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Kinematic Viscosities of Poly(ethylene glycols)

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Kinematic viscosities data have been obtained as a function of temperature for poly(ethylene glycols) with different molecular weights. The viscosity measurements were performed at ambient pressure and several temperatures ranging from 293.15 (or above their melting points) to 363.15 K. A generalized correlation based on the number of carbon atoms was developed, resulting in an average absolute deviation of 1.6% between experimental and calculated results.

Introduction

Poly(ethylene glycols) (PEGs) comprise a series of linear chain polymers of oxyethylene units with a wide variety of applications in the pharmaceutical, chemical, cosmetic, and food industries (Powell, 1980). Their low toxicity and high water solubility enable their use for purification of biological materials (Silva et al., 1997; Coimbra et al., 1994, 1995, 1998; Mei et al., 1995) and as an additive in the production of edible films for food coating (Chinnan and Park, 1995; Ninni et al., 1999). Many other applications in the automotive, petroleum, and textile industries are also mentioned in the literature (Powell, 1980; Lee and Teja, 1990). Prior works have reported the kinematic viscosity of lower glycols (Lee and Teja, 1990) and aqueous solutions containing PEGs with different molecular weights (González-Tello et al., 1994). In the present work, we report the viscosities of PEGs with the molecular weights 200, 400, 600, 1000, 1500, and 3350. Furthermore, the viscosity data for each PEG were correlated as a function of temperature, and a generalized correlation based on the number of carbon atoms was also developed.

Experimental Section

Materials and Analytical Procedures. All PEGs employed in the present work were obtained from Sigma, except for PEG 1500, which was purchased from Fluka. They were analytical grade and used as received. Their polydispersity index was determined by gel permeation chromatography (GPC) using an Ultrahydrogel column Waters device. The following experimental conditions were used for the GPC: water as the mobile phase at a rate of 0.8 μL/min, injection temperature of 313.15 K, sample injection of 100 μL, and a refraction index detector.

The water content of each PEG was determined by Karl Fischer titration using a Methrom device. The characteristics of the polymers used in the present work are given in Table 1.

Table 1. Polymer Characterization

PEG	avg MW	polydispersity index	water content (mass %)	NCN[a]	TCN[b]
200	202	1.095	0.20 ± 0.02	8	8
400	400	1.086	0.23 ± 0.02	18	18
600	616	1.069	0.27 ± 0.02	26	28
1000	991	1.044	1.44 ± 0.02	44	44
1500	1359	1.022	1.05 ± 0.05	68	60
3350	2816	1.043	0.69 ± 0.07	152	128

[a] Nominal carbon number based on the molecular weight (MW) according to the PEG denomination. [b] True carbon number based on the average MW determined by GPC.

Apparatus and Measuring Procedures. Kinematic viscosities were measured with calibrated Cannon Fenske glass capillary viscometers (sizes 75, 100, 150, 200, 350, and 400), made by Cannon Instrument Co. The viscometers were placed inside a thermostated liquid bath (Cole Parmer Instrument Co.) for keeping temperature constant during each measurement. Thermometers (Cole Parmer Instrument Co.) with subdivisions of 0.1 K were used for monitoring bath temperature. This assembly maintains a temperature uniformity of ±0.05 K. The kinematic viscosities ν were calculated from the efflux time θ and the instrument constant c by using the following equation:

$$\nu = c\theta \tag{1}$$

Values for c were provided by the viscometer manufacturer, and the correction for temperature effects was considered. An electronic timer (accuracy: 1/100 s) was used for measuring the efflux time. At each temperature the viscosity was measured at least five times to give the average values presented below.

Results and Discussion

The PEG kinematic viscosities are summarized in Table 2. The highest standard deviation observed in the experimental measures was $0.090 \times 10^{-6}\ \mathrm{m^2{\cdot}s^{-1}}$ (PEG 1500 at 323.15 K), and the lowest one, $0.0006 \times 10^{-6}\ \mathrm{m^2{\cdot}s^{-1}}$ (PEG 400 at 323.15 K), resulting in a mean standard deviation of $0.017 \times 10^{-6}\ \mathrm{m^2{\cdot}s^{-1}}$ for the whole set of experimental data. The highest variation coefficient obtained was 0.084% (PEG 1500 at 323.15 K), suggesting an excellent reproducibility for the measured efflux times.

The viscosity data were correlated by using the following equation:

$$\ln \nu/10^{-6}\ \mathrm{m^2{\cdot}s^{-1}} = A + B/(T/\mathrm{K} - C) \tag{2}$$

where T is the absolute temperature. The values of parameters A, B, and C were determined by regression using the Statistical Analysis System (SAS, Cary, NC)

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Table 2. Experimental Kinematic Viscosities of PEGs

	$\nu/10^{-6}\ m^2 \cdot s^{-1}$					
T/K	PEG 200	PEG 400	PEG 600	PEG 1000	PEG 1500	PEG 3350
293.15	57.33	101.61				
298.15		80.55	123.51			
303.15	34.71	62.39	94.29			
311.15				103.10		
313.15	22.36	39.93	59.53			
318.15				80.10	128.75	
323.15	15.41	25.75	40.22	65.48	107.68	
328.15						278.86
333.15	11.16	18.40	28.76	46.52	71.81	236.34
343.15	8.35	13.66	20.34	34.18	53.14	173.16
353.15	6.48	10.96	15.60	25.46	40.63	132.26
363.15	5.15	8.73	12.28	20.01	31.86	103.90

Table 3. Parameters of Eq 2

PEG	A	B	C	AAD/%	$SD/10^{-6}\ m^2 \cdot s^{-1}$
200	−2.419	770.4	174.0	1.0	0.2
400	−1.956	771.1	176.2	2.4	1.3
600	−1.673	771.0	179.3	1.0	0.5
1000	−1.214	759.1	182.5	1.4	2.7
1500	−0.7722	771.0	181.2	1.3	1.8
3350	0.4374	770.2	179.9	0.2	0.6

package. The parameters are given in Table 3, which also shows the values for the average absolute deviation (AAD) and the standard deviation (SD), calculated according to eqs 3 and 4, respectively:

$$\mathrm{AAD} = \left[\left(\sum_{i=1}^{n}\left(\frac{|\nu_{\mathrm{exp},i} - \nu_{\mathrm{cal},i}|}{\nu_{\mathrm{exp},i}}\right)\right)\right] \times \frac{100}{n} \qquad (3)$$

$$\mathrm{SD} = \left[\frac{\sum_{i=1}^{n}(\nu_{\mathrm{exp},i} - \nu_{\mathrm{cal},i})^2}{(n-p)}\right]^{1/2} \qquad (4)$$

where $\nu_{\mathrm{exp},i}$ and $\nu_{\mathrm{cal},i}$ are the experimental and calculated values for the kinematic viscosities, respectively, n is the number of experimental points, and p is the number of adjusted parameters. The deviations are <1.5%, except for the equation for PEG 400, which has a mean deviation of 2.4%. The highest SD is $2.7 \times 10^{-6}\ m^2 \cdot s^{-1}$.

Following the suggestion of Lee and Teja (1990) for lower glycols, a generalized correlation based on the numbers of carbon atoms N was also developed. For the parameter A in eq 2 a quadratic form on N is assumed, and for the parameter C a sigmoidal (Boltzman-type) dependence is assumed. The parameters were generalized as follows:

$$A = a_0 + a_1 N + a_2 N^2$$

$$B = b_0$$

$$C = (c_0 - c_1)/\{1 + \exp[(N - c_2)/c_3]\} + c_1 \qquad (5)$$

Two different values for the number of carbon atoms (N) were considered: the first one was calculated using the molecular weight given by the PEG denomination, such as PEG 400 or PEG 1500, and was named the nominal carbon number (NCN); the second one was calculated according to the average molecular weight (MW) determined by GPC and named the true carbon number (TCN). Both values are given in Table 1, and it should be noted that they were rounded to the closest even number. The difference between the two carbon numbers is significant for PEG 1500 and PEG 3350.

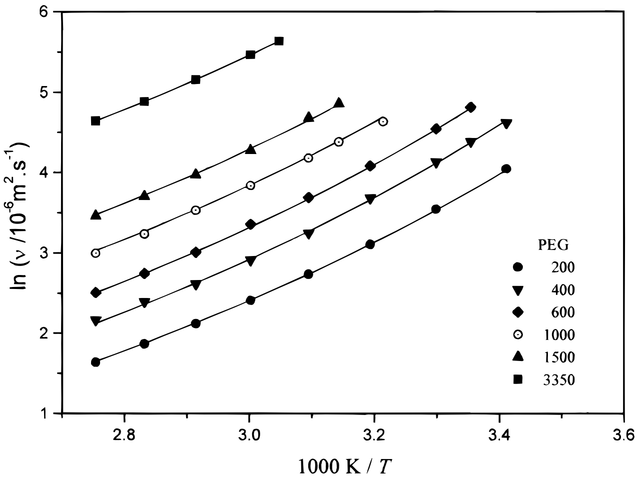

Figure 1. Experimental and correlated viscosities of PEGs. The points are experimental values, and the curves represent the correlated viscosities.

Table 4. Parameters of Eq 5

$a_0 = -2.738$
$a_1 = 4.114 \times 10^{-2}$
$a_2 = -1.276 \times 10^{-4}$
$b_0 = 770.2$

$c_0 = -131.3$
$c_1 = 179.9$
$c_2 = -24.48$
$c_3 = 8.319$

Table 5. Prediction of Kinematic Viscosity Data Available in the Literature (Powell, 1980)

PEG	avg MW range	NCN range	T/K	$\nu_{\mathrm{exp}}/10^{-6}\ m^2 \cdot s^{-1}$	$\nu_{\mathrm{calc}}/10^{-6}\ m^2 \cdot s^{-1}$	AD[a]
200	190−210	8	298.15	40	43.6	8.9
			372.05	4.3	4.34	0.93
300	285−315	12−14	298.15	69	57.2−64.3	6.8
			372.05	5.8	5.30−5.81	0.17
400	380−420	16−18	298.15	90	71.7−79.3	11.9
			372.05	7.3	6.34−6.90	5.6
600	570−630	26−28	298.15	131	112.1−121.0	7.6
			372.05	10.5	9.38−10.1	4.0
1000	950−1000	42−46	372.05	17−19[b]	16.0−18.0	5.7
1500	1300−1500	58−68	372.05	25−32[b]	25.2−32.4	3.1
2000	1900−2200	86−100	372.05	47	47.7−60.8	17.3

[a] Absolute deviation calculated by AD = $(|\nu_{\mathrm{exp}} - \nu_{\mathrm{calc}}|/\nu_{\mathrm{exp}}) \times 100$; ν_{calc} estimated using an average value for the NCN. [b] AD is based on the average experimental viscosity.

Using both definitions for the number of carbon atoms, the constants of eq 5 were obtained by regression of all the data determined in the present work. In the case of the NCN, an AAD of 3.8% and a SD of $2.5 \times 10^{-6}\ m^2 \cdot s^{-1}$ were obtained, but choosing the TCN as the number of carbon atoms, the AAD and the SD become significantly lower, 1.6% and $1.5 \times 10^{-6}\ m^2 \cdot s^{-1}$, respectively. For this last case the values of the constants are given in Table 4. Figure 1 shows the experimental data and the viscosities obtained by the best-generalized correlation. A good agreement between calculated and experimental values is obtained.

Kinematic viscosity data available in the literature (Powell, 1980) were used for checking the prediction capacity of the model with the parameters given in Table 4. The experimental values, the polymer characteristics and the predicted results are shown in Table 5. A range of predicted values was estimated using the NCN range calculated according to the information about molecular weight given by Powell (1980). Using an average value for this NCN range, an AAD of 6.6% was obtained. Although the deviations are comparatively higher than those obtained for the correlation of our experimental data, it should be noted that for this prediction we had to use an average nominal number of carbon atoms. Unfortunately, more detailed information about the polymer dispersity, about its true average molecular weight, as well as about the product purity is not available in the literature reporting the viscosity data. Furthermore, in most cases the experimental viscosities are within or close to the range of predicted values.

But the use of this generalized equation for extrapolation purposes upon the number of carbon atoms should be avoided. As the parameter A has a quadratic dependence on the number of carbon atoms, the deviations between experimental and calculated viscosities may become higher as the molecular weight increases.

Conclusions

Viscosities of poly(ethylene glycols) with molecular weights ranging from 200 to 3350 were determined experimentally. The measurements were performed at temperatures ranging from 293.15 K (or above product melting point) to 363.15 K. A generalized equation based on the number of carbon atoms was developed, and it correlates well with the experimental data with an average absolute deviation of 1.6%. This equation has been further tested for prediction purposes, using viscosity data taken from the literature for poly(ethylene glycols) in the molecular weight range 200 to 2000. In this molecular weight range the predicted values are relatively close to the experimental ones.

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