J. Chem. Eng. Data 1993, 38, 401-403

Densities and Viscosities for Propylene Glycol Monomethyl Ether + Water

Abburi Krishnaiah,[†] **Brett P. Gampper, and Dabir S. Viswanath***

Department of Chemical Engineering, University of Missouri, Columbia, Missouri 65211

Densities and viscosities were measured over the entire range of composition for propylene glycol monomethyl ether (PGME) + water from 298.15 to 328.15 K at four isotherms. Excess volumes derived from the experimental density data were fitted to a Redlich–Kister-type relation. Excess volumes are negative over the whole range of mole fractions, and temperature has no appreciable influence on excess volumes. Values of $\Delta\eta$ which refer to the deviations of the viscosities of mixtures from the ideal mole fraction rule have been evaluated. $\Delta\eta$ values were positive over the entire range of mole fractions and temperatures.

Introduction

A knowledge of densities and viscosities of fluids and fluid mixtures is essential to understand the molecular interactions between unlike molecules, to develop new theoretical models, and also for engineering applications in the process industry. The variation of these properties with temperature and composition for mixtures containing polar and hydrogen-bonded components may be complex due to a decrease and/or an increase in hydrogen-bonding interaction due to mixing. In the present study densities and viscosities were measured for the industrially important system propylene glycol monomethyl ether (PGME) + water over the entire range of composition from 298.15 to 328.15 K at 10 K intervals. No data could be found for this system in the literature sources, except the pure component data on PGME (*1*).

Experimental Section

Materials. Propylene glycol monomethyl ether (Aldrich, 98%) was dried over anhydrous calcium chloride, and fractionally distilled in an all-glass distillation apparatus. The middle fraction boiling at 393.05 K was collected into a dry glass bottle and sealed under nitrogen. The purified sample had a boiling point of 393.05 K at 760 mmHg, a density of 0.917 45 g cm^{-3}, and a refractive index of 1.4016 at 298.15 K. These values are in excellent agreement with the reported values (*1*) of 393.25 K, 0.917 72 g cm^{-3}, and 1.4017, respectively. Deionized water was distilled twice, and the fraction boiling at 373.10 K was collected. The purity of the distilled water sample was ascertained by comparing the measured normal boiling point (373.10 K), density (0.997 09 g cm^{-3}), and refractive index (1.3324) at 298.15 K with the values reported in the literature (2), 373.15 K, 0.997 05 g cm^{-3}, and 1.3325, respectively. On the basis of these, the purity of the compounds was assessed to be better than 99.8 mol %.

Preparation of Mixtures. Mixtures were prepared in air-tight bottles on a mass basis using a Sartorius analytical balance series R with an RS 232-C port and accurate to ±0.1 mg. Precautions were taken that the components were not exposed to the atmosphere during the preparation of the mixtures and subsequent measurements. The bottles were fitted with air-tight septa, evacuated, weighed, and filled with PGME, the low-volatility component. The space above the liquid was evacuated and weighed to make certain that any residual air is removed. The second component, water, was injected into the bottles through the septa and weighed. In all cases care was taken not to have any space above the liquid; if any space was left, it was filled with nitrogen gas. This procedure eliminated loss due to evaporation, and the error was minimized. Thus, the possible error in the mole fraction was estimated to be less than ±5 × 10^{-4}.

Table I. Volume of the Pycnometer (V) and Viscometer Constant (k) at Different Temperatures

T/K	V/cm^3	$k \times 10^3$/(cm^2 s^{-2})
298.15	8.2299	3.9744
308.15	8.2320	3.9711
318.15	8.2355	3.9665
328.15	8.2404	3.9606

Apparatus. Densities of liquids and liquid mixtures were measured using a bicapillary pycnometer described earlier (*3*). The pycnometer was calibrated with deionized double-distilled water at each temperature, and the average of 10 measurements did not differ more than ±0.0005 cm^3. Volumes of the pycnometer at different temperatures are given Table I. Density values are reproducible to ±5 × 10^{-5} g cm^{-3}. Excess volumes were computed from the density and composition using the equation

$$V^E/(\mathrm{cm^3\,mol^{-1}}) = \{[x_1M_1 + (1 - x_1)M_2]/\rho_m\} - x_1M_1/\rho_1 - (1 - x_1)M_2/\rho_2 \quad (1)$$

where x_1 is the mole fraction of PGME, M_1 and M_2 represent molecular masses, and ρ_m, ρ_1, and ρ_2 are the densities of the mixture, PGME, and water, respectively. Excess volumes are accurate to ±0.002 cm^3 mol^{-1}.

Viscosities were measured using a suspended-level Ubbelohde viscometer. The viscometer was calibrated at each temperature using distilled water. The viscometer constant, k, was calculated from the viscosity, η_w, density, ρ_w, and flow time, t_w, of water using the relation $k = \eta_w/\rho_w t_w$. The k values tabulated in Table I are the average of 10 measurements, and these measurements did not differ more than ±0.0005 cm^2 s^{-2}. An electronic stopwatch capable of measuring time to ±0.01 s was used for the time measurement. Kinetic energy corrections were negligible. The estimated error in viscosity was ±5 × 10^{-4} mPa s. The performance of the viscometer was assessed by measuring and comparing the viscosities of the pure components with the values reported in the literature.

---

* To whom correspondence should be addressed.

[†] On leave from the Department of Chemistry, Sri Venkateshwara University College of Engineering, Tirupati 517502, India.

0021-9568/93/1738-0401$04.00/0

Table II. Densities, Viscosities, and Excess Volumes for Propylene Glycol Monomethyl Ether (1) + Water (2)

x_1	ρ/(g cm^{-3})	η/(mPa s)	V^E/(cm^3 mol^{-1})	$\Delta\eta$/(mPa s)	x_1	ρ/(g cm^{-3})	η/(mPa s)	V^E/(cm^3 mol^{-1})	$\Delta\eta$/(mPa s)
		298.15 K					318.15 K		
0.0000	0.997 05	0.8903	0.000	0.000	0.0000	0.990 22	0.5972	0.0000	0.0000
0.0222	0.996 48	1.2896	−0.164	0.381	0.0222	0.987 57	0.8257	−0.1577	0.2176
0.0396	0.997 48	1.6511	−0.321	0.728	0.0396	0.987 52	0.9800	−0.3124	0.3633
0.1131	0.995 11	3.0345	−0.842	2.050	0.1131	0.980 80	1.5795	−0.8204	0.9267
0.1959	0.985 15	3.7305	−1.156	2.677	0.1959	0.968 38	1.9251	−1.1285	1.2314
0.3010	0.971 99	3.8641	−1.349	2.723	0.3010	0.953 14	2.0154	−1.2985	1.2699
0.3583	0.964 26	3.8108	−1.332	2.622	0.3583	0.945 33	1.9781	−1.3002	1.2044
0.4651	0.952 70	3.5149	−1.263	2.238	0.4651	0.934 34	1.8412	−1.3035	1.0148
0.5264	0.947 06	3.1243	−1.190	1.796	0.5264	0.927 96	1.7443	−1.2068	0.8878
0.7332	0.931 79	2.4136	−0.807	0.913	0.7332	0.911 95	1.4203	−0.8195	0.4619
0.8372	0.925 01	2.0935	−0.484	0.506	0.8372	0.905 49	1.2775	−0.5444	0.2678
0.9035	0.921 40	1.9293	−0.282	0.287	0.9035	0.901 51	1.1891	−0.317	0.147
1.000	0.916 99	1.7226	0.000	0.000	1.0000	0.896 65	1.0899	0.000	0.000
		308.15 K					328.15 K		
0.0000	0.994 03	0.7190	0.000	0.000	0.0000	0.985 70	0.5042	0.000	0.000
0.0222	0.992 68	1.0000	−0.167	0.266	0.0222	0.981 85	0.6617	−0.149	0.148
0.0396	0.993 27	1.2360	−0.330	0.491	0.0396	0.980 35	0.7906	−0.290	0.269
0.1131	0.988 17	2.1189	−0.833	1.326	0.1131	0.970 93	1.2107	−0.754	0.657
0.1959	0.977 04	2.6146	−1.151	1.767	0.1959	0.957 85	1.4719	−1.057	0.882
0.3010	0.962 41	2.7304	−1.319	1.814	0.3010	0.942 79	1.5400	−1.247	0.904
0.3583	0.955 00	2.6625	−1.330	1.709	0.3583	0.935 57	1.5191	−1.283	0.858
0.4651	0.943 58	2.4381	−1.294	1.415	0.4651	0.923 18	1.4231	−1.218	0.715
0.5264	0.938 06	2.3001	−1.244	1.237	0.5264	0.917 25	1.3843	−1.150	0.649
0.7332	0.922 16	1.8231	−0.854	0.624	0.7332	0.900 93	1.1840	−0.738	0.358
0.8372	0.915 50	1.6103	−0.557	0.343	0.8372	0.894 17	1.0298	−0.429	0.158
0.9035	0.911 59	1.4898	−0.334	0.179	0.9035	0.890 55	0.9901	−0.233	0.089
1.0000	0.906 59	1.3736	0.000	0.000	1.0000	0.886 47	0.9436	0.000	0.000

Table III. Values of the Coefficients of Equation 3

T/K	a_0	a_1	a_2	a_3	a_4	sd	AAD
			V/(cm^3 mol^{-1})				
298.15	18.069	72.040	14.264	−6.137		0.013	0.001
308.15	18.123	73.385	13.187	−5.399		0.014	0.001
318.15	18.193	74.509	13.108	−5.348		0.013	0.001
328.15	18.277	75.752	13.220	−5.000		0.060	0.002
			η/(mPa s)				
298.15	0.8903	25.330	−69.570	69.306	−24.230	0.031	0.023
308.15	0.7190	16.748	−45.784	45.877	−16.144	0.010	0.019
318.15	0.5972	11.789	−32.195	32.164	−11.724	0.0003	0.011
328.15	0.5042	8.387	−22.302	22.175	−7.821	0.0005	0.016

Table IV. Values of the Coefficients of Equation 4

T/K	b_0	b_1	b_2	b_3	b_4	b_5	sd	AAD
				V^E/(cm^3 mol^{-1})				
298.15	−4.8927	2.6685	−2.6784	0.608 69	2.2959		0.0025	0.0096
308.15	−5.0186	2.2510	−2.4045	0.670 55	1.3323		0.0048	0.0112
318.15	−4.9454	2.2987	−2.2988	0.484 78	1.6141		0.0062	0.0104
328.15	−4.7366	2.4790	−1.3966	0.658 87	1.5208		0.0004	0.0043
				$\Delta\eta$/(mPa s)				
298.15	7.9378	−7.7421	9.1721	−16.4360	−5.1260	19.144	0.0030	0.0193
308.15	5.2299	−5.1882	6.3231	−9.0458	−4.0061	9.9352	0.0151	0.0489
318.15	3.7558	−3.7113	4.0317	−4.7856	−1.9972	4.9736	0.0136	0.0282
328.15	2.7388	−2.3987	2.4421	−4.1919	−1.0936	3.6945	0.0166	0.0239

Experimental viscosity values were used to calculate $\Delta\eta$ using the relation

$$\Delta\eta = \eta_{\text{mix}} - x_1\eta_1 - (1 - x_1)\eta_2 \qquad (2)$$

where η_{mix}, η_1, and η_2 are viscosities of the mixture, PGME, and water respectively. $\Delta\eta$ values are accurate to ±0.001 mPa s.

A thermostatically controlled, well-stirred water bath with temperature controlled to ±0.02 K was used for all the measurements. Temperature was measured using a 2804A Hewlett-Packard quartz thermometer with a resolution of better than ±0.01 K.

Results and Discussion

Experimental data on the density, viscosity, derived excess volume, and $\Delta\eta$ for the PGME + water system as a function of the mole fraction of PGME at 298.15, 308.15, 318.15, and 328.15 are shown in Table II. Molar volumes and viscosities have been fitted to the relation

$$Z = \sum a_i x^i \qquad (3)$$

where Z is V/(cm^3 mol^{-1}) or η/(mPa s). The values of the coefficients a_i are tabulated in Table III along with the standard deviation (sd) and average absolute deviation (AAD). Excess volumes and $\Delta\eta$ at various temperatures have been fitted to the Redlich–Kister-type equation

$$G = x_1 x_2 \{\sum b_i (x_1 - x_2)^i\} \qquad (4)$$

where b_i's are adjustable parameters and G is V^E/(cm^3 mol^{-1}) or $\Delta\eta$/(mPa s). Equation 4 was fitted at each temperature by the least-squares technique. The values of the coefficients (b_i) are summarized in Table IV along with the average absolute deviation and standard deviation for each isotherm.

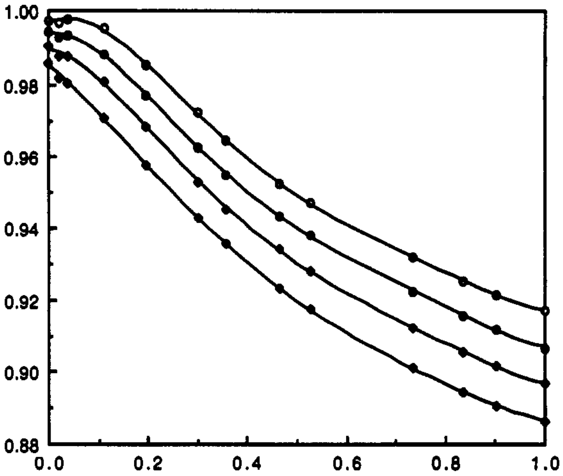

Figure 1. Mole fraction versus density for propylene glycol monomethyl ether (1) + water (2): (○) 298.15 K, (●) 308.15 K, (◇) 318.15 K, (◆) 328.15 K, (x axis) x_1, (y axis) ρ/(g cm^{-3}).

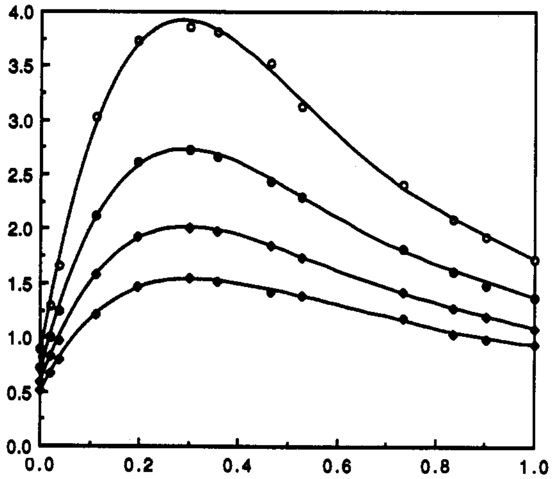

Figure 2. Mole fraction versus viscosity for propylene glycol monomethyl ether (1) + water (2): (○) 298.15 K, (●) 308.15 K, (◇) 318.15 K, (◆) 328.15 K, (x axis) x_1, (y axis) η/(mPa s).

The average absolute deviation was computed using the equation

$$\mathrm{AAD} = \sum [\{G_{\mathrm{exptl}} - G_{\mathrm{calcd}}\}/G_{\mathrm{exptl}}]/n \qquad (5)$$

where n represents the number of experimental points excluding the end points. Composition–density and composition–viscosity plots are shown in Figures 1 and 2 along with the calculated values. The AAD and the solid curves in Figures 1 and 2 indicate that the calculated and experimental values are in excellent agreement at different temperatures. Figure 3 shows excess volumes as a function of composition at different temperatures.

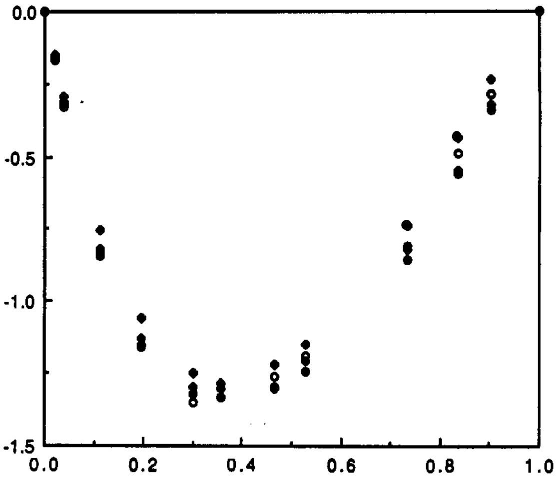

Figure 3. Mole fraction versus excess volume for propylene glycol monomethyl ether (1) + water (2): (○) 298.15 K, (●) 308.15 K, (◇) 318.15 K, (◆) 328.15 K, (x axis) x_1, (y axis) V^E/(cm^3 mol^{-1}).

Excess volumes are negative and $\Delta\eta$ are positive over the entire range of composition at all the temperatures studied. Excess volumes become less negative with an increase in temperature; however, the effect of temperature on excess volume is not appreciable. $\Delta\eta$ decreases with an increase in temperature. Negative excess volumes and rather large positive $\Delta\eta$ indicate the existence of strong intermolecular interactions between unlike molecules compared to like molecules. Further, the variation of these properties with temperature indicates that an increase of temperature results in a decrease in the interaction between PGME and water molecules.

Literature Cited

(1) Daubert, T. E.; Danner, R. P. DIPPR Project 801, Data Compilation, Tables of Physical and Thermodynamic Properties of Pure Compounds, Extant 1992.
(2) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents: Physical Properties and Methods of Purification*; Wiley-Interscience: New York, 1986.
(3) Krishnaiah, A.; Naidu, P. R. *J. Chem. Eng. Data* **1980**, *25*, 135.

Received for review August 20, 1992. Revised January 14, 1993. Accepted February 17, 1993. The support of the AIChE Design Institute for Physical Properties Project 805 is acknowledged.