536	1.08262	−1.122
0.6867	1.12899	−1.276	0.6867	1.08789	−1.064
0.1852	1.13034	−0.358	0.1852	1.08945	−0.314
0.3411	1.13020	−0.659	0.3411	1.08929	−0.569
T = 298.15 K			T = 348.15 K		
0.9963	1.00907	−0.062	0.9963	0.98514	−0.054
0.9928	1.01933	−0.124	0.9928	0.99378	−0.107
0.9876	1.03276	−0.222	0.9876	1.00489	−0.185
0.9822	1.04494	−0.326	0.9822	1.01478	−0.266
0.9768	1.05529	−0.429	0.9768	1.02307	−0.343
0.9627	1.07566	−0.674	0.9627	1.03928	−0.523
0.9571	1.08166	−0.759	0.9571	1.04407	−0.585
0.9472	1.09020	−0.890	0.9472	1.05098	−0.682
0.9007	1.10979	−1.242	0.9007	1.06781	−0.964
0.8536	1.11613	−1.350	0.8536	1.07403	−1.070
0.6867	1.12086	−1.228	0.6867	1.07954	−1.022
0.1852	1.12215	−0.350	0.1852	1.08131	−0.304
0.3411	1.12202	−0.640	0.3411	1.08113	−0.552
T = 308.15 K			T = 358.15 K		
0.9963	1.00561	−0.060	0.9963	0.97866	−0.052
0.9928	1.01545	−0.120	0.9928	0.98707	−0.103
0.9876	1.02829	−0.213	0.9876	0.99786	−0.178
0.9822	1.03987	−0.312	0.9822	1.00744	−0.254
0.9768	1.04968	−0.408	0.9768	1.01546	−0.327
0.9627	1.06898	−0.638	0.9627	1.03114	−0.496
0.9571	1.07466	−0.717	0.9571	1.03578	−0.554
0.9472	1.08278	−0.840	0.9472	1.04249	−0.646
0.9007	1.10161	−1.178	0.9007	1.05904	−0.914
0.8536	1.10786	−1.287	0.8536	1.06533	−1.018
0.6867	1.11267	−1.185	0.6867	1.07115	−0.978
0.1852	1.11395	−0.342	0.1852	1.07317	−0.292
0.3411	1.11383	−0.624	0.3411	1.07295	−0.530
T = 318.15 K			T = 363.15 K		
0.9963	1.00141	−0.058	0.9928	0.98354	−0.101
0.9928	1.01090	−0.117	0.9876	0.99418	−0.173
0.9876	1.02321	−0.205	0.9822	1.00362	−0.248
0.9822	1.03429	−0.299	0.9768	1.01152	−0.318
0.9768	1.04364	−0.390	0.9627	1.02696	−0.482
0.9627	1.06199	−0.606	0.9571	1.03153	−0.539
0.9571	1.06740	−0.681	0.9472	1.03816	−0.627
0.9472	1.07514	−0.797	0.9007	1.05461	−0.888
0.9007	1.09333	−1.120	0.8536	1.06095	−0.991
0.8536	1.09953	−1.229	0.6867	1.06692	−0.954
0.6867	1.10445	−1.145			
0.1852	1.10577	−0.335			
0.3411	1.10565	−0.607			

Table 9. Adjusted Parameters, A_i, of the Redlich−Kister Correlation[23] (Equation 5) for the (Monoethylene Glycol + Water) System at Various Temperatures, T

T/K	A_0	A_1	A_2	σ (eq 5)[a]
283.15	−1.553	−0.730	0.254	0.019
293.15	−1.415	−0.624	0.256	0.008
303.15	−1.304	−0.558	0.221	0.006
313.15	−1.211	−0.507	0.183	0.005
323.15	−1.133	−0.466	0.165	0.006
333.15	−1.067	−0.435	0.183	0.006
343.15	−0.992	−0.393	0.032	0.003
353.15	−0.933	−0.364	0.020	0.002
363.15	−0.878	−0.338	0.019	0.002

[a] σ, standard deviation, defined by eq 5.

Table 10. Adjusted Parameters, A_i, of the Redlich−Kister Correlation[23] (Equation 5) for the (Polyethylene Glycol-400 + Water) System at Various Temperatures, T

T/K	A_0	A_1	A_2	A_3	A_4	σ (eq 5)[a]
278.15	−4.958	−2.748	−2.415	−4.845	−11.251	0.035
288.15	−3.903	−3.330	−2.026	−6.216	−8.345	0.031
298.15	−3.772	−3.202	−2.001	−5.722	−7.614	0.027
308.15	−3.721	−3.137	−1.332	−5.092	−8.044	0.112
318.15	−3.593	−3.014	−1.476	−4.792	−7.205	0.020
328.15	−3.501	−2.931	−1.181	−4.375	−7.157	0.016
338.15	−3.393	−2.842	−1.002	−4.045	−6.923	0.195
348.15	−3.302	−2.720	−0.700	−3.762	−6.898	0.011
358.15	−3.178	−2.615	−0.530	−3.453	−6.729	0.009

[a] σ standard deviation, defined by eq 5.
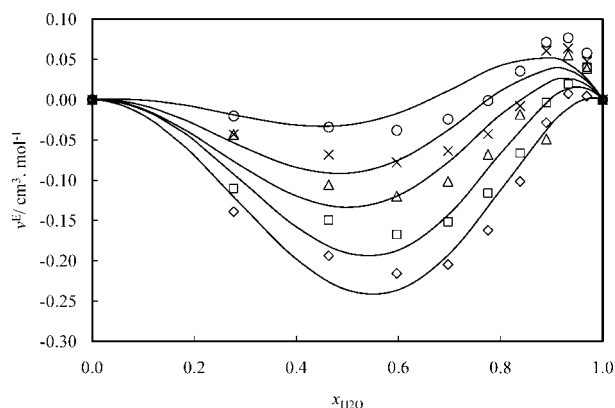
Figure 4. Excess molar volumes (v^E) for the (monoethylene glycol + water) system reported by Yang et al.[12] at various temperatures showing a local maxima in addition to a minima. Symbols: ○, 353.15 K; ×, 343.15 K; Δ, 333.15 K; □ 323.15 K; ◇, 313.15 K. Solid curves: correlated values from Yang et al.[12]

Figure 5. Excess molar volumes (v^E) for the (monoethylene glycol + water) system at various temperatures determined in this work. Symbols: ×, 363.15 K; □, 333.15 K; ◇, 313.15 K; Δ, 293.15 K; ○, 283.15 K. Solid curves: calculated with eq 4 and parameters provided in Table 9.

Figure 6. Excess molar volumes (v^E) for the (diethylene ethylene glycol + water) system at various temperatures determined in this work and comparison with the literature data.[16] Symbols: Δ, 348.15 K; □, 328.15 K; ○, 288.15 K. Hollow symbols are data from the literature,[16] and solid symbols are data from our work. Solid curves: correlated values from the literature.[16]
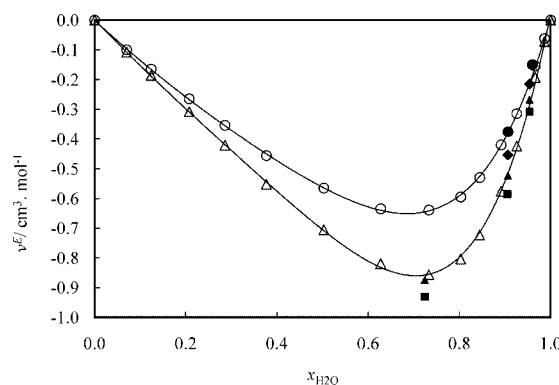
Figure 7. Excess molar volumes (v^E) for the (triethylene glycol + water) binary system at different temperatures determined by Valtz et al.[17] and comparisons with our data. Hollow symbols represent data from the literature;[17] solid symbols represent our data. Symbols: ○, 353.15 K; Δ, 293.15 K; ●, 308.15 K; ▲, 288.15 K; ◆, 298.15 K; ■, 278.15 K. Solid curves: correlated values from the literature.[17]

water), (TEG + water), and (PEG-400 + water), respectively. A comparison of molar excess volumes is also made among all the studied systems at fixed temperature in Figure 9.

Our results strongly suggest that the excess molar volumes for the (glycol + water) systems studied in this work are negative in the whole compositions and throughout the temperature ranges studied here. A graphical representation of excess molar volumes at 358.15 K for all the glycol aqueous solutions studied here is given in Figure 9. The volumetric properties of MEG aqueous solutions studied in ref 12 are presented in Figure 4 showing both negative and positive excess molar volumes. The excess molar volumes calculated from our density data for the aqueous MEG solutions presented in Figure 5 show disagreement to the positive maxima. Figures 6 to 8 and Figure 9 show that there are no positive excess molar volumes for the other systems. The increase of the moles of glycols in water results in more negative excess molar volumes than the increase in the same number of moles of water in glycols. This trend goes on increasing from MEG to PEG-400

containing systems at constant temperature. The excess volume for all the systems goes on decreasing with the increase in temperature.

Conclusions

In this paper, atmospheric density data for the (glycol + water) systems are reported in the whole range of compositions and at
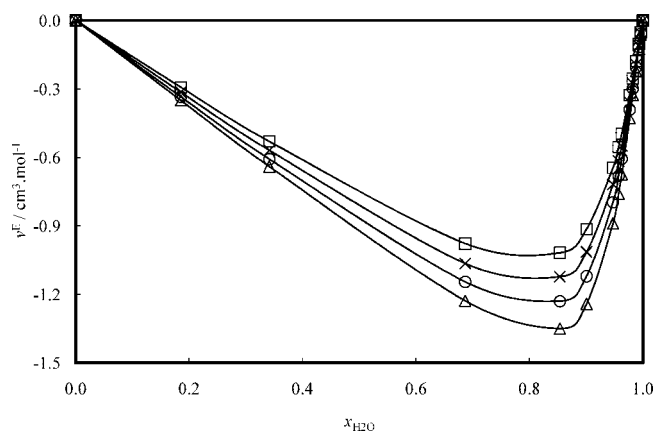
Figure 8. Excess molar volumes (v^E) for the (polyethylene glycol-400 + water) system at various temperatures determined in this work. Symbols: □, 358.15 K; ×, 338.15 K; ○, 318.15 K; △, 298.15 K. Solid curves correlated values with eq 4 and parameters provided in Table 10.
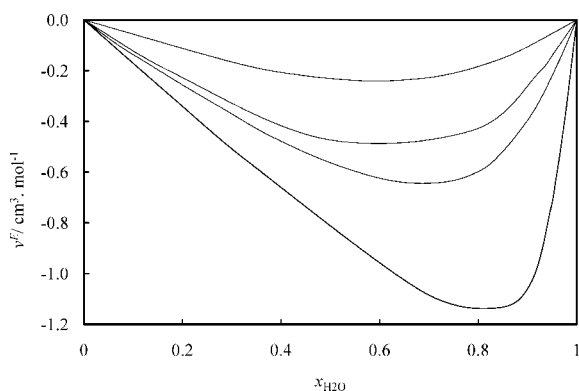

Figure 9. Excess molar volumes (v^E) determined in this work for various glycol aqueous solutions at 358.15 K. Solid curves are tendency behavior for mono-, di-, tri-, and polyethylene glycol-400 aqueous solutions, respectively, from top to bottom.

various temperatures generally from (273.15 to 363.15) K. The studied glycols are: mono-, di-, and triethylene glycol and polyethylene glycol with an average molar mass of 400 g·mol⁻¹. All these systems show complete miscibility, and the excess molar volumes were found to be negative. The excess molar volumes of some aqueous glycols were correlated using the Redlich−Kister[23] correlation, and the new parameters are reported.

Literature Cited

(1) Morénas, M.; Douhéret, G. Thermodynamic Behavior of Some Glycol - Water Mixtures, Excess and Partial Molar Volumes. *Thermochim. Acta* **1978**, *25*, 217–224.

(2) Müller, E. A.; Rasmussen, P. Densities and Excess Volumes in Aqueous Poly (Ethylene Glycol) Solutions. *J. Chem. Eng. Data* **1991**, *36*, 214–217.

(3) Obermeier, E.; Fischer, S.; Bohne, D. Thermal Conductivity, Density, Viscosity, and Prandtl - Numbers of Di- and Triethylene Glycol - Water Mixtures. *Ber. Bunsenges. Phys. Chem.* **1985**, 805–809.

(4) Bohne, D.; Fischer, S.; Obermeier, E. Thermal Conductivity, Density, Viscosity, and Prandtl - Numbers of Ethylene Glycol - Water Mixtures. *Ber. Bunsenges. Phys. Chem.* **1984**, *88*, 739–742.

(5) Goerge, J.; Sastry, N. V. Partial Excess Molar Volumes, Partial Excess Isentropic Compressibilities and Relative Permitivities of Water + Ethane-1,2-Diol Derivative and Water + 1,2-dimethoxyethane at Different Temperatures. *Fluid Phase Equilib.* **2004**, *216*, 307–321.

(6) Sun, T.; Teja, A. S. Density, Viscosity, and thermal Conductivity of Aqueous Ethylene, Diethylene, and Triethylene, Glycol Mixtures Between 290K and 450 K. *J. Chem. Eng. Data* **2003**, *48*, 198–202.

(7) Ray, A.; Némethy, G. Densities and Partial Molal Volumes of Water - Ethylene Glycol Mixtures. *J. Chem. Eng. Data* **1973**, *18*, 309–311.

(8) Hout, J-.Y.; Battistel, E.; Lumry, R.; Villeneuve, G.; Lavalle, J-.F.; Anusiem, A.; Jolicoeur, C. A. Comprehensive Thermodynamic Investigation of Water - Ethylene Glycol Mixtures at 5, 25, and 45 °C. *J. Solution Chem.* **1988**, *17*, 601–631.

(9) Lee, H.; Hong, W.-H.; Kim, H. Excess Volumes of Binary and Ternary Mixtures of Water, Methanol, and Ethylene Glycol. *J. Chem. Eng. Data* **1990**, *35*, 371–374.

(10) Tsierkezos, N. G.; Molinou, I. E. Thermodynamic Properties of Water + Ethylene Glycol at 283.15, 293.15, and 313.15 K. *J. Chem. Eng. Data* **1998**, *43*, 989–993.

(11) Geyer, H.; Ulbig, P.; Görnert, M. Measurement of Densities and Excess Molar Volumes for (1,2-Ethanediol, or 1,2-Propanediol, or 1,2-Buntanediol + Water) at the Temperature (278.15, 288.15, 298.15, 308.15, 318.15) K and for (2,3-Butanediol + Water) at the Temperature (308.15, 313.15, and 318.15) K. *J. Chem. Thermodyn.* **2000**, *32*, 1585–1596.

(12) Yang, C.; Ma, P.; Jing, F.; Tang, D. Excess Molar Volumes, Viscosities, and Heat Capacities for the Mixtures of Ethylene Glycol + Water from 273.15K to 353.15 K. *J. Chem. Eng. Data* **2003**, *48*, 836–840.

(13) Hynčica, P.; Hnedkovský, L.; Cibulka, I. Partial Molar Volumes of Organic Solutes in Water. XIV. Polyhydric Alcohols Derived from Ethane and Propane at Temperature T = 298 K to T = 573 K and at Pressures up to 30 MPa. *J. Chem. Thermodyn.* **2006**, *38*, 801–809.

(14) Kushare, S. K.; Dagade, D. H.; Patil, K. J. Volumetric and Compressibility Properties of Liquid Water as a Solute in Glycolic, Propylene carbonate, and Tetramethylurea Solutions at T = 298.15 K. *J. Chem. Thermodyn.* **2008**, *40*, 78–83.

(15) Tsierkezos, N. G.; Molinou, I. E. Transport Properties of 2:2 Symmetrical Electrolytes in (Water + Ethylene Glycol) Binary Mixtures at T = 293.15 K. *J. Chem. Thermodyn.* **2006**, *38*, 1422–1431.

(16) Bernal-Garcia, J. M.; Guzmán-López, A.; Cabrales-Torres, A.; Rico-Ramírez, V.; Iglesias-Silva, G. A. Supplementary Densities and Viscosities of Aqueous Solutions of Diethylene Glycol from (283.15 to 353.15) K. *J. Chem. Eng. Data* **2008**, *53*, 1028–1031.

(17) Valtz, A.; Teodorescu, M.; Wichterle, I.; Richon, D. Liquid Densities and Excess Molar Volumes for Water + Diethylene Glycolamine, and Water, Methanol, Ethanol, 1-Propanol + Triethylene Glycol Binary Systems at Atmospheric Pressure and Temperatures in the Range of 283.15−363.15 K. *Fluid Phase Equilib.* **2004**, *215*, 129–142.

(18) Kirincic, S.; Klofutar, C. A. Volumetric Study of Aqueous Solutions of Poly(ethylene Glycol)s at 298.15 K. *Fluid Phase Equilib.* **1998**, *149*, 233–247.

(19) Han, F.; Zhang, J.; Chen, G.; Wei, X. Density, Viscosity, and Excess Properties for Aqueous Poly(ethylene Glycol) Solutions from (298.15 to 323.15) K. *J. Chem. Eng. Data* **2008**, *53*, 2598–2601.

(20) Bettin, H.; Spieweck, F. : Die Dichte von Wasser als Funktion der Temperatur bach Einführung der Internationalen Temperaturskala von 1990. *PTB-Mitt.* **1990**, *100*, 195–196.

(21) Daubert, T. E.; Danner, R. P.; Sibel, H. M.; Stebbins, C. C. Physical and Thermodynamic Properties of Pure Chemicals. *Data Compilation*; Taylor & Francis: Washington, D. C., 1997.

(22) Component Plus 3.0.0.0 relased by ProSim Softwares and Services in Process Simulations: France, SA 2001. http://www.prosim.net.

(23) Redlich, O.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345–348.

(24) Twu, C. H. An Internally Consistent Correlation for Predicting the Critical Properties and Molecular Weights of Petroleum and Coal-Tar Liquids. *Fluid Phase Equilib.* **1984**, *16*, 137–150.

(25) Bernal-Garcia, J. M.; Ramos-Estrada, M.; Iglesias-Silva, G. A.; Hall, K. R. Densities and Excess Molar Volumes of Aqueous Solutions of n-Methyldiethanolamine (MDEA) at Temperatures from (283.15 to 363.15) K. *J. Chem. Eng. Data* **2003**, *48*, 864–866.

(26) Azizian, S.; Bashavard, N. Surface Properties of Diluted Solutions of Cyclohexanol and Cyclopentanol in Ethylene Glycol. *J. Colloid Interface Sci.* **2005**, *282*, 428–433.