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Density, Viscosity, and Surface Tension at 293.15 K and Liquid−Liquid Equilibria from 301.15 K to 363.15 K under Atmospheric Pressure for the Binary Mixture of Diethylene Glycol Diethyl Ether + Water

Xin-Xue Li, Ying-Xin Liu, and Xiong-Hui Wei*

Department of Applied Chemistry, College of Chemistry and Molecular Engineering, Peking University,
Beijing 100871, China

Densities, viscosities, and surface tension have been measured as a function of composition for the binary liquid mixture of diethylene glycol diethyl ether + water at 293.15 K under atmospheric pressure. Densities were determined using a capillary pycnometer. Viscosities were measured with a Ubbelohde capillary viscometer. Surface tension was measured by means of the drop-volume technique. The estimated uncertainties of the measurements were ±0.1% for density, ±0.3% for viscosity, and $\pm 0.04\ \mathrm{mN \cdot m^{-1}}$ for surface tension. Liquid−liquid equilibrium data were also measured for the binary mixture in the temperature range from 301.15 K to 363.15 K. The compositions of both the top and bottom phases were analyzed by gas chromatography.

Introduction

Glycol ethers are important industrial solvents. 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 meting point. 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.[1,2] In addition, the glycol ethers can also be used as polar additives in anionic polymerization and automotive brake fluid.

A binary mixture of diethylene glycol diethyl ether (DEGDEE, $C_2H_5(OC_2H_4)_2C_2H_5$) with water has been used as a scrubbing liquid for the absorption of carbonyl sulfide from syngas 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 element sulfur in liquid redox process. Process design using this system requires accurate thermophysical property data. Although there are some papers concerning measurements of density and viscosity for pure DEGDEE or its mixtures with organic solvent,[1−3] no data about the mixture of DEGDEE (1) + water (2) was found in the literature. Surface tension was also measured for the binary liquid mixture at 293.15 K under atmospheric pressure because it plays an important role in mass transfer processes such as distillation, extraction, crystallization, and absorption.[4]

The mutual solubility of the two components increases as the temperature decreases with a lower critical solution temperature (LCST). To elucidate the structures and properties of the interface between two phases in the vicinity of the critical solution temperature, Aratono[5] had determined the LCST by measuring the phase-separation and phase-mixing temperatures in the vicinity of the LCST under atmospheric pressure. The detailed procedure was described in their papers. The mass fraction w_1 and temperature T_c of LCST are 0.690 and 299.52 K, respectively. However, their measurements were limited to narrow temperature ranges only about 3 K above the LCST. In this work, liquid−liquid equilibrium (LLE) data were measured in the temperature range from 301.15 K to 363.15 K. The compositions of both top and bottom phases were analyzed by gas chromatography.

Experimental Section

Materials. DEGDEE (Fluka,GC>99%) was dried over ferrous sulfate (AR) 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.[3] The purity of the final samples, as found by gas chromatograph, was better than 99.4 mass %. Bidistilled water was used. Table 1 shows the measured density and viscosity of DEGDEE together with those reported in the literature for comparison.

Apparatus and Procedure. The densities of the pure liquids and the mixtures were measured with a 5-$\mathrm{cm^3}$ capillary pycnometer. Degassed pure water was used as a calibrating substance. 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, surface tension, and LLE. Binary mixtures were prepared by mass, using an analytical balance with a precision of ±0.0001 g (TG328B, Shanghai, China). The uncertainty of the density measurements was estimated to be ±0.1%.

The viscosities were determined at 293.15 K with a capillary viscometer of the 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 uncertainty of the viscosity measurements was estimated to be ±0.3%.

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* To whom correspondence may be addressed. Tel.: +86-10-82642177. Fax: +86-10-62751529. E-mail: xhwei@pku.edu.cn.

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Table 1. Comparison of Measured Densities (ρ) and Viscosities (η) of DEGDEE with Literature Values at 293.15 K and Phase Equilibria Data of DEGDEE (1) + Water (2) at 301.15 K and 302.15 K

Density and Viscosity	
this work	lit
ρ/(kg·m^{-3})	
907.3	907.9[1]
η/(mPa·s)	
1.346	1.358[2]
Phase Equilibria	
this work	lit
301.15 (K), Top Phase, w_1[a]	
0.7937	0.7921[5]
301.15 (K), Bottom Phase, w_1	
0.5875	0.5804[5]
302.15 (K), Top Phase, w_1	
0.8042	0.8066[5]
302.15 (K), Bottom Phase, w_1	
0.5631	0.5571[5]

[a] w_1 is the mass fraction of DEGDEE.

The drop-volume method was employed to measure surface tension, γ, for binary mixtures of DEGDEE with water over the whole composition range. All samples were equilibrated to 293.15 ± 0.1 K under atmospheric pressure. The uncertainty of the surface tension measurements was estimated to be ±0.04 mN·m^{-1}.

LLE data above the LCST were determined as follows: mixtures corresponding to a mass fraction around 0.690 at each temperature were stirred for 2 h in thermostatic equilibrium and then left to stand and equilibrate. After 5 h, samples of the conjugate phase were withdrawn and their compositions were determined by gas chromatograph.

An Agilent 6890N gas chromatograph with a 2m × $^1/_8$ in. Porapak Q packed column and a TCD linked to a HP6890 workstation was used to determine the concentration of DEGDEE and water. The carrier gas was hydrogen (flow rate of 50 mL/min). Oven temperature was 513.15 K. An injection volume of 1 μL was chosen. In all cases, the injections were repeated at least three to four times and the average results were reported. The average deviation of the peak area ratio of DEGDEE/water was $\pm 8 \times 10^{-4}$.

For the calibration of the gas chromatograph, the external standard method was used.[6] A series of standards with composition lying close to the equilibrium curve were prepared and analyzed, and the ratio of the mass-fraction composition DEGDEE/water was regressed to the corresponding peak-area ratios. Analysis of a series of samples of known composition indicated that the maximum relative error between the measured and true composition was 0.2% mass.

Results and Discussion

A comparison of our measurements of density, viscosity, and LLE with the data in the literature was shown in Table 1. It is necessary to point out that LLE data in Table 1 were obtained by linear interpolation from Aratono's experimental results.[5] A reasonable agreement was found between our experimental values and those of the literature.

Table 2 gives the experimental results of the densities, viscosities, and surface tensions at 293.15 K at various mass fractions. The plot of the densities against the mass fraction of the DEGDEE is given in Figure 1. It is shown that, with increasing mass fraction of DEGDEE, the density decreases to a little degree at first then increases up to a maximum value greater than the density of pure

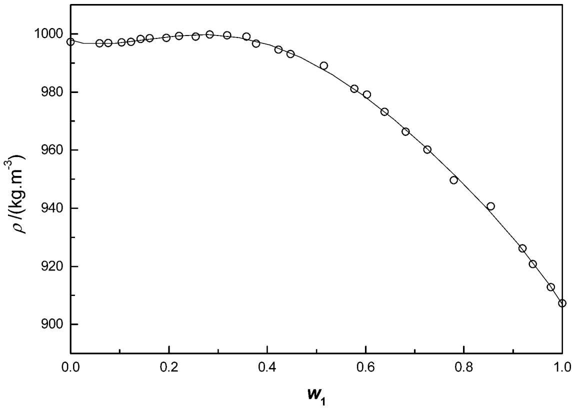

Figure 1. Liquid densities vs mass fraction, w, for diethylene glycol diethyl ether (1) + water (2) at 293.15 K.

Table 2. Densities (ρ), Viscosities (η), and Surface Tension (γ) for the Mixture of DEGDEE (1) + Water (2) at 293.15 K

w_1	ρ/(kg·m^{-3})	η/(mPa·s)	γ/(mN·m^{-1})
0.0000	997.2	1.002	72.75
0.0033			69.73
0.00984			66.53
0.01771			56.82
0.03207			45.57
0.05896	996.7	1.180	36.39
0.07683	996.9	1.265	
0.1038	997.1	1.451	
0.1227	997.2	1.551	
0.1425	998.2	1.701	
0.1611	998.5	1.839	35.71
0.1951	998.6	2.149	
0.2207	999.3	2.414	
0.2547	999.1	2.707	34.92
0.2828	999.8	2.961	
0.3185	999.5	3.302	
0.3578	999.1	3.637	34.11
0.3773	996.6	3.781	
0.4231	994.6	4.088	
0.4474	993.1	4.218	32.30
0.5151	989.0	4.462	
0.5769	981.1	4.452	30.54
0.6029	979.1	4.403	
0.6385	973.1	4.270	30.21
0.6814	966.4	4.033	
0.7256	960.1	3.741	
0.7794	949.6	3.189	30.46
0.8549	940.7	2.599	30.20
0.9195	926.2	1.943	
0.9401	920.7	1.75	30.01
0.9769	912.8	1.467	
1.000	907.3	1.346	29.27

Table 3. Phase Composition for the Mixture of DEGDEE (1) + Water (2) at Various Temperatures

T/K	top phase, w_1	bottom phase, w_1
301.15	0.7937	0.5875
302.15	0.8042	0.5631
303.15	0.8137	0.5452
308.15	0.8488	0.4616
313.15	0.8664	0.3912
318.15	0.8834	0.3419
323.15	0.8934	0.3046
333.15	0.9016	0.2329
343.15	0.9045	0.1754
353.15	0.9079	0.1421
363.15	0.9088	0.1277

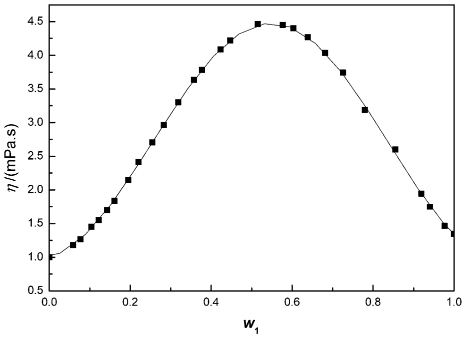

Figure 2. Viscosities vs mass fraction, *w*, for diethylene glycol diethyl ether (1) + water (2) at 293.15 K.

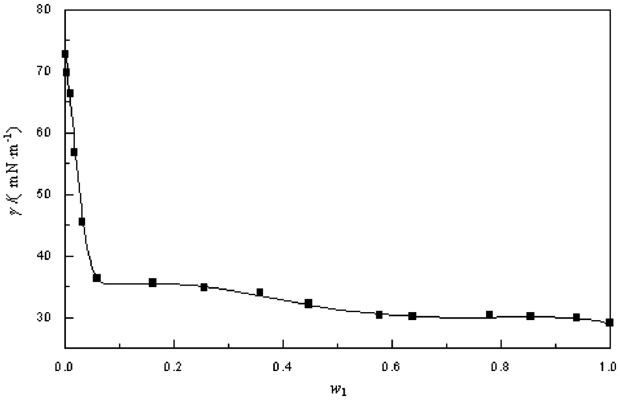

Figure 3. Surface tension vs mass fraction, *w*, for diethylene glycol diethyl ether (1) + water (2) at 293.15 K.

water (the mass fraction of DEGDEE is around 0.3), decreases sharply after that.

Figure 2 shows that the viscosity is positive deviation over the entire range of composition. It reaches a peak around the mass fraction of DEGDEE 0.5. The reason needs to be investigated further.

The surface tension curve of DEGDEE/water system at 293.15K is shown in Figure 3. Obviously, DEGDEE has marked surface activity. There are similar results reported for ethylene glycol dimethyl ether.[4]

A partial phase diagram, temperature vs DEGDEE mass fraction, for the DEGDEE/water system is shown in Figure 4. The values of the mass fractions and temperatures of LCST were obtained from the literature.[5] It can be seen that the effect of temperature on the top phase is more pronounced than that on the bottom phase.

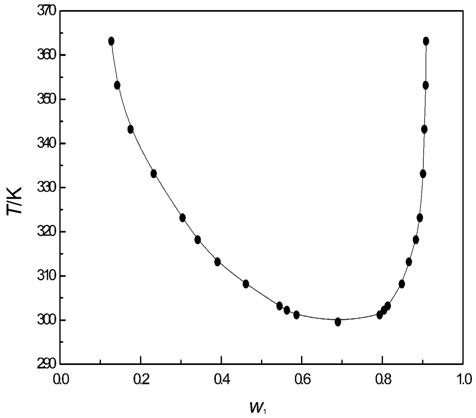

Figure 4. Partial phase diagram (temperature vs mass fraction, *w*) of diethylene glycol diethyl ether (1) + water (2).

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