Density and Viscosity of the Binary Mixture of Triethylene Glycol Monoethyl Ether + Water from (293.15 to 333.15) K at Atmospheric Pressure

Guo-Min Xu,[†] Xin-Xue Li,*,[‡] Yi-Jiang Hu,[‡] Yan-Wei Wang,[‡] Gui-Chen Fan,[‡] and Min Zhang[‡]

Department of Petroleum Engineering, Daqing Petroleum Institute, Daqing 163318, China, and Department of Chemistry, University of Science and Technology Beijing, Beijing 100083, China

---

As part of our systematic program on the thermodynamic study of an aqueous solution of glycol ethers, this work reports new measurements of densities and viscosities for the binary liquid mixture of triethylene glycol monoethyl ether ($CH_3CH_2(OCH_2CH_2)_3OH$) + water as a function of composition in the temperature range from (293.15 to 333.15) K at atmospheric pressure. Densities were determined using a capillary pycnometer. Viscosities were measured with an Ubbelohde capillary viscometer. From the experimental data, the excess molar volumes, V^E, and viscosity deviations, $\delta\eta$, were calculated. These data have been correlated by the Redlich−Kister type equations to obtain their coefficients and standard deviations. The results suggest that the molecular interaction between triethylene glycol monoethyl ether and water is stronger than that of diethylene glycol monoethyl ether and water.

Introduction

This paper is a continuation of our systematic program on the thermodynamic study of the binary mixtures of glycol ethers and water.[1–3] Glycol ethers are widely used industrial solvents with the highest potential for gas sweetening.[4] They can be used as scrubbing liquids in the cleaning of exhaust air and gas streams from industrial production plants because of their favorable properties such as low vapor pressure, low toxicity, low viscosity, high chemical stability, and low melting temperature.[5] Binary mixtures of glycol ethers and water have been used in the absorption of carbonyl sulfide (COS) from synthesis gas for reasons of either protecting catalyst activity in subsequent operations or preventing corrosion and air pollution. The key advantage of using the binary mixtures of glycol ethers and water as absorption liquids of COS is that both solubility and hydrolysis rate are enhanced. Process design using these systems requires accurate thermophysical property data.

Glycol ethers are nonionic amphiphile molecules and are very effective as surfactants with a large number of applications.[6] They can be used as polar additives in anionic polymerization and automotive brake fluid. Short-chain polyethylene glycol monoalkylethers are used in various biotechnical and biomedical applications, constituting a simple model of biological systems.[7]

In addition, glycol ethers, with the combination of ether, alcohol, and hydrocarbon chain in one molecule, provide versatile solvency characteristics with both polar and nonpolar properties. It is well-known that polyether (PEO) is important in many industrial, environmental, and biological applications because of its specific hydrophilic properties. The hydration of PEO ascribes to terminal hydroxyl groups as well as the ether oxygens along the polymer backbone. To explicate the role played by the polyether backbone, Fenn et al.[8] had studied tetraethylene glycol dimethyl ether (TEGDE)/water systems by using ultrafast infrared (IR) polarization selective pump−probe spectroscopy of water's hydroxyl stretch. So, short-chain glycol ethers are useful in studying molecular interactions and arrangements through the mixing deviation from ideality.

Experimental Section

Materials. Triethylene glycol monoethyl ether (TEGMEE, CAS 112-50-5) was purchased from Aldrich, and its mass fraction purity was 97.8 %. After being purified by vacuum distillation, the mass fraction of TEGMEE was higher than 99 % as determined by gas chromatography. Prior to measurements, it was dried over 0.4 nm molecular sieves and partially degassed under vacuum. Doubly distilled water was used.

Apparatus and Procedure. The densities of the pure liquids and the mixtures were measured with a 10 cm^3 capillary pycnometer. Degassed pure water was used as calibrating substances. A thermostatically controlled water bath whose temperature was controlled to ± 0.01 K was used for all the density measurements and the following measurements of viscosity. Binary mixtures were prepared by mass, using an electronic analytical balance (HANGPING FA2104, Shanghai, China) with a precision of ± 0.0001 g. The uncertainty in mole fraction was estimated to be ± 0.0001. The relative uncertainty of the density measurements was estimated to be ± 0.1 %.

The viscosities were determined with a capillary viscometer of Ubbelohde type which was calibrated by measurement of the viscosity of pure water. The flow-time measurements were made using an accurate stopwatch with an uncertainty of ± 0.01 s. The average of six sets of flow times for each fluid was taken for the purpose of the calculation of viscosity. The flow times were reproducible to ± 0.06 s. The relative uncertainty of the viscosity measurements was estimated to be ± 0.2 %.

Results and Discussion

There are few data on density and viscosity of TEGMEE in the literature. A comparison of our measurements of density and viscosity with the data in the literature was shown in Table 1. It is necessary to point out that the viscosity data of pure TEGMEE at 293.15 K are not found in the literature. So the

---

* Corresponding author. Tel.: +86-10-62333871. Fax: +86-10-62332462. E-mail: lxx1969@pku.org.cn.
[†] Daqing Petroleum Institute.
[‡] University of Science and Technology Beijing.

10.1021/je9008014

Table 1. Comparison of Measured Densities (ρ) and Viscosities (η) of TEGMEE with Literature Values at (298.15 and 308) K

	ρ/g·cm^{-3}		η/mPa·s	
T/K	this work	lit.	this work	lit.
298.15	1.0163	1.0161[a,c,e] 1.01703[b] 1.01619[d]	6.739	7.042[e]
308.15	1.0081	1.00880[f]		

[a] From ref 9. [b] From ref 10. [c] From ref 11. [d] From ref 12. [e] From ref 13. [f] From ref 14.

viscosity of pure TEGMEE at 298.15 K was measured for comparison. A reasonable agreement was found between our experimental density value and those in the literature, and the relative difference in viscosity value between this work and the literature is low within the limitations of available information.

The experimental results of the densities and viscosities for TEGMEE (1) + water (2) from (293.15 to 333.15) K at various mole fractions are listed in Table 2.

Excess molar volumes V^E and viscosity deviations $\delta\eta$ were calculated from the experimental results according to the following equations, respectively

$$V^E = \frac{x_1M_1 + x_2M_2}{\rho_M} - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2} \tag{1}$$

$$\delta\eta = \eta_M - (x_1\eta_1 + x_2\eta_2) \tag{2}$$

where x_1 and x_2 are the mole fractions; M_1 and M_2 are molar masses; ρ_1 and ρ_2 are the densities; and η_1 and η_2 are the viscosities of pure components 1 and 2, respectively. The subscript M represents mixture properties. The values calculated for V^E and $\delta\eta$ were also listed in Table 2.

The values of V^E and $\delta\eta$ were fitted by a Redlich−Kister type polynomial[15]

$$Y = x_1x_2\sum_{k=0}^{m} A_k(x_1 - x_2)^k \tag{3}$$

where $Y = V^E$ or $\delta\eta$ and the coefficients of A_k are parameters that were obtained by fitting the equations to the experimental values with a least-squares method, which were given in Table 3. The tabulated standard deviation σ was defined as

$$\sigma = \left[\frac{\sum(Y - Y_{cal})^2}{n - p}\right]^{1/2} \tag{4}$$

where Y refers to V^E or $\delta\eta$; n is the number of data points; and p is the number of coefficients. The subscript cal represents calculated value.

Figure 1 shows that the excess molar volumes are negative over the entire range of composition with a minimum around $x_1 = 0.28$ at all temperatures. The negative V^E values indicate that there is a volume contraction on mixing. Figure 2 shows that the viscosity deviations are positive over the entire range of composition with a maximum around $x_1 = 0.28$ for all temperatures. It is shown that the curves in Figures 1 and 2 are not symmetrical. It can also be observed that the values of V^E and $\delta\eta$ are affected by temperature and composition. The deviation becomes more with decreasing temperature. The effect of temperature on viscosity is more pronounced than that on density.

Table 2. Densities ρ, Excess Molar Volumes V^E, Viscosities η, and Viscosity Deviations $\delta\eta$ for the Mixture of TEGMEE (1) + Water (2) at Temperatures from T = (293.15 to 333.15) K

	T/K					T/K				
x_1	293.15	303.15	313.15	323.15	333.15	293.15	303.15	313.15	323.15	333.15
	ρ/g·cm^{-3}					V^E/cm^3·mol^{-1}				
0.0000	0.9982	0.9957	0.9922	0.9881	0.9832	0.0000	0.0000	0.0000	0.0000	0.0000
0.01119	1.0069	1.0037	0.9997	0.9951	0.9896	−0.1276	−0.1265	−0.1263	−0.1260	−0.1231
0.02492	1.0166	1.0126	1.0075	1.0021	0.9957	−0.3014	−0.2975	−0.2847	−0.2778	−0.2650
0.04128	1.0262	1.0207	1.0148	1.0087	1.0019	−0.5114	−0.4875	−0.4664	−0.4537	−0.4410
0.06284	1.0351	1.0287	1.0218	1.0144	1.0062	−0.7567	−0.7247	−0.6884	−0.6526	−0.6125
0.09179	1.0408	1.0328	1.0253	1.0174	1.0085	−0.9820	−0.9174	−0.8725	−0.8306	−0.7759
0.1317	1.0427	1.0349	1.0265	1.0181	1.0087	−1.1563	−1.1106	−1.0416	−0.9899	−0.9211
0.1905	1.0422	1.0339	1.0255	1.0168	1.0073	−1.3063	−1.2551	−1.1896	−1.1310	−1.0586
0.2885	1.0387	1.0298	1.0214	1.0127	1.0031	−1.3786	−1.3095	−1.2469	−1.1924	−1.1106
0.4019	1.0336	1.0249	1.0165	1.0077	0.9985	−1.2524	−1.2062	−1.1441	−1.0832	−1.0258
0.4747	1.0311	1.0223	1.0139	1.0052	0.9961	−1.1467	−1.0979	−1.0354	−0.9830	−0.9338
0.6076	1.0273	1.0185	1.0102	1.0016	0.9925	−0.8926	−0.8524	−0.7997	−0.7589	−0.7087
0.7399	1.0244	1.0155	1.0074	0.9988	0.9898	−0.5994	−0.5538	−0.5276	−0.4885	−0.4504
0.8176	1.0229	1.0141	1.0061	0.9976	0.9886	−0.4005	−0.3723	−0.3632	−0.3398	−0.3021
0.8956	1.0218	1.0131	1.0051	0.9966	0.9877	−0.2272	−0.2193	−0.2142	−0.1932	−0.1725
1.0000	1.0206	1.0119	1.0039	0.9955	0.9867	0.0000	0.0000	0.0000	0.0000	0.0000
	η/mPa·s					$\delta\eta$/mPa·s				
0.0000	1.005	0.8007	0.6560	0.5494	0.4688	0.000	0.000	0.000	0.000	0.000
0.01119	1.484	1.129	0.9341	0.7411	0.6117	0.4030	0.2740	0.2386	0.1606	0.1188
0.02492	2.221	1.595	1.261	1.0127	0.8193	1.047	0.6733	0.5171	0.3941	0.2967
0.04128	3.256	2.344	1.747	1.369	1.092	1.971	1.343	0.9453	0.7050	0.5341
0.06284	4.832	3.349	2.429	1.859	1.433	3.400	2.243	1.551	1.135	0.8286
0.09179	6.993	4.589	3.265	2.436	1.853	5.365	3.343	2.285	1.632	1.186
0.1317	9.102	5.955	4.072	3.015	2.252	7.203	4.515	2.951	2.100	1.499
0.1905	10.54	7.032	4.899	3.558	2.652	8.241	5.306	3.571	2.480	1.772
0.2885	11.29	7.522	5.382	3.942	2.923	8.326	5.320	3.708	2.592	1.832
0.4019	11.34	7.547	5.391	3.965	3.006	7.606	4.795	3.317	2.300	1.670
0.4747	10.93	7.378	5.226	3.885	2.953	6.701	4.272	2.895	2.018	1.460
0.6076	10.06	6.868	4.953	3.735	2.879	4.929	3.117	2.153	1.499	1.099
0.7399	9.168	6.386	4.586	3.552	2.774	3.138	1.992	1.319	0.9482	0.7084
0.8176	8.738	6.178	4.457	3.509	2.728	2.181	1.407	0.9157	0.6895	0.4947
0.8956	8.353	5.884	4.315	3.437	2.697	1.266	0.7340	0.4984	0.4009	0.2953
1.0000	7.796	5.657	4.185	3.326	2.627	0.000	0.000	0.000	0.000	0.000

Table 3. Coefficients of the Redlich−Kister Equation and Standard Deviation for Excess Molar Volume and Viscosity Deviation for TEGMEE (1) + Water (2)

T/K	property	A_0	A_1	A_2	A_3	A_4	A_5	σ
293.15	V^E/cm^3·mol^{-1}	−4.3603	3.4733	−3.5820	3.2729			0.022
	$\delta\eta$/mPa·s	25.2566	−19.9333	27.6832	−65.2684	−11.9819	80.8437	0.25
303.15	V^E/cm^3·mol^{-1}	−4.1662	3.4236	−3.3546	2.9884			0.019
	$\delta\eta$/mPa·s	15.9661	−13.2956	18.9276	−36.9424	−10.3377	44.3862	0.13
313.15	V^E/cm^3·mol^{-1}	−3.9311	3.2833	−3.2905	2.6679			0.017
	$\delta\eta$/mPa·s	11.0049	−10.2668	11.6939	−18.7614	−6.1032	23.0346	0.056
323.15	V^E/cm^3·mol^{-1}	−3.7294	3.1504	−3.0866	2.6250			0.015
	$\delta\eta$/mPa·s	7.6539	−7.1939	8.2275	−11.7122	−3.0514	14.1963	0.040
333.15	V^E/cm^3·mol^{-1}	−3.5182	2.9496	−2.7231	2.6256			0.018
	$\delta\eta$/mPa·s	5.5838	−4.9531	5.2526	−8.1966	−1.2262	9.2358	0.029

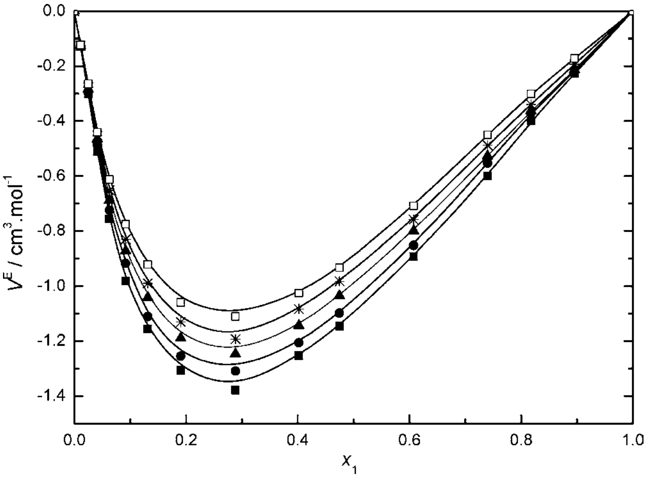

Figure 1. Excess molar volume V^E vs mole fraction x of TEGMEE for TEGMEE (1) + water (2): ■, 293.15 K; ●, 303.15 K; ▲, 313.15 K; ∗, 323.15 K; □, 333.15 K. The symbols represent experimental values, and the solid curves represent the values calculated from eq 3.

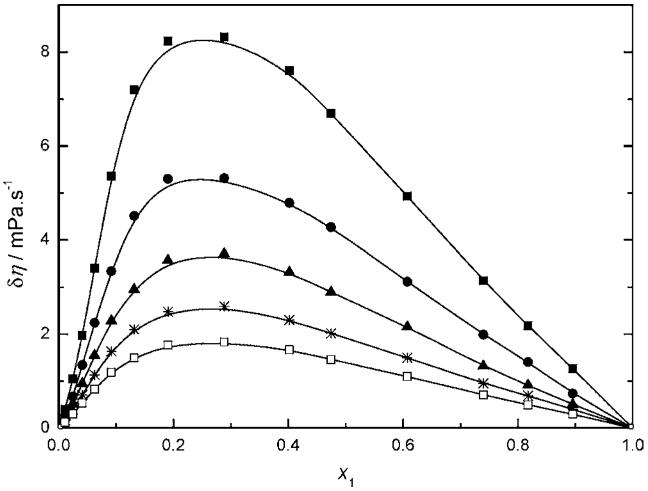

Figure 2. Viscosity deviation $\delta\eta$ vs mole fraction x of TEGMEE for TEGMEE (1) + water (2): ■, 293.15 K; ●, 303.15 K; ▲, 313.15 K; ∗, 323.15 K; □, 333.15 K. The symbols represent experimental values, and the solid curves represent the values calculated from eq 3.

As reported in the literature,[7] the molecular interactions in the aqueous solution of alkoxyethanols are complicated due to the presence of the O and OH groups in the same molecule, which allows self-association via inter- and intramolecular hydrogen bonds. The conformational behavior around the C−C bond and C−O bonds in the oxyethylene chain in water suggest the presence of several types of hydrogen bonds between the molecule of amphiphile and water. Katsumoto et al.[16] had investigated the molecular interaction occurring in the system 2-butoxyethanol in water by infrared (IR) spectroscopy combined with quantum chemical calculations. They found that the blue shift of the υ_{CH} bands due to the butoxy group of C_4E_1 originates mainly from the formation of H-bonds between the ether oxygen atom and water molecules. ^{1}H NMR spectra of aqueous solutions of some *n*-alkoxyethanols (C_1E_m, $m = 1, 2, 3$) over the whole composition range at 298.15 K had been used to study the behavior of binary liquid mixtures. Spectroscopic results confirm the strong interactions between components involving hydrogen bonds.[17]

Compare the properties of TEGMEE + water with that of diethylene glycol monoethyl ether (DEGMEE) measured by us. It can be found that the negative values of the excess molar volumes and the positive values of the viscosity deviations of the TEGMEE/water system are larger than that of the DEGMEE/water system, which suggests that the interactions between TEGMEE and water through hydrogen bonding are stronger than that of DEGMEE and water. The only difference between TEGMEE and DEGMEE molecules lies in that the former has three oxyethylene units while the latter has two. Thus it can be concluded that the molecular interaction of glycol ether with water is enhanced by increasing the oxyethylene units with the same hydrocarbon chain.

Supporting Information Available:

Experimental data summary. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Li, X. X.; Liu, Y. X.; Wei, X. H. Density, Viscosity, and Surface Tension at 293.15 K and Liquid-Liquid Equilibria from 301.15 to 363.15 K under Atmospheric Pressure for the Binary Mixture of Diethylene Glycol Diethyl Ether + Water. *J. Chem. Eng. Data* **2004**, *49*, 1043–1045.

(2) Li, X. X.; Zhao, G.; Liu, D. S.; Cao, W. W. Excess Molar Volume and Viscosity Deviation for the Binary Mixture of Diethylene Glycol Monobutyl Ether + Water from (293.15 to 333.15) K at Atmospheric Pressure. *J. Chem. Eng. Data* **2009**, *54*, 890–892.

(3) Li, X. X.; Zhou, W. D.; Li, X. Y.; Sun, J. L.; Jiang, W. Density, viscosity, and excess properties of the binary mixture of diethylene glycol monomethyl ether + water at T = (293.15, 303.15, 313.15, 323.15, 333.15) K under atmospheric pressure. *J. Mol. Liq.* **2009**, *148*, 73–76.

(4) Henni, A.; Tontiwachwuthikul, P.; Chakma, A. Solubility Study of Methane and Ethane in Promising Physical Solvents for Natural Gas Sweetening Operations. *J. Chem. Eng. Data* **2006**, *51*, 64–67.

(5) Esteve, X.; Conesa, A.; Coronas, A. Liquid Densities, Kinematic Viscosities, and Heat Capacities of Some Alkylene Glycol Dialkyl Ethers. *J. Chem. Eng. Data* **2003**, *48*, 392–397.

(6) Mozo, I.; García de la Fuente, I.; González, J. A.; Cobos, J. C. Thermodynamics of Mixtures Containing Alkoxyethanols. XXIV. Densities, Excess Molar Volumes, and Speeds of Sound at (293.15, 298.15, and 303.15) K and Isothermal Compressibilities at 298.15 K for 2-(2-Alkoxyethoxy)ethanol + 1-Butanol Systems. *J. Chem. Eng. Data* **2007**, *52*, 2086–2090.

(7) Piekarski, H.; Tkaczyk, M.; Góralski, P. Thermochemical properties of electrolyte solutions in {2-(2-methoxyethoxy)ethanol + water} and

(2-isopropoxyethanol + water) mixtures at 298.15 K. *J. Chem. Thermodyn.* **2004**, *36*, 259–266.

(8) Fenn, E. E.; Moilanen, D. E.; Levinger, N. E.; Fayer, M. D. Water Dynamics and Interactions in Water-Polyether Binary Mixtures. *J. Am. Chem. Soc.* **2009**, *131*, 5530–5539.

(9) Pal, A.; Dass, J. Excess molar volumes and excess partial molar volumes of triethylene glycol monoethyl ether-n-alcohol mixtures at 25 °C. *J. Solution Chem.* **1999**, *28*, 237–245.

(10) Douhéret, G.; Davis, M. I.; Ulloa, J.; Høiland, H.; Fjellanger, I. J. Ultrasonic speeds and volumetric properties of binary mixtures of water with 2-[2-(2-alkoxyethoxy)ethoxy]ethanols at 298.15 K. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 2369–2379.

(11) Pal, A.; Sharma, S. Ultrasonic speeds and isentropic functions of [2-{2-(2-alkoxyethoxy)ethoxy}ethanol + di-n-butylether] at the temperature 298.15 K. *J. Chem. Thermodyn.* **1998**, *30*, 767–776.

(12) Sen, D.; Kim, M. G. Excess molar volumes and excess molar enthalpies of the binary mixtures of 1,2-dichloropropane with di- and triethylene glycol mono alkyl ethers at T=298.15 K. *Fluid Phase Equilib.* **2008**, *285*, 30–35.

(13) Pal, A.; Sharma, S. Viscosities and Densities of Some n-alkoxyethanols with trichloroethylene and tetrachloroethylene at 298.15 K. *J. Chem. Eng. Data* **1998**, *43*, 21–24.

(14) Castellari, C. Excess molar enthalpies and hydrogen bonding in binary mixtures containing ethers and benzyl alcohol at 308.15 K and atmospheric pressure. *J. Chem. Eng. Data* **2006**, *51*, 599–603.

(15) Redlich, O.; Kister, A. T. Algebraic representation of thermodynamic properties and the classification of solutions. *Ind. Eng. Chem.* **1948**, *40*, 345–348.

(16) Katsumoto, Y.; Komatsu, H.; Ohno, K. Origin of the Blue Shift of the CH Stretching Band for 2-Butoxyethanol in Water. *J. Am. Chem. Soc.* **2006**, *128*, 9278–9279.

(17) Yadav, M. Kr.; Kumar, A. ^{1}H NMR studies of aqueous solutions of some n-alkoxyethanols (C_1E_m, m=1,2,3) or polyethers ($C_1E_mC_1$, m=1,2,3,4) at 298.15 K. *J. Mol. Liq.* **2005**, *121*, 94–98.

Received for review October 4, 2009. Accepted December 7, 2009.

JE9008014