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Kinematic Viscosities of Poly(ethylene glycol) Aqueous Solutions

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Kinematic viscosities of aqueous mixtures containing poly(ethylene glycol)s (PEGs) with nominal molecular masses ranging from (200 to 10 000) g·mol^{-1} have been determined at various concentrations and temperatures. The binary experimental data were used to adjust the parameters of a Kumar-like equation. Relative errors around 5.5% were observed between calculated and experimental results. The adjusted parameters also allowed the viscosity prediction for multicomponent mixtures, with an overall deviation of 9.9%.

Introduction

Poly(ethylene glycol) (PEG) is a linear, neutral polyether, available in a variety of molecular masses, soluble in water and in most organic solvents.[1] PEG has a variety of properties that make it suitable for applications in the biomedical and biotechnological areas. These properties include the formation of two-phase systems with aqueous solutions of other polymers or salts, its nontoxicity, and the formation of complexes with metal cations and so forth.[2]

Aqueous two-phase systems are increasingly used for separation of biomolecules, cells, and cell particles.[3,4] Such systems are composed of two incompatible polymers, for example, dextran and poly(ethylene glycol) (PEG), or of one polymer (PEG) and a salt (usually a phosphate or sulfate salt). The use of PEGs in aqueous two-phase systems (ATPS) has been reported by several authors,[5−7] since such systems allow the separation and purification of biomolecules in a gentle environment and extraction using ATPS can be performed continuously in available commercial separators.[8−10] The advantages of using aqueous two-phase extraction lie in volume reduction, high capacity, and fast separation; moreover, it is relatively straightforward to scale up a separation process.[11]

In addition to the knowledge of phase equilibrium, data on the properties of the phases are necessary for the design of ATPS extraction processes in large-scale applications. The knowledge of physical properties, such as the viscosities of aqueous mixtures containing PEGs, is important because these solutions are used in many industrial and biotechnological applications.[12] However, it is not viable to measure viscosities at all conditions of interest, and consequently, methods for the estimation of viscosities at various temperatures, concentrations, and solute types are of great practical interest. Numerous empirical and semiempirical methods have been proposed to calculate liquid viscosity of mixtures,[13−17] but some equations are inappropriate for concentrated and/or multicomponent mixtures.

In the present work, the reformulated Kumar's equation[15] was employed to correlate and predict kinematic viscosities of aqueous solutions containing PEGs in a wide range of polymer concentrations and at different temperatures. The difference between the data treatment from this work and those of other related works[14,17−19] is that the viscosities of concentrated PEG solutions were employed together with literature viscosity data at various temperatures, concentrations, and PEG molecular masses. Moreover, for each polymer employed, the hydration numbers were estimated and compared with available values in the literature.[20−24] A generalized correlation for estimating kinematic viscosities of PEG aqueous solutions as a function of polymer molecular mass, concentration, and temperature was also developed.

Table 1. Average Relative Molar Masses (M_n), Polydispersity Indexes, and Water Contents of PEGs Used in This Work

PEG	avg rel molar mass (M_n)	polydispersity index	water content (mass %)
200	202	1.095	0.20 ± 0.02
400	400	1.086	0.23 ± 0.02
600	616	1.069	0.27 ± 0.02
1000	987	1.067	1.54 ± 0.02
1500	1529	1.069	1.10 ± 0.02
3350	2806	1.073	0.75 ± 0.01
8000	7975	1.099	0.36 ± 0.08
10 000	10 475	1.106	0.66 ± 0.05

Experimental Section

Materials. Analytical grade PEGs with nominal molecular masses ranging from (200 to 10 000) g·mol^{-1} were purchased from SIGMA and used without further purification. Water was distilled, deionized, with a Mili-Q water system (Millipore, USA) and used to prepare the PEG solutions. The solutions were prepared on a mass basis using an analytical balance (Sartorius Analytic, GmbH) accurate to ±0.0001 g. PEG concentrations in the solutions varied up to 50 mass % for systems containing PEGs 200, 400, 600, 1000, and 1500, up to 30 mass % for PEG 3350, and up to 25 mass % for PEGs 8000 and 10 000. The estimated error in the mass fractions was 2 in 10 000. PEGs were characterized according to their molecular masses and water content using the procedures described in a previous article.[25] The characteristics of the polymers used in the present work are given in Table 1. The water content in the polymer samples was taken into account to calculate the solution concentrations.

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Apparatus and Procedures. Calibrated Cannon-Fenske glass capillary viscometers (sizes 50, 75, 100, 150, and 200) were used to measure the kinematic viscosities (Cannon Instrument Co., USA). The viscometers were placed in a water bath (Anton Paar, Austria) to hold the temperature constant within ±0.1 °C. The measurements were performed at temperatures varying between (293.15 and 323.15) K. An electronic timer with 0.01-s accuracy was used to measure the efflux time. The experiments were replicated at least three times for each PEG mixture, and the results given below are the average values. The standard deviations of the viscosity determinations varied within the range 1.9×10^{-7} $m^2 \cdot s^{-1}$ to 1.1×10^{-9} $m^2 \cdot s^{-1}$, and the lowest figures were obtained for the lowest viscosity values. The variation coefficient ranged from 0.1% to 0.7%, so that the uncertainty of the experimental measurements can be estimated as being not higher than 0.7%.

Results and Discussion

The kinematic viscosities for the binary and multicomponent PEG solutions determined in this work are given in Tables 2−4.

Kumar's Equation for Viscosity Correlation in PEG Mixtures. The Kumar expression[26] is one of the equations presented in the literature to calculate dynamic viscosities of solutions as a function of solute concentration. Initially, Kumar's expression was formulated to estimate viscosities in aqueous and nonaqueous salt solutions. Such correlation involves two parameters, the hydration number and the ion−solvent interaction coefficient, as given below:

$$\frac{\eta}{\eta_0} = 1 + \frac{bx}{1 - hx} \tag{1}$$

where η is the solution dynamic viscosity, η_0 is the solvent dynamic viscosity, x is the solute mole fraction, and b and h are the solute−solvent interaction coefficient and the hydration number (number of molecules of bound solvent per molecule of solute), respectively.

The Kumar expression was later reformulated[15] to allow the calculation of kinematic viscosities of aqueous solutions containing salts or organic solutes. The resulting equation is a function of the relative density between solution and solvent, of the solute mass fraction, and of the temperature. Pereira et al.[15] investigated the predictive capacity of the equation for ternary, quaternary, and quinary solutions.

The reformulated Kumar equation was used in this work to correlate and predict the kinematic viscosities of the aqueous PEG mixtures. The equations for binary and multicomponent systems are given as follows:

$$\nu_{\mathrm{rel}} = \frac{1}{\rho_{\mathrm{rel}}}\left[1 + \frac{Bw}{1 - Hw}\right] \tag{2}$$

$$\nu_{\mathrm{rel}} = \frac{1}{\rho_{\mathrm{rel}}}\left[1 + \frac{\sum_i Bw_i}{1 - \sum_i Hw_i}\right] \tag{3}$$

where the parameters B and H are interpreted, respectively, as a coefficient of solute−solvent interaction and as the number of solvent molecules solvating the solute, both functions of the temperature; w is the mass fraction of solute; ν_{rel} and ρ_{rel} are the ratios between the kinematic viscosities and densities of the solution and the corresponding values for the pure solvent, respectively; and i represents the solutes in the multicomponent mixture. The dependence of the parameters B and H on the temperature is given by the polynomials in $(T - T_{\mathrm{ref}})$, as follows:

Table 2. Kinematic Viscosities, ν, in Aqueous Solutions of PEGs at 293.15 K and Various Mass Fractions, w

w	$\nu/10^{-6}$ $m^2 \cdot s^{-1}$	w	$\nu/10^{-6}$ $m^2 \cdot s^{-1}$	w	$\nu/10^{-6}$ $m^2 \cdot s^{-1}$
PEG 400		PEG 600		PEG 1000	
0.0248	1.121	0.0249	1.143	0.0243	1.169
0.0497	1.239	0.0501	1.311	0.0492	1.356
0.0748	1.379	0.0749	1.470	0.0737	1.588
0.1002	1.543	0.0996	1.656	0.0985	1.854
0.1529	1.941	0.1491	2.143	0.1477	2.510
0.1998	2.415	0.1994	2.793	0.1960	3.406
0.2998	3.956	0.2993	4.900	0.2953	6.304
PEG 1500		PEG 3350			
0.0246	1.216	0.0248	1.345		
0.0498	1.456	0.0492	1.747		
0.0741	1.751	0.0744	2.267		
0.0992	2.094	0.0995	2.936		
0.1482	2.994	0.1489	4.669		
0.1980	4.252	0.1983	7.215		
0.2967	8.443	0.2987	16.693		

$$B = B_{\mathrm{ref}} + \sum_n B_n (T - T_{\mathrm{ref}})^n \tag{4}$$

$$H = H_{\mathrm{ref}} + \sum_n H_n (T - T_{\mathrm{ref}})^n \tag{5}$$

where T_{ref} is the reference temperature, equal to 298.15 K.

As can be seen, eqs 2 and 3 require the information of densities of pure water and of aqueous PEG solutions. For this reason, linear equations were fitted to experimental density data of PEGs in water[19,27] at 298.15 K. The coefficients of the linear equations are given in Table 5. In addition, to estimate the densities of the PEG + water mixtures at temperatures other than 298.15 K, the densities of the PEG solutions at 298.15 K, relative to water (subscript w) at the same reference temperature, were multiplied by the density of water at the desired temperature:

$$\rho_i(T) = \frac{\rho_i(298.15\ \mathrm{K})}{\rho_{\mathrm{w}}(298.15\ \mathrm{K})}\rho_{\mathrm{w}}(T) \tag{6}$$

In dealing with multicomponent systems, a semiempirical equation was used to calculate the corresponding densities. It requires the densities of the binary solutions (solute + solvent) and is given by

$$\rho_{\mathrm{mix}} - \rho_{\mathrm{w}} = \sum_{i, i \neq \mathrm{w}} (\rho_i - \rho_{\mathrm{w}}) \tag{7}$$

where ρ_{mix}, ρ_{w}, and ρ_i represent the densities of the multicomponent mixture, of pure water, and of the binary aqueous mixtures containing component i, respectively. The summation in eq 7 should be performed on all the components i in the solution, except for the water. Equations 6 and 7 were used in a prior work[28] to estimate the densities of aqueous solutions containing different solutes, with very good agreement between experimental and calculated values.

By nonlinear regression[29] of eq 2, the values of B_{ref}, B_1, B_2 and H_{ref}, H_1, H_2 were obtained for each PEG + water system. A data bank comprising experimental viscosities of binary systems reported in this work and those from the literature,[18,21] in a wide range of PEG molecular masses, concentrations, and temperatures, was employed in the

Table 3. Kinematic Viscosities, ν, in Aqueous Solutions of PEGs at Various Temperatures, T, and Mass Fractions, w

T/K	w	$\nu/10^{-6}$ m^2·s^{-1}	w	$\nu/10^{-6}$ m^2·s^{-1}
	PEG 200		PEG 400	
293.15			0.2487	3.167
303.15	0.2399	1.829	0.2487	2.365
313.15	0.2399	1.416	0.2487	1.828
323.15	0.2399	1.148		
293.15	0.4902	7.231	0.4958	10.917
303.15	0.4902	4.971	0.4958	7.425
313.15	0.4902	3.649		
323.15	0.4902	2.835	0.4958	4.180
	PEG 600		PEG 1000	
293.15	0.2490	3.684	0.2275	4.425
303.15	0.2490	2.745	0.2275	3.237
313.15	0.2490	2.089	0.2275	2.539
323.15	0.2490	1.696	0.2275	2.028
293.15	0.4899	15.534	0.4777	21.823
303.15	0.4899	10.389	0.4777	14.524
313.15	0.4899	7.361	0.4777	10.256
323.15	0.4899	5.501	0.4777	7.502
	PEG 1500		PEG 3350	
293.15	0.1223	2.387	0.0969	2.965
303.15	0.1223	1.833	0.0969	2.329
313.15	0.1223	1.457	0.0969	1.838
323.15	0.1223	1.191	0.0969	1.496
293.15	0.2349	6.046	0.2492	12.125
303.15	0.2349	4.473	0.2492	8.863
313.15	0.2349	3.444	0.2492	6.757
323.15	0.2349	2.716	0.2492	5.312
293.15	0.4534	28.784	0.3389	22.824
303.15	0.4534	19.228	0.3389	16.250
313.15			0.3389	12.086
323.15	0.4534	9.967	0.3389	9.281
	PEG 8000		PEG 10 000	
293.15	0.0530	2.748	0.0499	3.119
303.15	0.0530	2.128	0.0499	2.376
313.15	0.0530	1.679	0.0499	1.922
323.15	0.0530	1.364	0.0499	1.519
293.15	0.1000	5.623		
303.15	0.1000	4.396	0.0977	5.196
313.15	0.1000	3.338	0.0977	4.037
323.15	0.1000	2.664	0.0977	2.980
293.15	0.2554	33.655		
303.15	0.2554	24.476	0.2441	31.977
313.15	0.2554	18.904	0.2441	24.496
323.15	0.2554	14.715	0.2441	19.314

Table 4. Kinematic Viscosities, ν, of Multicomponent Poly(ethylene glycol) Aqueous Solutions at Various Temperatures, T

T/K	w_1	w_2	w_3	w_4	$\nu/10^{-6}$ m^2·s^{-1}
	PEG 400 (1) + PEG 600 (2) + PEG 1000 (3) + PEG 1500 (4)				
293.15	0.1005	0.1006	0.0999	0.1032	11.430
303.15	0.1005	0.1006	0.0999	0.1032	8.166
313.15	0.1005	0.1006	0.0999	0.1032	5.936
323.15	0.1005	0.1006	0.0999	0.1032	4.657
	PEG 3350 (1) + PEG 8000 (2) + PEG 10 000 (3)				
293.15	0.0997	0.1012	0.0495		23.468
303.15	0.0997	0.1012	0.0495		17.170
313.15	0.0997	0.1012	0.0495		13.051
323.15	0.0997	0.1012	0.0495		10.248
	PEG 400 (1) + PEG 8000 (2)				
293.15	0.1003	0.1000			8.221
303.15	0.1003	0.1000			6.078
313.15	0.1003	0.1000			4.675
323.15	0.1003	0.1000			3.702

Table 5. Linear Fittings for the Densities of Poly(ethylene glycol) Aqueous Solutions

equation: $\rho/(10^3\ \mathrm{kg{\cdot}m^{-3}}) = a + bw$

PEG	a	b	R^2	PEG	a	b	R^2
300	0.996 04	0.166 97	*3,66*[a]	4000	0.996 01	0.178 36	*3,71*
400	0.996 11	0.169 85	*3,74*	6000	0.995 75	0.180 59	*3,72*
600	0.996 23	0.172 33	*3,68*	8000[b]	0.996 67	0.177 01	*3,49*
900	0.995 68	0.176 62	*3,76*	10 000	0.995 42	0.182 95	*3,75*
1000	0.995 70	0.176 30	*3,76*	12 000	0.995 86	0.182 34	*3,68*
1500	0.995 63	0.175 87	*3,72*	15 000	0.995 86	0.181 40	*3,76*
2000	0.995 77	0.178 62	*3,75*	20 000	0.996 04	0.180 68	*3,63*
3000	0.995 74	0.179 43	*3,71*	35 000	0.996 17	0.181 17	*3,80*
3350[b]	0.996 48	0.175 64	*3,67*				

[a] Correlation coefficients such as 0.999 80 given as *3*,80. [b] Experimental density data from ref 19. All other sets of density data were taken from ref 27.

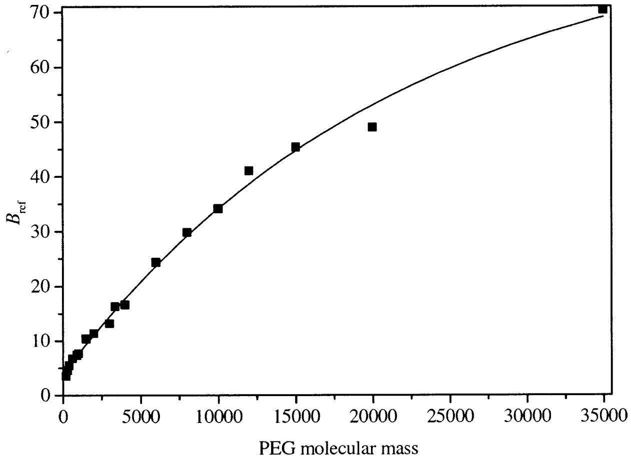

Figure 1. B_{ref} values as a function of PEG molecular mass.

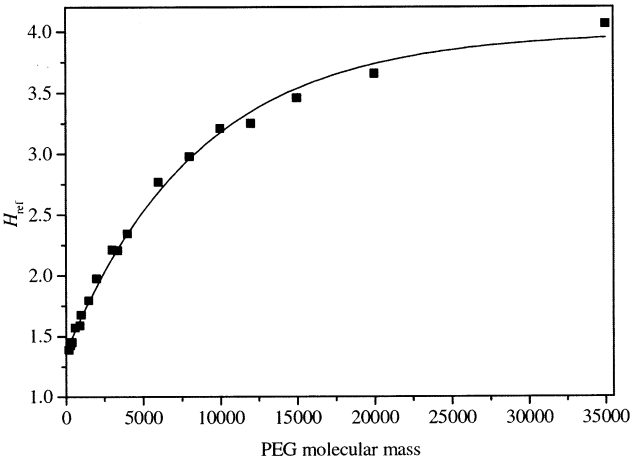

Figure 2. H_{ref} values as a function of PEG molecular mass.

correlations. The data bank comprises a total of 259 experimental points. The adjusted parameters, as well as the average absolute deviations (AADs) between experimental and calculated viscosities, are presented in Table 6. It was observed that H_{ref} and B_{ref} exhibit a dependence on the polymer molecular mass as depicted in Figures 1 and 2. For this reason, it is interesting to compare the H_{ref} values obtained in the present work with the hydration numbers reported in the literature, since there are reports about the variation of hydration numbers with molecular mass of different PEG molecules.

The number of water molecules, which are thought to be bounded in the PEG molecules, varies widely according to the experimental measurement techniques, which include conductometry,[24] differential scanning calorimetry (DSC),[20] IR spectrophotometry,[22] and viscometry.[21] Values between 0.9 and 6 water molecules per monomer were quoted.[23] It is also reported that PEGs of higher molecular masses show increased hydration.[20]

Table 6. Adjusted Coefficients of Eqs 2, 4, and 5 for Calculating Kinematic Viscosities of Aqueous PEG Solutions[a]

PEG	w	T/K	B_{ref}	$B_1/10^{-3}$	$B_2/10^{-3}$	H_{ref}	$H_1/10^{-3}$	$H_2/10^{-3}$	AAD[b]
200	≤0.49	303−323	3.4444	55.3	−2.38	1.3862	−5.44	0.106	5.9
300	≤0.29	298	4.5680	0.0	0.0	1.4256	0.0	0.0	2.4
400	≤0.50	293−323	5.4186	37.8	−2.38	1.4487	−12.7	0.29	3.4
600	≤0.49	293−323	6.7086	−1.05	−0.002	1.5693	−9.62	0.068	4.9
900	≤0.21	298	7.3506	0.0	0.0	1.5891	0.0	0.0	3.7
1000	≤0.50	293−323	7.6304	2.0	1.03	1.6762	0.385	−0.36	5.7
1500	≤0.45	293−323	10.3957	−1.89	1.10	1.7942	−7.76	0.0	7.9
2000	≤0.40	298	11.3580	0.0	0.0	1.9760	0.0	0.0	4.7
3000	≤0.12	298	13.1893	0.0	0.0	2.2100	0.0	0.0	2.7
3350	≤0.34	293−323	16.2610	−0.02	1.27	2.2050	1.94	0.039	10.8
4000	≤0.10	298	16.6385	0.0	0.0	2.3424	0.0	0.0	2.6
6000	≤0.25	298	24.3935	0.0	0.0	2.7669	0.0	0.0	7.8
8000	≤0.26	293−323	29.8474	−4.56	−4.60	2.9778	−8.34	0.253	4.3
10 000	≤0.24	293−323	34.1380	5.36	−10.3	3.2098	3.66	0.0	7.0
12 000	≤0.04	298	41.0170	0.0	0.0	3.2500	0.0	0.0	2.5
15 000	≤0.04	298	45.3602	0.0	0.0	3.4566	0.0	0.0	3.4
20 000	≤0.03	298	48.9736	0.0	0.0	3.6566	0.0	0.0	2.3
35 000	≤0.03	298	70.2625	0.0	0.0	4.0611	0.0	0.0	3.8
global									5.4

[a] Experimental viscosity data from the present work and from the literature.[18,21] [b] $\mathrm{AAD} = \left[\sum_{i=1}^{n}\left(\frac{|\nu_{\exp,i} - \nu_{\mathrm{calc},i}|}{\nu_{\exp,i}}\right)\right] \times \frac{100}{n}$

According to Moulik and Gupta,[22] 4 to 6 water molecules per oxygen for a PEG of molecular mass 20 000 have been obtained, and a minor temperature dependence of hydration has been observed. The same authors obtained hydration numbers (molecules of bound water per monomer unit) of 1.53 for PEG 400 and 1.93 for PEG 600. Bahri and Guveli[30] reported that 0.16 to 3.20 water molecules may bind a single oxygen center for PEGs with molecular masses in the range (200 to 1000) g·mol^{-1}. The hydration numbers obtained from viscometry were presented by Bisal et al.[24] for PEGs 200, 300, 400, 600, and 1000 with values equal to 0.79, 0.95, 1.07, 1.21, and 2.45, respectively. The hydration numbers determined by viscometry are also reported by Kirinčič and Klofutar.[21] These values varied from 2.06 to 28.44 for PEGs with molecular masses between (300 and 35 000) g·mol^{-1}. The explanation given for such high values was that, as the molecular mass increases, the polymer chain begins to fold in on itself, forming segment−segment interactions as it traps additional, more loosely bound water between the segments. A different result was obtained by DSC determinations of bound water.[20] In the work of Antonsen and Hoffman,[20] the amount of water bound per polymer repeated unit varied from 2.3 to 3.8, for PEG molecular masses between 200 and 2.3 × 10^5 g·mol^{-1}. They also observed that the amount bound at higher molecular masses is greater than that at low molecular masses.

Hence, comparing the H_{ref} values from Table 6 and the hydration numbers reported in the literature, it seems that in the present work the H_{ref} values might be interpreted as the number of molecules of bound water per oxyethylene unit. In general, on the basis of the figures presented previously, it can be observed that the hydration numbers at 298.15 K (H_{ref}) obtained in this work are in agreement with part of the data reported in the literature. Therefore, the physical meaning of eq 2 for calculating viscosities of aqueous PEG solutions becomes more consistent, despite some discrepancies described above. In any case, the data presented here are closely related to the general conclusion that something in the range of 1 to 4 water molecules are bound per repeated oxyethylene unit of the polymer and that the hydration numbers rise with the PEG molecular mass.

Considering that the values of B_{ref} and H_{ref} are functions of the polymer molecular masses (as shown in Figures 1 and 2), such values were regressed to an exponential type equation as given below:

$$Y_{ref} = C_1 + C_2 \exp(-M_w/C_3) \qquad (8)$$

where Y_{ref} is B_{ref} or H_{ref}, M_w is the molecular mass of the PEG molecule, and the C_i's are adjusted constants. Correlation coefficients of 0.9974 and 0.9977 were obtained in the regression for estimating B_{ref} and H_{ref} values, respectively. The molecular masses used in this correlation were the values given by the PEG denomination, such as PEG 1000 or PEG 3350. Although Table 1 gives the average molecular masses for the PEGs used in the present work, such information is not available for the viscosity data taken from the literature.

Table 7. Constants for the Generalized Equation

H[a]	B[a]
$C_1 = 3.990\ 96$	$C_1 = 83.9795$
$C_2 = -2.598\ 61$	$C_2 = -80.2152$
$C_3 = 7891.5$	$C_3 = 22077.1$
$H_1 = 1.08 \times 10^{-3}$	$B_1 = -0.1424$
$H_2 = -0.32 \times 10^{-3}$	$B_2 = 6.32 \times 10^{-3}$

[a] H_{ref} and B_{ref} are calculated by eq 8 using the parameters C_i given above.

Taking B_{ref} and H_{ref} as functions of the PEG molecular mass, a generalized correlation could be obtained using eq 2 for calculating the viscosities of the systems studied. Substituting eq 8 in eqs 4 and 5, a generalized expression was obtained for the H and B parameters of eq 2. The parameters of this generalized equation were estimated employing the entire set of experimental data. Results of the regression are given in Tables 7 and 8 and in Figures 3 and 4. The AAD value for the whole set of binary experimental data was 5.5% (Table 8). The systems containing PEG 200 or 3350 are those with the higher deviations between experimental and calculated viscosities. In the case of PEG 3350, the main reason for such deviation is probably the significant difference between the nominal and the average molecular masses (Table 1), a difference that is not so large for the other PEG denominations. In the case of PEG 200, the relatively low experimental viscosity values may have contributed to the large deviation observed, but it also seems that such values do not fit so

Table 8. Results of the Generalized Correlation for Viscosity Calculations

PEG	AAD %	PEG	AAD %
200	16.7	3350	7.6
300	4.4	4000	2.9
400	5.6	6000	6.8
600	5.2	8000	5.0
900	2.8	10 000	7.0
1000	6.4	12 000	2.8
1500	6.6	15 000	3.1
2000	3.6	20 000	3.5
3000	3.1	35 000	3.5
global			5.5

well in the suggested dependence of the parameters B_{ref} and H_{ref} on the polymer molecular mass. Some authors suggest that for poly(ethylene glycol)s of low molecular mass, such as PEG 200, only tightly bound water is associated to the polymer chain. For polymers of larger molecular mass, the chain begins to fold in on itself, trapping additional water between the segments of the polymer chain.[20,21] This observed difference in the polymer behavior, according to its molecular mass, might be the explanation for the larger deviation obtained for aqueous solutions of PEG 200.

It is also important to contrast the results of the correlation obtained in the present work with those reported in the literature for the viscosity of aqueous PEG systems. González-Tello et al.[19] reported an AAD value of 3.5% for dynamic viscosities (η) greater than 10 mPa·s, and a value of 17.5% for viscosities lower than 10 mPa·s. In that work, the equation proposed to calculate viscosities of aqueous PEG solutions takes into account the influences of poly(ethylene glycol) concentration and of the temperature, in the range (277 to 313) K. The same model equation was tested by Günduz[14] for PEG 8000 and dextran 580 000 in water at 293.15 K, with a resultant AAD of 1.9% and 1.5%, respectively. It must be stressed that in the latter case the results were obtained by adjusting four parameters for each polymer separately. For a mixture of both polymers (PEG + dextran) in water, a Grunberg equation was used to correlate the viscosities, resulting in an AAD of 6.8%.[14] A subsequent work of the same author[17] presented AAD values of up to 9.4% for aqueous mixtures of PEG + dextran of different molecular masses. Polymer concentrations of up to 7 mass % and temperatures between (303.15 and 343.15) K were considered.

Concluding the above remarks, it can be observed that the results achieved in the present work are in good agreement with the AAD values usually presented in the literature. The advantage of the equation presented here, in comparison with other equations, is that it has a generalized form in relation to PEG molecular mass, concentration of polymer, and temperature.

Viscosity Prediction in Multicomponent Systems. The predictive capacity of eq 3 to estimate the viscosities of the ternary, quaternary, and quinary aqueous PEG systems was investigated. The values of viscosity calculated by eq 3 were compared with the experimental data from Table 4. An AAD of 9.9% was obtained. It should be observed that the predicted values are in all cases lower than the experimental viscosities. Probably there is an additional effect on the viscosity, attributable to the relatively high concentration of polymers with different molecular masses. This effect is not properly described by the parameters adjusted to aqueous binary mixtures containing one polymer. Yet, it should be noted that the AAD values obtained in this work are similar to those reported in the literature for viscosity prediction of multicomponent mixtures. Cao et al.[16] reported deviations in the range (2.7 to 5.3)% for viscosity predictions by the GC-UNIMOD model. They used a large data bank, including mostly binary mixtures of alkanes, alcohols, ketones, ethers, and esters. Using the same model, Rabelo et al.[31] reported deviations in the range (0.8 to 14.0)% for some multicomponent fatty mixtures. The literature also mentions predictions of the GC-UNIMOD model for mixtures of some poly(ethylene glycol) dimethyl ethers and methanol over a wide range of temperatures. The reported average absolute deviations were around 20%. On the other hand, predictions with good accuracy were obtained by Pereira et al.[15] employing the modified Kumar equation to estimate viscosities of multicomponent mixtures. However, only low molecular mass solutes (salts, glycerin, monosaccharides, etc.) were employed at relatively low solute concentrations (up to 15 mass %).

In general, the results obtained in this work, either in correlation or in prediction, were satisfactory. Moreover, the obtained generalized equation based on the polymer molecular mass is a useful tool, since only a few parameters are required for viscosity estimations in systems containing PEGs with molecular masses between 200 and 35 000 g·mol^{-1}.

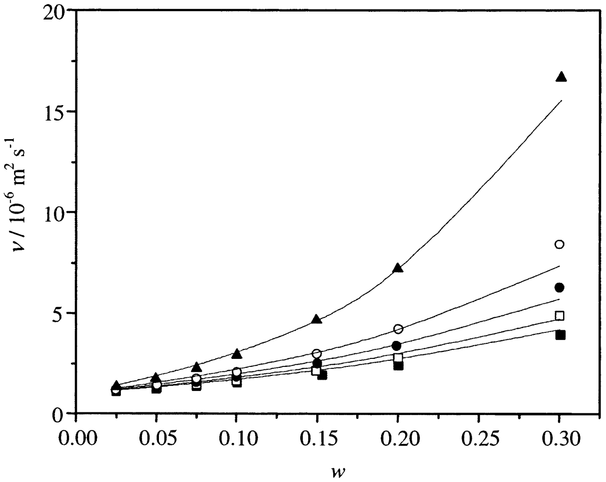

Figure 3. Experimental and calculated viscosities at 293.15 K and various concentrations: ■, PEG 400; □, PEG 600; ●, PEG 1000; ○, PEG 1500; ▲, PEG 3350; —, calculated values.

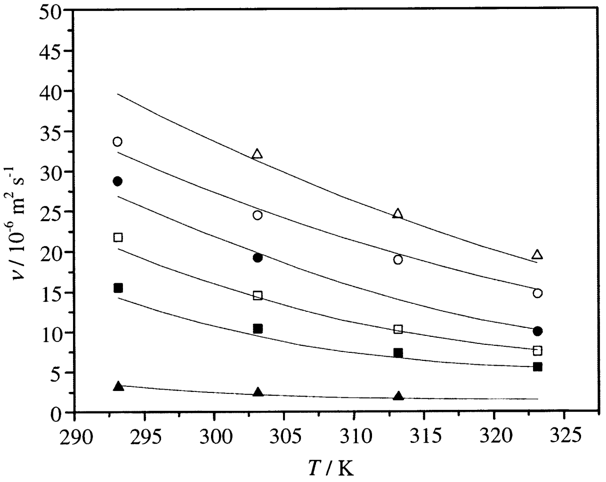

Figure 4. Experimental and calculated viscosities at various temperatures and concentrations: ▲, PEG 400, $w = 0.2487$; ■, PEG 600, $w = 0.4899$; □, PEG 1000, $w = 0.4777$; ●, PEG 1500, $w = 0.4534$; ○, PEG 8000, $w = 0.2554$; △, PEG 10 000, $w = 0.2441$; —, calculated values.

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