J. Chem. Eng. Data **2002,** *47,* 835−838

Kinematic Viscosities of Poly(ethylene glycol) Blends

Luciana Ninni, Wong H. Fung, and Antonio J. A. Meirelles*

LASEFI, Faculty of Food Engineering, State University of Campinas (UNICAMP), P.O. Box 6121,
13083-970 Campinas, São Paulo, Brazil

Kinematic viscosities of binary and multicomponent mixtures containing poly(ethylene glycols) were measured as a function of temperature. Viscosities of the binary mixtures were used to calculate the excess molar Gibbs energy of activation for viscous flow G^{*E}. The G^{*E} values are positive over the entire composition range and they increase as the difference in the molecular masses of the two polymers increases. The group-contribution viscosity model GC-UNIMOD was employed to correlate the viscosity of the binary systems and then to predict the viscosities of the multicomponent mixtures. Average absolute deviation around 3.5% was obtained for the viscosity calculations using the GC-UNIMOD model.

Introduction

Poly(ethylene glycol) (PEG) belongs to a class of synthetic polymers that finds several industrial applications because of their availability in a wide range of molecular masses besides having an unusual combination of properties such as water solubility, lubricity, and low toxicity. Blends of different molecular masses are desired to obtain combinations of properties. For instance, blends of PEG 300 and 1450 are available from most suppliers for use in pharmaceutical and cosmetic products. PEGs are also used as processing aids in making other products. An example is the use of molten PEGs in heat-transfer baths.[1] Hence, because of the industrial interest, experimental viscosity data and models for estimating viscosities of PEG mixtures are important. In a previous paper,[2] a generalized correlation based on the number of carbon atoms was developed for calculating kinematic viscosities of pure PEGs in a molecular mass range between 200 and 3350 as a function of temperature. In the case of mixtures, there are many empirical or semiempirical equations in the literature[3,4] for estimating viscosity data. Among them there is the group-contribution viscosity model GC-UNIMOD,[5] which requires binary interaction parameters between constituent groups of molecules in the mixture and viscosities of pure components. The GC-UNIMOD has been used to predict the viscosity of systems containing mixtures of organic solvents[3,4] and working fluid pairs such as methanol and some poly(ethylene glycol) dimethyl ether (PEGDME) mixtures.[6] In the case of the last mentioned system, the authors reported an average absolute deviation around 20% for viscosity predictions and observed that these predictions were getting worse with the increase of the molecular size of PEGDME.

The aim of this paper is to extend our prior studies[2] to binary and multicomponent blends of PEGs using the GC-UNIMOD model. Therefore, the kinematic viscosities of blends of PEGs covering a wide range of mixture molecular masses were measured at various temperatures, and the GC-UNIMOD model was used to correlate and predict these experimental data.

Table 1. Poly(ethylene glycol) Characterization

PEG	avg molecular mass (M_n)	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	987	1.067	1.54 ± 0.02	44	44
1500	1468	1.069	1.09 ± 0.01	68	66
3350	2806	1.073	0.75 ± 0.01	152	126

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

Experimental Section

Materials. The samples of poly(ethylene glycol) of different average molecular masses, ranging from (200 to 3350) g mol^{-1}, were supplied by Sigma, except PEG 1500, which was purchased from Fluka. They were analytical-grade reagents used without further purification. Their polydispersity index was determined by gel permeation chromatography (GPC) using a Ultrahydrogel column Waters device. The following experimental conditions were employed for the GPC runs: water as the mobile phase at a rate of 0.8 μL min^{-1}, injection temperature of 313.15 K, volume of the sample injected equal to 100 μL, and a refractive index detector.

The water content of the PEG samples was previously determined by Karl Fischer titration using a Metrohm device (Switzerland). In Table 1 the characteristics of the polymers used in this work are given together with the nominal and true carbon numbers for each PEG. The denomination nominal carbon number refers to carbon numbers calculated from the molecular mass given by PEG manufacturers such as PEG 200 and PEG 3350, while the true carbon number was evaluated from the results of the GPC molecular mass distribution.

Apparatus and Procedures. The solutions were prepared by mass on an analytical balance (Sartorius Analytic−GmbH) with ±0.1-mg accuracy. The estimated error in mass fraction was 1 in 10000. Calibrated Cannon-Fenske-type viscometers were used to measure the kinematic viscosities at different temperatures (Cannon Instrument Co.). The viscometer sizes were 150, 200, 300, and 350, appropriate for the range of viscosity values measured in

---

* To whom correspondence should be addressed. Phone: +55-19-3788-4037. Fax: +55-19-3788-4027. E-mail: tomze@ceres.fea.unicamp.br.

10.1021/je0155249 CCC: $22.00

Table 2. Viscosity of Binary Blends of Poly(ethylene glycol)s at Various Temperatures

T / K	w_1	ν / 10^{-6} m^2 s^{-1}	w_1	ν / 10^{-6} m^2 s^{-1}	w_1	ν / 10^{-6} m^2 s^{-1}
	200(1) + 400(2)		200(1) + 600(2)		400(1) + 600(2)	
293.15	0.4999	77.53	0.5031	93.89	0.5043	127.44
298.15	0.4999	59.73	0.5031	72.95	0.4999	99.61
303.15	0.4999	46.49	0.5031	58.41	0.5007	77.66
308.15	0.4999	37.18	0.5031	46.52	0.5007	60.86
313.15	0.4999	30.13	0.5031	37.90	0.5007	49.25
318.15	0.4999	24.73	0.5031	30.94	0.5007	40.49
323.15	0.4999	20.62	0.5031	25.80	0.5007	33.58
	600(1) + 1000(2)		400(1) + 1500(2)		600(1) + 3350(2)	
333.15	0.5001	36.19	0.4918	40.99	0.4999	97.32
343.15	0.5001	26.44	0.4918	29.81	0.4999	70.85
353.15	0.5001	21.27	0.4836	23.11	0.4999	54.27
363.15	0.5001	15.87	0.4836	18.20	0.4999	41.97
	1000(1) + 3350(2)		400(1) + 3350(2)			
333.15	0.5001	114.79	0.5000	88.09		
343.15	0.5001	84.10	0.5000	63.76		
353.15	0.5001	62.07	0.5000	48.92		
363.15	0.5001	49.94	0.5000	38.66		

Table 3. Viscosity of Binary Blends Containing Poly(ethylene glycol) 400 at Various Concentrations

T / K	w_1	ν / 10^{-6} m^2 s^{-1}	w_1	ν / 10^{-6} m^2 s^{-1}	w_1	ν / 10^{-6} m^2 s^{-1}
	400(1) + 600(2)		400(1) + 1500(2)		400(1) + 3350(2)	
293.15	0.1010	154.96				
293.15	0.2000	146.25				
293.15	0.2999	139.42				
293.15	0.3992	133.61				
293.15	0.7000	121.82				
293.15	0.8998	110.98				
293.15	0.9482	105.77				
333.15	0.0996	28.04	0.0511	70.91	0.0273	224.82
333.15	0.2001	26.87	0.0997	68.69	0.0513	219.00
333.15	0.2999	25.63	0.1513	63.49	0.1029	196.70
333.15	0.3992	24.84	0.2500	56.83	0.2000	162.98
333.15	0.5000	23.76	0.3496	50.02	0.2500	147.14
333.15	0.7000	21.80	0.7006	31.17	0.6998	52.48
333.15	0.8998	20.04	0.9003	23.27	0.8002	39.62
333.15	0.9482	19.78				

Table 4. Viscosities of Ternary Mixtures of Poly(ethylene glycol)s at Various Temperatures

T / K	w_1	w_2	ν / 10^{-6} m^2 s^{-1}	w_1	w_2	ν / 10^{-6} m^2 s^{-1}
	400(1) + 600(2) + 1000(3)			600(1) + 1000(2) + 1500(3)		
333.15	0.3339	0.3334	30.26	0.3332	0.3335	47.10
343.15	0.3339	0.3334	22.01	0.3332	0.3335	34.20
353.15	0.3339	0.3334	16.77	0.3332	0.3335	26.67
363.15	0.3339	0.3334	13.21	0.3332	0.3335	21.00
	400(1) + 1000(2) + 3350(3)			1000(1) + 1500(2) + 3350(3)		
333.15	0.3334	0.3331	71.25	0.3330	0.3334	109.27
343.15	0.3334	0.3331	52.29	0.3330	0.3334	79.28
353.15	0.3334	0.3331	38.85	0.3330	0.3334	60.59
363.15	0.3334	0.3331	31.23	0.3330	0.3334	47.59

the present work. The viscometers were placed in a constant temperature water bath controlled to ±0.1 °C. An electronic timer with 0.01-s accuracy was used for measuring the efflux time. The experiments were replicated at least five times for each PEG mixture and the results reported are the average values.

Results and Discussion

The viscosity data are presented in Tables 2−5 as a function of mass fraction (w) and temperature T. The kinematic viscosities ν were calculated from the efflux time and the instrument constant provided by the manufacturer.

Table 5. Viscosities of a Multicomponent Mixture of Poly(ethylene glycol)s at Various Temperatures

T / K	w_1	w_2	w_3	w_4	ν / 10^{-6} m^2 s^{-1}
	400(1) + 600(2) + 1000(3) + 1500(4) + 3350(5)				
333.15	0.2000	0.1997	0.1999	0.2002	61.40
343.15	0.2000	0.1997	0.1999	0.2002	44.84
353.15	0.2000	0.1997	0.1999	0.2002	34.13
363.15	0.2000	0.1997	0.1999	0.2002	26.77

Table 6. Coefficients of the Redlich−Kister Equation (A_p) and Average Absolute Deviations (AAD) between Experimental and Calculated G^{*E} Values

T / K	A_0	A_1	A_2	A_3	AAD
400(1) + 600(2)					
293.15	495.3292	70.6134	409.3651		5.30
333.15	1172.855	73.1809	1249.925		5.20
400(1) + 1500(2)					
333.15	6549.193	3957.076	2049.027	5960.119	4.01
400(1) + 3350(2)					
333.15	15771.32	8805.127	16811.02	22896.8	4.63

The maximal standard deviation of the measured viscosities was 1.3 × 10^{-7} m^2 s^{-1} and the minimal 1.9 × 10^{-9} m^2 s^{-1}, resulting in an average deviation of 2.6 × 10^{-8} m^2 s^{-1}. The average uncertainty of the viscosity values was estimated to be equal to 0.3%.

In this work, the GC-UNIMOD model was selected for viscosity calculations. Moreover, the viscosity data for the systems containing PEG 400 have been used to calculate the excess molar Gibbs energy of activation for viscous flow.

Excess Molar Gibbs Energy of Activation for Viscous Flow. Viscosities of binary mixtures (PEGs 400 + 600, 400 + 1500, and 400 + 3350) have been used to calculate the excess molar Gibbs energy of activation for viscous flow, G^{*E}, through the following equation,

$$G^{*E} = RT\left(\ln(\nu M) - \sum_{i=1}^{n} x_i \ln(\nu_i M_i)\right) \tag{1}$$

where M is the mixture molar mass, R is the gas constant, T is the absolute temperature, ν and ν_i are the kinematic viscosities of the mixture and of the pure components, respectively, x_i is the component i mole fraction, and n is the number of components in the mixture. The pure component viscosities were calculated using the equation proposed by Cruz et al.[2] and the true carbon numbers given in Table 1.

The G^{*E} (in J mol^{-1}) for the binary mixtures was fitted to a Redlich−Kister's equation,

$$G^{*E} = x_i x_j \sum_{p=0}^{l} A_p (x_i - x_j)^p \tag{2}$$

where x_i and x_j denotes the mole fractions of components i and j, respectively, and A_p values are adjustable parameters. The G^{*E} experimental values and the Redlich−Kister's fitted polynomials are plotted in Figure 1. The coefficients A_p and the average absolute deviations (AAD) between experimental and calculated G^{*E} values are given in Table 6. The G^{*E} values are positive over the entire composition range and they increase as the difference in the molecular masses of the two polymers increases. The increase of the temperature has a similar effect (Figure 1).

Table 7. Average Absolute Deviations (AAD) for the Viscosity Estimation

	AAD				AAD		
binary mixtures	option 1	option 2	option 3	multicomponent mixtures	option 1	option 2	option 3
200 + 400	4.16	4.20	4.74	400 + 600 + 1000	5.53	5.50	5.77
200 + 600	7.45	7.53	8.54	600 + 1000 + 1500	1.09	1.12	1.00
400 + 600	3.20	3.43	3.27	400 + 1000 + 3350	1.46	1.04	0.94
600 + 1000	2.20	2.18	2.28	1000 + 1500 + 3350	4.86	4.59	4.74
400 + 1500	2.89	2.75	3.07	400 + 600 + 1000 + 1500 + 3350	2.52	2.03	2.03
600 + 3350	1.90	1.10	1.09				
1000 + 3350	0.97	0.82	0.91				
400 + 3350	4.54	5.36	6.75				
global	3.62	3.76	4.14		3.09	2.86	2.90

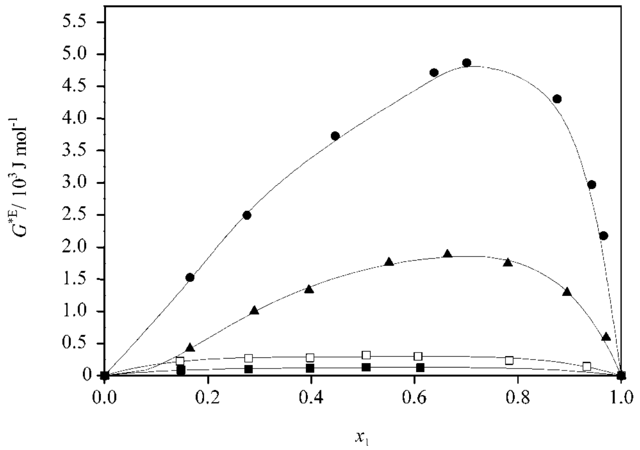

Figure 1. Excess molar Gibbs energy of activation for viscous flow of PEG binary mixtures: (■) 400 + 600 at 293.15 K; (□) 400 + 600 at 333.15 K; (▲) 400 + 1500; (●) 400 + 3350; (—) Redlich−Kister.

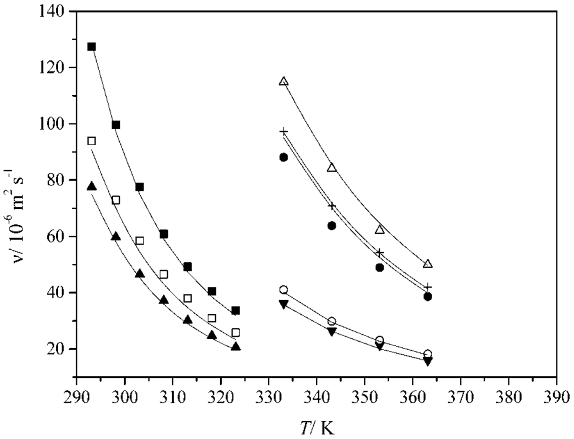

Figure 2. Experimental and correlated viscosities of binary PEG mixtures. Experimental data of Table 2: (▲) 200 + 400; (□) 200 + 600; (■) 400 + 600; (○) 400 + 1500; (●) 400 + 3350; (▼) 600 + 1000; (+) 600 + 3350; (△) 1000 + 3350; (—) GC-UNIMOD/option 2.

GC-UNIMOD Model. The GC-UNIMOD viscosity equation, like the UNIFAC[7] model, is expressed as the sum of combinatorial and residual terms. The combinatorial term of both the viscosity equation and the UNIFAC model is dependent on the molecular size and shape, while the residual term takes into account the interaction energy between different groups present in the mixture. To estimate the kinematic viscosities of the PEG mixtures, the viscosities of the pure components must be known. The equation for pure PEGs[2] was used for calculating the polymer viscosities required in the GC-UNIMOD model.

As a first attempt, the GC-UNIMOD model, with energy interaction parameters obtained from UNIFAC-VLE tables,[8] was tested for estimating the viscosities of the binary mixtures measured in this work. For these predictions the PEG molecule was divided into three functional groups: CH_2, OH, and CH_2O. An average absolute deviation of 15.9% was obtained. It was also verified that specially for the binary mixtures containing polymers with very different molecular masses (for example, the mixture of PEGs 600 and 3350) the model predictions were poor. A readjustment of the energy interaction parameters becomes necessary to improve the predictive capability of the model. The experimental data of the binary mixtures (Tables 2 and 3) were used for this re-adjustment.

As suggested by Herraiz et al.,[6] different possibilities of dividing the polymer molecules into functional groups were considered. PEG molecules can be divided into the following groups: OH, CH_2O, and CH_2 (option 1);[8] OH, CH_2CH_2O, and CH_2 (option 2);[9,10] or CH_2OH, CH_2O, and CH_2 (option 3).[11] As can be seen, three pairs of interaction parameters have to be adjusted in each one of the above options. The new parameters were obtained using a nonlinear estimation method.[12] The average absolute deviations (AAD) between experimental and estimated values were calculated according to the following equation,

Table 8. Energy Interaction Parameters (in Kelvin) for the GC-UNIMOD Model

	CH_2CH_2O	CH_2	OH
CH_2CH_2O		−93.8155	−250.3
CH_2	52.7182		−101.3
OH	41.4333	85.4514	

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

where $\nu_{\mathrm{exp},i}$ and $\nu_{\mathrm{calc},i}$ are the experimental and calculated kinematic viscosities, respectively, and m is the number of experimental points.

Better agreement between experimental and calculated data for the binary mixtures was obtained using options 1 and 2, with AAD global values of 3.62% and 3.76%, respectively (see Table 7). The GC-UNIMOD model was also capable of predicting rather well the viscosities of the multicomponent mixtures, but in this case options 2 and 3 result in slightly better AAD global values, around 2.9% (Table 7). The energy interaction parameters for option 2 are given in Table 8. Figure 2 shows the viscosity values calculated by the GC-UNIMOD model compared with the experimental binary data given in Table 2. The comparison for the ternary and quinary mixtures is shown in Figure 3.

As can be observed in Table 7, the highest AAD values were obtained for those binary mixtures containing PEGs 200 and/or 400. In the case of the multicomponent systems no experimental values were measured for mixtures con-

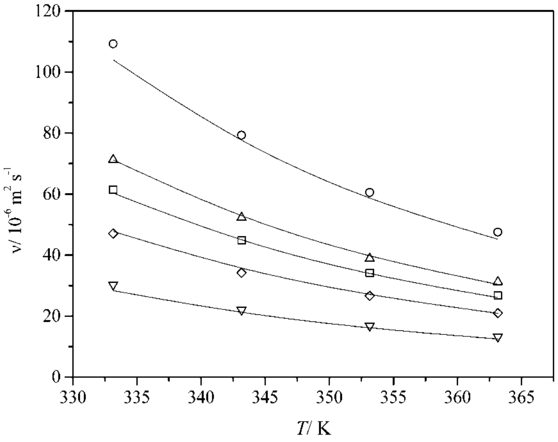

Figure 3. Experimental and predicted viscosities of multicomponent PEG mixtures: (▽) 400 + 600 + 1000; (△) 400 + 1000 + 3350; (□) 400 + 600 + 1000 + 1500 + 3350; (◇) 600 + 1000 + 1500; (○) 1000 + 1500 + 3350; (—) GC-UNIMOD/option 2.

taining PEG 200. Probably this is the reason the AAD values for the predictions (multicomponent mixtures) were slightly lower than those obtained for the correlation of the binary mixtures (Table 7).

The GC-UNIMOD model, with a new set of interaction parameters, works well for estimating the viscosity data measured in the present work. For comparison purposes, some correlation and prediction results reported in the literature should be mentioned. The authors of the GC-UNIMOD reported deviations in the range of 2.7 to 5.3% for predictions of mixture viscosities using energy interaction parameters from UNIFAC-VLE tables. It is also depicted in the literature[6] predictions of the GC-UNIMOD model for mixtures of some poly(ethylene glycol) dimethyl ethers and methanol over a wide range of temperatures. The results showed that the predictions were getting worse with the increase of the polymer molecular mass. The reported average absolute deviations were around 20%. Rabelo et al.[13] employed the GC-UNIMOD model for predicting the viscosity of fatty systems. In this case the AAD values varied in the range of 0.8 to 14.0%. The comparison can also include some empirical equations used for correlating experimental viscosities of aqueous systems containing PEGs. Some of these works[14−17] reported results for concentrated and/or diluted solutions with AAD values varying in the range of 1.2 to 6.8%.

The unique experimental data available in the literature[1] for PEG mixtures is the viscosity of a blend of PEGs 300 and 1500 at equal mass proportion of both compounds. This experimental point was compared to the value predicted by the GC-UNIMOD model (option 2), yielding an AAD value of 10.6%. Although such deviation is comparatively greater than those obtained for the correlation and prediction of our experimental data, it should be noted that for this prediction we had to use the nominal carbon number, not the true carbon number, to estimate the pure PEG viscosities.

Conclusions

In this work the kinematic viscosities of blends of poly(ethylene glycol)s with nominal molecular masses ranging from (200 to 3350) g mol^{-1} were determined at various temperatures. The GC-UNIMOD model was tested for correlating and predicting viscosity data. In most cases a good agreement between experimental and calculated values was obtained.

Literature Cited

(1) Powell, G. M. Polyethylene Glycol. In *Handbook of Water Soluble Gums and Resins*; Davidson, R. L., Ed.; McGraw-Hill Book Company: New York, 1980; Chapter 18.

(2) Cruz, M. S.; Chumpitaz, L. D. A.; Alves, J. G. L. F.; Meirelles, A. J. A. Kinematic Viscosities of Poly(Ethylene Glycols). *J. Chem. Eng. Data* **2000**, *45*, 61−63.

(3) Domínguez, M.; Pardo, J. I.; Gascón, I.; Royo, F. M.; Urieta, J. S. Viscosities of the Ternary Mixture (2-butanol + *n*-hexane + 1-butylamine) at 298.15 and 313.15 K. *Fluid Phase Equilib.* **2000**, *169*, 277−292.

(4) Nhaesi, A. H.; Asfour, A.-F A. Prediction of the Viscosity of Multi-Component Liquid Mixtures: a Generalized McAllister Three-Body Interaction Model. *Chem. Eng. Sci.* **2000**, *55*, 2861−2873.

(5) Cao, W.; Knudsen, K.; Fredenslund, A.; Rasmussen, P. Group-Contribution Viscosity Predictions of Liquid Mixtures Using UNIFAC−VLE Parameters. *Ind. Eng. Chem. Res.* **1993**, *32*, 2088−2092.

(6) Herraiz, J.; Shen, S.; Fernández, J.; Coronas, A. Thermophysical Properties of Methanol + Some Polyethylene Glycol Dimethyl Ether by UNIFAC and DISQUAC Group-Contribution Models for Absorption Heat Pumps. *Fluid Phase Equilib.* **1999**, *155*, 327−337.

(7) Fredenslund, A.; Jones, R. L.; Prausnitz, J. M. Group Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures. *AIChE J.* **1975**, *21*, 1086−1099.

(8) Skjold-Jorgensen, S.; Kolbe, B.; Gmehling, J.; Rasmussen, P. Vapor−Liquid Equilibria by UNIFAC Group-Contribution. Revision and Extension. *Ind. Eng. Chem. Process Des. Dev.* **1979**, *18*, 714−722.

(9) Ninni, L.; Camargo, M. S.; Meirelles, A. J. A. Water Activity in Poly(Ethylene Glycol) Aqueous Solutions. *Thermochim. Acta* **1999**, *328*, 169−176.

(10) Rasmussen, D.; Rasmussen, P. Phase Equilibria in Aqueous Polymer Solutions. *Chem. Eng. Prog.* **1989**, *85*, 50−56.

(11) Herskowitz, M.; Gottlieb, M. Vapor−Liquid Equilibrium in Aqueous Solutions of Various Glycols and Poly(ethylene glycols). 2. Tetraethylene Glycol and Estimation of UNIFAC Parameters. *J. Chem. Eng. Data* **1984**, *29*, 450−452.

(12) Marquardt, D. W. An Algorithm for Least-Square Estimation of Nonlinear Parameters. *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431−441.

(13) Rabelo, J.; Batista, E.; Cavaleri, F. W.; Meirelles, A. J. A. Viscosity Prediction for Fatty Systems. *J. Am. Oil Chem. Soc.* **2000**, *77*, 1255−1261.

(14) Gündüz, U. Evaluation of Viscosities of Polymer−Water Solutions Used in Aqueous Two-Phase Systems. *J. Chromatogr. B* **1996**, *680*, 263−266.

(15) Mei, L.-H.; Lin, D.-Q.; Zhu, Z.-Q.; Han, Z.-X. Densities and Viscosities of Polyethylene Glycol + Salt + Water Systems at 20 °C. *J. Chem. Eng. Data* **1995**, *40*, 1168−1171.

(16) González-Tello, P.; Camacho, F.; Blázquez, G. Density and Viscosity of Concentrated Aqueous Solutions of Polyethylene Glycol. *J. Chem. Eng. Data* **1994**, *39*, 611−614.

(17) Gündüz, U. Viscosity Prediction of Polyethylene Glycol−Dextran−Water Solutions Used in Aqueous Two-Phase Systems. *J. Chromatogr. B* **2000**, *743*, 181−185.

Received for review October 2, 2001. Accepted April 2, 2002. The authors gratefully acknowledge the financial support of FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo: 01/10137-6) and CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico: 521011/95-7, 466680/00-7, and 145941/99).

JE0155249