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

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This work reports new measurements of densities and viscosities for the binary liquid mixture of triethylene glycol monobutyl ether ($CH_3(CH_2)_3(OCH_2CH_2)_3OH$) + 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. Both excess molar volumes and viscosity deviations were correlated by the Redlich−Kister-type equations. The results suggest that the molecular interaction between triethylene glycol monobutyl ether and water is stronger than that of diethylene glycol monobutyl 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. Glycol ethers are important industrial solvents with the highest potential for gas sweetening.[1] 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.[2]

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.[3] The key advantage of using these systems as absorption liquids is that both solubility and hydrolysis rate of COS 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.[4] 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.[5]

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 useful to study molecular interactions and arrangements through deviation from ideal mixtures.

Experimental Section

Materials. Triethylene glycol monobutyl ether (TEGMBE, CAS 143-22-6) was purchased from Alfa Aesar, and its mass fraction purity was 99.9 %. TEGMBE was used as received. Prior to measurements, it was dried over 0.4 nm molecular sieves and partially degassed under vacuum. Doubly distilled water was used.

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

ρ/g·cm^{-3}		η/mPa·s	
this work	lit.	this work	lit.
0.9808	0.9868[a] 0.98056[b] 0.98275[c]	7.688	9.109[a]

[a] From ref 6. [b] From ref 7. [c] From ref 8.

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 for calibration. A thermostatically controlled water bath whose temperature was controlled to ± 0.01 K was used for all the density measurements and the measurements of viscosity. Binary mixtures were prepared by mass, using an electronic analytical balance (HANGPING FA2104, Shanghai, China) with 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 doubly distilled water. The flow-time measurements were made using an accurate stopwatch with 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 TEGMBE 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 TEGMBE at 293.15 K were not found in the literature. So the viscosity of pure TEGMBE 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

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Table 2. Densities ρ and Viscosities η for the Mixture of TEGMBE (1) + Water (2) at Temperatures from (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}					η/mPa·s		
0.0000	0.9982	0.9957	0.9922	0.9881	0.9832	1.005	0.8007	0.6560	0.5494	0.4688
0.009612	1.0041	1.0009	0.9965	0.9914	0.9859	1.536	1.175	0.9391	0.7657	0.6398
0.02136	1.0094	1.0047	0.9989	0.9925	0.9867	2.342	1.741	1.356	1.094	0.9018
0.03602	1.0119	1.0065	0.9997	0.9932	0.9863	3.496	2.526	1.935	1.519	1.226
0.05509	1.0135	1.0071	0.9998	0.9925	0.9850	5.103	3.614	2.685	2.137	1.629
0.08023	1.0136	1.0066	0.9986	0.9909	0.9833	7.018	4.832	3.562	2.692	2.116
0.1156	1.0119	1.0049	0.9969	0.9885	0.9805	9.156	6.189	4.476	3.293	2.525
0.1685	1.0089	1.0013	0.9933	0.9849	0.9768	11.21	7.424	5.289	3.913	2.972
0.2571	1.0041	0.9963	0.9875	0.9789	0.9704	12.63	8.311	5.912	4.406	3.346
0.3308	1.0004	0.9925	0.9836	0.9749	0.9665	12.68	8.439	6.038	4.477	3.399
0.4398	0.9959	0.9879	0.9791	0.9706	0.9624	12.35	8.238	5.926	4.406	3.371
0.5322	0.9930	0.9851	0.9762	0.9678	0.9596	11.78	7.929	5.747	4.329	3.319
0.5991	0.9912	0.9832	0.9745	0.9660	0.9578	11.36	7.685	5.612	4.257	3.266
0.7291	0.9886	0.9806	0.9718	0.9632	0.9552	10.51	7.271	5.407	4.147	3.188
0.8068	0.9874	0.9793	0.9704	0.9619	0.9539	10.13	7.083	5.264	4.088	3.119
0.8905	0.9862	0.9781	0.9692	0.9606	0.9525	9.778	6.856	5.143	3.936	3.051
1.0000	0.9848	0.9767	0.9678	0.9593	0.9512	9.282	6.528	4.979	3.769	2.978

Table 3. Parameters in Equations 1 and 2 for Density and Viscosity Data of TEGMBE (1) + Water (2)

x_1	a_0 / g·cm^{-3}	a_1·10^4 / g·cm^{-3}	σ / g·cm^{-3}	η_0·10^4 / mPa·s	E_a / kJ·mol^{-1}	σ / mPa·s
0.009612	1.1395	−4.59	0.0008	9.1	18.10	0.016
0.02136	1.1788	−5.76	0.0005	6.7	19.87	0.031
0.03602	1.2015	−6.45	0.0005	4.5	21.78	0.045
0.05509	1.2238	−7.16	0.0004	3.4	23.40	0.071
0.08023	1.2375	−7.63	0.0003	2.4	25.09	0.099
0.1156	1.2445	−7.92	0.0005	1.5	26.80	0.11
0.1685	1.2454	−8.06	0.0003	1.2	27.80	0.16
0.2571	1.2530	−8.48	0.0003	1.3	27.92	0.21
0.3308	1.2510	−8.54	0.0003	1.6	27.50	0.18
0.4398	1.2432	−8.43	0.0002	1.8	27.18	0.19
0.5322	1.2397	−8.41	0.0003	2.2	26.47	0.18
0.5991	1.2376	−8.40	0.0002	2.6	25.99	0.18
0.7291	1.2356	−8.42	0.0003	4.2	24.63	0.14
0.8068	1.2349	−8.44	0.0003	4.9	24.18	0.13
0.8905	1.2352	−8.49	0.0003	5.2	23.99	0.11
1.0000	1.2329	−8.46	0.0002	6.0	23.49	0.12

relative difference in viscosity value between this work and the literature is low.

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

In this paper, to show the temperature dependence of density and viscosity, the measured densities are presented as functions of temperature by the linear relation, eq 1, while viscosities are presented by the Arrhenius-like equation, eq 2.[9]

$$\rho = a_0 + a_1(T/\mathrm{K}) \tag{1}$$

$$\eta = \eta_0 \mathrm{e}^{E_a/RT} \tag{2}$$

where a_0, a_1, η_0, and E_a are the undetermined parameters. The fitted results were given in Table 3.

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

$$V^E = \frac{x_1M_1 + x_2M_2}{\rho_M} - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2} \tag{3}$$

$$\delta\eta = \eta_M - (x_1\eta_1 + x_2\eta_2) \tag{4}$$

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 listed in Table 4.

The excess mole volumes and viscosity deviations were fitted by a Redlich−Kister-type polynomial[10]

$$Y = x_1x_2\sum_{k=0}^{m} A_k(x_1 - x_2)^k \tag{5}$$

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 5 and Table 6.

The correlated results for densities, viscosities, excess mole volumes, and viscosity deviations were given in Table 3, Table 5, and Table 6, in which the tabulated standard deviation σ was defined as

$$\sigma = \left[\frac{\sum (Y_{\mathrm{exp}} - Y_{\mathrm{cal}})^2}{n - p}\right]^{1/2} \tag{6}$$

where Y refers to ρ, η, V^E, or $\delta\eta$; n is the number of data points; and p is the number of coefficients. The subscripts exp and cal represent the experimental value and the calculated value, respectively.

Figure 1 shows that the excess molar volumes are negative over the entire range of composition with a minimum around $x_1 = 0.26$ at all temperatures. The negative V^E indicate that there

Table 4. Excess Molar Volumes V^E and Viscosity Deviations $\delta\eta$ for the Mixture of TEGMBE (1) + Water (2) at Temperatures from (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
	V^E/cm^3·mol^{-1}					$\delta\eta$/mPa·s				
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.000	0.000	0.000	0.000	0.000
0.009612	−0.1437	−0.1422	−0.1366	−0.1270	−0.1231	0.4514	0.3193	0.2416	0.1854	0.1469
0.02136	−0.3050	−0.2844	−0.2610	−0.2328	−0.2303	1.160	0.8180	0.6077	0.4758	0.3794
0.03602	−0.4376	−0.4124	−0.3763	−0.3547	−0.3336	2.193	1.519	1.123	0.8536	0.6668
0.05509	−0.5843	−0.5448	−0.5063	−0.4727	−0.4417	3.642	2.498	1.791	1.410	1.022
0.08023	−0.7298	−0.6836	−0.6346	−0.5977	−0.5698	5.349	3.572	2.559	1.884	1.446
0.1156	−0.8647	−0.8318	−0.7951	−0.7410	−0.7047	7.194	4.726	3.320	2.371	1.766
0.1685	−1.0024	−0.9586	−0.9389	−0.8927	−0.8580	8.810	5.658	3.905	2.821	2.080
0.2571	−1.1141	−1.0765	−1.0292	−0.9799	−0.9238	9.497	6.038	4.145	3.029	2.232
0.3308	−1.1073	−1.0734	−1.0266	−0.9733	−0.9240	8.937	5.744	3.952	2.863	2.100
0.4398	−1.0036	−0.9734	−0.9460	−0.9171	−0.8883	7.705	4.918	3.369	2.441	1.799
0.5322	−0.8765	−0.8676	−0.8371	−0.8264	−0.7997	6.370	4.080	2.790	2.066	1.515
0.5991	−0.7593	−0.7445	−0.7459	−0.7265	−0.7006	5.396	3.453	2.366	1.779	1.294
0.7291	−0.5397	−0.5371	−0.5365	−0.5072	−0.5168	3.470	2.295	1.599	1.250	0.8897
0.8068	−0.4069	−0.3940	−0.3820	−0.3731	−0.3866	2.447	1.662	1.120	0.9410	0.6258
0.8905	−0.2408	−0.2336	−0.2270	−0.2020	−0.1990	1.402	0.9551	0.6374	0.5196	0.3478
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.000	0.000	0.000	0.000	0.000

Table 5. Fit Parameters in the Redlich−Kister Equation of Excess Molar Volume V^E for TEGMBE (1) + Water (2)

T/K	A_0	A_1	A_2	A_3	A_4	A_5	σ / cm^3·mol^{-1}
293.15	−3.7172	3.4230	−1.5380	−2.9128	−2.5995	6.6135	0.014
303.15	−3.6385	3.1579	−1.4610	−2.2321	−2.2463	5.6064	0.015
313.15	−3.5341	2.6364	−1.5803	−0.1822	−1.7129	3.0932	0.014
323.15	−3.4426	2.3859	−1.1922	0.3263	−1.6825	2.4321	0.013
333.15	−3.3104	2.1434	−1.4841	−0.08055	−1.0383	3.1111	0.014

Table 6. Fit Parameters in the Redlich−Kister Equation of Viscosity Deviation $\delta\eta$ for TEGMBE (1) + Water (2)

T/K	A_0	A_1	A_2	A_3	A_4	A_5	σ / mPa·s
293.15	27.0089	−24.1684	31.3410	−59.1965	−10.6746	69.2286	0.16
303.15	17.2850	−15.6517	20.2727	−32.9133	−4.8743	35.6876	0.11
313.15	11.8529	−10.8144	13.8439	−21.3099	−2.5210	20.7687	0.077
323.15	8.7097	−7.7291	10.7673	−11.5417	−2.2722	9.0138	0.052
333.15	6.4117	−5.7867	7.0877	−9.0440	−0.5043	6.6334	0.035

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 $x_1 = 0.26$ for all temperatures. It can be seen that the curves in Figures 1 and 2 are not symmetrical. Both V^E and $\delta\eta$ indicate that the molecular interaction between TEGMBE and water is strong. It can also be observed that this kind of interaction is affected by temperature and composition. The interaction becomes stronger with decreasing temperature. The effect of temperature on viscosity is sharper than that on density.

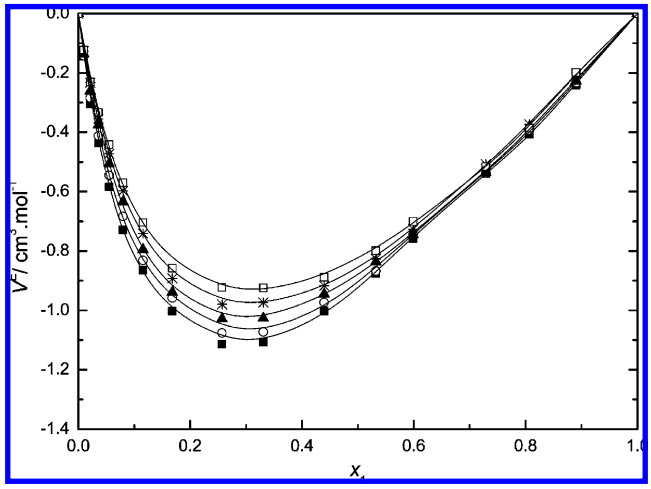

Figure 1. Excess molar volume V^E vs mole fraction x of TEGMBE for TEGMBE (1) + water (2): ■, 293.15K; ○, 303.15 K; ▲, 313.15 K; *, 323.15 K; □, 333.15 K. The symbols represent experimental values, and the solid curves represent the values calculated from eq 5.

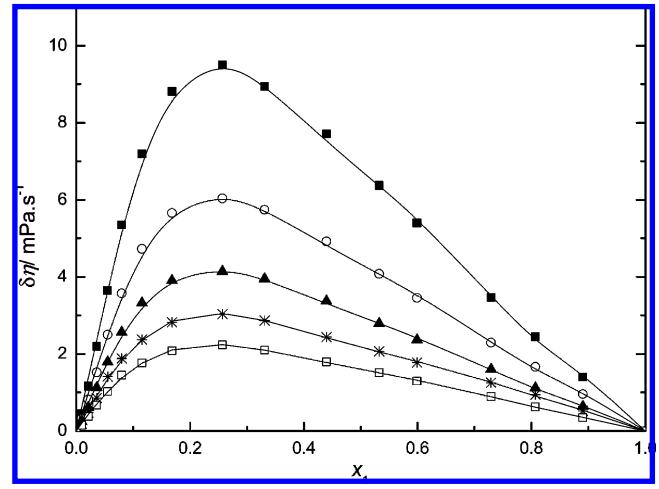

Figure 2. Viscosity deviation $\delta\eta$ vs mole fraction x of TEGMBE for TEGMBE (1) + water (2): ■, 293.15 K; ○, 303.15 K; ▲, 313.15 K; *, 323.15 K; □, 333.15 K. The symbols represent experimental values, and the solid curves represent the values calculated from eq 5.

As reported in the literature,[4,5] 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 suggests the presence of several types of hydrogen bonds between the amphiphile molecule and water. ^{1}H NMR spectra of aqueous solutions of some *n*-alkoxyethanols (C_1E_m, $m = 1, 2, 3$) over the whole composition rang 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.[11]

The properties of TEGMBE + water can be compared with that of diethylene glycol monobutyl ether (DEGMBE) + water measured by us previously.[12] The negative values of the excess molar volumes and the positive values of the viscosity deviations are larger than that of DEGMBE, which suggest that the interactions between TEGMBE and water through hydrogen bonding are stronger than that of DEGMBE and water. The only difference between TEGMBE and DEGMBE 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 within the same hydrocarbon chain.

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