1028 *J. Chem. Eng. Data* **2008,** *53,* 1028–1031

Supplementary Densities and Viscosities of Aqueous Solutions of Diethylene Glycol from (283.15 to 353.15) K

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This paper presents atmospheric pressure liquid densities and viscosities for mixtures of diethylene glycol + water over the entire composition range at temperatures from (283.15 to 353.15) K. Density is measured using a vibrating tube densimeter, and two different Cannon-Fenske viscosimeters are used for the viscosity measurements. The excess molar volumes are calculated from experimental measurements. Excess molar volumes present negative deviations from ideality at all the investigated temperatures and become more negative with decreasing temperature. From (293.15 to 343.15) K, the viscosity deviation as a function of composition changes sign from negative to positive in the water-rich region. A Redlich–Kister-type equation correlates the viscosity deviations.

Introduction

The physical properties such as density and viscosity of pure diethylene glycol (DEG) and their mixtures with water are needed for the design of natural gas dehydration processes, air conditioning systems, etc.

In this work, densities of aqueous solutions of DEG are measured with a vibrating tube densimeter from (283.15 to 353.15) K. Also, kinematic viscosities of these aqueous solutions are measured using Cannon-Fenske viscosimeters from (293.15 to 353.15) K. Excess molar volumes and viscosity deviations are correlated using Redlich–Kister-type[1] equations.

Experimental

Apparatus and Procedures. An explanation of the vibrating tube densimeter has been given before.[2] The reproducibility in the density and temperature measurements provided by the manufacturer is $\pm$ 0.001 $\text{kg}\cdot\text{cm}^{-3}$ and $\pm$ 0.001 K, respectively. The uncertainty of the thermometer and the density measurements is $\pm$ 0.01 K on ITS-90 and better than $\pm 3\cdot10^{-5}$ $\text{g}\cdot\text{cm}^{-3}$, respectively. The uncertainty in the excess volume is 0.008 $\text{cm}^3\cdot\text{mol}^{-1}$. Kinematic viscosities are measured using two different Cannon-Fenske viscosimeters, sizes 25 and 50 with flow ranges of $(0.5 \text{ to } 2)\cdot10^{-6}$ $\text{m}^2\cdot\text{s}^{-1}$ and $(0.8 \text{ to } 4)\cdot10^{-6}$ $\text{m}^2\cdot\text{s}^{-1}$, respectively. Measurements are performed following the ASTM 445 standard. The viscosimeters reside in a Polyscience constant-temperature water bath that is controlled within $\pm$ 0.01 K. A digital thermometer F250 (Automatic System) is used to measure the temperature with an accuracy of 0.01 K. The efflux time is measured with an accuracy of 0.01 s. Each datum is an average of at least five runs with a maximum deviation in the kinematic viscosity of $\pm$ 0.1 %, and the estimated accuracy[2] in the dynamic viscosity is better than $\pm$ 0.004 $\text{mPa}\cdot\text{s}$.

Table 1. Comparison of Experimental Densities and Viscosities of DEG

	$\rho/\text{g}\cdot\text{cm}^{-3}$		$\eta/\text{mPa}\cdot\text{s}$	
T/K	this work	lit.	this work	lit.
283.15	1.12424			
288.15	1.12065			
293.15	1.11705	1.1158[7]	36.433	33.6[7] 36.2[10]
298.15	1.11347	1.11281[6]		
303.15	1.10988	1.1095[5]	22.091	
308.15	1.10629	1.1062[5]		
313.15	1.10270	1.1014[7]	14.563	12.8[7] 14.7[10]
318.15	1.09911			
323.15	1.09551		10.029	
328.15	1.09191			
333.15	1.08830	1.0874[7]	7.220	6.02[7] 7.38[10]
338.15	1.08468			
343.15	1.08105		5.369	
348.15	1.07740			
353.15	1.07374		4.139	

Samples. Water grade HPLC is supplied by Fischer Co. with a mole fraction purity greater than 99.95 %. DEG is provided from Sigma with a stated mole fraction purity of 99.0 %. Pure components are used as received. The mixtures are prepared gravimetrically using an analytical balance (Ohaus model AS120S) with a precision of $\pm$ 0.1 mg. The overall uncertainty in the mole fractions is better than $\pm$ 0.002.

Results and Discussion

Pure water density values have been measured previously by Bernal-García et al.[3] These values compared with those obtained from the standard equation of state for water[4] agree within 0.005 %.

A comparison of the pure DEG densities and viscosities is given in Table 1. DEG density measurements agree with those from Pal et al.,[5] Dethlefsen at al.,[6] and Kumagai et al.[7] within an average absolute percentage deviation of (0.02, 0.06, and 0.1) %. Densities and excess molar volumes of (DEG + water)

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10.1021/je700672f CCC: $40.75

Table 2. Experimental Densities and Excess Volumes for DEG (1) + Water (2)

x_1	ρ / $g \cdot cm^{-3}$	V^E / $cm^3 \cdot mol^{-1}$	ρ / $g \cdot cm^{-3}$	V^E / $cm^3 \cdot mol^{-1}$	ρ / $g \cdot cm^{-3}$	V^E / $cm^3 \cdot mol^{-1}$	ρ / $g \cdot cm^{-3}$	V^E / $cm^3 \cdot mol^{-1}$
	T = 283.15 K		T = 288.15 K		T = 293.15 K		T = 298.15 K	
0.0000	0.99970	0.0000	0.99910	0.0000	0.99820	0.0000	0.99704	0.0000
0.0255	1.01973	−0.0983	1.01861	−0.0948	1.01727	−0.0920	1.01572	−0.0899
0.0565	1.04015	−0.2300	1.03842	−0.2206	1.03653	−0.2127	1.03450	−0.2063
0.1027	1.06334	−0.4125	1.06091	−0.3950	1.05839	−0.3800	1.05577	−0.3670
0.1966	1.09118	−0.6514	1.08801	−0.6255	1.08481	−0.6023	1.08156	−0.5816
0.3010	1.10634	−0.7547	1.10288	−0.7270	1.09940	−0.7019	1.09589	−0.6791
0.3989	1.11362	−0.7491	1.11006	−0.7231	1.10648	−0.6995	1.10289	−0.6780
0.5006	1.11788	−0.6828	1.11429	−0.6603	1.11068	−0.6399	1.10707	−0.6212
0.6011	1.12039	−0.5795	1.11680	−0.5618	1.11319	−0.5456	1.10959	−0.5307
0.7003	1.12198	−0.4559	1.11839	−0.4426	1.11479	−0.4305	1.11119	−0.4194
0.8051	1.12307	−0.3068	1.11947	−0.2977	1.11587	−0.2899	1.11227	−0.2822
0.8920	1.12364	−0.1696	1.12005	−0.1652	1.11645	−0.1609	1.11286	−0.1569
1.0000	1.12424	0.0000	1.12065	0.0000	1.11705	0.0000	1.11347	0.0000
	T = 303.15 K		T = 308.15 K		T = 313.15 K		T = 318.15 K	
0.0000	0.99555	0.0000	0.99403	0.0000	0.99221	0.0000	0.99021	0.0000
0.0255	1.01397	−0.0899	1.01183	−0.0823	1.00999	−0.0861	1.00773	−0.0850
0.0565	1.03233	−0.2025	1.03002	−0.1961	1.02757	−0.1920	1.02501	−0.1885
0.1027	1.05307	−0.3572	1.05027	−0.3455	1.04739	−0.3362	1.04441	−0.3280
0.1966	1.07828	−0.5645	1.07494	−0.5459	1.07156	−0.5303	1.06813	−0.5159
0.3010	1.09236	−0.6596	1.08880	−0.6390	1.08522	−0.6212	1.08161	−0.6045
0.3989	1.09929	−0.6592	1.09567	−0.6397	1.09203	−0.6223	1.08837	−0.6063
0.5006	1.10345	−0.6051	1.09982	−0.5881	1.09618	−0.5734	1.09253	−0.5597
0.6011	1.10597	−0.5179	1.10236	−0.5048	1.09873	−0.4931	1.09508	−0.4815
0.7003	1.10758	−0.4099	1.10397	−0.3999	1.10035	−0.3905	1.09671	−0.3818
0.8051	1.10867	−0.2759	1.10506	−0.2692	1.10145	−0.2630	1.09783	−0.2574
0.8920	1.10927	−0.1536	1.10568	−0.1504	1.10209	−0.1474	1.09849	−0.1450
1.0000	1.10988	0.0000	1.10629	0.0000	1.10270	0.0000	1.09911	0.0000
	T = 323.15 K		T = 328.15 K		T = 333.15 K		T = 338.15 K	
0.0000	0.98803	0.0000	0.98569	0.0000	0.98319	0.0000	0.98055	0.0000
0.0255	1.00537	−0.0851	1.00286	−0.0850	1.00022	−0.0851	0.99746	−0.0855
0.0565	1.02233	−0.1853	1.01953	−0.1825	1.01662	−0.1800	1.01361	−0.1777
0.1027	1.04136	−0.3204	1.03821	−0.3135	1.03499	−0.3070	1.03168	−0.3009
0.1966	1.06465	−0.5023	1.06113	−0.4896	1.05755	−0.4775	1.05392	−0.4662
0.3010	1.07797	−0.5889	1.07429	−0.5739	1.07058	−0.5597	1.06684	−0.5463
0.3989	1.08469	−0.5911	1.08098	−0.5766	1.07725	−0.5626	1.07349	−0.5491
0.5006	1.08885	−0.5466	1.08516	−0.5338	1.08143	−0.5213	1.07769	−0.5095
0.6011	1.09142	−0.4704	1.08774	−0.4598	1.08404	−0.4498	1.08033	−0.4399
0.7003	1.09307	−0.3734	1.08941	−0.3656	1.08574	−0.3577	1.08206	−0.3505
0.8051	1.09421	−0.2519	1.09057	−0.2467	1.08693	−0.2416	1.08327	−0.2367
0.8920	1.09488	−0.1422	1.09126	−0.1393	1.08763	−0.1362	1.08399	−0.1339
1.0000	1.09551	0.0000	1.09191	0.0000	1.08830	0.0000	1.08468	0.0000
	T = 343.15 K		T = 348.15 K		T = 353.15 K			
0.0000	0.97776	0.0000	0.97484	0.0000	0.97179	0.0000		
0.0255	0.99457	−0.0859	0.99157	−0.0864	0.98850	−0.0882		
0.0565	1.01051	−0.1762	1.00727	−0.1738	1.00407	−0.1750		
0.1027	1.02829	−0.2952	1.02484	−0.2902	1.02130	−0.2852		
0.1966	1.05024	−0.4553	1.04651	−0.4451	1.04272	−0.4350		
0.3010	1.06306	−0.5334	1.05924	−0.5208	1.05538	−0.5087		
0.3989	1.06969	−0.5362	1.06588	−0.5239	1.06202	−0.5118		
0.5006	1.07393	−0.4982	1.07014	−0.4871	1.06632	−0.4765		
0.6011	1.07659	−0.4305	1.07284	−0.4214	1.06905	−0.4124		
0.7003	1.07836	−0.3435	1.07463	−0.3365	1.07089	−0.3301		
0.8051	1.07960	−0.2324	1.07591	−0.2280	1.07220	−0.2237		
0.8920	1.08034	−0.1316	1.07667	−0.1292	1.07299	−0.1269		
1.0000	1.08105	0.0000	1.07740	0.0000	1.07374	0.0000		

mixtures from (283.15 to 353.15) K in the entire composition range are given in Table 2. Obermeier et al.[8] presented a correlation for the density and viscosity of (DEG + water) using data from (263.15 to 413.15) K and (0.25, 0.5, and 0.75) mass fraction. Our values agree with their equation within an average absolute percentage deviation of 0.16 %. Figure 1 presents the percentage deviation of all density values from this equation. Excess molar volumes have been calculated by Pal et al.[5] at (303.15 and 308.15) K. A comparison between their excess molar volume and our values shows an average absolute deviation of ± 0.003 $cm^3 \cdot mol^{-1}$. The excess molar volume presents negative deviations from ideality at the temperatures selected in this work. Negative deviations of the excess molar volume decrease as the temperature increases. We represent the excess molar volume with a Redlich–Kister[1,2] equation. Table 3 shows the values of the parameters at each temperature together with its standard deviation from the fit.

We have compared our water viscosities with values calculated from a standard equation of water.[9] Our values agree within an absolute average deviation of 0.012 mPa·s. We have

Table 3. Parameters for the Redlich–Kister Equation for the Excess Molar Volume

T/K	a_0	a_1	a_2	a_3	σ/cm^3·mol^{-1}
283.15	−2.7605	1.8764	−0.6024	−0.4162	0.0114
288.15	−2.6701	1.7867	−0.5583	−0.4037	0.0107
293.15	−2.5876	1.7021	−0.5251	−0.3778	0.0100
298.15	−2.5117	1.6246	−0.4991	−0.3425	0.0092
303.15	−2.4452	1.5520	−0.4921	−0.2828	0.0081
308.15	−2.3775	1.4903	−0.4629	−0.2846	0.0086
313.15	−2.3158	1.4228	−0.4580	−0.2213	0.0069
318.15	−2.2580	1.3683	−0.4538	−0.1882	0.0062
323.15	−2.2028	1.3159	−0.4508	−0.1472	0.0053
328.15	−2.1499	1.2644	−0.4497	−0.1013	0.0047
333.15	−2.0988	1.2158	−0.4489	−0.0535	0.0040
338.15	−2.0496	1.1703	−0.4535	−0.0120	0.0033
343.15	−2.0023	1.1241	−0.4608	0.0352	0.0026
348.15	−1.9563	1.0829	−0.4672	0.0752	0.0022
353.15	−1.9111	1.0327	−0.4824	0.1500	0.0015

Table 4. Experimental Viscosities and Viscosity Deviations of DEG (1) + Water (2)

x_i	η/mPa·s	η/mPa·s	η/mPa·s	η/mPa·s	η/mPa·s	η/mPa·s	η/mPa·s
	T = 293.15 K	T = 303.15 K	T = 313.15 K	T = 323.15 K	T = 333.15 K	T = 343.15 K	T = 353.15 K
0.0000	1.013	0.811	0.667	0.561	0.477	0.413	0.362
0.0255	1.429	1.115	0.959	0.754	0.62	0.527	0.465
0.0565	2.223	1.674	1.298	1.031	0.849	0.71	0.606
0.1027	3.639	2.629	1.984	1.545	1.236	1.011	0.848
0.1966	7.452	5.148	3.716	2.783	2.147	1.703	1.392
0.3010	12.597	8.358	5.847	4.231	3.202	2.514	2.043
0.3989	17.482	11.397	7.761	5.509	4.103	3.15	2.502
0.5006	22.222	14.15	9.506	6.694	4.917	3.731	2.942
0.6011	26.004	16.34	10.927	7.635	5.534	4.217	3.283
0.7003	29.456	18.481	12.217	8.477	6.12	4.617	3.593
0.8051	32.256	19.998	13.198	9.115	6.492	4.863	3.818
0.8920	34.041	21.187	13.93	9.635	6.874	5.121	4.024
1.0000	36.433	22.091	14.563	10.029	7.22	5.369	4.139

compared our DEG viscosities with measurements from Kumagai et el.[7,10] First, they measured the viscosity of DEG using a rolling-ball viscosimeter. Their data[7] agree with our measurements within an average absolute deviation of 13.7 %. Later, they[10] realized their measurements have a high experimental error, and they remeasured them with an improved capillary viscosimeter. Their new data[10] agree with our measurements within an average absolute percentage deviation of 1.4 %. Experimental viscosities of (DEG + water) from (293.15 to 353.15) K are shown in Table 4. Viscosities of aqueous DEG have been measured by Obermeier et al.[8] and Sun and Teja.[11] Figure 2 presents the deviation of the viscosity values from a correlating equation developed by Obermeier et al.[8] Our viscosity measurements agree with the equation within an average absolute percentage deviation of 2.57 %. Viscosity deviations have been calculated as earlier[12] from the viscosity measurements. Figure 3 shows that viscosity deviations present a change of sign from negative to positive in the water-rich region with a maximum at $x_1 \approx 0.60$. This behavior was mentioned before by Sun and Teja,[11] and it has been confirmed in this work. We have correlated the viscosity deviations using a Redlich–Kister equation,[1,12] and the adjusted parameters

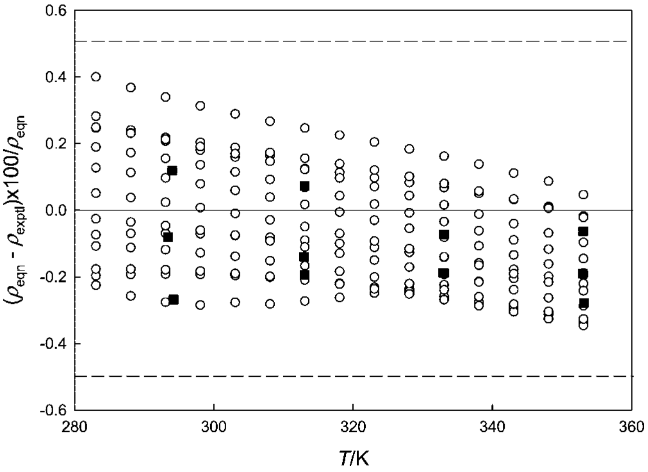

Figure 1. Percentage error of the DEG + water densities from calculated values from an equation reported by Obermeier et al.:[8] ○, this work; ■, Sun and Teja.[11] Dashed line represents the uncertainty given by Obermeier et al.[8] of their equation.

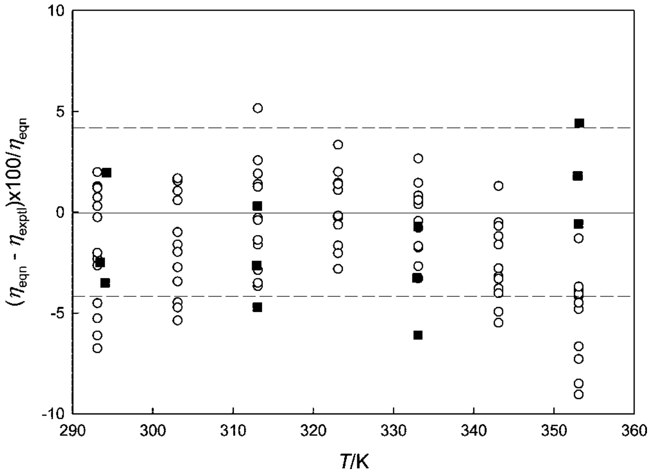

Figure 2. Percentage error of the DEG + water viscosities from calculated values from an equation reported by Obermeier et al.:[8] ○, this work; ■, Sun and Teja.[11] Dashed line represents the uncertainty given by Obermeier et al.[8] of their equation.

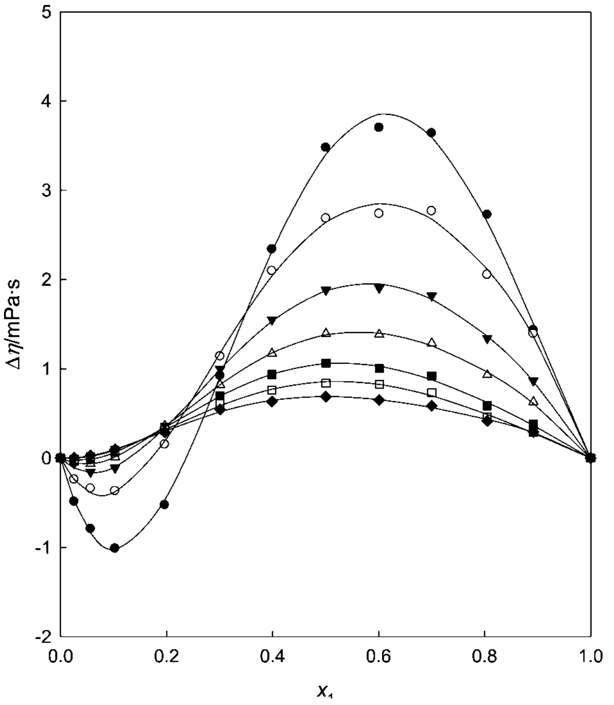

Figure 3. Viscosity deviations for aqueous solutions of DEG: ●, 293.15 K; ○, 303.15 K; ▲, 313.15 K; Δ, 323.15 K; ■, 333.15 K; □, 343.15 K; ♦, 353.15 K.

Table 5. Parameters for the Redlich–Kister Equation for the Viscosity Deviations

T/K	a_0	a_1	a_2	a_3	σ/mPa·s
293.15	13.5942	15.7992	−18.0389	1.4915	0.0732
303.15	10.5553	8.1437	−8.7395	5.2970	0.0630
313.15	7.4914	4.1761	−5.6408	3.3477	0.0285
323.15	5.5224	2.1866	−3.6077	2.7329	0.0171
333.15	4.2346	0.8503	−3.1424	1.7181	0.0218
343.15	3.4268	0.5149	−2.3341	1.0771	0.0192
353.15	2.7663	−0.0005	−1.1703	1.9057	0.0147

together with their standard deviation are in Table 5. We have also compared our mixture viscosities with those calculated from the Kendall and Monroe Relation[13] and the Arrhenius equation.[14] These two methods fail to predict accurately the viscosity of the mixtures considered in this work. It is worth mentioning that the values obtained from these equations are used as ideal contributions to the excess viscosity. When they are used as such a contribution, our data present positive deviations from them at all temperatures and compositions.

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Received for review November 14, 2007. Accepted February 12, 2008. Instituto Tecnológico de Celaya, CONACyT, Texas A&M University, and the Texas Engineering Experiment Station have provided financial support for this work.

JE700672F