Densities and Viscosities of Seven Glycol Ethers from 288.15 K to 343.15 K

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Densities and viscosities of seven glycol ethers consisting of 1-methoxy-2-propanol, 3-methoxy-1-butanol, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, diethylene glycol dimethyl ether, ethylene glycol *tert*-butyl methyl ether, and diethylene glycol diethyl ether were measured from 288.15 K to 343.15 K at atmospheric pressure. Densities were determined using a vibrating-tube densimeter. Viscosities were measured with an automatic Ubbelohde capillary viscometer. The estimated uncertainties of the measurements were ±0.1% for density and ±0.9% for viscosity. The data were correlated using simple expressions and were also used to develop a model for the viscosity based on the Hildebrand fluidity equation.

Introduction

The glycol ethers are important industrial solvents. Process design using these fluids requires accurate thermophysical property data. However, few such data have been published in the literature. In this paper, the densities and viscosities of seven glycol ethers were measured from (288.15 to 343.15) K at atmospheric pressure. The seven glycol ethers chosen were 1-methoxy-2-propanol (MP), 3-methoxy-1-butanol (MB), ethylene glycol dimethyl ether (EGDME), ethylene glycol diethyl ether (EGDEE), diethylene glycol dimethyl ether (DEGDME), ethylene glycol *tert*-butyl methyl ether (EGTBME), and diethylene glycol diethyl ether (DEGDEE). Among these substances, the density and viscosity data have been reported previously for 1- methoxy-2-propanol at temperatures from (293.15 to 328.15) K (De Lorenzi et al., 1996), ethylene glycol dimethyl ether at (298.15 and 303.15) K (Pal and Sharma, 1999), and diethylene glycol dimethyl ether at temperatures from (298.15 to 318.15) K (Aminabhavi et al., 1994).

Various methods have been developed to relate liquid viscosity with the density. Early in the twentieth century, Batschinski (1913) observed that the reciprocal of the viscosity, the fluidity, of nonassociated liquids is linearly related to their molar volumes. Later, Hildebrand (1971) showed that, for a simple liquid, the fluidity depends on the relative expansion of the liquid, $V/V_0 - 1$, and modified the original Batschinski equation to obtain

$$\phi = B(V/V_0 - 1) \qquad (1)$$

where ϕ is the fluidity, V is the molar volume, V_0 is the intrinsic volume defined as the molar volume at zero fluidity corresponding to the solid-state volume but retaining rotational motion, and B is a constant which is a measure of the molecule's ability to absorb externally applied momentum due to its mass, shape, and flexibility. In this work a model based on the Hildebrand equation was developed to correlate the viscosities of these substances.

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Table 1. Comparison of Measured Densities (ρ), Viscosities (η), and Refractive Indices (n_D) of Pure Components with Literature Values at 298.15 K

	ρ/(kg·m^{-3})		η/(mPa·s)		n_D	
compound	this work	lit.	this work	lit.	this work	lit.
MP	916.4	916.50[a] 916.3[b] 916.99[c]	1.681	1.6714[a] 1.7226[c]	1.401 27	
MB	923.2		3.210		1.414 19	
EGDME	861.5	863.70[d] 862.6[f] 861.32[g]	0.417	0.455[e] 0.417[f] 0.424[g]	1.378 11	1.3770[d] 1.37811[e]
EGDEE	836.0	835.10[d]	0.593		1.390 05	1.3898[d]
DEGDME	938.5	938.4[e] 938.9[c]	0.989	0.989[e] 0.985[c]	1.405 85	1.4058[e]
EGTBME	840.7		0.778		1.396 09	
DEGDEE	902.1	903.5[h]	1.238	1.241[h]	1.409 62	

[a] De Lorenzi et al., 1996. [b] Pal et al., 1997. [c] Krishnaiah et al., 1993. [d] Kusano, 1978. [e] Riddick et al., 1986. [f] Pal and Sharma, 1999. [g] Das and Hazra, 1994. [h] Pal and Sharma, 1998.

Experimental Section

The chemicals used were of analytical grade and obtained from Aldrich and Tedia. All components were dried over molecular sieves (Aldrich, 0.3 nm) and used without further purification. The purity of all chemicals was checked by gas chromatography. In all cases chemicals with a purity >99.2 mass % were used for the experimental investigations. The measured properties of pure components are listed in Table 1 together with the literature values. Refractive indices, n_D, of pure chemicals were measured with an Abbe refractometer, Atago RX-5000, with an accuracy of ±0.000 01 unit.

All dried liquids were boiled to remove dissolved air. Densities were measured by using a DMA-58 vibrating-tube densimeter (Anton-Paar, Austria) with a stated precision of 0.02 kg/m^3. The temperature in the measuring cell was regulated to ±0.01 K. The uncertainty of the density measurements was estimated to be ±0.1%.

The kinematic viscosities were determined with a commercial capillary viscometer of the Ubbelohde type. The kinematic viscosity (ν) was then calculated from the

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Table 2. Density of Seven Glycol Ethers at Various Temperatures

	ρ/kg·m^{-3}						
T/K	MP	MB	EGDME	EGDEE	DEGDME	EGTBME	DEGDEE
288.15	925.9	932.8	872.4	846.1	948.4	850.5	911.7
293.15	921.4	928.2	867.0	840.9	943.4	845.6	906.8
298.15	916.4	923.2	861.5	836.0	938.5	840.7	902.1
303.15	911.4	918.4	855.7	830.8	933.5	835.8	897.3
308.15	906.6	913.5	850.2	825.7	928.5	830.9	892.5
313.15	901.7	908.5	844.6	820.5	923.5	826.1	887.6
318.15	896.7	903.6	839.0	815.3	918.6	821.1	882.8
323.15	891.8	898.5	833.3	810.1	913.6	816.1	878.0
328.15	886.7	893.5	827.5	804.9	908.5	811.1	873.1
333.15	881.7	888.4	821.8	799.5	903.4	806.1	868.2
338.15	876.6	883.0	816.0	794.3	898.4	801.0	863.4
343.15	871.3	877.6	810.1	788.9	893.2	795.9	858.4

Table 3. Correlation Results from Eq 3 for Density

compound	a_1	a_2	a_3 ($\times 10^4$)	AAD %	MAD %
1-methoxy-2-propanol	1134.3	−0.495 90	−7.8751	0.007	0.016
3-methoxy-1-butanol	1111.8	−0.302 07	−11.071	0.007	0.015
ethylene glycol dimethyl ether	1125.8	−0.666 69	−7.3786	0.006	0.015
ethylene glycol diethyl ether	1091.1	−0.691 86	−5.5005	0.004	0.012
diethylene glycol dimethyl ether	1204.0	−0.791 60	−3.3187	0.003	0.007
ethylene glycol *tert*-butyl methyl ether	1086.1	−0.672 12	−5.0549	0.003	0.009
diethylene glycol diethyl ether	1168.4	−0.826 17	−2.2448	0.003	0.008

following relationship

$$\nu \equiv \eta/\rho = k(t - \theta) \qquad (2)$$

where t is the flow time, η is the absolute viscosity, ρ is the density, and k and θ are respectively the viscometer constant and the Hagenbach correction (Hardy, 1962). The constants k for several viscometers were provided by the manufacturer (SCHOTT-GERÄTE, Germany) and checked at room temperature by measurement of the viscosity of pure water. The viscometer was kept in a D20 KP (LAUDA, Germany) thermostat controlled to ±0.01 K with a PID regulator. The flow-time measurements were made with an electronic stopwatch having a precision of ±0.01 s. The uncertainty of the viscosity measurements was estimated to be ±0.9%. The densities and viscosities of these substances were measured at temperatures ranging from 288.15 K to 343.15 K. An average of at least three measurements was calculated for each temperature.

Results and Discussion

Table 2 lists the results of the measurements of the densities of the glycol ethers studied in this work. The density data of glycol ether were fit using the polynomial

$$\rho/(\mathrm{kg\cdot m^{-3}}) = a_1 + a_2(T/\mathrm{K}) + a_3(T/\mathrm{K})^2 \qquad (3)$$

where a_1, a_2, and a_3 are constants and T is the temperature in K. The correlation results from eq 3 are given in Table 3. A comparison of our measurements of density with the data in the literature appears in Figure 1. In all cases a reasonable agreement between our measurements of density and the data of the literature is obtained.

Table 4 contains the results for the absolute viscosities of the glycol ethers determined from the kinematic viscosities and the densities measured in this work. The data were regressed using the equation

$$\ln[\eta/(\mathrm{mPa\cdot s})] = b_1 + b_2/(T/\mathrm{K}) + b_3/(T/\mathrm{K})^2 \qquad (4)$$

where b_1, b_2, and b_3 are constants. Table 5 gives the correlation results from eq 4. A comparison of our measurements of viscosity with the data in the literature is shown in Figure 2. A reasonable agreement was found between our measurements of viscosity and those of the literature.

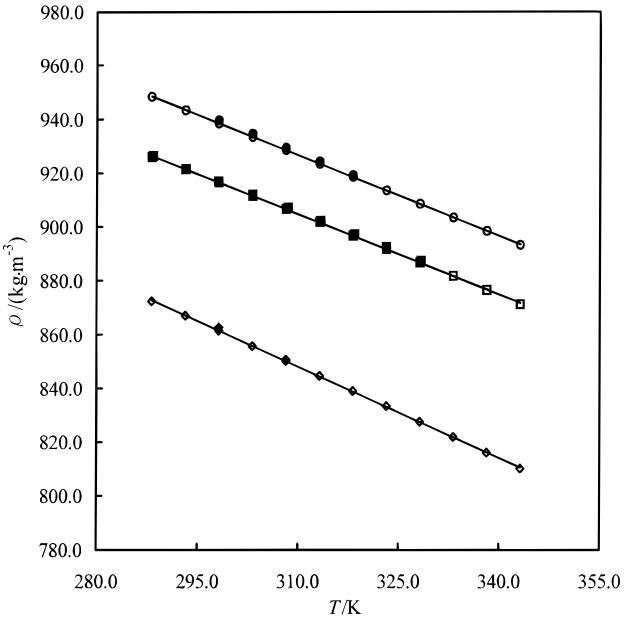

Figure 1. Variation of density with temperature for ○, diethylene glycol dimethyl ether, (○, this work; ●, Aminabhavi et al., 1994), 1-methoxy-2- propanol, (□, this work; (■, De Lorenzi et al., 1996), and ethylene glycol dimethyl ether (◇, this work; ▲ Pal and Sharma, 1999).

For most nonassociated liquids, Hidebrand's equation of fluidity is obeyed over wide temperature ranges. However, when the fluidities of the seven glycol ethers were plotted against their molar volumes, smooth curves were obtained with increasing curvature as the temperature was lowered. Hildebrand's equation was not strictly obeyed, indicating that the fluidity is not linearly related to molar volume. The plots are shown in Figure 3. The viscosity data were then modeled using a modification of the Hildebrand equation with the fluidity being a nonlinear function of the

Table 4. Absolute Viscosity of Seven Glycol Ethers at Various Temperatures

	η/mPa·s						
T/K	MP	MB	EGDME	EGDEE	DEGDME	EGTBME	DEGDEE
288.15	2.175	4.326	0.468	0.685	1.177	0.917	1.498
293.15	1.902	3.683	0.441	0.636	1.081	0.844	1.358
298.15	1.681	3.210	0.417	0.593	0.989	0.778	1.238
303.15	1.488	2.822	0.394	0.556	0.916	0.721	1.134
308.15	1.332	2.523	0.374	0.522	0.853	0.672	1.045
313.15	1.196	2.236	0.355	0.491	0.796	0.628	0.996
318.15	1.080	1.986	0.338	0.463	0.745	0.588	0.897
323.15	0.981	1.770	0.322	0.437	0.699	0.551	0.837
328.15	0.895	1.598	0.308	0.414	0.656	0.519	0.783
333.15	0.818	1.447	0.294	0.393	0.617	0.489	0.732
338.15	0.753	1.317	0.281	0.375	0.583	0.463	0.668
343.15	0.685	1.196	0.269	0.357	0.552	0.439	0.648

Table 5. Correlation Results from Eq 4 for Viscosity

compound	b_1	b_2	b_3 ($\times 10^{-2}$)	AAD %	MAD %
1-methoxy-2-propanol	−2.4954	−373.47	3792.0	0.08	0.17
3-methoxy-1-butanol	−3.5665	441.83	2896.6	0.46	0.91
ethylene glycol dimethyl ether	−4.4548	1147.1	−237.64	0.07	0.16
ethylene glycol diethyl ether	−3.2752	434.53	1152.6	0.06	0.14
diethylene glycol dimethyl ether	−2.7580	226.39	1771.3	0.19	0.45
ethylene glycol *tert*-butyl methyl ether	−3.0529	295.37	1611.1	0.06	0.15
diethylene glycol diethyl ether	−2.1033	−205.44	2672.8	0.08	0.22

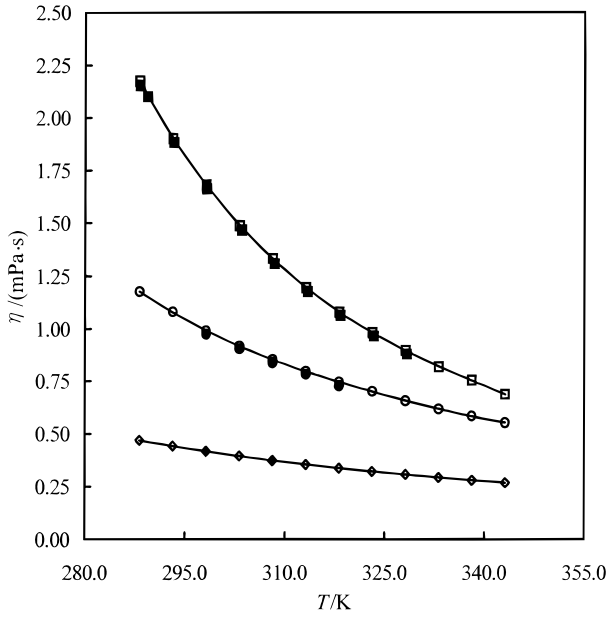

Figure 2. Variation of viscosity with temperature for 1-methoxy-2-propanol (□, this work; ●, De Lorenzi et al., 1996), diethylene glycol dimethyl ether (○, this work; ●, Aminabhavi et al., 1994), and ethylene glycol dimethyl ether, (◇, this work; ◆, Pal and Sharma, 1999).

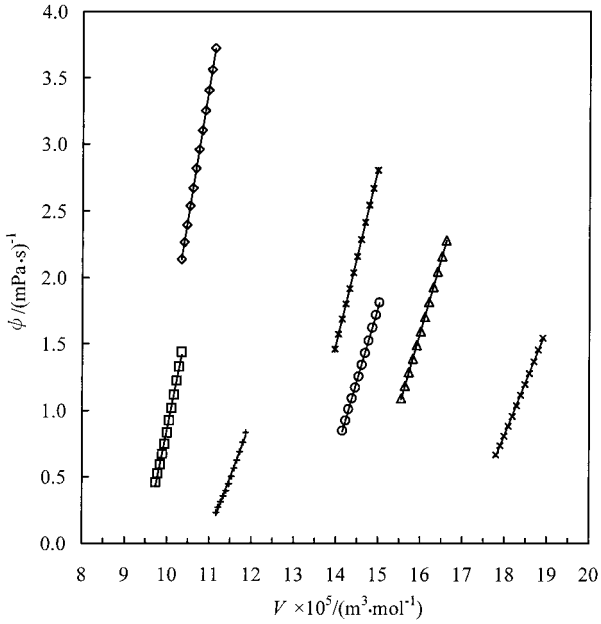

Figure 3. Plot of ϕ versus V: ◇, ethylene glycol dimethyl ether; □, 1-methoxy-2-propanol; +, 3-methoxy-1-butanol; ∗, ethylene glycol diethyl ether; ○, diethylene glycol dimethyl ether; △, ethylene glycol *tert*-butyl methyl ether; ×, diethylene glycol diethyl ether.

molar volume and the intrinsic volume V_0:

$$\phi = c_1(V/V_0 - 1)^{c_2 + c_3(V/V_0 - 1)} \quad (5)$$

To determine V_0, a second-degree function of the fluidity was fitted to the molar volumes using least squares. An approximate value of V_0 was obtained by extrapolation to zero fluidity. These extrapolated volumes ($V_{0\text{extrap}}$) should approach the "true" volumes if the fluidities and molar volumes were measured at temperatures approaching the freezing points of liquids (Liew et al., 1993). Since it was reasoned that the extrapolated volume was an approximate value for V_0, we proceed to vary the V_0 value and calculate the values of ϕ at different values of V/V_0 using eq 5 until the best correlation was obtained for each of the glycol ethers. The V_0 values, corresponding to the best correlations, were designated corrected intrinsic volumes, $V_{0\text{corr}}$.

When the molar volume of each substance was divided by the value of $V_{0\text{corr}}$, all the data sets could be reduced to a single curve, as shown in Figure 4. The curve shown in Figure 4 is given by

$$\phi \equiv 1/(\eta/\text{mPa·s}) = c_1(V/V_{0\text{corr}} - 1)^{c_2 + c_3(V/V_{0\text{corr}} - 1)} \quad (6)$$

where

$$c_1 = 0.105\ 365 \quad c_2 = -0.054\ 414\ 4 \quad c_3 = -9.990\ 20$$

Equation 6 may be used to calculate the viscosity of any

Table 6. Intrinsic Molar Volumes ($m^3 \cdot mol^{-1}$) and Correlation Results for the Viscosity Model of Eq 6

compound	$V_{0extrap}$ ($\times 10^5$)	V_{0corr} ($\times 10^5$)	AAD %	MAD %
1-methoxy-2-propanol	9.333	9.299	4.23	11.5
3-methoxy-1-butanol	10.684	11.032	1.23	2.98
ethylene glycol dimethyl ether	9.245	8.905	1.31	3.02
ethylene glycol diethyl ether	12.878	12.505	0.51	1.00
Diethylene glycol dimethyl ether	13.282	13.161	0.99	2.34
Ethylene glycol *tert*-butyl methyl ether	14.517	14.230	0.88	1.46
diethylene glycol diethyl ether	16.832	16.800	1.72	2.51

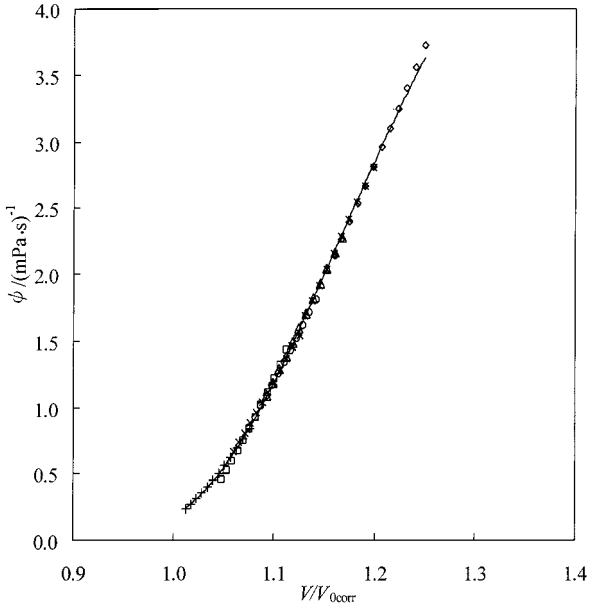

Figure 4. Plot of ϕ versus V/V_{0corr}: ◇, ethylene glycol dimethyl ether; □, 1-methoxy-2-propanol; △, ethylene glycol *tert*-butyl methyl ether; ∗, ethylene glycol diethyl ether; +, 3-methoxy-1-butanol; ×, diethylene glycol diethyl ether; ○, diethylene glycol dimethyl ether. The solid line corresponds to values calculated using eq 6.

glycol ether at a given temperature from knowledge of the molar volume (or density) and a single value of V_0 for each glycol ether. The advantage of using this model is the inclusion of the effect of temperature on the viscosity via the molar volume at given conditions. Using the values of V_{0corr} and the molar volumes of the glycol ethers, the viscosities were calculated using eq 6. When these viscosities were compared with the experimental values, an average deviation of 1.55% was obtained. Table 6 lists the values of V_0 and gives information about the calculated result for each of the glycol ethers.

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