Multicomponent Diffusion in Systems Containing Molecules of Different Size. 1. Mutual Diffusion in the Ternary System Poly(ethylene glycol) 2000 + Poly(ethylene glycol) 200 + Water

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The multicomponent approach for the description of liquid diffusion processes includes cross-term diffusion coefficients that describe the interaction between the flows of different solute components. We demonstrate that these cross-term diffusion coefficients can be large and thus necessary for the description of diffusion of polydisperse polymers. In this study, the four mutual diffusion coefficients have been measured at 25 °C for the ternary system PEG 2000 (1) [poly(ethylene glycol) 2000 g mol^{-1}] + PEG 200 (2) [poly(ethylene glycol) 200 g mol^{-1}] + water (0). Diffusion coefficients were measured at solute concentrations of 0.0827 mol dm^{-3} PEG 2000 and 0.076, 0.2293, and 0.4105 mol dm^{-3} PEG 200. One of the cross-terms, D_{21}, varies linearly with the concentration of PEG 200 at a constant concentration of PEG 2000 and, at the highest concentration of PEG 200, was larger than either of the main-diffusion coefficients D_{11} and D_{22}. The diffusion coefficients have been qualitatively interpreted in terms of molecular interactions and the excluded volume effect. We also report binary diffusion coefficients, densities, and viscosities for binary solutions of both PEG 200 and PEG 2000 in water at 25 °C.

Introduction

This paper examines the issue of interaction in multicomponent diffusion of different length components of the same polymer. The polymer, poly(ethylene glycol) (PEG) has been chosen for this study because of its use in crystallization of certain proteins and other biological macromolecules.[1,2]

The description of isothermal mutual diffusion of a system with n solutes, in terms of fundamental driving forces, requires a n^2 matrix of thermodynamic diffusion coefficients $[L_{ij}]$ relating the solute flux vectors $[J_i]$, on the solvent frame of reference (denoted by subscript "0" where $J_0 \equiv 0$), to the solute chemical potential gradient vectors $[\nabla \mu_i]$ according to[3]

$$-J_i = \sum_{j=1}^{n} (L_{ij})_0 \nabla \mu_j \qquad i = 1, ..., n \qquad (1)$$

In experimental studies, however, Fick's equation is used to described the transport in a multicomponent system[4,5] according to the equations

$$-J_i = \sum_{j=1}^{n} (D_{ij})_v \nabla C_j \qquad i = 1, ..., n \qquad (2)$$

Here the diffusion coefficients $(D_{ij})_v$ are on the volume-fixed reference frame defined by[6]

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$$\sum_{i=0}^{n+1} J_i \bar{V}_i = 0 \qquad (3)$$

The solvent frame $(D_{ij})_0$ may be calculated from the volume frame $(D_{ij})_v$ and the partial molar volumes of the components.[6] The thermodynamic diffusion coefficients are related to the solvent frame diffusion coefficients by the equations

$$(D_{ij})_0 = \sum_{k=1}^{n} (L_{ik})_0 \frac{\partial \mu_k}{\partial C_j} \qquad (4)$$

In what follows we will refer to the volume-fixed reference frame diffusion coefficients $(D_{ij})_v$ as D_{ij}.

In eq 2 we denote the D_{ii} as main-term diffusion coefficients and the D_{ij} $(i \neq j)$ as cross-term diffusion coefficients. The latter ones become zero at infinite dilution (pure solvent) for all mixtures containing no more than one electrolyte solute. However, one or more D_{ij} $(i \neq j)$ may be larger than any main-term diffusion coefficient at moderate to high solute concentrations,[7,8] especially if solutes of significant difference in molecular weight are included in the mixture.[9,10] There is a restriction that the determinant of the diffusion coefficient matrix must remain positive.[11]

From the technical point of view, the D_{ij} for a ternary system at mean concentrations $\bar{C}_1$ and $\bar{C}_2$ can be measured by performing two or more experiments at different ratios of $\Delta C_1/(\Delta C_1 + \Delta C_2)$, where ΔC_1 and ΔC_2 are the initial concentration differences across a free-diffusion boundary.[12]

A system in which a polydisperse sample has been added to a solvent will, in reality, contain many individual components. Denoting k as the number of components in the sample, the complete description of the isothermal transport in such a system requires k main-term diffusion

coefficients and $k(k-1)$ cross-term diffusion coefficients. An estimation of the molecular weight distribution may be made from considerations of how the polymer was formed and how it was purified. Also the HPLC will yield a distribution. However, without separating pure samples of each of the components in a polydisperse system, it is impossible to obtain all the D_{ij} for the full description. Sundelöf[13,14] derived equations for description of polydisperse systems by assuming that the cross-term diffusion coefficients are zero.

It should be possible to obtain information about the polydisperse character of a sample from the Ω_j (the fringe deviation function) values obtained in the full analysis of Gouy fringe patterns.[15,16] This requires some method for predicting the D_{ij} that will most influence the results. The validity of any theoretical model used for relating Ω_j to polydisperity will require experimental verification. This, in turn, will require multicomponent diffusion measurements on carefully chosen systems.

Background

There has always been an interest in the characterization of the polydispersity of polymers because of their importance in several fields such as biochemistry and the food industry.[17-20] Sundelöf presented a method for determination of the distribution of molecular size parameters, that uses a convolution procedure applied to the integral of the weight distribution function of diffusion coefficients.[13,14] The procedure, which neglects the cross-term diffusion coefficients, was applied to free-diffusion experiments with fair success. However, because $D_{ij} = 0$, for the $(i \neq j)$, approximation, the method would only apply to systems with relatively low solute concentrations or requires extrapolation of data to zero concentration.

To examine this issue, Cussler studied the ternary system polystyrene ($M_n = 182\,000$ g mol^{-1}) + polystyrene ($M_n = 217\,000$ g mol^{-1}) + toluene, in which the solutes were two polymers with mild polydispersity and different molecular weights.[21] His results, at the highest concentration explored, showed a large multicomponent effect, in which both D_{ij} ($i \neq j$) are large and their values reach the same magnitude of at least one of the main-term diffusion coefficients.

A few years ago Ambrosone presented an approach for determination of the size distribution of droplets in liquid using the NMR method.[22]

Some of us[23] used the Flory equation for the dependence of the limiting diffusion coefficients of monodisperse polymers on molecular weight to obtain the expressions for D_A (area/reduced height ratio of the refractive index gradient curve)[15] and Q_0 (area under the fringe deviation graph)[16] at infinite dilution. These equations hold for a general molecular weight distribution. They have then been used to analyze the effect of polydispersity on the parameters measured by the Gouy technique for several polydisperse polymers. These were poly(ethylene glycol) (PEG), poly(acrylic acid), and sodium polyacrylate.

The experimental work presented here expands our knowledge of the effect of the polydispersity on diffusive transport.[23,24] This work is part of a series of careful free-diffusion studies on systems containing solutes that belong to the same homologous series.[25-28]

This paper reports ternary diffusion coefficients for the system PEG 2000 + PEG 200 + water, in which both samples have a mild polydispersity. In the following we will refer to PEG 2000 as solute 1 and to PEG 200 as solute 2.
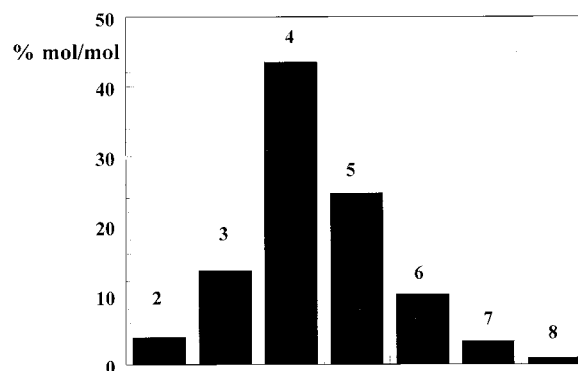

Figure 1. Distribution of the PEG oligomers for PEG 200 determined by a chromatographic technique.

The transport properties of PEG samples are also of interest in the protein crystallization field.[29,30] Besides certain common salts (NaCl, KSCN, $(NH_4)_2SO_4$, KCl, $MgCl_2$) the PEG is one of the most used components in the liquid phase in protein crystallization.[1,2,31] Hence, the second purpose of this paper is to collect data on the PEG systems to investigate the effect of this polymers on transport in multicomponent systems in which one of the components is a protein. This is the beginning of an extensive research project to characterize transport in protein systems with a polymeric precipitant, for protein crystal growth,[32] especially for diffusion modeling in microgravity conditions.[29,33,34]

Experimental Section

The experimental work was performed at the University of Naples and at the Texas Christian University, TCU.

Material. All compounds were purchased from Aldrich and used without further purification and are polydisperse. For PEG 200, the composition distribution was determined by high performance liquid chromatography. The results are in agreement with the values given by the supplier (see Figure 1) and with the predicted Poisson distribution.[35] The experimental analysis showed a larger amount of the tetramer, although all oligomers from 2 to 8 are detectable. The weight average molecular weight for PEG 200 is $M_w = 221.23$ g mol^{-1}, $M_n = 212.72$ g mol^{-1}, and $M_w/M_n = 1.04$. For PEG 2000 we accepted the data of the supplier (lot 06423HZ): $M_n = 1919$ g mol^{-1}, $M_w = 2034$ g mol^{-1}, and $M_w/M_n = 1.06$. In what follows, the M_w values have been used as molecular weight.

All solutions were prepared by mass using appropriate buoyancy corrections. Double distilled water was used in all cases.

Chromatography. The distribution function of the PEG 200 sample was determined by HPLC. PEG 200 derivatized with 3,5-dinitrobenzoyl chloride was used as suggested by Desbene et al.[36] The elution gradient technique was used with solvent A (99/1 v/v) = n-heptane/$(CH_2Cl_2$ + (2-propanol) (95/5 v/v)) and solvent B (50/50 v/v) = heptane/$(CH_2Cl_2$ + (2-propanol) (95/5 v/v)). The sample was injected on a 25×0.4 cm^2 column of Merck Lichrospher 100 Diol. The solvent feed rate was 1 cm^3 min^{-1}, and the sample was eluted with a gradient: B was increased from 0 to 100% during the first 50 min, then only B was fed for 15 min, and from 65 to 80 min B was decreased from 100 to 0%. The UV detector was set at 254 nm.[37]

The different oligomers were recognized by injecting standard monodisperse samples furnished from the Nikkol Chemical Co. and by observing proportionality between retention times and number of ethylene oxide adducts.

Table 1. Experimental Densities of the Binary Systems PEG 200 + Water and PEG 2000 + Water at 25 °C

m_2 mol kg^{-1}	d_2 kg dm^{-3}	C_2 mol dm^{-3}	ν_2 dm^3 kg^{-1}	m_2 mol kg^{-1}	d_2 kg dm^{-3}	C_2 mol dm^{-3}	ν_2 dm^3 kg^{-1}
			PEG 200 + Water				
0.013 56	0.997 469	0.013 49	0.8554	0.462 09	1.011 067	0.423 86	0.8514
0.041 13	0.998 386	0.040 69	0.8551	0.483 64	1.011 858	0.441 98	0.8512
0.051 44	0.998 891	0.050 80	0.8549	0.483 90	1.011 617	0.442 20	0.8512
0.058 78	0.998 913	0.057 96	0.8549	0.532 57	1.013 049	0.482 64	0.8510
0.076 86	0.999 487	0.075 54	0.8547	0.628 14	1.015 677	0.560 12	0.8505
0.102 02	1.000 435	0.099 80	0.8544	0.646 52	1.017 346	0.574 73	0.8504
0.110 86	1.000 583	0.108 27	0.8543	0.704 44	1.018 399	0.620 22	0.8501
0.122 06	1.000 778	0.118 97	0.8542	0.730 27	1.018 364	0.640 22	0.8500
0.148 31	1.001 692	0.143 85	0.8539	0.813 15	1.020 419	0.703 27	0.8497
0.149 07	1.001 737	0.144 56	0.8539	0.862 41	1.021 558	0.739 95	0.8496
0.153 23	1.001 942	0.148 48	0.8539	0.863 36	1.021 753	0.740 65	0.8496
0.200 91	1.003 419	0.193 01	0.8534	0.928 35	1.023 300	0.788 15	0.8494
0.204 41	1.003 405	0.196 24	0.8534	1.025 57	1.025 649	0.857 38	0.8492
0.208 33	1.002 913	0.199 87	0.8533	1.067 60	1.026 620	0.886 67	0.8491
0.240 92	1.004 274	0.229 77	0.8530	1.081 76	1.026 985	0.896 45	0.8491
0.252 89	1.005 033	0.240 67	0.8529	1.160 19	1.028 874	0.949 85	0.8490
0.254 43	1.004 985	0.242 07	0.8529	1.128 48	1.027 490	0.928 42	0.8490
0.270 31	1.005 634	0.256 45	0.8528	1.255 56	1.031 061	1.013 07	0.8489
0.303 57	1.006 442	0.286 30	0.8525	1.373 72	1.033 599	1.088 92	0.8488
0.310 09	1.006 679	0.292 11	0.8525	1.498 31	1.036 198	1.166 06	0.8487
0.365 86	1.008278	0.341 27	0.8520	1.616 34	1.038 639	1.236 59	0.8486
0.419 89	1.009 820	0.387 98	0.8516	1.618 83	1.038 676	1.238 05	0.8486
0.420 27	1.010 263	0.388 31	0.8516	1.644 11	1.037 884	1.252 83	0.8486
0.420 35	1.009 815	0.388 38	0.8516	1.831 66	1.042 806	1.359 28	0.8486
			PEG 2000 + Water				
0.015 48	1.002 016	0.015 04	0.8400	0.143 86	1.035 778	0.115 28	0.8475
0.020 81	1.003 735	0.020 04	0.8396	0.150 59	1.037 287	0.119 58	0.8487
0.024 64	1.005 006	0.023 58	0.8394	0.151 32	1.037 411	0.120 04	0.8489
0.028 36	1.005 961	0.026 97	0.8392	0.161 12	1.039 628	0.126 16	0.8509
0.045 34	1.010 966	0.041 97	0.8387	0.176 68	1.042 747	0.135 53	0.8544
0.045 43	1.010 998	0.042 04	0.8387	0.182 06	1.039 590	0.138 12	0.8557
0.052 96	1.013 117	0.048 44	0.8387	0.184 95	1.044 142	0.140 33	0.8564
0.043 78	1.010 528	0.040 62	0.8387	0.211 03	1.049 231	0.154 92	0.8636
0.064 05	1.016 412	0.057 60	0.8389	0.250 95	1.056 752	0.175 57	0.8767
0.070 02	1.015 682	0.062 25	0.8391	0.280 62	1.061 403	0.189 62	0.8880
0.077 54	1.018 005	0.068 19	0.8395	0.289 19	1.062 393	0.193 45	0.8915
0.084 35	1.021 848	0.073 57	0.8399	0.309 39	1.065 315	0.202 29	0.9002
0.097 97	1.025 219	0.083 75	0.8411	0.348 29	1.071 331	0.218 41	0.9186
0.098 73	1.025 574	0.084 32	0.8411	0.369 18	1.074 147	0.226 48	0.9292
0.119 13	1.030 189	0.098 79	0.8435	0.389 59	1.075 440	0.233 75	0.9402
0.128 55	1.032 313	0.105 20	0.8449	0.396 95	1.076 095	0.236 34	0.9443

Figure 1 shows the mole fraction of the different oligomers contained in the PEG 200.

Density. Density data were collected in Naples using a Paar Model 602 density meter that was regulated at 25.00 ± 0.01 °C with a digital thermometer System Tecnik Model AB S1220 as the temperature device. Density data were also collected at the TCU with a Mettler-Paar DMA40 density meter that was thermostated with water from a large, well-regulated (25.00 ± 0.01 °C) water bath. The density meter was connected to a computer for time averaging to give 2 ppm precision. The density meter calibrations were done with doubly distilled water ($d =$ 0.9970 44 kg dm^{-3}) and air whose density was calculated from ambient conditions corrected to 25 °C.

The densities of the PEG 200 and PEG 2000 aqueous solutions reported in Table 1 were interpolated with a polynomial whose coefficients were determined by the method of least squares

$$d/\text{g cm}^{-3} = 0.997\,044 + \sum_{j=1}^{n} a_j\, m/\text{mol kg}^{-1} \quad (5)$$

Here m_i is the PEG molality. Molar concentrations were obtained from the weight ratio using the densities computed from eq 5.

The partial specific volumes of PEG 200 and PEG 2000 were computed from density equations using the expression

$$\bar{v}_i = \frac{\left[d_i M_w - (1000 + m_i M_w)\left(\frac{\partial d_i}{\partial m_i}\right) \right]}{M_w d_i^2} \quad (6)$$

The limiting partial specific volumes at infinite dilution are 0.8556 and 0.8413 dm^3 kg^{-1} for PEG 200 and PEG 2000, respectively, in agreement with literature data.[38] Table 1 lists the results for the binary systems PEG 200 + water and PEG 2000 + water.

The densities of the top and bottom solutions (corresponding to the ternary free diffusion experiments) were measured for each set of ternary diffusion experiments with the same mean concentrations ($\bar{C}_1$, $\bar{C}_2$). The method of least squares was used to determine the values of $\bar{d}$, H_1, and H_2 in the following equation:

$$d = \bar{d} + H_1(C_1 - \bar{C}_1) + H_2(C_2 - \bar{C}_2) \quad (7)$$

The ternary density values are reported in Table 4. Table 5 lists $\bar{d}$, H_1, and H_2 for the mean compositions of all the sets of diffusion experiments.

Table 2. Relative Viscosities for the Binary Systems PEG 200 + Water and PEG 2000 + Water at 25 °C

C_2 mol dm^{-3}	η_2/η_0	C_2 mol dm^{-3}	η_1/η_0
PEG 200 + Water		**PEG 2000 + Water**	
0.052 71	1.0362	0.015 04	1.3081
0.051 93	1.0166	0.023 58	1.5272
0.098 30	1.0876	0.042 04	2.0440
0.147 22	1.1056	0.040 62	2.0661
0.193 06	1.1373	0.057 59	2.6680
0.241 10	1.1777	0.073 55	3.4338
0.242 98	1.1836	0.083 74	3.9544
0.341 27	1.2831	0.098 79	4.0163
0.387 98	1.3295	0.084 30	4.9272
0.423 86	1.3773	0.105 20	5.4109
0.480 10	1.4277	0.119 58	6.6292
0.601 91	1.5709	0.138 67	7.2890
0.857 38	1.9074	0.126 14	7.3219
0.896 45	1.9758	0.140 35	8.3163
0.949 85	2.0619	0.154 93	8.9101
1.013 07	2.1637	0.135 52	10.7357
1.136 99	2.3802	0.175 49	14.2903
1.170 16	2.4456	0.189 55	17.2510
1.238 05	2.6063	0.193 43	18.1164
1.359 28	2.8809	0.202 30	20.9130
		0.218 32	25.3449
		0.226 40	27.8211

Viscosity. Viscosity data were collected in Naples with an Ubbelhode viscometer, at (25.00 ± 0.01) °C, on solutions prepared by mass. The following equations gave the best fit based on the method of least squares:

$$\eta_1/\eta_0 = 1.000 + (3.23 \pm 0.40)C_1 - (1.97 \pm 0.53)C_1^2 + (2.56 \pm 0.17)C_1^3 \quad (8)$$

$$\eta_2/\eta_0 = 1.000 + (0.721 \pm 0.027)C_2 + (0.251 \pm 0.062)C_2^2 + (0.170 \pm 0.034)C_2^3 \quad (9)$$

The data are listed in Table 2.

Diffusion Measurements. Diffusion measurements were performed both in Naples and at TCU. The diffusion measurements corresponding to the binary systems PEG 2000 + water and PEG 200 + water (Table 3) and to the three compositions of the ternary system PEG 2000 + PEG 200 + water denoted by A2, B, and C (Tables 4 and 5) were performed in Naples. The measurements corresponding to the ternary composition A1 (Tables 4 and 5) were performed at TCU. The purpose was to compare the data obtained with the diffusiometer in Naples having an optical arm b = 193.38 cm with those obtained at TCU with the Gosting diffusiometer[39] with b = 308.885 cm. Both instruments were operated in the Gouy mode. The Gosting diffusiometer has better optics as well as the greater b

Table 4. Ternary Experimental Data at 25 °C Meausered at Texas Christian University (A1) and at University of Naples at Three Compositions (A2, B, C)

$\bar{C}_1 = 0.0827$ mol dm^{-3}; $\bar{C}_2 = 0.0762$ mol dm^{-3}				
	A1.a	A1.b	A1.c	A1.d
C_1/mol dm^{-3}	0.0827	0.0827	0.0827	0.0827
C_2/mol dm^{-3}	0.0760	0.0760	0.0760	0.7698
ΔC_1/mol dm^{-3}	0.00069	0.00305	0.00390	0.00163
ΔC_2/mol dm^{-3}	0.0284	0.0065	−0.0006	0.0238
d_{top}/kg dm^{-3}	1.026051	1.026079	1.026104	1.026266
d_{bot}/kg dm^{-3}	1.028407	1.028424	1.028417	1.028595
α_1	0.2007	0.8292	1.0153	0.4147
J_m	43.31	45.99	48.83	49.58
$10^5 D_A$/cm^2 s^{-1}	0.5140	0.2580	0.2203	0.3891
$10^4 Q_0$	−237.6	36.05	8.65	−56.5

$\bar{C}_1 = 0.0828$ mol dm^{-3}; $\bar{C}_2 = 0.0761$ mol dm^{-3}				
	A2.a	A2.b	A2.c	A2.d
C_1/mol dm^{-3}	0.0829	0.0828	0.0828	0.0828
C_2/mol dm^{-3}	0.0761	0.0761	0.0760	0.761
ΔC_1/mol dm^{-3}	0.00001	0.00340	0.00543	0.00679
ΔC_2/mol dm^{-3}	0.06984	0.03493	0.01399	0.00003
d_{top}/kg dm^{-3}	1.024970	1.025382	1.025393	1.025279
d_{bot}/kg dm^{-3}	1.025520	1.026715	1.026141	1.026492
α_1	0.00204	0.5013	0.8006	0.9997
J_m	73.39	73.39	73.59	73.56
$10^5 D_A$/cm^2 s^{-1}	0.6530	0.3581	0.2660	0.2216
$10^4 Q_0$	−473.2	−10.9	39.4	9.7

$\bar{C}_1 = 0.0832$ mol dm^{-3}; $\bar{C}_2 = 0.2293$ mol dm^{-3}					
	B.a	B.b	B.c	B.d	B.e
C_1/mol dm^{-3}	0.0832	0.0832	0.0832	0.0832	0.0832
C_2/mol dm^{-3}	0.2293	0.2294	0.2293	0.2293	0.2293
ΔC_1/mol dm^{-3}	0.00133	0.0054	0.00336	−0.00002	0.00676
ΔC_2/mol dm^{-3}	0.0561	0.0139	0.0350	0.0701	−0.0001
d_{top}/kg dm^{-3}	1.031369	1.031353	1.031385	1.031351	1.031207
d_{bot}/kg dm^{-3}	1.033705	1.033658	1.033648	1.033729	1.033687
α_1	0.1942	0.7963	0.4934	−0.00214	0.7963
J_m	73.53	72.36	73.08	74.13	72.35
$10^5 D_A$/cm^2 s^{-1}	0.4902	0.2618	0.3536	0.6368	0.2206
$10^4 Q_0$	−218.4	84.01	13.7	−485.1	86.8

$\bar{C}_1 = 0.0827$ mol dm^{-3}; $\bar{C}_2 = 0.0762$ mol dm^{-3}				
	C.a	C.b	C.c	C.d
C_1/mol dm^{-3}	0.0829	0.0829	0.0829	0.0829
C_2/mol dm^{-3}	0.4104	0.4106	0.4106	0.4105
ΔC_1/mol dm^{-3}	0.0000	0.0051	0.0013	0.0032
ΔC_2/mol dm^{-3}	0.0699	0.0138	0.0558	0.0350
d_{top}/kg dm^{-3}	1.039874	1.039863	1.039870	1.039878
d_{bot}/kg dm^{-3}	1.083916	1.083728	1.083720	1.083712
α_1	0.0000	0.7890	0.1873	0.4840
J_m	73.53	72.36	73.08	74.13
$10^5 D_A$/cm^2 s^{-1}	0.5959	0.2549	0.4816	0.335
$10^4 Q_0$	−454	131.1	−197.5	40.7

distance. The results obtained with the two diffusiometers were in good agreement, although the accuracy of the TCU apparatus is better by a factor of 1.5−2. The errors on the

Table 3. Binary Experimental and Derived Data for the Systems PEG 200 + Water and PEG 2000 + Water at 25 °C[a]

C_2 mol dm^{-3}	ΔC_2 mol dm^{-3}	J_m	$10^5 D_A$ cm^2 s^{-1}	$10^4 Q_0$	C_1 mol dm^{-3}	ΔC_1 mol dm^{-3}	J_m	$10^5 D_A$ cm^2 s^{-1}	$10^4 Q_0$
PEG 200 + Water					**PEG 2000 + Water**				
0.04452	0.0621	63.31	0.6221	27	0.00984	0.002 39	42.32	0.1910	7
0.08846	0.0610	63.08	0.6109	15	0.0235	0.006 94	73.41	0.2019	10
0.08852*	0.0484	58.97	0.6139	17	0.0452	0.006 47	68.67	0.2083	11
0.1701	0.0524	54.87	0.6000	23	0.0840*	0.008 01	50.63	0.2253	7
0.4151	0.0537	58.71	0.5686	13	0.1177	0.004 76	51.21	0.2365	6
0.5975	0.0455	47.49	0.5464	19	0.1728	0.006 47	71.06	0.2519	8
0.7216	0.0367	38.07	0.5343	17	0.2353	0.002 66	28.84	0.2447	7
0.9075	0.0417	45.31	0.5090	23					
1.4178	0.0506	50.68	0.4700	20					
2.1798	0.0746	77.50	0.3665	18					

[a] * denotes data collected at the Texas Christian University.

Table 5. Ternary Diffusion Data for the PEG 2000 (1) + PEG 200 (2) + Water System at 25 °C

	A1	A2	B	C
C_1/mol dm^{-3}	0.0827	0.0828	0.0832	0.0829
C_2/mol dm^{-3}	0.0762	0.0761	0.2293	0.4105
d/kg dm^{-3}	1.02700 ± 0.00004	1.02730 ± 0.00003	1.03400 ± 0.00005	1.04101 ± 0.00004
H_1/kg mol^{-1}	0.337 ± 0.008	0.335 ± 0.005	0.341 ± 0.004	0.340 ± 0.004
H_2/kg mol^{-1}	0.032 ± 0.001	0.0343 ± 0.0005	0.0336 ± 0.0005	0.0326 ± 0.0004
$\bar{V}_1$/cm^3 mol^{-1}	1703	1704	1697	1695
$\bar{V}_2$/cm^3 mol^{-1}	190	188	188	189
$\bar{V}_0$/cm^3 mol^{-1}	18.08	18.07	18.05	18.02
$10^3 R_1$/dm^3 mol^{-1}	12.384 ± 0.004	10.670 ± 0.004	10.545 ± 0.005	10.869 ± 0.007
$10^3 R_2$/dm^3 mol^{-1}	1.103 ± 0.005	0.948 ± 0.005	0.957 ± 0.005	1.062 ± 0.004
$10^5 D_{11}$/cm^2 s^{-1}	0.2201 ± 0.0014	0.2206 ± 0.0011	0.2046 ± 0.0007	0.1872 ± 0.0027
$10^5 D_{12}$/cm^2 s^{-1}	0.0141 ± 0.0003	0.0135 ± 0.0001	0.0136 ± 0.0001	0.0123 ± 0.0002
$10^5 D_{21}$/cm^2 s^{-1}	0.0671 ± 0.0085	0.0548 ± 0.0084	0.4041 ± 0.0139	0.6324 ± 0.0105
$10^5 D_{22}$/cm^2 s^{-1}	0.3316 ± 0.0021	0.3405 ± 0.0019	0.3256 ± 0.0020	0.3220 ± 0.0028
$\|D_{ij}\|$	0.0720	0.0744	0.0611	0.0525

diffusion coefficients of the binary systems are estimated to be some units per thousand.

Tiselius cells were used, and the boundary was formed by withdrawing solution at the center of the cell with a needle attached to a tube that goes through a peristaltic pump. The needle was always carefully withdrawn at the start of the experiment while very slowly withdrawing solution into the needle to prevent contamination by back-flow of solution from the needle. At TCU, the Gouy fringes were photographed on the Kodak IIG plates. Exposure times and widths of the light source slit were adjusted during the experiment in order to obtain pictures of each fringe pattern that were uniform in net exposure and easily read on an optical comparator. The fraction part of the fringe, the decimal value of the total number of fringes J_m, was obtained using the standard Gosting technique.[39] The fringe positions were read with a precision of 1 μm by using a Gaertner comparator.[40,41]

At Naples the Gouy fringes were scanned with a photo-diode mounted on stage driven by a stepping-motor and processed directly on a Fx II MacIntosh. Fringe position versus time was determined, and those data of both binary and ternary systems were analyzed by the PQ[42] program and the Albright[43] programs. For the ternary systems, the parameters D_A and Q_0 were extracted from fringe position data and the D_{ij} coefficients were computed according to the procedure described by Fujita and Gosting.[16] This classic procedure was used even if the components are polydisperse; in fact, their polydispersity is very mild and does not affect the interferometric analysis. A work in preparation in Sartorio's Lab will be devoted to the interferometric analysis of ternary systems containing very polydisperse solute, whose weight distribution function is a Schulz function.[23] The D_{ij} coefficients were also computed using the new procedure that simultaneously fit the fringe positions from the full set of experiments proposed by Miller.[44] The two procedures gave essentially the same results. Table 4 (A1, A2, B, C) shows the results of these interferometric measurements and includes the mean concentrations and the concentration increment across the boundary ΔC_i; the refractive index fraction, α_i; the fringe number, J_m; the measured volume-fixed diffusion coefficient D_A, and Q_0. Table 5 includes the mean concentrations of both solutes, the partial molar volume $\bar{V}_i$ of the i-th solute, the refractive index increment $R_i = (\partial n/\partial C_i)$, and the experimental diffusion coefficients relative to the volume-fixed frame of reference.[6] R_i values, corresponding to the two instruments, are different because of a different wavelength of the light source.

Table 6. Results of the Fitting of Eqs 2−4 to the Experimental Viscosity[a]

sample	[η]	K_H	K_M	C_m/mol dm^{-3}
PEG 200	0.672 ± 0.007	1.29 ± 0.06	0.79 ± 0.03	4.6 ± 0.1
PEG 2000	17.9 ± 0.3	1.3 ± 0.2	0.46 ± 0.01	0.463 ± 0.008

[a] The [η] value was reported from the eq 4 fitting.

Results and Discussion

Binary Systems PEG 200 (2) + H$_2$O (0) and PEG 2000 (1) + H$_2$O (0). Viscosity. The relative viscosity, η_r, for solutions of the two binary systems, is shown in Table 2. The η_r dependence on concentration can be described, in dilute solution, by the Einstein equation for hard spheres:[3]

$$\eta_r = 1 + 2.5\phi \qquad (10)$$

where ϕ is the solute volume fraction. This equation can be used only at high dilution for the PEG 200 and very high dilution for the PEG 2000 solutions. For moderately concentrated polymer solutions the Huggins equation

$$\eta_{sp}/C = [\eta] + K_H[\eta]^2 C \qquad (11)$$

or the Martin equation

$$\ln(\eta_{sp}/C) = \ln[\eta] + K_M[\eta]C \qquad (12)$$

gives a better functional description.[45] Equation 11 is the same functional expression of the Lee−Teja equation useful for the concentration and temperature dependence.[46] In eqs 10 and 11, [η] is the intrinsic viscosity, K_H and K_M are the Huggins and Martin coefficients, and $\eta_{sp} = \eta_r - 1$ represents the specific viscosity. The Fedors equation[47]

$$[\eta] = 2(\eta_r^{1/2} - 1)(1/C - 1/C_m) \qquad (13)$$

gives the best fit of our data over the whole concentration range. The parameter C_m represents the maximum concentration to which particles can pack. The parameters of the previous equations are reported in Table 6. The volume fraction corresponding to C_m is near unity for both PEG 200 and PEG 2000, but the K_H is far from 0.25, as expected for good solvents in such conditions.[47]

In a previous paper, some of us calculated the PEG diffusion coefficients at infinite dilution at 25 °C[24] using the Flory scaling law

$$D_i^\infty = (10.6 \pm 0.3)M_{w,i}^{-(0.527\pm0.006)} \text{ cm}^2\text{ s}^{-1} \qquad (14)$$

The Flory exponent γ, obtained by the exponent rule[48]

$$a_\eta = -(1 - 3\gamma) \tag{15}$$

is in good agreement with the Mark–Hawink coefficient, a_η, from the literature.[49-51] The intrinsic viscosities, evaluated from our PEG 200 and PEG 2000 viscosity data, give an average molecular weight respectively of 260 and 2414 g mol^{-1}. These values are larger than the numerical average molecular weights (213 ± 10) and (1919 ± 100) g mol^{-1}, respectively, and hence larger than the Gouy average weights, proved lower than the numerical average $(145 \pm 25$ and 1874 ± 250 g mol$^{-1})$.[23]

Diffusion. The diffusion coefficients of the binary systems PEG 200 + water and PEG 2000 + water are shown in Table 3. Their concentration dependences are quite different. Diffusion coefficients of PEG 200 decrease as concentration increases, whereas for PEG 2000 they increase.

Nevertheless, the viscosity for the PEG 2000 + water system has an increasing trend as a function of the concentration, and this increase is larger than that for the PEG 200 + water system at the same net mass of solute increase (see Table 3). Therefore, the experimental D trends are in contrast with the usual case where an increase of viscosity leads to a decrease of the solute diffusion coefficients. This behavior suggests a diffusion mechanism that involves the length of PEG in a complex way.[24]

The decreasing trend of D as a function of concentration for PEG 200 was also found for other low molecular weight PEG solutes.[52] This is the expected case where an increase of the viscosity leads to a decrease of the diffusion coefficient.

The increase of the diffusion coefficient for PEG 2000 as its concentration increases can be attributed to the concentration dependence of the thermodynamic driving force, perhaps coupled with a change in the effective spherical radius of the polymer. For higher molecular weight PEG polymers, the increase of the thermodynamic driving force for solute diffusion overcomes the slowing effect of increased viscosity.

For a better understanding of the above argument it is useful to rewrite eq 4 for binary systems as follows[53]

$$D = \frac{RTL}{C}\left(1 + C\frac{\partial \ln \gamma}{\partial C}\right) = \frac{RTL}{C}B \tag{16}$$

where C is the solute concentration, γ is the activity coefficient of the solute in the molar concentration scale, L/C is the mobility, and B is the thermodynamic term, that arises by assuming that the chemical potential gradient is the driving force for diffusion. The values of the diffusion coefficient are affected by both the mobility and thermodynamic factor behavior.[24,52,54]

For PEG 200 the mobility decrease overcomes the increase of B as the concentration is raised and this leads to the decrease of the diffusion coefficient. For PEG 2000, B increases sufficiently to overcome a decreased mobility to cause an increase of the diffusion coefficients.[24]

Consideration of the Flory–Huggins equations for entropy of mixing of a solvent with large random coil polymers indicates that in this case chemical potential is related to volume fraction, and this leads to a greater driving force for diffusion for longer polymers.

The general conclusions reported above are analyzed in detail, in ref 24, for several mild polydisperse PEG samples including the two here reported. To avoid unnecessary repetition, ref 24 should be read in conjunction with the present paper.

Ternary System PEG 2000 (1) + PEG 200 (2) + H$_2$O (0). Interpretation of Size and Sign of Diffusion Coefficients of Solutes in Liquid Mixtures. A. Basic Effects That Influence the Size and Sign of Diffusion Coefficients. The following list should not be viewed as rigorous or complete. It is for nonelectrolyte systems, and these effects may have some overlap. However, the list does itemize many of the important concepts. The two main categories, dragging effects and chemical potential effects, come from the description of transport of a component as being due to the product of thermodynamic transport coefficients and chemical potential driving (see eq 4). The list does not include effects attributable to charges on ions or charge sites on molecules whose net charge is zero.

(1) Dragging Effects. (a) Direct Frictional Interaction. Now we consider direct contact "friction" between two molecules that mutually affects their motion. This would be in the category of a frictional effect that appears (mostly) in the magnitude of the thermodynamic transport coefficients. This is the effect that impedes intradiffusion. This would be a consequence of weak interactions between solute molecules that cause mutual dragging and thus a positive correlation of motion. If the dragging effect between the two types of solute molecules is greater than that between solute and solvent molecules, the dragging effect will tend to contribute to positive cross-term diffusion coefficients.

(2) Chemical Potential Effects. (a) Salting-in Effect. Short-range attractive interactions between solutes cause salting-in. This argument of attractive interaction implies a greater interaction between solute component molecules than between a solute molecule and the solvent. This effect includes a chemical equilibrium process leading to formation of a complex.[55] Salting-in lowers the chemical potential. If large enough, this effect generally leads to negative cross-term diffusion coefficients.[55,7] This will be the case when the diffusivity of the complex is lower than that of either of the species that form it.[56]

(b) Salting-out Effect. Repulsive forces between the solutes are associated with the concept of salting-out. Salting-out increases the chemical potentials of the solutes. This effect will contribute to positive cross-term diffusion coefficients.[7,57]

(c) Excluded Volume Effect. The excluded volume effect may be categorized as a salting-out effect, but because of its importance we treat it separately. The most inclusive definition of excluded volume is the impossibility that any part of two rigid bodies will occupy the same volume in the solution at the same time. In this definition, the excluded volume is the effective volume of a solution that, strictly for steric reasons, is not available to particles of species i as the result of the introduction of one particle of the species j.[58] In this definition the position of i will be defined as a point located within i and the volume excluded to i must include the geometry of i as well. For this article we consider the specific case where the molecular size of one of the components (e.g. a large polymer) is much greater than the molecular size of the other components in the system. In this limit the excluded volume due the large component, in dilute solutions, is practically equal to the volume fraction of the large molecule and the geometry of a smaller component i can be ignored with respect to interaction of the small molecule with the large molecule. An implication is that an interstitial solution of mixtures of small solvent and solute molecules between the

large molecules will have much the same properties of the mixture by itself at the same concentration of the interstitial solution.

In a ternary solution, the concentration gradient of the larger molecule component will cause an effective gradient of the smaller molecule component in the interstitial solution when at the same time the stoichiometric concentration of the smaller molecule component is uniform. From eq 2 we can see that for this case the flow of the smaller molecule component is due to the concentration gradient of the larger molecule component times the corresponding cross-term diffusion coefficient. This cross-term diffusion coefficient will be positive and increases in proportion to the concentration of the smaller molecule component.

(d) Large Molecule Concentration Effect. By this effect we mean the nonlinear concentration dependence of the activity coefficients for the large molecules, due to crowding. This may be approximated by the Percus–Yevick equation[59] for hard spheres in continuum. This is a thermodynamic effect that depends on the concentration of the large molecule component but does not directly use attractive or repulsive forces between molecules except for hard sphere collision. However, this has the same general effect of a repulsive force between molecules of the large molecule component.

(e) Mixing of pPolymer Effect. The Flory–Huggins equation for entropy of mixing of polymers with solvent is another thermodynamic effect that may be viewed separately.[60] Application of this combinatorial effect shows chemical potential to be related to volume fraction for polymers.

B. Application of These Effects for Interpretation of the Results Presented Here. The experimental cross-term diffusion coefficient values, reported in Table 5 and drawn in Figure 2 as a function of the PEG 200 molar concentration, are always positive and therefore can be due only to the dragging effect 1a or to the chemical potential effects 2b, 2c, 2d, and 2e. However, these effects do not equally contribute to determine the values of the two cross-term diffusion coefficients. In fact, they are very different in magnitude. D_{21} is quite large and increases linearly with the concentration of PEG 200, while D_{12} is small and decreases in the whole range of concentration explored with PEG 200.

At the highest concentration explored ($C_2 \cong 0.4$ mol dm^{-3}), D_{21} is larger than both main-term diffusion coefficients and specifically about 2 times the D_{22}. At this concentration the ratio D_{21}/D_{11} is about 3; thus, diffusion of each PEG 2000 molecule is accompanied by a flux of three PEG 200 molecules in the absence of a PEG 200 concentration gradient. On the other hand, the ratio D_{12}/D_{22} is about 1/26, which means only one molecule of PEG 2000 will accompany 26 molecules of PEG 200 when there is only a concentration gradient of PEG 200.

Interpretation of the diffusion coefficients follows from the list of effects given above. The large D_{21} values could be due to a prevalent contribution of the excluded volume effect, 2c, and this is compatible with the relative sizes of PEG 2000 and PEG 200. In fact, effect 2e is low, because we are changing the PEG 200 concentration and not the PEG 2000's one, and the other effects are probably not large enough to account for the magnitudes of these cross-diffusion coefficients. The dominant thermodynamic term for D_{21} from eq 4 will be $L_{22}(\partial\mu_2/\partial C_1)$. Here L_{22} relates directly to the main-term diffusion coefficient for PEG200 and $(\partial\mu_2/\partial C_1)$ is formally the salting-out term which can be estimated as an excluded volume effect.
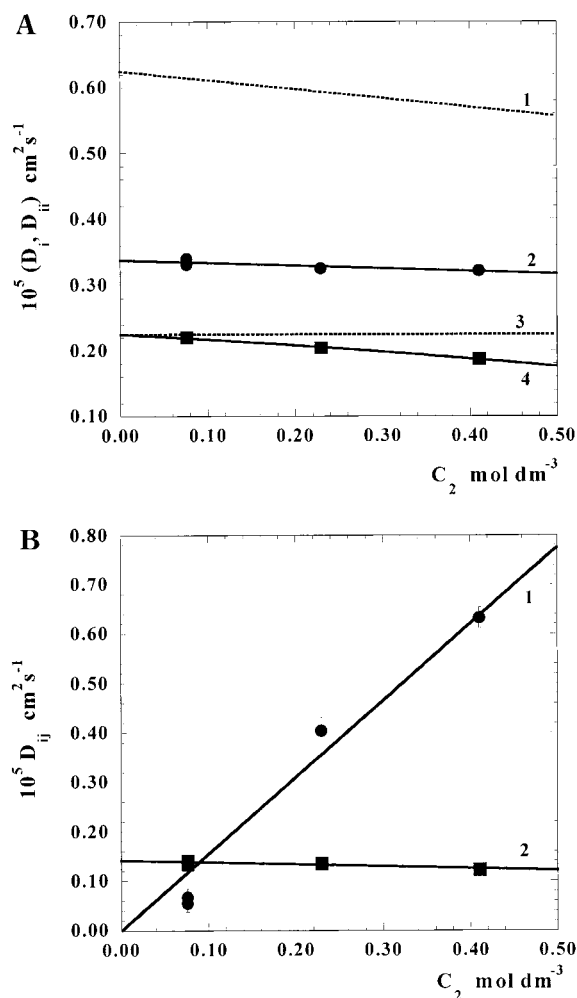

Figure 2. Ternary diffusion coefficients of the PEG 2000 + PEG 200 + water system at 25 °C. (A) Comparison between D_{ii} and the corresponding D_i: D_2, curve 1; D_{22}, curve 2; D_1, curve 3; D_{11}, curve 4. (B) Cross-term diffusion coefficients. The D_{12} value is multiplied by 10.

For D_{12} an excluded volume effect should not be taken into account, and its value mostly relates to effects 1a and 2b, even if 2d and 2e are probably not negligible. The expression for D_{12} from eq 4 is $L_{11}(\partial\mu_1/\partial C_2) + L_{12}(\partial\mu_2/\partial C_2)$. The thermodynamic factor $(\partial\mu_1/\partial C_2)$ is again a salting-out term. This term cannot be calculated using the excluded volume argument. L_{11} will relate strongly to D_{11}. The L_{12} coefficient could be negative, but it is likely to be small because the components are nonelectrolytes.

The excluded volume effect also contributes to large values of D_{21} for a mixture of the protein lysozyme (component 1) and the salt components (2) NaCl,[9,26,61] NH₄-Cl,[62] KCl, MgCl₂, and CaCl₂.[63] In these cases the ratio D_{21}/D_{22} is nearly the same for each type of salt at the same salt concentration and it linearly depends on the concentration of the salt. Also, this quotient is insensitive to the concentration of the protein. This behavior also applies to the case of lysozyme chloride and PEG 400 (2), where cross-term coefficients are not affected by long-range electrostatic forces.[64] These facts show clearly that an excluded volume effect is also the proper interpretation in these cases.

In the past many researchers have studied transport properties of polyelectrolytes in the presence of simple electrolytes or another polyelectrolyte[65,66] and have found large coupled flows of the lighter with the heavier molecule.[67,68] The author's prediction[68] of the cross-term dif-

fusion coefficients on the basis of electrostatic solute–solute interactions leads to estimated values somewhat smaller than the experimental ones, and the differences seem to increase with the concentration of the solutes in solution. The authors suggest that, even in these systems, besides the electrostatic effects and the other effects, there is the excluded volume effect, which makes a major contribution.

The main-term diffusion coefficients, D_{11} and D_{22}, are drawn with the corresponding binary coefficients D_1 and D_2 in Figure 2a as a function of PEG 200 concentration, C_2. They are both smaller than the corresponding binary diffusion coefficients and both decrease as the PEG 200 molar concentration increases. The difference between D_2 and D_{22} is quite large, about 0.3×10^{-5} cm^2 s^{-1}, and reflects the obstruction effect of PEG 2000 to the motion of PEG 200 molecules. The D_{11} values are close to the corresponding D_1 value considered at the same constant PEG 2000 concentration. The largest difference, observed at the highest explored PEG 200 concentration, is about 0.04×10^{-5} cm^2 s^{-1}. This is due to the small obstruction effect of the PEG 200 molecule on the motion of the bigger PEG 2000 molecule. The D_{11} concentration trend depends on the increasing PEG 200 obstruction effect at increasing number of PEG 200 molecules in solution.

Finally, we point out that even though a salting out effect could formally be invoked to rationalize the diffusion coefficients, all the solutions we used have been prepared as transparent solutions with a short time of dissolution. In fact, even if the molecular radius ratio of the two polymers is in the range of possible flocculation,[69,70] the compositions of the present study are far from these conditions. Furthermore, the determinant of the diffusion coefficients is always large and this ensures that the experimental conditions are far from the spinodal curve where the value of the determinant must vanish (see Table 5).[57,71]

Conclusion

We have studied the hydrodynamic and thermodynamic effects on the correlation of motion in multicomponent systems. We argue that for the PEG 2000 (1) + PEG 200 (2) + H$_2$O systems an excluded volume effect is the main contributor to the size of the D_{21} cross-term diffusion coefficients. This paper has shown that even for systems containing nonionic components the cross-term diffusion coefficients can be large even at moderate concentration when the excluded volume effect is dominant. This is a first step for describing polydisperse samples through a multicomponent approach, including main-term and cross-term diffusion coefficients.

A comparative analysis of chromatography, viscosity, and Gouy interferometry confirms the different average molecular weights provided by these different techniques for polydisperse samples.

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