

Density, Viscosity and Thermal Conductivity of Aqueous Solutions of Propylene Glycol, Dipropylene Glycol, and Tripropylene Glycol between 290 K and 460 K

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The density, viscosity, and thermal conductivity of propylene glycol + water, dipropylene glycol + water, and tripropylene glycol + water mixtures were measured at temperatures ranging from 290 K to 460 K and concentrations ranging from 25 mol % glycol to 100 mol % glycol. Our data generally agreed with the limited data available in the literature and were correlated using empirical expressions, the modified rough hard-sphere model, and the generalized corresponding states principle (GCSP). The GCSP method, with two adjustable parameters for each property, offers the potential for judicious extrapolation of density and transport property data for all glycol + water mixtures.

Introduction

Measurements of the density, viscosity, and thermal conductivity of aqueous systems at high temperatures and pressures are of interest in the development of thermophysical property models, as such systems generally exhibit large departures from ideal behavior. As a continuation of our previous work on water + polyethylene glycol mixtures,¹ we report new data on the thermophysical properties of aqueous propylene, dipropylene, and tripropylene glycol mixtures. Literature data^{2–4} have been reported only for water + propylene glycol at ambient conditions. Our work, therefore, extends the experimental information to a wider range of temperatures and also allows us to compare two models for their ability to correlate and extrapolate such information.

Experimental Section

Materials. Reagent-grade propylene glycol (PG), dipropylene glycol (DPG), and tripropylene glycol (TPG) were purchased from Aldrich Company and used in the experiments without further purification. The stated minimum purity of these reagents was 99.5 mol %, 99 mol %, and 97 mol % respectively, with the impurities consisting mainly of isomers. Glycol + water mixtures were prepared gravimetrically using double-distilled water.

Measurements. Densities and viscosities of mixtures were measured using a pycnometer and a capillary viscometer. The pycnometer was calibrated using mercury, and the viscometer was calibrated by the manufacturer using viscosity standards. Both pycnometer and viscometer were placed inside a high-pressure view cell for visual observation of liquid levels. The view cell was placed in a thermostated vessel in order to maintain the contents at a constant temperature and pressurized to suppress boiling of the liquids. Temperature uncertainty was estimated to be ± 0.1 K. Triplicate measurements were carried out for density and viscosity at each temperature. The reproducibility of the density and viscosity measurements was $\pm 0.1\%$ and $\pm 1\%$, respectively, whereas the uncertainty was estimated to be $\pm 0.2\%$ for density and $\pm 2\%$ for viscosity.

Table 1. Densities of Glycol + Water Mixtures

$x_1 = 0.25$		$x_1 = 0.50$		$x_1 = 0.75$	
T/K	$\rho/\text{kg}\cdot\text{m}^{-3}$	T/K	$\rho/\text{kg}\cdot\text{m}^{-3}$	T/K	$\rho/\text{kg}\cdot\text{m}^{-3}$
Propylene Glycol (1) + Water (2)					
296.65	1040	297.05	1042	296.80	1038
313.05	1028	313.05	1029	313.05	1026
333.10	1013	333.10	1013	333.10	1010
353.05	996.5	353.05	996.8	353.05	993.8
363.30	988.0	363.40	987.9	363.35	985.1
373.45	979.3	383.50	970.3	378.35	971.6
381.55	971.3	395.75	958.1	388.50	963.2
390.55	963.4	407.45	947.1	398.30	954.2
407.75	947.5	424.95	929.6	408.15	944.7
424.55	930.2	439.95	914.7	411.75	940.7
444.55	908.3			428.15	924.7
				441.45	912.7
Dipropylene Glycol (1) + Water (2)					
295.05	1040	293.40	1034	293.90	1028
313.05	1026	313.05	1019	313.05	1013
333.10	1010	333.10	1003	333.10	997.0
353.10	992.8	353.10	986.0	353.10	980.5
368.25	979.2	372.20	969.5	372.20	964.3
395.95	953.1	382.50	960.1	382.50	955.2
408.35	941.3	392.40	951.0	392.30	946.2
426.75	922.7	394.25	949.4	402.30	936.9
444.65	904.1	407.85	936.8	405.35	934.5
		426.35	918.8	418.35	923.0
		445.25	899.1	437.25	904.2
				455.15	887.2
Tripropylene Glycol (1) + Water (2)					
295.40	1037	294.80	1028	295.35	1021
313.05	1023	313.05	1013	313.05	1007
333.05	1006	333.10	996.8	333.10	990.4
353.05	989.0	353.05	979.9	353.10	973.7
368.25	975.3	368.25	966.8	368.25	960.5
378.15	966.7	378.50	957.4	378.55	951.3
393.05	953.0	388.40	947.8	388.40	942.4
409.05	936.6	394.05	944.0	398.35	933.3
426.65	918.9	408.65	930.6	408.30	924.3
446.15	897.8	426.75	913.2	414.15	918.6
		446.85	892.5	429.25	904.7
				445.00	889.5

Additional details relating to the apparatus and experimental procedure are given elsewhere.^{5–7}

Thermal conductivity was measured using the relative transient hot-wire method. In the case of the pure glycols,

Table 2. Viscosities of Glycol + Water Mixtures

$x_1 = 0.25$		$x_1 = 0.50$		$x_1 = 0.75$	
T/K	$\eta/\text{mPa}\cdot\text{s}$	T/K	$\eta/\text{mPa}\cdot\text{s}$	T/K	$\eta/\text{mPa}\cdot\text{s}$
Propylene Glycol (1) + Water (2)					
296.65	7.39	297.05	17.5	296.80	32.4
313.05	3.90	313.05	8.47	313.05	14.4
333.10	2.12	333.10	4.14	333.10	6.46
353.05	1.32	353.10	2.36	353.05	3.45
363.30	1.09	363.40	1.84	363.35	2.66
373.45	0.915	383.50	1.22	378.35	1.87
384.15	0.778	398.75	0.952	388.50	1.52
394.55	0.657	411.45	0.793	398.30	1.27
411.75	0.525	428.95	0.618	408.15	1.08
429.55	0.426	443.95	0.517		
449.55	0.344				
Dipropylene Glycol (1) + Water (2)					
295.05	22.3	293.40	59.9	293.90	88.5
313.05	9.14	313.05	18.6	313.05	25.8
333.10	4.30	333.10	7.68	333.10	9.71
353.10	2.42	353.10	3.89	353.10	4.71
368.25	1.72	372.20	2.33	372.20	2.73
378.75	1.41	382.50	1.85	382.50	2.14
397.45	0.983	392.40	1.53	392.30	1.72
411.35	0.803	395.75	1.45	402.30	1.43
429.75	0.630	410.85	1.11	406.85	1.33
447.65	0.512	429.35	0.829	421.35	1.05
		448.25	0.640	440.25	0.795
				458.15	0.641
Tripropylene Glycol (1) + Water (2)					
295.40	36.7	294.80	66.6	295.35	71.2
313.05	14.2	313.05	22.4	313.05	24.6
333.05	6.27	333.10	9.12	333.10	9.92
353.05	3.36	353.05	4.50	353.10	4.93
368.25	2.30	368.25	2.96	368.25	3.21
378.15	1.84	378.50	2.32	378.55	2.53
394.55	1.35	388.40	1.88	388.40	2.03
412.05	1.01	395.15	1.67	398.35	1.66
429.65	0.785	411.65	1.26	408.30	1.44
449.15	0.615	429.75	0.952	412.45	1.31
		449.85	0.738	428.25	1.02
				446.55	0.791

a bare platinum wire was employed to measure the thermal conductivity. In the case of aqueous mixtures, a Pyrex capillary filled with liquid mercury was employed to act as an insulated hot-wire, as described in our earlier work.⁶⁻⁸ Both hot-wire cells were placed inside a thermostated high-pressure vessel that maintained a constant temperature in the cell within ± 0.1 K. The effective length of the wire was obtained by calibration using IUPAC-suggested values of the thermal conductivity of water⁹ and dimethylphthalate.¹⁰ Each reported value of the measured thermal conductivity was obtained by averaging the results of five experiments. The values were reproducible within $\pm 1\%$ and were estimated to have an uncertainty of $\pm 2\%$. Further details of the experimental apparatus and technique are given elsewhere.⁶⁻⁸

Results and Discussion

Tables 1–3 list the experimental densities, viscosities, and thermal conductivities of glycol + water mixtures containing (25, 50, and 75) mol % glycol. Table 4 lists the same properties for the pure glycols. The temperature range of the measurements was 293 K to 458 K, and pressures were in the range of 0.1 to 2.2 MPa in order to suppress boiling of the liquids. These pressures were not expected to affect the measured densities, viscosities, or thermal conductivities to any appreciable extent.⁹ However, for the sake of completeness, it should be noted that the following pressures were used: for $T/K < 370$, $P/\text{MPa} = 0.1$; for $370 < T/K < 390$, $P/\text{MPa} = 1.1$; for $390 < T/K <$

Table 3. Thermal Conductivities of Glycol + Water Mixtures

$x_1 = 0.25$		$x_1 = 0.50$		$x_1 = 0.75$	
T/K	$\lambda/\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$	T/K	$\lambda/\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$	T/K	$\lambda/\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
Propylene Glycol (1) + Water (2)					
299.6	0.322	298.9	0.243	298.5	0.212
322.1	0.337	324.2	0.250	323.7	0.214
347.2	0.348	349.1	0.254	348.2	0.215
372.1	0.353	372.1	0.255	372.8	0.215
396.4	0.353	397.1	0.255	396.0	0.214
420.4	0.347	420.2	0.253	420.8	0.212
440.4	0.338	440.8	0.249	442.0	0.210
Dipropylene Glycol (1) + Water (2)					
297.8	0.248	297.9	0.190	298.4	0.167
323.9	0.256	324.9	0.193	324.8	0.169
349.9	0.260	349.3	0.195	350.1	0.167
374.0	0.264	374.9	0.196	375.1	0.169
398.6	0.263	398.9	0.195	399.0	0.169
423.8	0.264	424.4	0.193	424.3	0.167
		448.8	0.187	448.9	0.163
Tripropylene Glycol (1) + Water (2)					
297.3	0.215	298.1	0.174	297.7	0.157
324.3	0.220	325.8	0.174	325.2	0.156
349.7	0.223	350.2	0.175	349.1	0.156
374.1	0.224	375.1	0.172	375.5	0.155
398.9	0.222	399.0	0.172	399.4	0.152
423.0	0.220	424.5	0.168	422.5	0.150
448.2	0.213	448.3	0.164	449.0	0.144

410, $P/\text{MPa} = 1.5$; for $410 < T/K < 430$, $P/\text{MPa} = 1.8$; for $T/K > 430$, $P/\text{MPa} = 2.2$. The thermal conductivity of DPG + water at 445 K and $x_1 = 0.25$ could not be measured because of the onset of convection in our apparatus.

The density ρ , the viscosity $\ln \eta$, and the thermal conductivity λ of glycol (1) + water (2) mixtures were correlated using the following expressions

$$\rho/(\text{kg m}^{-3}) = \sum \sum A_{ij} w_1^{i-1} t^{j-1} \quad (1a)$$

$$\ln \eta/(\text{mPa s}) = w_1 \ln \eta_1 + w_2 \ln \eta_2 +$$

$$(\ln \eta_1 - \ln \eta_2) w_1 w_2 (B_4 + B_5 w_1 + B_6 t + B_7 w_1^2) \quad (1b)$$

$$\lambda/(\text{W m}^{-1} \text{K}^{-1}) = w_1 \lambda_1 + w_2 \lambda_2 +$$

$$(\lambda_1 - \lambda_2) w_1 w_2 (C_4 + C_5 w_1 + C_6 t) \quad (1c)$$

where $t = T/K - 273.15$, w_1 is the mass fraction of glycol, $w_2 = 1 - w_1$, and i and j have values from 1 to 3 in eq 1a. The properties $\ln \eta_1$ (or λ_1) and $\ln \eta_2$ (or λ_2) are the values of $\ln \eta$ (or λ) for pure glycol and pure water, respectively. These properties are given by

$$\ln \eta_1/(\text{mPa s}) = B_1 + B_2 t + B_3 t^2 \quad (2a)$$

$$\lambda_1/(\text{W m}^{-1} \text{K}^{-1}) = C_1 + C_2/(t - C_3) \quad (2b)$$

These relationships for water were obtained by fitting literature data⁹ in the temperature range 293 K – 473 K, as follows

$$\ln \eta_2/(\text{mPa s}) = -3.758\,023 + 590.980\,8/(t + 137.264\,5) \quad (3a)$$

$$\lambda_2/(\text{W m}^{-1} \text{K}^{-1}) = 0.570\,990 + 0.167\,156 \times 10^{-2}t - 0.609\,054 \times 10^{-5}t^2 \quad (3b)$$

Equation 1c was proposed by Bohne et al.¹¹ to correlate the thermal conductivity of aqueous ethylene glycol as a function of temperature and mass fraction. Equation 1b is

Table 4. Densities, Viscosities, and Thermal Conductivities of Pure Glycols

propylene glycol		dipropylene glycol		tripropylene glycol	
<i>T</i> /K	ρ /kg·m ⁻³	<i>T</i> /K	ρ /kg·m ⁻³	<i>T</i> /K	ρ /kg·m ⁻³
298.85	1033	297.45	1020	295.01	1017
318.05	1018	313.05	1008	313.05	1003
339.00	1003	333.10	992.4	333.10	986.4
359.40	986.1	353.10	976.1	353.10	969.9
380.95	967.6	372.25	960.3	372.15	953.5
399.60	951.2	391.45	943.1	391.50	936.4
420.20	931.7	408.35	928.1	411.35	918.7
440.35	912.2	420.30	916.9	428.20	903.3
		428.30	909.6		
<i>T</i> /K	η /mPa·s	<i>T</i> /K	η /mPa·s	<i>T</i> /K	η /mPa·s
297.25	46.4	297.42	81.5	294.82	69.4
302.55	34.0	313.07	29.8	313.05	23.6
317.10	16.4	333.10	11.1	333.10	9.64
332.30	8.75	353.10	5.24	353.10	4.85
347.40	5.26	372.25	3.00	372.15	2.91
362.05	3.42	391.45	1.90	391.50	1.91
376.45	2.34	408.35	1.36	411.35	1.33
391.05	1.67	420.30	1.10	428.20	1.03
406.05	1.27	428.30	0.970		
420.85	0.982				
<i>T</i> /K	λ /W·m ⁻¹ ·K ⁻¹	<i>T</i> /K	λ /W·m ⁻¹ ·K ⁻¹	<i>T</i> /K	λ /W·m ⁻¹ ·K ⁻¹
299.1	0.196	298.2	0.156	298.1	0.152
313.6	0.195	309.8	0.157	326.1	0.152
332.9	0.195	316.9	0.156	351.1	0.150
352.3	0.194	347.4	0.156	376.2	0.148
371.6	0.193	363.0	0.156	399.4	0.145
391.1	0.192	377.6	0.155	424.9	0.140
411.4	0.190	391.6	0.154	449.6	0.135
430.4	0.187	405.7	0.153		
450.8	0.183	420.6	0.151		
		435.1	0.149		

Table 5. Coefficients A_{ij} and B_i of Eqs 1 and 2

	propylene glycol + water	dipropylene glycol + water	tripropylene glycol + water
ρ /kg·m ⁻³ Correlation			
A_{11}	1003.7	1003.8	1003.8
A_{21}	147.12	168.58	181.87
A_{31}	-99.617	-134.05	-151.40
A_{12}	-0.20062	-0.20207	-0.20159
A_{22}	-1.1024	-1.1338	-1.0231
A_{32}	0.63102	0.62288	0.46738
A_{13}	-2.5127×10^{-3}	-2.5073×10^{-3}	-2.5100×10^{-3}
A_{23}	2.6902×10^{-3}	2.3810×10^{-3}	1.6067×10^{-3}
A_{33}	-1.1267×10^{-3}	-5.8641×10^{-4}	3.5824×10^{-4}
AAD%	0.036	0.053	0.054
MAD%	0.083	0.118	0.197
$\ln \eta$ /mPa·s Correlation			
B_1	-3.9701	-3.6944	-3.4986
B_2	1000.8	878.20	853.42
B_3	-104.10	-84.119	-88.217
B_4	1.5232	1.6832	20.687
B_5	-5.0007	-5.1426	-50.423
B_6	9.8106×10^{-4}	2.8529×10^{-3}	2.2872×10^{-4}
B_7	3.2452	3.4638	31.372
AAD%	0.95	0.82	0.98
MAD%	2.73	2.18	2.80
λ /W·m ⁻¹ ·K ⁻¹ Correlation			
C_1	0.19116	0.15428	0.15028
C_2	1.1999×10^{-4}	7.0784×10^{-5}	4.5630×10^{-5}
C_3	-9.2459×10^{-7}	-6.1800×10^{-7}	-7.3863×10^{-7}
C_4	0.36220	0.40207	0.27899
C_5	9.0345×10^{-2}	1.9196×10^{-2}	2.3445×10^{-1}
C_6	-2.0935×10^{-4}	-2.3796×10^{-4}	-1.9210×10^{-4}
AAD%	0.51	0.35	0.46
MAD%	2.07	1.27	1.52

similar to eq 1c, except for the inclusion of the term $B_7 w_1^2$. Coefficients of eqs 1 and 2 (A_{ij} , B_i , and C_i) obtained by fitting data are given in Table 5, which also lists average absolute deviations (AAD) and maximum absolute deviation (MAD) between experimental data and smoothed (correlated) values.

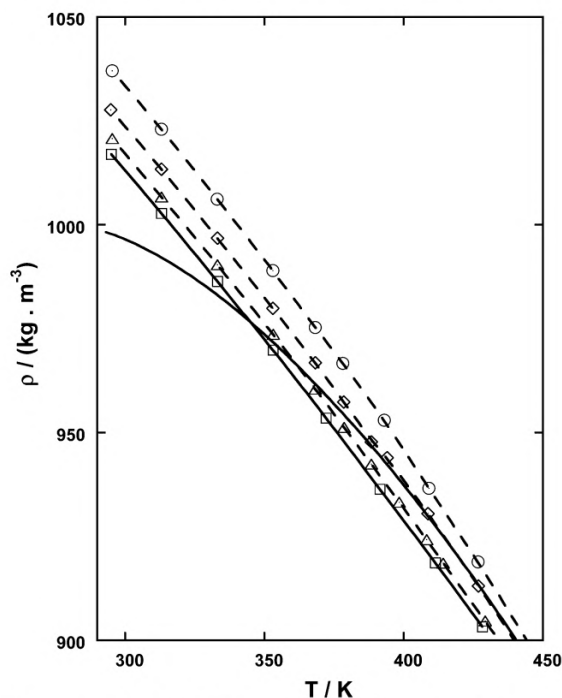


Figure 1. Density of TPG + water mixtures as a function of temperature. Experimental data: $\square$, 100 mol % glycol; $\triangle$, 75 mol % glycol; $\diamond$, 50 mol % glycol; $\circ$, 25 mol % glycol. Solid lines represent smoothed values of the pure components, whereas dashed lines represent calculated values using the GCSP method.

tions (MAD) between experimental data and smoothed (correlated) values. The calculated AAD and MAD are within experimental uncertainty for all three properties. Typical results for mixtures are given in Figures 1–3, where the experimental data and the correlations are shown as a function of temperature for 0, 25, 50, 75, and 100 mol % glycol. The results of pure PG, DPG, and TPG are given in Figures 4–6.

Comparison of our density and viscosity data and literature values for pure PG is shown in Figures 4 and 5. There is good agreement with literature values at low temperatures for both density and viscosity. There are very few reported mixture data in the literature. The few available mixture data at low temperatures were compared in terms of excess molar volume V^E , viscosity deviation $\Delta\eta$, and thermal conductivity deviation $\Delta\lambda$, defined as follows

$$V^E = x_1 M_1 (1/\rho_m - 1/\rho_1) + x_2 M_2 (1/\rho_m - 1/\rho_2) \quad (4a)$$

$$\Delta\eta = \eta_m - x_1 \eta_1 - x_2 \eta_2 \quad (4b)$$

$$\Delta\lambda = \lambda_m - x_1 \lambda_1 - x_2 \lambda_2 \quad (4c)$$

where subscripts m, 1, and 2 refer to the mixture, pure glycol, and pure water, respectively, and M is the molecular weight. Smoothed experimental values from eqs 1–3 were used in the comparisons. Figure 7 shows that our V^E and $\Delta\eta$ curves agree reasonably well with literature data in the entire concentration range.

V^E , $\Delta\eta$, and $\Delta\lambda$ values were also calculated for all glycol + water mixtures in the temperature range 293 K to 460 K. Excess volumes V^E were found to be negative at all temperatures but became less negative with increasing

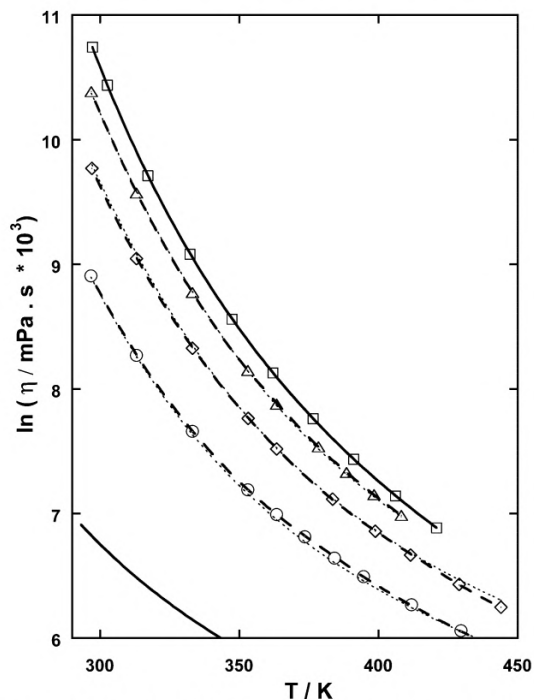


Figure 2. Viscosity of PG + water mixtures as a function of temperature. Experimental data: $\square$, 100 mol % glycol; $\triangle$, 75 mol % glycol; $\diamond$, 50 mol % glycol; $\circ$, 25 mol % glycol. Solid lines represent smoothed values of the pure components, whereas dashed lines represent calculated values using the modified rough-sphere method.

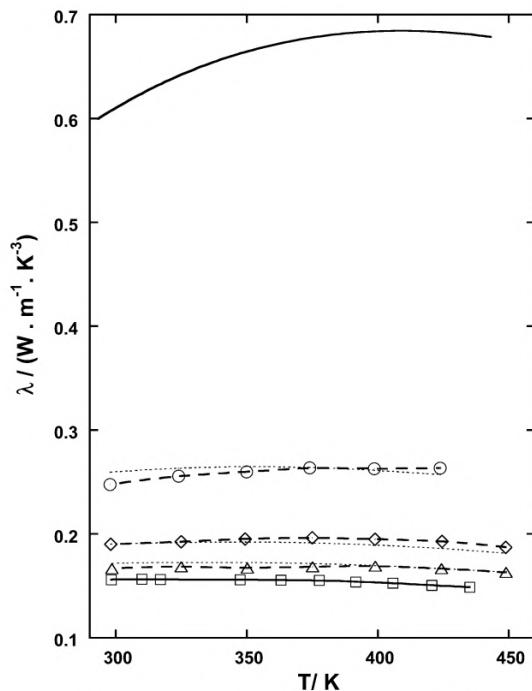


Figure 3. Thermal conductivity of DPG + water mixtures as a function of temperature. Experimental data: $\square$, 100 mol % glycol; $\triangle$, 75 mol % glycol; $\diamond$, 50 mol % glycol; $\circ$, 25 mol % glycol. Solid lines represent smoothed values of the pure components, whereas dashed lines represent calculated values using the modified rough sphere method.

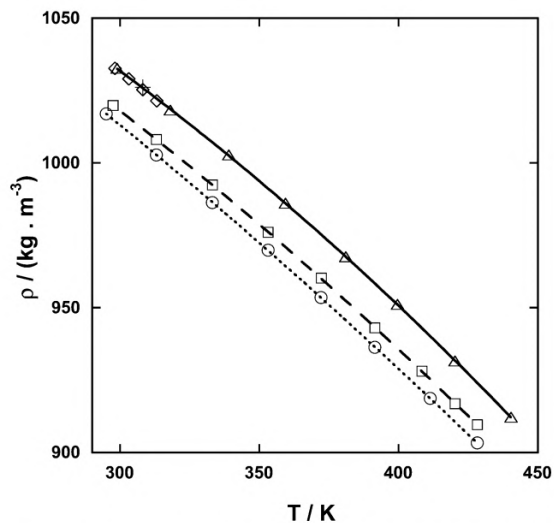


Figure 4. Density of glycols as a function of temperature. Symbols represent experimental data and lines represent smoothed data of this work for: $\triangle$, PG; $\square$, DPG; $\circ$, TPG. Also shown are the experimental data of $\diamond$, Sastry and Patel;³ +, Naidu et al.⁵

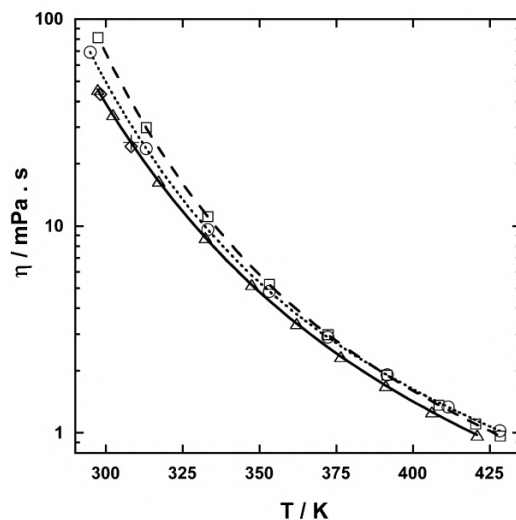


Figure 5. Viscosity of glycols as a function of temperature. Symbols represent experimental data and lines represent smoothed data of this work for: $\triangle$, PG; $\square$, DPG; $\circ$, TPG. Also shown are the experimental data of $\diamond$, Sastry and Patel;³ +, Naidu et al.⁵

temperature. This behavior is quite common in completely miscible water + polar organic mixtures and was reported previously by us in the case of polyethylene glycol + water mixtures¹. However, polypropylene glycol + water mixtures exhibit even more negative values of V^E . For example, the minimum value of V^E at $T = 303$ K in the PG + water system is -0.63 cm³ mol⁻¹ (Figure 7).

Thermal conductivity deviations were found to be negative for all mixtures studied at all temperatures. Also, $\Delta\lambda$ values became more negative with increasing temperature, and the relative deviations $\Delta\lambda/\lambda$ were quite large. This behavior was also reported previously by us in the case of polyethylene glycol + water mixtures.

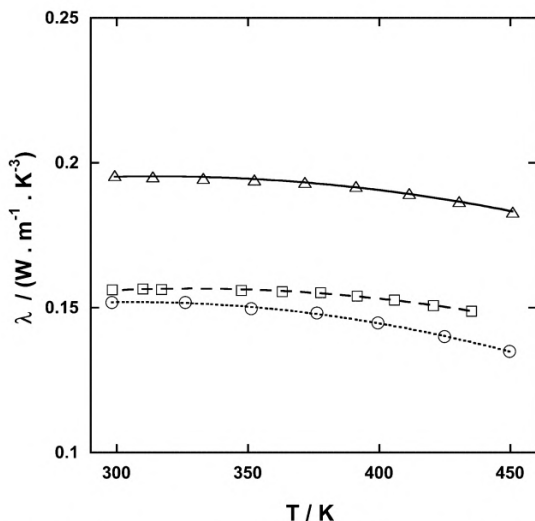


Figure 6. Thermal conductivity of glycols as a function of temperature. Symbols represent experimental data, and lines represent smoothed data of this work for: $\triangle$, PG; $\square$, DPG; $\circ$, TPG.

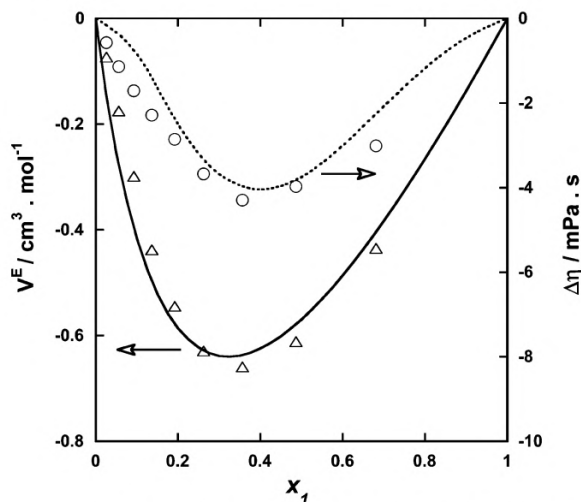


Figure 7. Excess volumes and viscosity deviations of PG + water mixtures at 303 K. Experimental data of $\triangle$, volume, and $\circ$, viscosity, by Kapadi et al.⁴ Solid line represents the smoothed data of this work.

The behavior of $\Delta\eta$ was complex. In the case of PG + H₂O, $\Delta\eta$ values were found to be negative at 303 K (see Figure 7) and then gradually became positive at high temperatures. The changes in $\Delta\eta$ were larger in aqueous polypropylene glycol systems. For example, the minimum value of $\Delta\eta$ at $T = 303$ K was -1.3 mPa s in the case of ethylene glycol + water,¹ whereas it was -4.1 mPa s in the case of PG + H₂O, as shown in Figure 7. Moreover, the $\Delta\eta$ values depend not only on the temperature but also on the concentration. This behavior, however, needs to be verified with additional experiments.

Modified Rough-Hard-Sphere Method

The rough-hard-sphere concept was proposed by Chandler¹² and extended by Assael et al.^{13,14} It postulated that the reduced viscosity η^* and reduced thermal conductivity

λ^* of rough hard spheres can be expressed as universal functions of the reduced volume V_r (V/V_0) as follows

$$\log(\eta^*/R_\eta) = 1.0945 - 9.26324 V_r^{-1} + 71.0385 V_r^{-2} - 301.9012 V_r^{-3} + 797.69 V_r^{-4} - 1221.977 V_r^{-5} + 987.5574 V_r^{-6} - 319.4636 V_r^{-7} \quad (5a)$$

$$\log(\lambda^*/R_\lambda) = 1.0655 - 3.538 V_r^{-1} + 12.120 V_r^{-2} - 12.469 V_r^{-3} + 4.562 V_r^{-4} \quad (5b)$$

where R_η and R_λ reflect the degree of coupling between translational and rotational motions of the molecules. In practice, these parameters are generally used to empirically account for deviations from the behavior of smooth hard spheres. The reduced viscosity and thermal conductivity are defined as

$$\eta^* = 6.035 \times 10^8 (1/MRT)^{0.5} \eta V^{2/3} \quad (6a)$$

$$\lambda^* = 1.936 \times 10^7 (M/RT)^{0.5} \lambda V^{2/3} \quad (6b)$$

where R is the gas constant and V is the molar volume of the substance. The transport properties of a fluid at a given temperature and pressure can thus be calculated using eqs 5 and 6, provided that the coupling parameters R_η and R_λ and the characteristic volume V_0 are known. Note that the volume V must also be available from experiment or from a pVT relation at the conditions of interest.

We have previously¹⁵ proposed an extension of the method to polar liquids using the following simple expressions for the characteristic volume V_0 and the coupling parameters R_η and R_λ

$$V_0 = D_1 \times 10^{-5} + D_2 \times 10^{-3}/T \quad (7a)$$

$$R_\eta = D_3 \quad (7b)$$

$$R_\lambda = D_4 + D_5 \times 10^{-3} T \quad (7c)$$

Equations 5–7 were used to correlate η and λ of 58 liquids over a wide range of temperatures. In the present work, the equations were used to correlate the data for pure water,⁹ polyethylene glycols,¹ and polypropylene glycols, and results are given in Table 6 together with the AAD and MAD.

The model can be extended to mixtures via the following mixing rules where K_1 and K_2 are used for correlating η

$$V_{0,m} = x_1^2 V_{0,1} + x_1 x_2 (V_{0,1} + V_{0,2})(1 - K_1) + x_2^2 V_{0,2} \quad (8a)$$

$$R_{\eta,m} = x_1^2 R_{\eta,1} + x_1 x_2 (R_{\eta,1} + R_{\eta,2})(1 - K_2) + x_2^2 R_{\eta,2} \quad (8b)$$

$$R_{\lambda,m} = x_1^2 R_{\lambda,1} + 2x_1 x_2 (R_{\lambda,1} R_{\lambda,2})^{0.5} (1 - K_3) + x_2^2 R_{\lambda,2} + x_1 x_2 (x_1 - x_2) (R_{\lambda,1} R_{\lambda,2})^{0.5} K_4 \quad (8c)$$

and K_3 (symmetrical contributions) and K_4 (unsymmetrical contributions) are used for correlating λ since $V_{0,m}$ has a small effect on λ . The results are given in Table 7 with the average deviations being 3.3% for η and 1.5% for λ .

Generalized Corresponding States Method

The two-reference-fluid generalized corresponding states principle (GCSP) has been used previously by us^{16–20} to correlate thermophysical property data with considerable

Table 6. Coefficients of Eq 7

	D_1	D_2	D_3	D_4	D_5	η (%)		λ (%)	
						AAD	MAD	AAD	MAD
water	0.5934	2.060	0.6012	-0.6404	5.340	0.27	0.89	0.11	0.50
EG ^a	2.970	4.882	1.077	0.07776	3.522	0.32	0.83	0.52	1.22
DEG ^b	5.002	8.751	1.448	0.1092	5.072	0.49	1.59	0.67	0.97
TEG ^c	7.071	12.34	1.815	0.3119	6.665	0.46	1.03	0.37	0.70
PG	3.504	8.214	1.382	-0.2302	4.342	1.61	2.92	0.14	0.29
DPG	5.216	18.10	2.124	-0.8661	8.371	2.00	3.23	0.12	0.24
TPG	8.041	23.75	2.440	-0.5885	10.48	1.76	3.09	0.79	1.44

^a Ethylene glycol. ^b Diethylene glycol. ^c Triethylene glycol.**Table 7. Coefficients of Eq 8**

	K_1	K_2	K_3	K_4	η (%)		λ (%)	
					AAD	MAD	AAD	MAD
EG ^a + H ₂ O	0.036	-0.579	0.258	0.225	2.06	6.16	0.91	2.00
DEG ^b + H ₂ O	0.023	-0.846	0.304	0.615	3.17	8.79	2.20	4.94
TEG ^c + H ₂ O	0.003	-0.830	0.324	0.632	2.95	6.82	1.36	3.63
PG + H ₂ O	0.044	-0.694	0.335	0.523	2.09	6.16	1.12	3.44
DPG + H ₂ O	0.030	-0.923	0.309	0.678	4.77	12.3	1.89	4.83
TPG + H ₂ O	-0.001	-0.846	0.319	0.687	4.71	11.6	1.78	3.61

^a Ethylene glycol. ^b Diethylene glycol. ^c Triethylene glycol.

success. The GCSP relates the quantities $Z_C V_R$, $\ln(\eta\xi)$, or $\lambda\phi$ of the mixture to the properties of two reference fluids r1 and r2 at the same reduced temperature T_R and reduced pressure P_R as follows

$$Z_C V_R = x_1(Z_C V_R)^{(r1)} + x_2(Z_C V_R)^{(r2)} \quad (9a)$$

$$\ln(\eta\xi) = x_1 \ln(\eta\xi)^{(r1)} + x_2 \ln(\eta\xi)^{(r2)} \quad (9b)$$

$$\lambda\phi = x_1(\lambda\phi)^{(r1)} + x_2(\lambda\phi)^{(r2)} \quad (9c)$$

in which

$$\xi = V_C^{2/3} T_C^{-1/2} M^{1/2} \quad (10a)$$

$$\phi = V_C^{2/3} T_C^{-1/2} M^{1/2} \quad (10b)$$

In the above equations, Z is the compressibility and V the volume. The subscript C denotes the critical point, and superscripts r1 and r2 denote the properties of two reference fluids. These equations can be extended to mixtures using

$$V_C = \sum x_i x_j V_{C_{ij}} \quad (11a)$$

$$T_C V_C = \sum x_i x_j T_{C_{ij}} V_{C_{ij}} \quad (11b)$$

$$Z_C = \sum x_i Z_{C_i} \quad (11c)$$

where subscripts i or j denote pure component properties. When ($i \neq j$)

$$V_{C_{ij}} = (1/8)(V_{C_i}^{1/3} + V_{C_j}^{1/3})^3 \theta_{ij} \quad (12a)$$

$$T_{C_{ij}} V_{C_{ij}} = (T_{C_i} T_{C_j} V_{C_i} V_{C_j})^{1/2} \psi_{ij} \quad (12b)$$

θ_{ij} and ψ_{ij} are binary interaction parameters that must be obtained by fitting experimental data. Critical properties of pure glycols and water required in the calculations were obtained from the literature.²¹ Other required properties were calculated from eqs 2 and 3. It was found that density and viscosity could be correlated better using mass-fraction-

Table 8. GCSP Correlations of Density, Viscosity, and Thermal Conductivity of Glycol + Water Mixtures

	data	AAD (%)	MAD (%)	θ_{12}	ψ_{12}
Density					
PG + H ₂ O ^a	33	0.07	0.19	1.119	1.164
DPG + H ₂ O ^a	32	0.05	0.17	1.260	1.369
TPG + H ₂ O ^a	33	0.07	0.17	1.358	1.523
Viscosity					
PG + H ₂ O ^a	30	1.92	6.11	0.664	0.672
DPG + H ₂ O ^a	33	1.64	3.84	-0.0536	0.0128
TPG + H ₂ O ^b	33	3.39	12.16	0.934	0.516
Thermal Conductivity					
PG + H ₂ O ^b	21	0.63	1.89	1.696	1.532
DPG + H ₂ O ^b	20	0.84	1.60	2.191	1.765
TPG + H ₂ O ^b	21	0.99	2.56	2.535	1.962

^a Mass-fraction-based mixing rules. ^b Mole-fraction-based mixing rules.

based mixing rules, whereas thermal conductivity could be better correlated using mole-fraction-based mixing rules. Binary interaction parameters determined using the GCSP model are listed in Table 8 together with the corresponding AAD and MAD. The deviations were generally within experimental uncertainty and smaller than the corresponding deviations using the modified rough-hard-sphere model. The results demonstrate that it is possible to correlate all data within experimental uncertainty using only two adjustable parameters per binary system for each property.

Conclusions

Densities, viscosities, and thermal conductivities of PG + water, DPG + water, and TPG + water were measured at temperatures ranging from 290 K to 460 K and glycol concentrations from 25 to 100 mol %. Our data generally agreed with available literature data within experimental uncertainty. The temperature behavior of the excess properties was also examined, and large deviations from ideal behavior were observed. The data were correlated using an empirical relationship, the modified rough-hard-sphere method, and the GCSP method. The GCSP method was able to correlate each property over the entire range of temperatures studied using two adjustable parameters per property. This suggests that the method may be used for

interpolation and judicious extrapolation of transport property data for glycol + water mixtures.

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Literature Cited

- (1) Sun, T. F.; Teja, A. S. Density, Viscosity, and Thermal Conductivity of Aqueous Ethylene, Diethylene, and Triethylene Glycol Mixtures between 290 K and 450 K. *J. Chem. Eng. Data* **2003**, *48*, 198–202.
- (2) Sastry, N. V.; Patel, M. C. Densities, Excess Molar Volumes, Viscosities, Speed of Sound, Excess Isentropic Compressibilities, and Relative Permittivities for Alkyl (Methyl, Ethyl, Butyl, and Isoamyl) Acetates + Glycols at Different Temperatures. *J. Chem. Eng. Data* **2003**, *48*, 1019–1027.
- (3) Naidu, B. V. K.; Rao, K. C.; Subha, M. C. Densities and Viscosities of Mixtures of Some Glycols and Polyglycols in Dimethyl Sulfoxide at 308.15 K. *J. Chem. Eng. Data* **2002**, *47*, 379–382.
- (4) Kapadi, U. R.; Hundiware, D. G.; Patil, N. B.; Lande, M. K.; Patil, P. R. Studies of Viscosity and Excess Molar Volume of Binary Mixtures of Propane-1,2 Diol with Water at Various Temperatures. *Fluid Phase Equilib.* **2001**, *192*, 63–70.
- (5) Sun, T. F.; Ly, D.; Teja, A. S. Densities of Acetic Acid + Water Mixtures at High Temperatures and Concentrations. *Ind. Eng. Chem. Res.* **1995**, *34*, 1327–1331.
- (6) Bleazard, J. G.; Sun, T. F.; Johnson, R. D.; DiGuilio, R. M.; Teja, A. S. The Transport Properties of Seven Alkanediols. *Fluid Phase Equilib.* **1996**, *117*, 386–393.
- (7) Bleazard, J. G.; Sun, T. F.; Teja, A. S. The Thermal Conductivity and Viscosity of Acetic Acid–Water Mixtures. *Int. J. Thermophys.* **1996**, *17*, 111–120.
- (8) DiGuilio, R. M.; Teja, A. S. Thermal Conductivity of Poly(ethylene glycols) and Their Binary Mixtures. *J. Chem. Eng. Data* **1990**, *35*, 117–121.
- (9) Meyer, C. A. ASME Steam Tables: Thermodynamics and Transport Properties of Steam, 6th ed.; American Society of Mechanical Engineering: New York, 1993.
- (10) Marsh, K. N. Ed. *Recommended Reference Materials for the Realization of Physicochemical Properties*; Blackwell Scientific Publications: Boston, 1987.
- (11) Bohne, D.; Fischer, S.; Obermeier, E. Thermal Conductivity, Density, Viscosity, and Prandtl Numbers of Ethylene Glycol + Water Mixtures. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 739–742.
- (12) Chandler, D. Rough Hard Sphere Theory of the Self-Diffusion Constant for Molecular Liquids. *J. Chem. Phys.* **1975**, *62*, 1358–1363.
- (13) Assael, M. J.; Dymond, J. H.; Papadaki, M.; Patterson, P. M. Correlation and Prediction of Dense Fluid Transport Coefficients. I. *n*-Alkanes. *Int. J. Thermophys.* **1992**, *13*, 269–281.
- (14) Assael, M. J.; Dymond, J. H.; Papadaki, M.; Patterson, P. M. Correlation and Prediction of Dense Fluid Transport Coefficients. III. *n*-Alkane Mixtures. *Int. J. Thermophys.* **1992**, *13*, 659–669.
- (15) Bleazard, J. G.; Teja, A. S. Extension of the Rough Hard-Sphere Theory for Transport Properties to Polar Liquids. *Ind. Eng. Chem. Res.* **1996**, *35*, 2453–2459.
- (16) Teja, A. S. A Corresponding States Equation for Saturated Liquid Densities. 1. Applications to LNG. *AIChE J.* **1980**, *26*, 337–345.
- (17) Teja, A. S.; Rice, P. Generalized Corresponding States Method for the Viscosities of Liquid Mixtures. *I&EC Fundamentals* **1981**, *20*, 77–81.
- (18) Teja, A. S.; Rice, P. The Measurement and Prediction of the Viscosities of Some Binary Liquid Mixtures Containing *n*-Hexane. *Chem. Eng. Sci.* **1981**, *36*, 7–11.
- (19) Teja, A. S.; Rice, P. A Generalized Corresponding States Method for the Prediction of the Thermal Conductivity of Liquids and Liquid Mixtures. *Chem. Eng. Sci.* **1981**, *36*, 417–422.
- (20) Teja, A. S.; Rice, P. The Prediction of the Thermal Conductivity of Binary Aqueous Mixtures. *Chem. Eng. Sci.* **1982**, *37*, 788–790.
- (21) Rowley, R. L.; Wilding, W. V.; Oscarson, J. L.; Zundel, N. A.; Marshall, T. L.; Daubert, T. E.; Danner, R. P. *DIPPR Data Compilation of Pure Compound Properties*; Design Institute for Physical Properties (DIPPR), American Institute of Chemical Engineers: New York, 2002.

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