*J. Chem. Eng. Data* **2004,** *49,* 1311−1317

# 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 ±0.1% and ±1%, respectively, whereas the uncertainty was estimated to be ±0.2% for density and ±2% for viscosity. Additional details relating to the apparatus and experimental procedure are given elsewhere.[5−7]

**Table 1. Densities of Glycol + Water Mixtures**

| $x_1 = 0.25$ | | $x_1 = 0.50$ | | $x_1 = 0.75$ | |
|---|---|---|---|---|---|
| $T$/K | $\rho$/kg·m$^{-3}$ | $T$/K | $\rho$/kg·m$^{-3}$ | $T$/K | $\rho$/kg·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 |

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

10.1021/je049960h CCC: $27.50

**Table 2. Viscosities of Glycol + Water Mixtures**

| $x_1 = 0.25$ | | $x_1 = 0.50$ | | $x_1 = 0.75$ | |
|---|---|---|---|---|---|
| $T$/K | $\eta$/mPa·s | $T$/K | $\eta$/mPa·s | $T$/K | $\eta$/mPa·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 water[9] 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 ±1% and were estimated to have an uncertainty of ±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 $T/\mathrm{K} < 370$, $P/\mathrm{MPa} = 0.1$; for $370 < T/\mathrm{K} < 390$, $P/\mathrm{MPa} = 1.1$; for $390 < T/\mathrm{K} < 410$, $P/\mathrm{MPa} = 1.5$; for $410 < T/\mathrm{K} < 430$, $P/\mathrm{MPa} = 1.8$; for $T/\mathrm{K} > 430$, $P/\mathrm{MPa} = 2.2$. 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.

**Table 3. Thermal Conductivities of Glycol + Water Mixtures**

| $x_1 = 0.25$ | | $x_1 = 0.50$ | | $x_1 = 0.75$ | |
|---|---|---|---|---|---|
| $T$/K | $\lambda$/W·m$^{-1}$·K$^{-1}$ | $T$/K | $\lambda$/W·m$^{-1}$·K$^{-1}$ | $T$/K | $\lambda$/W·m$^{-1}$·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 |

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

$$\rho/(\mathrm{kg\ m^{-3}}) = \Sigma\,\Sigma\, A_{ij}\, w_1^{\,i-1}\, t^{\,j-1} \tag{1a}$$

$$\ln \eta/(\mathrm{mPa\ s}) = w_1 \ln \eta_1 + w_2 \ln \eta_2 + (\ln \eta_1 - \ln \eta_2) w_1 w_2 (B_4 + B_5 w_1 + B_6 t + B_7 w_1^{2}) \tag{1b}$$

$$\lambda/(\mathrm{W\ m^{-1}\ K^{-1}}) = w_1 \lambda_1 + w_2 \lambda_2 + (\lambda_1 - \lambda_2) w_1 w_2 (C_4 + C_5 w_1 + C_6 t) \tag{1c}$$

where $t = T/\mathrm{K} - 273.15$, $w_1$ 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 $\lambda_1$) and ln $\eta_2$ (or $\lambda_2$) are the values of ln $\eta$ (or $\lambda$) for pure glycol and pure water, respectively. These properties are given by

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

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

These relationships for water were obtained by fitting literature data[9] in the temperature range 293 K − 473 K, as follows

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

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

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 | |
|---|---|---|---|---|---|
| $T$/K | $\rho$/kg·m$^{-3}$ | $T$/K | $\rho$/kg·m$^{-3}$ | $T$/K | $\rho$/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 | | |
| $T$/K | $\eta$/mPa·s | $T$/K | $\eta$/mPa·s | $T$/K | $\eta$/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 | | | | |
| $T$/K | $\lambda$/W·m$^{-1}$·K$^{-1}$ | $T$/K | $\lambda$/W·m$^{-1}$·K$^{-1}$ | $T$/K | $\lambda$/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 |
|---|---|---|---|
| | $\rho$/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 |
| $A_{13}$ | $-2.5127 \times 10^{-3}$ | $-2.5073 \times 10^{-3}$ | $-2.5100 \times 10^{-3}$ |
| $A_{23}$ | $2.6902 \times 10^{-3}$ | $2.3810 \times 10^{-3}$ | $1.6067 \times 10^{-3}$ |
| $A_{33}$ | $-1.1267 \times 10^{-3}$ | $-5.8641 \times 10^{-4}$ | $3.5824 \times 10^{-4}$ |
| 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 |
| $B_6$ | $9.8106 \times 10^{-4}$ | $2.8529 \times 10^{-3}$ | $2.2872 \times 10^{-4}$ |
| $B_7$ | 3.2452 | 3.4638 | 31.372 |
| AAD% | 0.95 | 0.82 | 0.98 |
| MAD% | 2.73 | 2.18 | 2.80 |
| | $\lambda$/W·m$^{-1}$·K$^{-1}$ Correlation | | |
| $C_1$ | 0.19116 | 0.15428 | 0.15028 |
| $C_2$ | $1.1999 \times 10^{-4}$ | $7.0784 \times 10^{-5}$ | $4.5630 \times 10^{-5}$ |
| $C_3$ | $-9.2459 \times 10^{-7}$ | $-6.1800 \times 10^{-7}$ | $-7.3863 \times 10^{-7}$ |
| $C_4$ | 0.36220 | 0.40207 | 0.27899 |
| $C_5$ | $9.0345 \times 10^{-2}$ | $1.9196 \times 10^{-2}$ | $2.3445 \times 10^{-1}$ |
| $C_6$ | $-2.0935 \times 10^{-4}$ | $-2.3796 \times 10^{-4}$ | $-1.9210 \times 10^{-4}$ |
| AAD% | 0.51 | 0.35 | 0.46 |
| MAD% | 2.07 | 1.27 | 1.52 |

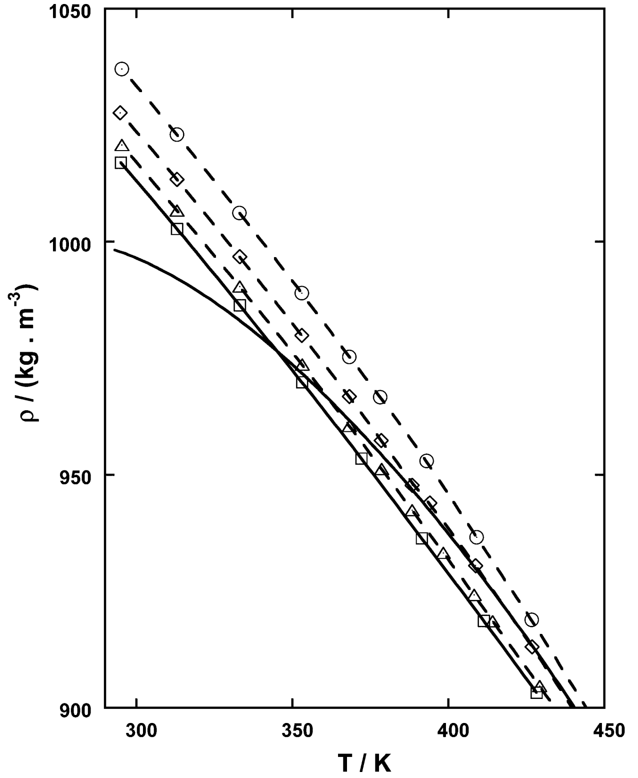

**Figure 1.** Density of TPG + water mixtures as a function of temperature. Experimental data: □, 100 mol % glycol; △, 75 mol % glycol; ◇, 50 mol % glycol, ○, 25 mol % glycol. Solid lines represent smoothed values of the pure components, whereas dashed lines represent calculated values using the GCSP method.

similar to eq 1c, except for the inclusion of the term $B_7w_1^2$. 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 deviations (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

$$V^E = x_1M_1(1/\rho_m - 1/\rho_1) + x_2M_2(1/\rho_m - 1/\rho_2) \quad (4a)$$

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

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

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

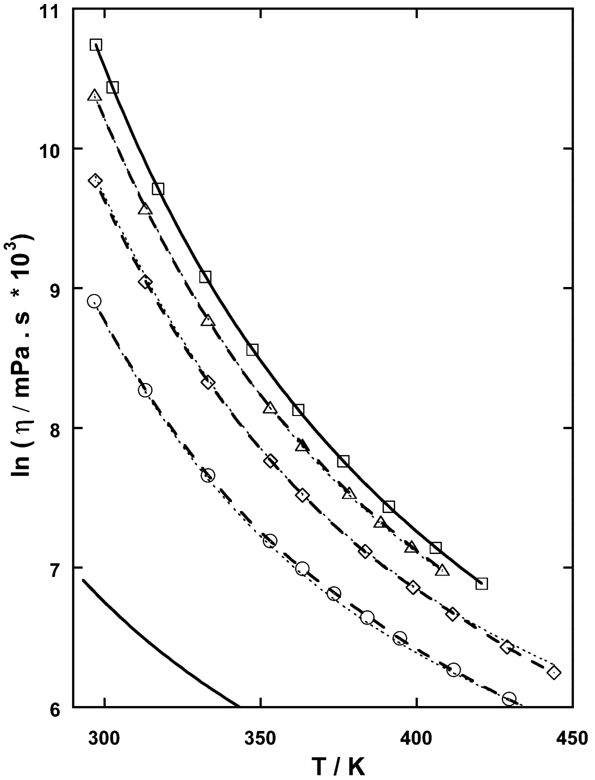

**Figure 2.** Viscosity of PG + water mixtures as a function of temperature. Experimental data: □, 100 mol % glycol; △, 75 mol % glycol; ◇, 50 mol % glycol, ○, 25 mol % glycol. Solid lines represent smoothed values of the pure components, whereas dashed lines represent calculated values using the modified rough-hard-sphere method.

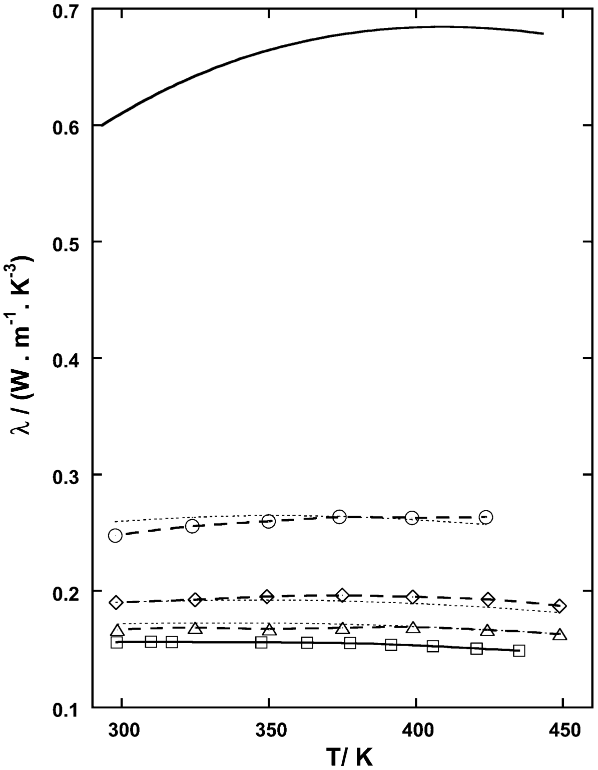

**Figure 3.** Thermal conductivity of DPG + water mixtures as a function of temperature. Experimental data: □, 100 mol % glycol; △, 75 mol % glycol; ◇, 50 mol % glycol, ○, 25 mol % glycol. Solid lines represent smoothed values of the pure components, whereas dashed lines represent calculated values using the modified rough hard sphere method.

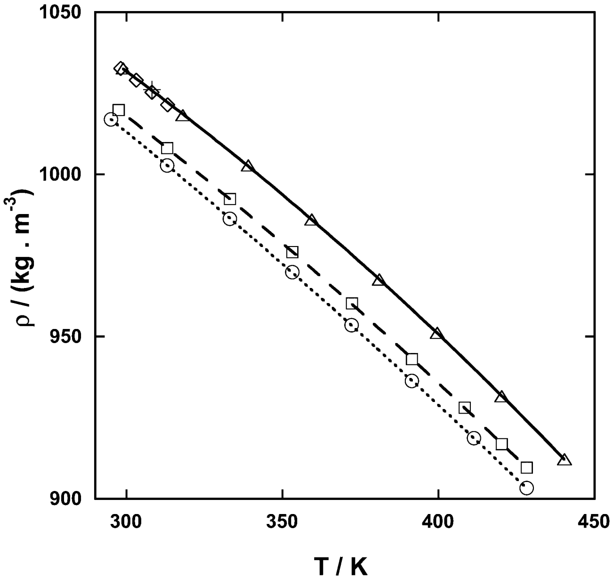

**Figure 4.** Density of glycols as a function of temperature. Symbols represent experimental data and lines represent smoothed data of this work for: −△−, PG; −□−, DPG; −○−, TPG. Also shown are the experimental data of ◇, Sastry and Patel;[3] +, Naidu et al.[5]

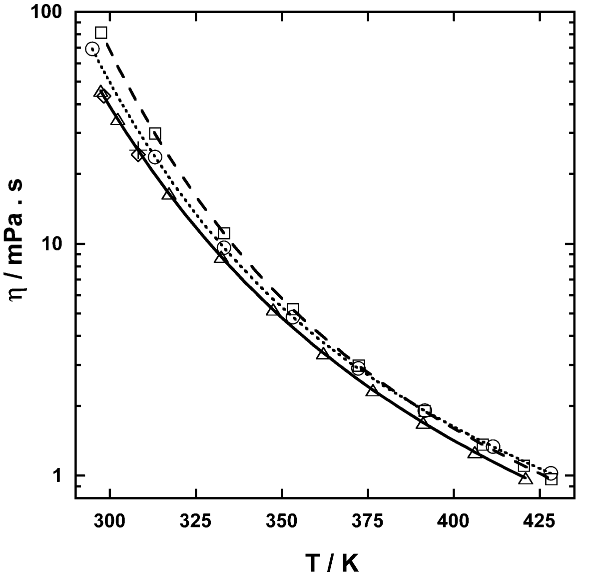

**Figure 5.** Viscosity of glycols as a function of temperature. Symbols represent experimental data and lines represent smoothed data of this work for: −△−, PG; −□−, DPG; −○−, TPG. Also shown are the experimental data of ◇, Sastry and Patel;[3] +, Naidu et al.[5]

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 mixtures[1]. 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 $-0.63$ cm$^3$ 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.

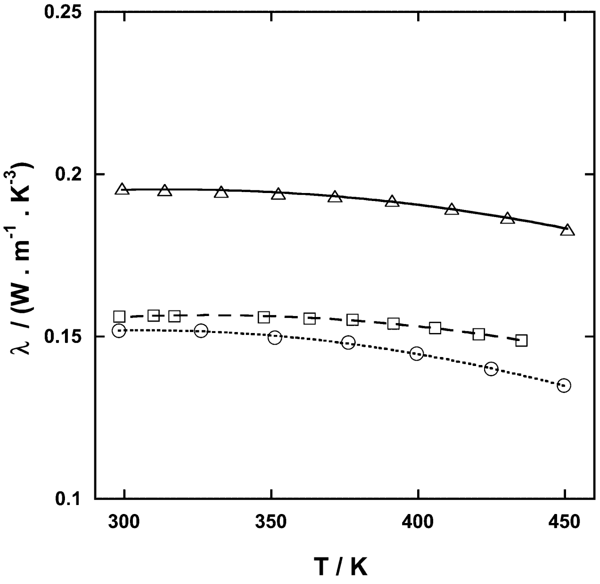

**Figure 6.** Thermal conductivity of glycols as a function of temperature. Symbols represent experimental data, and lines represent smoothed data of this work for: −△−, PG; −□−, DPG; −○−, TPG.

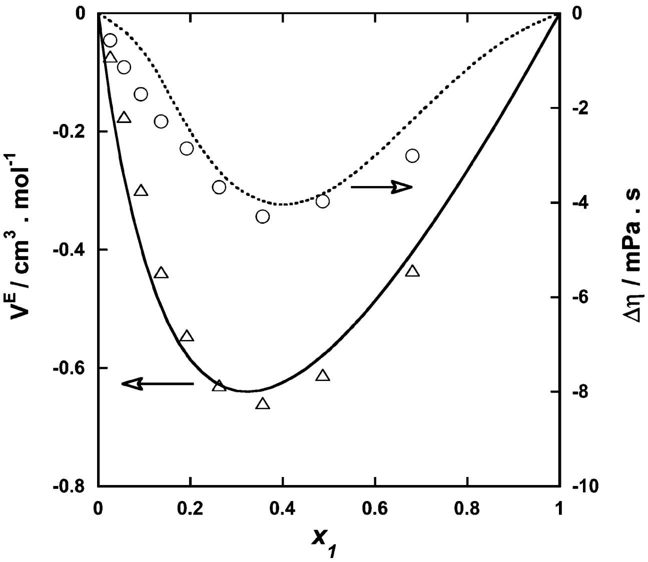

**Figure 7.** Excess volumes and viscosity deviations of PG + water mixtures at 303 K. Experimental data of △, volume, and ○, viscosity, by Kapadi et al.[4] Solid line represents the smoothed data of this work.

The behavior of $\Delta\eta$ was complex. In the case of PG + $H_2O$, $\Delta\eta$ 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 + $H_2O$, 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 Chandler[12] and extended by Assael et al.[13,14] It postulated that the reduced viscosity $\eta^*$ and reduced thermal conductivity $\lambda^*$ of rough hard spheres can be expressed as universal functions of the reduced volume $V_r$ ($V/V_o$) as follows

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

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

where $R_\eta$ and $R_\lambda$ 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 $R_\eta$ and $R_\lambda$ and the characteristic volume $V_o$ 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 previously[15] proposed an extension of the method to polar liquids using the following simple expressions for the characteristic volume $V_o$ and the coupling parameters $R_\eta$ and $R_\lambda$

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

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

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

Equations 5−7 were used to correlate $\eta$ and $\lambda$ 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 $\eta$

$$V_{o,m} = x_1^2V_{o,1} + x_1x_2(V_{o,1} + V_{o,2})(1 - K_1) + x_2^2V_{o,2} \quad (8a)$$

$$R_{\eta,m} = x_1^2R_{\eta,1} + x_1x_2(R_{\eta,1} + R_{\eta,2})(1 - K_2) + x_2^2R_{\eta,2} \quad (8b)$$

$$R_{\lambda,m} = x_1^2R_{\lambda,1} + 2x_1x_2(R_{\lambda,1}R_{\lambda,2})^{0.5}(1 - K_3) + x_2^2R_{\lambda,2} + x_1x_2(x_1 - x_2)(R_{\lambda,1}R_{\lambda,2})^{0.5}K_4 \quad (8c)$$

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

## 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**

| | | | | | | $\eta$ (%) | | $\lambda$ (%) | |
|---|---|---|---|---|---|---|---|---|---|
| | $D_1$ | $D_2$ | $D_3$ | $D_4$ | $D_5$ | 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**

| | | | | | $\eta$ (%) | | $\lambda$ (%) | |
|---|---|---|---|---|---|---|---|---|
| | $K_1$ | $K_2$ | $K_3$ | $K_4$ | AAD | MAD | AAD | MAD |
| EG[a] + $H_2O$ | 0.036 | −0.579 | 0.258 | 0.225 | 2.06 | 6.16 | 0.91 | 2.00 |
| DEG[b] + $H_2O$ | 0.023 | −0.846 | 0.304 | 0.615 | 3.17 | 8.79 | 2.20 | 4.94 |
| TEG[c] + $H_2O$ | 0.003 | −0.830 | 0.324 | 0.632 | 2.95 | 6.82 | 1.36 | 3.63 |
| PG + $H_2O$ | 0.044 | −0.694 | 0.335 | 0.523 | 2.09 | 6.16 | 1.12 | 3.44 |
| DPG + $H_2O$ | 0.030 | −0.923 | 0.309 | 0.678 | 4.77 | 12.3 | 1.89 | 4.83 |
| TPG + $H_2O$ | −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

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

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

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

in which

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

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

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

$$V_C = \Sigma\Sigma\, x_i x_j V_{C_{ij}} \tag{11a}$$

$$T_C V_C = \Sigma\Sigma\, x_i x_j T_{C_{ij}} V_{C_{ij}} \tag{11b}$$

$$Z_C = \Sigma\, x_i Z_{C_i} \tag{11c}$$

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

$$V_{C_{ij}} = (^1/_8)(V_{C_i}^{1/3} + V_{C_j}^{1/3})^3 \theta_{ij} \tag{12a}$$

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

$\theta_{ij}$ and $\psi_{ij}$ 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-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.

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

| | data | AAD (%) | MAD (%) | $\theta_{12}$ | $\psi_{12}$ |
|---|---|---|---|---|---|
| | | Density | | | |
| PG + $H_2O$[a] | 33 | 0.07 | 0.19 | 1.119 | 1.164 |
| DPG + $H_2O$[a] | 32 | 0.05 | 0.17 | 1.260 | 1.369 |
| TPG + $H_2O$[a] | 33 | 0.07 | 0.17 | 1.358 | 1.523 |
| | | Viscosity | | | |
| PG + $H_2O$[a] | 30 | 1.92 | 6.11 | 0.664 | 0.672 |
| DPG + $H_2O$[a] | 33 | 1.64 | 3.84 | −0.0536 | 0.0128 |
| TPG + $H_2O$[b] | 33 | 3.39 | 12.16 | 0.934 | 0.516 |
| | | Thermal Conductivity | | | |
| PG + $H_2O$[b] | 21 | 0.63 | 1.89 | 1.696 | 1.532 |
| DPG + $H_2O$[b] | 20 | 0.84 | 1.60 | 2.191 | 1.765 |
| TPG + $H_2O$[b] | 21 | 0.99 | 2.56 | 2.535 | 1.962 |

[a] Mass-fraction-based mixing rules. [b] Mole-fraction-based mixing rules.

## 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.

## Acknowledgment

Partial financial support for this work was provided by industrial members of the Fluid Properties Research Program at Georgia Tech.

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Received for review January 14, 2004. Accepted May 27, 2004.

JE049960H