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Densities, Viscosities, and Derived Functions of Binary Mixtures: (Tetraethylene Glycol Dimethyl Ether + Water) from 298.15 K to 343.15 K

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This paper reports the density and viscosity of aqueous tetraethylene glycol dimethyl ether (TTEGDME) solutions at five temperatures in the range of 298.15 K to 343.15 K over the whole concentration range. The results are compared with data published in the literature. The excess molar volumes, the partial molar volumes at infinite dilution, Grunberg−Nissan parameters, and viscosity deviations were derived.

Introduction

If acid gas impurities make up a large proportion of a gas stream, removing them by heat-regenerable solvents may be out of proportion with the value of the treated gas. In this case, nonreactive organic polar solvents can provide a more economical solution. Tetraethylene glycol dimethyl ether (tetraglyme, TTEGDME) is one of these solvents. It was initially selected as one of two promising solvents by Zawacki et al.[1] from a group of more than 100 physical solvents for its capacity for acid gas removal. TTEGDME is one of the solvents that make up Selexol, a widely used commercial solvent. TTEGDME is used as an inert solvent in many organometallic reactions involving alkali metals such as lithium, sodium, and potassium. Its outstanding stability even at high pH makes it an excellent solvent for reactions with strong bases. It found applications in adhesives, electrodeposition, and paints and as a cosolvent in the allylation and alkylation of uracil derivatives.[2] It has received considerable attention in absorption refrigeration technology. TTEGDME has also been of interest to researchers in their attempts to understand interactions of water with amphiphilic molecules.[3]

Our laboratory has been active in measuring the physical and transport properties of chemical and physical solvents of interest to the gas processing industry. In this study, we have measured the density and viscosity of aqueous TTEGDME solutions at various temperatures (298.15 K to 343.15 K) to cover a wide range of temperature found in industrial applications.

Experimental Section

TTEGDME (>99% pure) was purchased from Lancaster (Pelham, NH) and was used without further purification. The solutions were prepared by mass on an analytical balance (model Ap 205 D, Ohaus, Florham Park, NJ) with ±0.01 mg accuracy. The uncertainty in the mole fraction is less than ±0.0001. TTEGDME was kept over molecular sieves in a glass container. The densities of the binary mixtures were measured with an Anton Paar DMA-4500 density meter. Calibration was done using air and water at ambient temperature. The densities of water were measured in the temperature range of (15 °C to 80 °C) and were compared with the values measured by Bettin et al.[4] provided by Anton Paar in the instruction manual. The calibration was accepted if the measurements were within $\pm 5 \times 10^{-5}$ g·cm^{-3} of the published values. The uncertainties of our densities are about $\pm 5 \times 10^{-5}$ g·cm^{-3} when compared with the densities of pure MDEA published in the literature[5] in the temperature range of (25 °C to 80 °C). The densities of water were measured using deionized water.[6] Density measurements were reproducible to $\pm 2 \times 10^{-5}$ g·cm^{-3}.

For the viscosity measurements, the temperature was controlled by means of a digital controller (±0.004 °C) in a well-stirred water bath to better than ±0.01 °C as measured by a Cole-Parmer resistance thermometer (model H-01158-65, Anjou, Québec, Canada). Viscosities were determined with three different viscometers to cover, with precision, the range of temperature from (25 °C to 70 °C). A series of Cannon-Ubbelohde viscometers (Cole-Parmer) were used. The efflux time was measured with a handheld digital stopwatch capable of measuring time to within ±0.01 s. Experiments were repeated a minimum of four times at each temperature for all compositions. The equation for kinematic viscosity, according to Poiseuille's law, is

$$\nu = k_1 t - \frac{k_2}{t} \qquad (1)$$

where t is the efflux time and k_1 and k_2 are the viscometer constants. The second term representing the correction due to the kinetic energy was found to be negligible.[7] The value of the dynamic viscosity (η) was obtained by multiplying the measured kinematic viscosity (ν) by the measured density. Calibration constants for the viscometers were checked using high-purity ethylene glycol (EG), diethylene glycol (DEG), and water. A review of published values of the kinematic and dynamic viscosities of EG and DEG, with new experimental data, was published by Lee and Teja.[8] Values of the viscosity of water were taken from Stokes

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Table 1. Review of the Literature Data for the Density and Viscosity of Pure TTEGDME

	ρ/(g·cm^{-3})		η/(mPa·s)	
T/K	this work	literature	this work	literature
298.15	1.00665	1.00657[18] 1.00627[3] 1.00662[19] 1.00653[20] 1.0059[21] 1.0063[22]	3.38	3.294[14] 3.394[22] 3.313[10]
313.15	0.99328	0.99270[16] 0.99274[23] 0.9925[24]		
323.15	0.98405	0.9833[24] 0.98323[16]		
333.15	0.97480	0.97424[16] 0.9741[24]		

Table 2. Densities of Water (1) + TTEGDME (2) at Various Temperatures

	T/K				
x_2	298.15	313.15	323.15	333.15	343.15
			ρ/(g·cm^3)		
0.0000	0.99704	0.99221	0.98804	0.98312	0.97777
0.0199	1.01395	1.00673	1.00125	0.99513	0.98858
0.0510	1.02021	1.01189	1.00570	0.99034	0.99192
0.1066	1.03890	1.02570	1.00667	1.00747	0.99809
0.1950	1.03366	1.01980	1.01040	1.00092	0.99128
0.3008	1.02607	1.01212	1.00275	0.99327	0.98367
0.4088	1.02042	1.00646	0.99707	0.98760	0.97807
0.5116	1.01656	1.00260	0.99321	0.98377	0.97427
0.6252	1.01352	1.00260	0.99321	0.98377	0.97427
0.7016	1.01164	0.99766	0.98833	0.97895	0.96956
0.8037	1.00981	0.99586	0.98565	0.97724	0.96788
0.9044	1.00844	0.99451	0.98523	0.97595	0.96666
0.9505	1.00783	0.99392	0.98467	0.97540	0.96613
1.0000	1.00665	0.99328	0.98405	0.97480	0.96555

and Mills.[9] From the overall average percent deviation of the means of the average efflux time and the accuracy of the density measurement, we estimate the uncertainty of the dynamic viscosity to be ±1.0%.

Results and Discussion

Values of the density and viscosity for pure TTEGDME are compared with published literature values and are shown in Table 1. It is very probable that the scatter found in the density and viscosity data for pure solvent is due to the differences in purity of the commercial TTEGDME (98% and 99%) and the different methods used to purify it further.

Experimentally measured densities of the aqueous TTEGDME solutions at (25, 40, 50, 60, and 70) °C throughout the whole concentration range are listed in Table 2. The curves show an increase in the density with maxima at around 10 mol %. The density values of the binary mixtures were used to calculate the excess molar volume, $V^E{}_m$, as

$$V^E{}_m = V_m - V^\circ{}_1 x_1 - V^\circ{}_2 x_2 \tag{2}$$

where V_m is the molar volume of the mixture and $V^\circ{}_1$ and $V^\circ{}_2$ are those of pure water and pure TTEGDME, respectively; x_1 and x_2 are the mole fractions of pure water and TTEGDME, respectively. Figure 1 displays the dependence of $V^E{}_m$ on the composition at various temperatures. In all cases, $V^E{}_m$ is negative as is common for other completely miscible (water + polar organic) solvents with a minimum at around 25 mol % TTEGDME. These $V^E{}_m$ values become less negative with increasing temperature, as is also common. V^E curves are very unsymmetrical.

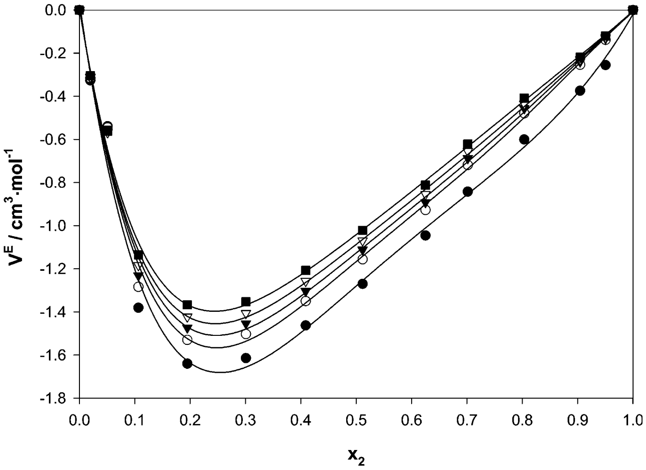

Figure 1. Excess molar volumes of the water (1) + TTEGDME (2) system at various temperatures: ●, 298.15 K; ○, 313.15 K; ▼, 323.15 K; ▽, 333.15 K; ■, 343.15 K.

Table 3. Redlich−Kister Equation-Fitting Coefficients of the Excess Volumes for Water (1) + TTEGDME (2) from 298.15 K to 343.15 K

T/K	a_0	a_1	a_2	a_3	σ/(cm^3·mol^{-1})
298.15	−5.102	−5.142	−5.721		0.08
313.15	−4.668	−4.339	−4.727	−2.684	0.06
323.15	−4.493	−4.186	−4.573	−2.717	0.05
333.15	−4.312	−4.049	−4.507	−2.767	0.04
343.15	−4.120	−3.940	−4.367	−2.687	0.03

A Redlich−Kister[10] relation was used to correlate the excess volume data:

$$V^E{}_m/\text{cm}^3\cdot\text{mol}^{-1} = x_1 x_2 \sum_{i=0}^{n} a_i (x_1 - x_2)^i \tag{3}$$

The coefficients and the standard deviation (σ) are presented in Table 3. Hepler[11] and Neal and Goring[12] recognized the usefulness of thermal expansion data for revealing correlations between the molecular structure of solutes and their effects on water structure. They suggested using the sign of the second derivative of the partial molar volume at infinite dilution of the solute with respect to temperature $(\partial^2 V^\circ{}_2/\partial T^2)_P$ to classify solutes as “structure makers” or “structure breakers”. A positive sign corresponds to a structure-making solute, and a negative sign corresponds to a structure-breaking solute.

The partial molar volume of water at infinite dilution in TTEGDME ($V^\infty{}_1$) and TTEGDME at infinite dilution in water ($V^\infty{}_2$) were obtained using the method proposed by Maham et al.[13] The apparent molar volumes were first calculated as

$$V_{\phi,1} = V^\circ{}_1 + \frac{V^E{}_m}{1 - x_2} \tag{4}$$

$$V_{\phi,2} = V^\circ{}_2 + \frac{V^E{}_m}{x_2} \tag{5}$$

where $V^\circ{}_1$ and $V^\circ{}_2$ are the molar volumes and x_1 and x_2 are the mole fractions of pure water and TTEGDME, respectively. An extrapolation of the regressed values of $V_{\phi,1}$ (as a function of x_2) to $x_2 = 1$ leads to $V^\infty{}_1$, and a similar extrapolation of $V_{\phi,2}$ values to $x_2 = 0$ led to $V^\infty{}_2$. Partial molar volumes at infinite dilution are listed in Table 4. $V^\infty{}_2$

Table 4. Partial Molar Volumes, V^{∞}_1 (Water) and V^{∞}_2 (TTEGDME) at Infinite Dilution from 298.15 K to 343.15 K

T/K	V^{∞}_1/(cm^3·mol^{-1})	V^{∞}_2/(cm^3·mol^{-1})
298.15	14.6	204.4
313.15	14.9	207.6
323.15	15.1	209.6
333.15	15.4	211.7
343.15	15.6	214.0

Table 5. Viscosities for TTEGDME (2) + Water (1) Mixtures at Various Temperatures

	T/K				
x_2	298.15	313.15	323.15	333.15	343.15
	η/(mPa·s)				
0.0000	0.8903	0.6531	0.5470	0.4660	0.4049
0.0199	3.11	2.11	1.71	1.41	1.18
0.0510	4.04	2.64	2.12	1.69	1.41
0.1066	6.17	3.62	2.70	2.08	1.67
0.1950	6.22	3.77	2.86	2.24	1.80
0.3008	5.29	3.39	2.63	2.12	1.73
0.4088	4.59	3.08	2.42	1.97	1.65
0.5116	4.14	2.82	2.26	1.86	1.56
0.6252	3.81	2.65	2.15	1.78	1.51
0.7016	3.65	2.57	2.10	1.75	1.50
0.8037	3.51	2.49	2.060	1.73	1.47
0.9044	3.41	2.44	2.010	1.69	1.45
0.9505	3.37	2.42	2.002	1.69	1.41
1.0000	3.38	2.42	2.004	1.69	1.42

values varied linearly with temperature. According to the criterion described above, the solute (TTEGDME) would be considered to have no net effect on the structure of water. For all of the values of the molar volumes at infinite dilution, V^{∞}_2 values were smaller than the corresponding molar values of pure TTEGDME (V°_2). It is important to note that the apparent volume ($V_{\phi,2}$) has maxima in the water-rich region around 10 mol % at all temperatures corresponding to the maxima in density values. The change in the excess volume can be explained by the TTEGDME molecule fitting (partially) into the empty space in liquid water. This picture does not invoke either the structure-making or the structure-breaking properties and is consistent with the observation that $(\partial^2 V^{\infty}_2/\partial T^2)_P$ values are approximately equal to zero.

Experimentally measured viscosities of the binary solutions of aqueous TTEGDME solutions at (25, 40, 50, 60, and 70) °C are listed in Table 5. The largest viscosity values were those at 20 mol % at all temperatures.

Experimental viscosity values of the binary mixtures were used to calculate the viscosity deviation, defined by

$$\Delta\eta = \eta - \eta_1 x_1 - \eta_2 x_2 \tag{6}$$

where η is the viscosity of the mixture and η_1 and η_2 are those of pure water and pure TTEGDME, respectively; x_1 and x_2 are the mole fractions of the pure components. The viscosity deviation represents deviations from a rectilinear dependence of viscosity on mole fraction. Figure 2 displays the dependence of $\Delta\eta$ on the composition and temperature. Values of $\Delta\eta$ were positive with a maximum around 15 mol % for all temperatures. Pal et al.[14] reported slightly negative values of $\Delta\eta$ for composition values greater than 92 mol % in a similar study at 25 °C. This might be due to their lower value of TTEGDME viscosity.

The calculated values of $\Delta\eta$ were correlated with a Redlich−Kister[10] relation

$$\Delta\eta/\text{mPa·s} = x_1 x_2 \sum_{i=0}^{n} a_i (x_1 - x_2)^i \tag{7}$$

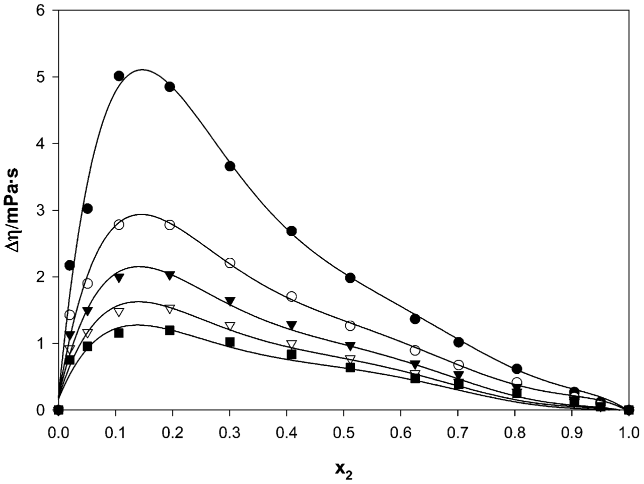

Figure 2. Viscosity deviations for the water (1) + TTEGDME (2) system at various temperatures: ●, 298.15 K; ○, 313.15 K; ▼, 323.15 K; ▽, 333.15 K; ■, 343.15 K.

Table 6. Redlich−Kister Equation-Fitting Coefficients of the Viscosity Deviations for Water (1) + TTEGDME (2) from 298.15 K to 343.15 K

T/K	a_0	a_1	a_2	a_3	a_4	σ/(mPa·s)
298.15	8.187	10.535	14.919	32.751	25.741	0.23
313.15	5.398	5.834	5.256	19.173	19.481	0.17
323.15	4.188	3.915	2.575	14.849	16.483	0.15
333.15	3.331	2.885	1.049	11.386	13.778	0.13
343.15	2.803	2.052	0.361	9.066	11.639	0.11

where x_1 is the mole fraction of water and x_2 is the mole fraction of TTEGDME. The coefficients and the standard deviation (σ) are presented in Table 6. The Grunberg−Nissan[15] parameters (d_{12}) were calculated for all compositions and temperatures. They were all positive and varied from a maximum of 62 in the water-rich region (2 mol %) to 1.3 in the TTEGDME-rich region (95 mol %). The value of the parameters drops very quickly in the water-rich region to reach an almost-constant value at concentrations greater than 30 mol %. The positive values of the coefficients suggest the predominance of interaction forces through hydrogen bonding as supported by the negative values of the excess volumes. The interpretation of the thermodynamic properties of mixtures containing water is still a subject of controversy. Some authors attribute the behavior to hydrogen bonding (ether−water in this mixture), and others attribute it to changes in the water structure.[16] More information about the short-range dynamics of aqueous solutions of poly(ethylene glycol) dimethyl ethers (PEGDME) in water can be found in a study published by Trouw et al.[17]

Conclusions

This paper reports experimental data for the densities and viscosities of the aqueous TTEGDME solutions over a range of temperature from 298.15 K to 343.15 K. The calculated V^{E}_{m} values for the aqueous TTEGDME solutions were all negative at all temperatures and compositions. The criterion proposed by Hepler suggests that the addition of TTEGDME to water had no effect on its structure! The viscosity deviations $\Delta\eta$ for TTEGDME + water were positive at all concentrations and temperatures. The positive values of the Grunberg−Nissan parameters and the excess volumes at all temperatures and compositions suggest the predominance of interaction forces. All excess volume and viscosity deviation curves were unsymmetrical.

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