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

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Densities and viscosities have been measured as a function of composition for the binary liquid mixture of diethylene glycol monobutyl ether $CH_3(CH_2)_3O(CH_2)_2O(CH_2)_2OH$ + water 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 Ubbelohde capillary viscometer. From the experimental data, the excess molar volumes V^E and viscosity deviations $\delta\eta$ were calculated. This binary system shows negative deviations in excess molar volumes from the ideal behavior. Excess molar volumes and viscosity deviations were correlated by the Redlich−Kister type equations to obtain their coefficients and standard deviations.

Introduction

Glycol ethers are important industrial solvents. They can be used as scrubbing liquids for the absorption of acid gases 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.[1] They are increasingly used as additives to gasoline due their octane-enhancing and pollution-reducing properties. On the other hand, hydroxyethers are nonionic amphiphile molecules, very effective as surfactants with a large number of applications.[2] Short-chain polyethylene glycol monoalkylethers are used in various biotechnical and biomedical applications, constituting a simple model of biological systems.[3] Also, in the last years, some authors have proposed new organic working pairs containing ethylene glycol ethers as absorbent fluids for absorption heat pumps and chillers.[4,5] In addition, the glycol ethers can also be used as polar additives in anionic polymerization and automotive brake fluid.

Diethylene glycol monobutyl ether (DEGMBE) is a colorless liquid which is miscible with water and most organic solvents. It is widely used as a solvent, especially in the printing ink and paint industries. Diethylene glycol monobutyl ether is also found in products such as floor cleaners, floor wax strippers, floor finishes, spray cleaners, penetrating oils, metal cleaners, and paint removers. Recently, it is found that DEGMBE is an effective component of new natural gas hydrate kinetic inhibitors.

The binary mixture of DEGMBE with water has been used as scrubbing liquids for the absorption of carbonyl sulfide from synthesis gas in our research. The key advantage of this system is that carbonyl sulfide absorbed can hydrolyze to H_2S which can be easily oxidized to the element sulfur in the liquid redox process. Process design using this system requires accurate thermophysical property data. On the other hand, the mixing deviation from ideality is useful in the study of molecular interactions and arrangements.[6] The data of densities and viscosities for the mixture of DEGMBE + water were not found in the literature.

Table 1. Comparison of Measured Densities (ρ) and Viscosities (η) of DEGMBE with Literature Values at Temperatures from (293.15 to 333.15) K

	ρ/g·cm^{-3}		η/mPa·s	
T/K	this work	lit.	this work	lit.
293.15	0.9529	0.9522[a]		
		0.95281[b]		
		0.952196[c]		
298.15			4.98	5.052[d]
303.15	0.9435	0.9438[a]		
313.15	0.9359	0.9353[a]		
323.15	0.9266	0.9266[a]		
333.15	0.9184	0.9178[a]		

[a] From ref 7. [b] From ref 8. [c] From ref 2. [d] From ref 9.

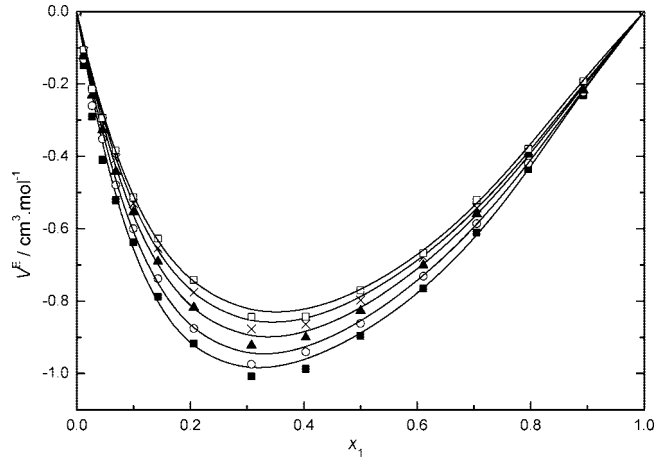

Figure 1. Excess molar volume V^E vs mole fraction x of DEGMBE for DEGMBE (1) + water (2): ■, 293.15 K; ○, 303.15 K; ▲, 313.15 K; ×, 323.15 K; □, 333.15 K. The symbols represent experimental values, and the solid curves represent the values calculated from eq 5.

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Table 2. Densities ρ and Viscosities η for the Mixture of DEGMBE (1) + Water (2) at Temperatures from (293.15 to 333.15) K

	ρ/g·cm^{-3}					η/mPa·s				
x_1	T/K = 293.15	303.15	313.15	323.15	333.15	293.15	303.15	313.15	323.15	333.15
0.000	0.9982	0.9957	0.9922	0.9881	0.9832	1.005	0.8007	0.6560	0.5494	0.4688
0.01221	1.0009	0.9968	0.9923	0.9870	0.9814	1.52	1.15	0.908	0.738	0.609
0.02709	1.0019	0.9964	0.9906	0.9849	0.9788	2.26	1.64	1.27	1.02	0.833
0.04539	1.0006	0.9934	0.9874	0.9806	0.9741	3.18	2.31	1.76	1.38	1.12
0.06890	0.9978	0.9907	0.9839	0.9762	0.9690	4.35	3.10	2.32	1.79	1.42
0.09981	0.9941	0.9866	0.9793	0.9716	0.9643	5.57	3.93	2.88	2.19	1.71
0.1428	0.9901	0.9818	0.9742	0.9658	0.9580	6.78	4.74	3.44	2.58	1.97
0.2062	0.9843	0.9757	0.9677	0.9589	0.9508	7.94	5.44	3.88	2.87	2.19
0.3078	0.9768	0.9679	0.9599	0.9508	0.9426	8.42	5.78	4.16	3.07	2.35
0.4037	0.9711	0.9618	0.9539	0.9448	0.9367	8.24	5.75	4.16	3.08	2.37
0.5015	0.9664	0.9571	0.9492	0.9401	0.9319	7.84	5.55	4.04	3.02	2.33
0.6107	0.9624	0.9530	0.9451	0.9360	0.9279	7.35	5.27	3.86	2.91	2.26
0.7050	0.9595	0.9501	0.9422	0.9331	0.9249	6.94	5.00	3.70	2.81	2.19
0.7958	0.9571	0.9477	0.9398	0.9307	0.9226	6.56	4.76	3.54	2.71	2.13
0.8932	0.9549	0.9455	0.9377	0.9286	0.9204	6.20	4.49	3.38	2.61	2.06
1.000	0.9529	0.9435	0.9357	0.9266	0.9185	5.84	4.23	3.22	2.51	2.00

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

x_1	a_0	a_1·10^4	σ/g·cm^{-3}	b_0	b_1	σ/mPa·s
0.01221	1.1445	−4.88	0.0006	2.009·10^{18}	−7.347	0.024
0.02709	1.1712	−5.77	0.0002	2.269·10^{20}	−8.110	0.050
0.04539	1.1933	−6.58	0.0003	2.537·10^{21}	−8.474	0.055
0.06890	1.2093	−7.21	0.0002	1.008·10^{23}	−9.067	0.071
0.09981	1.2128	−7.46	0.0001	2.068·10^{24}	−9.555	0.079
0.1428	1.2251	−8.02	0.0002	2.088·10^{25}	−9.928	0.080
0.2062	1.2299	−8.38	0.0002	4.449·10^{26}	−10.44	0.11
0.3078	1.2273	−8.55	0.0002	2.497·10^{26}	−10.33	0.11
0.4037	1.2223	−8.58	0.0004	4.961·10^{25}	−10.05	0.093
0.5015	1.2183	−8.60	0.0004	8.607·10^{24}	−9.746	0.078
0.6107	1.2142	−8.60	0.0004	1.595·10^{24}	−9.460	0.068
0.7050	1.2119	−8.62	0.0004	4.255·10^{23}	−9.238	0.066
0.7958	1.2089	−8.60	0.0004	1.199·10^{23}	−9.025	0.067
0.8932	1.2064	−8.59	0.0004	4.013·10^{22}	−8.842	0.076
1.000	1.2038	−8.57	0.0004	1.081·10^{22}	−8.622	0.087

Experimental Section

Materials. Diethylene glycol monobutyl ether, DEGMBE (CAS 112-34-5 Fluka, GC > 99 mass %), was dried over ferrous sulfate (A.R.) and then fractionally distilled under reduced nitrogen gas pressure. Prior to measurements, it was dried over 0.4 nm molecular sieves and partially degassed under vacuum. Bidistilled water was used.

Apparatus and Procedure. The densities of the pure liquids and the mixtures were measured with a 5 cm^3 capillary pycnometer. Degassed pure water was used as calibrating substances. A thermostatically controlled, well-stirred 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 checked by measurement of the viscosity of pure water. The flow-time measurements were made using an accurate stopwatch with a precision of ± 0.01 s. The average of five or 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 ± 0.3 %.

Results and Discussion

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 DEGMBE at 293.15 K is not found in the literature, and the values searched from different Web sites are not identical. There is no way to compare. So the viscosity of pure DEGMBE at 298.15 K was measured for comparison. A reasonable agreement was found between our experimental values and those of the literature.

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

In this paper, the measured densities and viscosities are presented as functions of temperature by the following equations, respectively

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

$$\eta = b_0(T/\mathrm{K})^{b_1} \tag{2}$$

where a_0, a_1, b_0, and b_1 are the undetermined parameters.

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

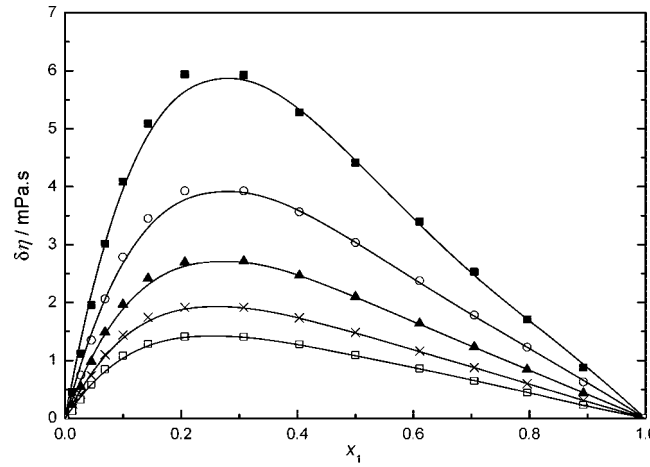

Figure 2. Viscosity deviation $\delta\eta$ vs mole fraction x of DEGMBE for DEGMBE (1) + water (2): ■, 293.15 K; ○, 303.15 K; ▲, 313.15 K; ×, 323.15 K; □, 333.15 K. The symbols represent experimental values, and the solid curves represent the values calculated from eq 5.

Table 4. Excess Molar Volumes, V^E, and Viscosity Deviations $\delta\eta$ for the Mixture of DEGMBE (1) + Water (2) at Temperatures from (293.15 to 333.15) K

	V^E/cm^3·mol^{-1}					$\delta\eta$/mPa·s				
x_1	T/K = 293.15	303.15	313.15	323.15	333.15	293.15	303.15	313.15	323.15	333.15
0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.000	0.000	0.000	0.000	0.000
0.01221	−0.1478	−0.1320	−0.1226	−0.1108	−0.1050	0.455	0.302	0.220	0.165	0.121
0.02709	−0.2904	−0.2597	−0.2318	−0.2231	−0.2146	1.12	0.748	0.548	0.413	0.322
0.04539	−0.4097	−0.3521	−0.3278	−0.3045	−0.2942	1.96	1.35	0.984	0.741	0.581
0.06890	−0.5211	−0.4794	−0.4426	−0.4060	−0.3842	3.02	2.06	1.49	1.10	0.847
0.09981	−0.6372	−0.5995	−0.5551	−0.5306	−0.5140	4.08	2.79	1.96	1.44	1.09
0.1428	−0.7869	−0.7383	−0.6909	−0.6539	−0.6268	5.09	3.45	2.41	1.75	1.28
0.2062	−0.9176	−0.8757	−0.8173	−0.7754	−0.7416	5.94	3.93	2.69	1.92	1.41
0.3078	−1.0085	−0.9745	−0.9225	−0.8765	−0.8437	5.93	3.93	2.72	1.92	1.41
0.4037	−0.9878	−0.9405	−0.9007	−0.8633	−0.8430	5.28	3.56	2.46	1.74	1.28
0.5015	−0.8967	−0.8616	−0.8266	−0.7968	−0.7709	4.41	3.03	2.10	1.48	1.09
0.6107	−0.7650	−0.7312	−0.7009	−0.6787	−0.6676	3.40	2.37	1.64	1.16	0.859
0.7050	−0.6109	−0.5859	−0.5590	−0.5428	−0.5209	2.53	1.79	1.23	0.875	0.648
0.7958	−0.4363	−0.4193	−0.3952	−0.3842	−0.3789	1.71	1.23	0.84	0.600	0.444
0.8932	−0.2311	−0.2223	−0.2176	−0.2121	−0.1922	0.875	0.628	0.435	0.309	0.230
1.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.000	0.000	0.000	0.000	0.000

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

T/K	A_0	A_1	A_2	A_3	σ/cm^3·mol^{-1}
293.15	−3.5765	1.8168	−1.9007	2.2124	0.029
303.15	−3.4410	1.8659	−1.6846	1.6111	0.021
313.15	−3.2971	1.7777	−1.4419	1.3361	0.019
323.15	−3.1765	1.6391	−1.3039	1.2401	0.017
333.15	−3.0967	1.5204	−1.1175	1.3359	0.017

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

T/K	A_0	A_1	A_2	A_3	σ/mPa·s
293.15	17.8650	−20.5359	14.6628	−1.6432	0.13
303.15	12.1830	−12.6467	9.9083	−2.9357	0.090
313.15	8.3888	−8.4962	7.1012	−3.0155	0.055
323.15	5.8962	−5.7938	5.4186	−3.0617	0.038
333.15	4.3299	−4.0917	4.15120	−2.8293	0.028

viscosities of pure components 1 and 2, respectively. The subscript M represents mixture properties. The excess mole volumes and viscosity deviations were correlated by a Redlich−Kister-type polynomial[10]

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

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 are 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

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

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 30 mol % for DEGMBE at all temperatures. It indicates that the interaction between DEGMBE molecules and water molecules is strong. This kind of interaction is also affected by temperature and composition. The interaction becomes stronger with decreasing temperature. Figure 2 shows that the viscosity deviations are positive over the entire range of composition with a maximum around 25 mol % for all temperatures. As the literature reported, 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 molecules of amphiphile and water.[3] The positive values of the viscosity deviations suggest that the interaction forces through hydrogen bonding play an important role.

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