the sample fluid and perfluoro-polyethers, to E. I. du Pont de Nemours & Co., Wilmington, DE, for kindly furnishing the sample fluid, and to Shin-etsu Chemicals Co., Ltd., Tokyo, Japan, for furnishing the silicone oil. We are also greatly indebted to the National Research Laboratory of Metrology, Tsukuba, Japan, for the calibration of the thermometer. The assistance of Hitoshi Tanaka, who made elaborate observations with the present authors, is gratefully acknowledged. The financial support by the Grants-in-Aid for Scientific Research Fund in 1988-1989 (Project No. 63603024 and No. 01603022) by the Ministry of Education, Science and Culture, Japan, and the financial support by the Tokyo Electric Power Co., Inc., are gratefully acknowledged.

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# Viscosities of Poly(ethylene glycols)

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**Kinematic viscosities of the first six members of the poly(ethylene glycol) homologous series were measured at ambient pressure and several temperatures ranging from 293 to 423 K. A generalized correlation for the viscosity of poly(ethylene glycols) was also developed in terms of the number of carbon atoms. Excellent agreement was obtained between experimental and calculated viscosities.**

## Introduction

The poly(ethylene glycols) ($HOCH_2CH_2(OCH_2CH_2)_{n-1}OH$) have found a wide variety of applications in the automotive, pharmaceutical, petroleum, cosmetic, textile, and other industries. As a result, the measurement and correlation of their thermophysical properties have attracted a great deal of attention and effort. Gallaugher and Hibbert (*1*, *2*) reported the freezing point, vapor pressure, surface tension, and other physical properties of poly(ethylene glycols) and their derivatives. The thermal conductivity of the lower glycols was studied by Fischer (*3*), whereas Thomas et al. (*4*) and Bohne et al. (*5*) measured the viscosity of ethylene glycol. More recently, the density and thermal conductivity of the higher glycols were reported by Tawfik and Teja (*6*) and DiGuilio and Teja (*7*). Generalized correlations were also developed by these investigators. In the present study, we report the measurements of the viscosity of the first six members of the homologous series of poly(ethylene glycols) and develop a general correlation for the viscosity applicable to all members of the homologous series.

## Experimental Section

Kinematic viscosities ($\nu$) were measured by using a calibrated Cannon-Ubbelohde capillary viscometer made by International Research Glassware. According to Poiseuille's law, the kinematic viscosity is given by

$$\nu = C_1 t - C_2/t \qquad (1)$$

where $t$ is the efflux time, and $C_1$ and $C_2$ are the viscometer constants. The correction due to kinetic energy, represented by $C_2/t$ in the above expression, can generally be neglected if an appropriately sized viscometer is used, so that measurements of the kinematic viscosity can be obtained directly from the measurements of the efflux times. The viscometers were placed inside thermostated liquid baths in order to keep the temperature constant during the measurement. Two temperature baths, one filled with water and the other with oil, were used in this study. The water bath was used for low-temperature measurements, whereas the oil bath was used at high temperatures (beyond 350 K). The water-bath temperature could be held within ±0.03 K with use of a Haake recirculation temperature controller (Type E3). The oil-bath temperature was controlled by a Haake controller (Type D3) within ±0.1 K. Temperature measurement was done by a four-wire platinum resistance thermometer (YSI), which had previously been calibrated with a NBS calibrated standard platinum resistance thermometer (Leeds and Northrup Co., Serial No. 709892). The accuracy of the temperature measurement was estimated to be ±0.1 K. An electronic timer accurate to 1/100 s was used to obtain the efflux time.

***Materials.*** Ethylene glycol (99.8%) and tri(ethylene glycol) (99.5%) were obtained from Fisher Scientific Co. Di(ethylene glycol) (99%), tetra(ethylene glycol) (99%), penta(ethylene glycol) (95%), and hexa(ethylene glycol) (98%) were obtained from the Aldrich Chemical Co. These chemicals were used as received.

Table I. Experimental Viscosities of Ethylene Glycol

| this work | | | ref 4 | | ref 5 | |
|---|---|---|---|---|---|---|
| $T$, K | $\nu$, cSt | $\mu$,[a] cP | $T$, K | $\nu$, cSt | $T$, K | $\mu$, cP |
| 293.9 | 18.04 | 20.16 | 290.25 | 21.58 | 273.25 | 56.53 |
| 313.3 | 8.535 | 9.409 | 298.25 | 15.13 | 282.45 | 34.15 |
| 333.3 | 4.673 | 5.076 | 307.95 | 10.47 | 298.15 | 16.63 |
| 353.3 | 2.877 | 3.078 | 329.35 | 5.26 | 303.05 | 13.61 |
| 373.3 | 1.941 | 2.043 | 336.95 | 4.29 | 313.15 | 9.407 |
| 393.4 | 1.379 | 1.428 | 347.35 | 3.340 | 333.35 | 5.030 |
| 413.5 | 1.039 | 1.057 | 356.45 | 2.661 | 353.15 | 3.068 |
| 423.7 | 0.925 | 0.933 | 374.95 | 1.923 | 373.35 | 2.016 |
| | | | 383.25 | 1.645 | | |
| | | | 392.75 | 1.426 | | |
| | | | 404.25 | 1.206 | | |
| | | | 413.85 | 1.053 | | |
| | | | 422.75 | 0.940 | | |
| | | | 433.05 | 0.831 | | |

[a] The generalized density correlation of Tawfik and Teja was used.

## Results and Discussion

The kinematic viscosity of ethylene glycol measured in this study is presented in Table I. Also listed in Table I are the literature values of Bohne et al. (*5*) and Thomas et al. (*4*), as well as absolute viscosities obtained by using the generalized density correlation of Tawfik and Teja (*6*). Excellent agreement was found between the three sets of data, with average absolute deviations (AAD) between our data and literature values being of the order of 1.0%. Viscosities of di-, tri-, tetra-, penta-, and hexa(ethylene glycols) are summarized in Table II. At least five samples were taken at each temperature to give the average values listed in these tables. The reproducibility of multiple samples was ±0.4%, and the accuracy of the data was estimated to be ±1.5%. A graphical representation of the

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**Table II. Experimental Viscosities of Poly(ethylene glycols)**

| substance | $T$, K | $\nu$, cSt | $\mu$, cP |
|---|---|---|---|
| di(ethylene glycol) | 294.3 | 30.64 | 34.43 |
| | 303.6 | 20.00 | 22.33 |
| | 313.3 | 13.47 | 14.94 |
| | 333.3 | 6.953 | 7.607 |
| | 353.3 | 4.124 | 4.446 |
| | 373.4 | 2.691 | 2.858 |
| | 393.4 | 1.899 | 1.985 |
| | 413.4 | 1.402 | 1.442 |
| | 426.6 | 1.182 | 1.203 |
| tri(ethylene glycol) | 294.8 | 39.63 | 44.49 |
| | 303.3 | 26.39 | 29.47 |
| | 313.3 | 17.35 | 19.25 |
| | 333.3 | 8.762 | 9.593 |
| | 353.3 | 5.110 | 5.518 |
| | 373.3 | 3.327 | 3.543 |
| | 393.3 | 2.304 | 4.217 |
| | 413.5 | 1.700 | 1.756 |
| | 426.6 | 1.424 | 1.456 |
| tetra(ethylene glycol) | 293.8 | 50.13 | 56.18 |
| | 303.4 | 31.17 | 34.74 |
| | 313.3 | 20.32 | 22.51 |
| | 333.3 | 10.15 | 11.11 |
| | 353.3 | 5.910 | 6.387 |
| | 373.2 | 3.818 | 4.073 |
| | 393.4 | 2.665 | 2.805 |
| | 413.5 | 1.960 | 2.034 |
| | 425.7 | 1.668 | 1.716 |
| penta(ethylene glycol) | 294.2 | 60.28 | 67.52 |
| | 303.3 | 37.90 | 42.29 |
| | 313.3 | 24.49 | 27.13 |
| | 333.3 | 12.06 | 13.20 |
| | 353.3 | 6.972 | 7.536 |
| | 373.1 | 4.492 | 4.794 |
| | 393.2 | 3.125 | 3.291 |
| | 413.5 | 2.299 | 2.388 |
| | 425.6 | 1.955 | 2.013 |
| hexa(ethylene glycol) | 293.2 | 75.18 | 84.09 |
| | 303.4 | 44.13 | 49.09 |
| | 313.4 | 28.36 | 31.38 |
| | 333.4 | 13.86 | 15.16 |
| | 353.4 | 7.974 | 8.625 |
| | 373.4 | 5.126 | 5.480 |
| | 393.4 | 3.544 | 3.743 |
| | 413.5 | 2.616 | 2.728 |
| | 423.6 | 2.296 | 2.379 |

**Table III. Constants of Equation 2**

| substance | $A$ | $B$ | $C$ | AAD% | MAD% |
|---|---|---|---|---|---|
| ethylene glycol | −3.6333 | 997.25 | 143.66 | 0.24 | 0.41 |
| di(ethylene glycol) | −3.3439 | 960.48 | 154.64 | 0.45 | 0.92 |
| tri(ethylene glycol) | −3.1329 | 941.32 | 158.88 | 0.27 | 0.69 |
| tetra(ethylene glycol) | −2.8522 | 885.06 | 165.14 | 0.34 | 0.63 |
| penta(ethylene glycol) | −2.6551 | 864.38 | 168.29 | 0.26 | 0.47 |
| hexa(ethylene glycol) | −2.4740 | 844.59 | 170.83 | 0.25 | 0.56 |

experimental data is given in Figure 1, where the logarithm of the viscosity is plotted against the reciprocal of temperature. The experimental data appear to be smooth but exhibit significant departure from the linear behavior predicted by the Andrade (*8*) equation.

The data measured in this work were correlated by using the following expression:

$$\ln \mu = A + \frac{B}{T - C} \qquad (2)$$

where $\mu$ is in centipoise and $T$ is in kelvin. $A$, $B$, and $C$ are fitted constants for each substance, and their values determined by regression are given in Table III. Equation 2 represents the experimental results very well with an AAD less than 0.5% and a maximum absolute deviation (MAD) less than 1.0% in every case. Also, the values of $A$, $B$, and $C$ were found to vary consistently with the number of carbon atoms in the glycol, suggesting the possibility of a generalized relationship for all the glycols.

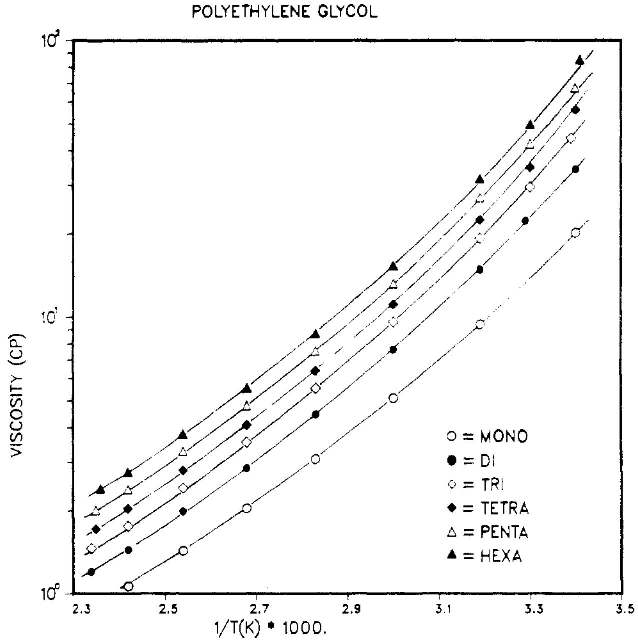

**Figure 1.** Experimental and correlated viscosities of the poly(ethylene glycols). Correlated viscosities are given by the solid lines.

**Table IV. Constants of Equation 3**

$a_0 = -3.54678$
$a_1 = 0.075394$
$b_0 = 915.232$
$c_0 = 163.178$
$c_1 = -43.1557$
$c_2 = 1.60992$

Equation 2 was therefore further generalized in terms of the number of carbon atoms ($N$) as follows:

$$A = a_0 + a_1 N$$
$$B = b_0$$
$$C = c_0 + c_1 \exp(-N/c_2) \qquad (3)$$

Values of $a_0$, $a_1$, $b_0$, $c_0$, $c_1$, and $c_2$ obtained by regression of all the data simultaneously are given in Table IV. An AAD of 1.1% was obtained for 53 data points covering the six glycols in this investigation. The good agreement between calculated and experimental values is demonstrated in Figure 1.

## Conclusion

Viscosities of the first six poly(ethylene glycols) were determined experimentally in this study. The measurements covered temperatures from room temperature to 423 K. Generally, our data are in good agreement with the data reported in the literature. In the case of ethylene glycol, the average deviation between our measurements and literature values was found to be less than 1%. A generalized correlation for the prediction of viscosities of poly(ethylene glycols) as a function of carbon number was also developed.

**Registry No.** Ethylene glycol, 107-21-1; tri(ethylene glycol), 112-27-6; di(ethylene glycol), 111-46-6; tetra(ethylene glycol), 112-60-7; penta(ethylene glycol), 4792-15-8; hexa(ethylene glycol), 2615-15-8; poly(ethylene glycol), 25322-68-3.

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# Vapor Pressures of 1,4-Dimethylbenzene, 1,4-Di(methyl-$d_3$)benzene, and 1,4-Dimethylbenzene-$d_{10}$ at 20–50 °C

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**The vapor pressures of $p$-$(CH_3)_2C_6H_4$ ($d_0$), $p$-$(CD_3)_2C_6H_4$ ($d_6$), and $p$-$(CD_3)_2C_6D_4$ ($d_{10}$) were measured by a static method from 20 to 50 °C. The ratio of the vapor pressure of $d_6$ to that of $d_0$ decreases from $1.07_2$ at 20 °C to $1.05_7$ at 50 °C, and that of $d_{10}$ to that of $d_0$ decreases from $1.08_4$ at 20 °C to $1.06_5$ at 50 °C. For the vaporization process, $\Delta H^\circ_{298}$ (kJ/mol) and $\Delta S^\circ_{298}$ (J/(K mol)) were found to be 43.0 and 107.0 for $d_0$, 42.6 and 106.3 for $d_6$, and 42.5 and 106.1 for $d_{10}$, respectively. The substitution of a deuterium atom for a hydrogen on the methyl groups appears to affect the properties more than such a substitution on the aromatic ring.**

## Introduction

The vapor pressure of 1,4-dimethylbenzene ($d_0$) has been reported by several investigators, most extensively by the National Bureau of Standards (*1*) from 27 to 149 °C. Pitzer and Scott (*2*) also report values over a more limited temperature range, but there appear to be no published data on its two most common isotopomers, 1,4-di(methyl-$d_3$)benzene ($d_6$) and 1,4-dimethylbenzene-$d_{10}$ ($d_{10}$). For these, the Aldrich Chemical Co. catalog, 1988-9, gives the normal boiling points as 135.4 and 135 °C, respectively, both lower than that of $d_0$, 138.350 °C (*1*). It became necessary to measure the ratios of the vapor pressures of $d_6$ and $d_{10}$ to that of $d_0$ in the neighborhood of room temperature in order to interpret earlier data on the fractionation of isotopic molecules based on inclusion phenomena (*3*). An accuracy of about 1% in the vapor pressure ratios was all that was needed, and this required only an accuracy of about 0.7% in the individual vapor pressures. All three isomers, $d_0$, $d_6$, and $d_{10}$, were determined, the $d_0$ partly to confirm the reliability of the technique used.

## Experimental Section

The three isomers were Aldrich Chemical Co. products. Gold Label $d_0$ (99+%) was distilled from $LiAlH_4$ under dry nitrogen, collected over a 0.5-deg range at atmospheric pressure, and stored under dry nitrogen. The $d_6$ and $d_{10}$ were 99+ atom % deuterium and were given no further treatment except for drying with molten sodium, as was also the $d_0$, described below.

The apparatus, shown schematically in Figure 1, was patterned after that used by Davis and Schiessler (*4*), but the design and procedure were modified somewhat. Seven mercury float valves, a, were controlled by mercury in reservoirs attached by tubes b and b′ to the manifold, c, through stopcocks, s. With the mercury in place, only one (capillary) tube, b′, led out of the system itself. The manifold permitted evacuation or introduction of dry nitrogen and led to the usual large mercury manometer, a McLeod gauge capable of measuring pressures down to 5 μmHg, a dry ice trap, and a mechanical pump. Nitrogen was admitted when needed by passage through Drierite and a dry ice trap. The whole apparatus occupied a segment of a cylinder, as in ref 4, and could be immersed in a water thermostat, controlled to ±0.02 °C while still attached to the pump. All the stopcocks were below the water level. The differential mercury manometer, m, had an internal diameter of 15 mm. The differences in the levels in the two arms were measured to 0.01 mm with a Gaertner cathetometer outside of the thermostat, which was also used for measuring the meniscus heights in the two manometer arms. Temperatures were read with a −1 to 51 °C thermometer graduated in tenths and certified by the National Bureau of Standards. The readings were corrected for any differences in meniscus heights in the two arms, as well as to 0 °C.

The procedure was as follows. Although a few direct measurements of the difference between the vapor pressures of $d_{10}$ and $d_0$ were made, it was found that more reliable results could be obtained by measuring the pure substances separately, with one arm of the manometer always evacuated. Furthermore, metallic sodium, not $CaH_2$, was used to remove any traces of water. The sodium was placed in the refluxing tube, r, which remained attached to, but could be isolated from, the apparatus by closing the appropriate valve. Further dehydration could then be accomplished, if desired, by returning the sample to r.

After the introduction of the sodium (cut in a dry nitrogen atmosphere in a glovebag) into r with a stream of dry nitrogen sweeping through the apparatus, about 5 cm$^3$ of $d_0$, $d_6$, or $d_{10}$ was added, similarly, the sample frozen in dry ice, and r sealed. The apparatus was evacuated, nitrogen admitted, and the sample refluxed for several minutes, during which time the sodium melted to form a shiny sphere. The sample was again frozen, the system evacuated, dry nitrogen introduced, and the refluxing repeated. The sample was again frozen, the system evacuated, and part of it distilled into bulb e, which contained a small Teflon-covered stirring bar. The remainder of the original sample, along with the sodium, was isolated in r. The mercury in the apparatus was then degassed by pumping at 5 μmHg or less while irradiating with a heat lamp. Finally, the sample in e was degassed by pumping at 25 °C (with magnetic stirring) for 2 or 3 min. While pumping was continued, the sample was frozen and pumped down to 5 μmHg for 10 or 15 min. The arms of the manometer were then divorced by closing the appropriate valve, the whole apparatus was immersed in the thermostat, and the left-hand side of the manometer kept continually at 5 μmHg or less by pumping. After

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