

Multicomponent Diffusion in Systems Containing Molecules of Different Size. 4. Mutual Diffusion in the Ternary System Tetra(ethylene glycol)–Di(ethylene glycol)–Water

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The effect of the molecular volume on the diffusion coefficients has been investigated for ternary systems. Mutual diffusion coefficients, D_{ij} , for the ternary system tetra(ethylene glycol)–di(ethylene glycol)–water at eight mean compositions were measured by Gouy interferometry at 25 °C. The data show the effect of the total concentration on the main- and cross-term diffusion coefficient values. We used these data to check, at high concentration, the predictive values of our recent semiempirical equations for nonelectrolyte solutions. The differences between the experimental and predicted diffusion coefficients found at the higher concentrations are discussed in terms of solute–solute nonbonding interactions.

Introduction

In an n -component system, the diffusion transport is described by the phenomenological linear nonequilibrium thermodynamic equation

$$J_i = - \sum_{j=1}^{n-1} (L_{ij})_0 \left(\frac{\partial \mu_j}{\partial x} \right) \quad i = 1, 2, \dots, n-1 \quad (1)$$

where J_i is the flux of component i , μ_i is its chemical potential, x is the one-dimensional axis for the one-dimensional diffusion, and $(L_{ij})_0$ are the thermodynamic diffusion coefficients on the solvent frame of reference. Because of the difficulty in determining experimentally the $\nabla \mu_i$ values, from an experimental point of view, the flow of each component may also be described by a general form of Fick's 1st law

$$J_i = - \sum_{j=1}^{n-1} (D_{ij})_V \left(\frac{\partial C_j}{\partial x} \right) \quad i = 1, 2, \dots, n-1 \quad (2)$$

where C_i is the molar concentration of component i and $(D_{ij})_V$ are the diffusion coefficients in the volume fixed reference frame. From $(D_{ij})_V$ and the knowledge of the partial molar volumes of the components in solution, it is possible to obtain $(D_{ij})_0$. The relation between the diffusion coefficients, $(D_{ij})_0$, and the thermodynamic transport coefficients, $(L_{ij})_0$, may be written as

$$(D_{ij})_0 = \sum_{k=1}^{n-1} (L_{ik})_0 \left(\frac{\partial \mu_k}{\partial C_i} \right) \quad k = 1, 2, \dots, n-1 \quad (3)$$

For binary systems eq 3 reduces to

$$D_i = L_i \frac{RT}{C_i} \left(1 + C_i \frac{\partial \ln \gamma_i}{\partial C_i} \right) = M_i \left(1 + C_i \frac{\partial \ln \gamma_i}{\partial C_i} \right) \quad (4)$$

where γ_i is the activity coefficient in the molarity scale, the term in parentheses is denoted as the "thermodynamic factor",

and M_i is denoted as "mobility". Then the experimental diffusion coefficients depend on two factors that are in some way related: a factor that accounts for the variation of the chemical potential of component i on its concentration and the factor M_i , which is strictly related to the motion of the particles in solution. All of the diffusion coefficients mentioned in the following discussion will be for the volume fixed frame of reference.

Depending on the nature of solute–solute interactions in solutions, these two factors have a different effect in determining the experimental diffusion coefficient values. Weak nonbonding or strong solute–solute interactions,^{1,2} salting-in or salting-out^{3–6} effects, and excluded-volume effects^{7–10} can contribute in different ways to the diffusion coefficient values.

The excluded-volume contribution can assume a significant role in a system where large-volume solutes are present and when the solute–solute interactions are weak. This is the case of nonelectrolyte solutions at moderate concentration and of solutions of synthetic or natural macromolecules.^{11,12} The effect of the volume contribution on the diffusion coefficient values has been extensively studied for binary systems from a theoretical point of view.^{13–21} For a single hard-sphere of radius σ_i diffusing in a solvent of viscosity η^0 in the limit of infinite dilution, the well-known Stokes–Einstein equation holds:

$$D_i^\infty \equiv M_i^\infty = \frac{kT}{\alpha \pi \sigma_i \eta^0} \quad (5)$$

where α is a parameter depending on the relative sizes of the solute and solvent.²² For the dependence of the diffusion coefficient on the concentration, Carter and Phillies proposed the following equation:²¹

$$D_i = D_i^\infty (1 - 0.898\phi_i - 19.01\phi_i^2 - 70\phi_i^3) \quad (6)$$

where ϕ_i is the volume fraction of the solute in solution. This equation takes into account the variations of both the thermodynamic factor and the mobility of the diffusing particles as the solute volume fraction increases. In particular, for noninteracting hard-sphere solutions, the thermodynamic factor increases while the mobility decreases at increasing solute concentration. This last variation is predominant, and a general

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decrease of the diffusion coefficients is then predicted by eq 6. The increasing trends often experimentally observed in polymeric systems must be ascribed to a larger increase, than that predicted for a hard-sphere system, of the thermodynamic factor on the concentration.^{23–26} The corresponding equation for the viscosity of a binary system of hard spheres at finite concentration is the well-known Einstein relation²⁷

$$\eta_i = \eta^0(1 + 2.5\phi_i) \quad (7)$$

Unfortunately, no extension of eqs 6 and 7 to multicomponent systems is present in the literature.

Recently we proposed very simple semiempirical equations to predict the four diffusion coefficients of ternary systems of weakly interacting nonelectrolytic solutes.⁷ We tried to correlate the main diffusion coefficients to the limiting diffusion coefficient of the corresponding binary system and to the “effective” volume of diffusing particles, V_i . This value can be obtained by fitting the following linear equation to the binary experimental diffusion data in dilute solution:

$$D_i = D_i^\infty(1 - 0.898\phi_i) \quad (8)$$

considering $\phi_i = C_i V_i$, where C_i is the molar concentration and V_i is expressed in $\text{dm}^3 \text{mol}^{-1}$.

In a dilute ternary solution of weakly interacting particles, we can reasonably assume that the difference between D_i and D_{ii} is simply ascribed to a decrease of the mobility of component i because of the increase in the crowding of the solution by adding solute j . Another transport property that accounts for the increase of the solute volume fraction is the solution viscosity (see eq 7). Then it is reasonable to try to correlate the D_i and D_{ii} values using the viscosities of the corresponding systems. We have then proposed the following semiempirical relation to predict the ternary main diffusion coefficients by the corresponding binary ones:

$$D_{ii} = D_i \frac{\eta_i}{\eta_{ij}} \quad (9)$$

where η_i and η_{ij} are the relative viscosities of the binary and ternary systems at the same concentration of component i . We have also proposed the following equation for the viscosity of a ternary system with noninteracting solutes:

$$\eta_{ij} = \eta^0[1 + 2.5(\phi_i + \phi_j)] \quad (10)$$

The main diffusion coefficient can finally be written as

$$D_{ii} = D_i^\infty(1 - 0.898\phi_i) \frac{1 + 2.5\phi_i}{1 + 2.5(\phi_i + \phi_j)} \quad (11)$$

This relation permits the calculation of the value of the main terms by the concentration dependence of the diffusion coefficients of the corresponding binaries. This equation can be approximated by

$$D_{ii} = D_i^\infty(1 - 0.898\phi_i - 2.5\phi_j) \quad (12)$$

For the cross-terms, we proposed a very simple relation based on the difference between the stoichiometric and the effective concentrations of the solutes in solution. Because of the nonzero volume of the solute j in solution, even in the absence of a stoichiometric concentration gradient of component i , a concentration gradient of component j , ∇C_j , will produce a

correlated effective concentration gradient of component i , ∇C_i^* , given by the relation

$$\frac{\nabla C_i^*}{\nabla C_j} = \frac{C_i \phi_j}{C_j(1 - \phi_j)^2} \quad (13)$$

The flux of component i under the concentration gradient of component j , ∇C_j , described by the diffusion coefficient D_{ij} , is then assumed to be equivalent to the flux of i produced by its own effective concentration gradient ∇C_i^* . Because the diffusion of a component under its own concentration gradient is described by the corresponding main diffusion coefficient, we can use the relation

$$D_{ii} \nabla C_i^* = D_{ij} \nabla C_j \quad (14)$$

to obtain

$$D_{ij} = D_{ii} \frac{C_i \phi_j}{C_j(1 - \phi_j)^2} = D_{ii} \frac{C_i V_j}{(1 - C_j V_j)^2} \quad (15)$$

Equations 11 and 15 now permit the calculation of the main- and cross-term diffusion coefficients only from the knowledge of the dependence of the corresponding two binary diffusion coefficients on the concentration.

The agreement between the experimental and predicted values was tested on three different ternary systems containing oligomer of poly(ethylene glycol) (PEG*i*, with i being the polymerization degree): PEG5(5)–PEG3(3)–H₂O at five compositions with a total molar concentration equal to $C_t = C_5 + C_3 = 0.3000 \text{ mol dm}^{-3}$,⁷ PEG4(4)–PEG2(2)–H₂O at four compositions with a total molar concentration equal to $C_t = C_4 + C_2 = 0.4500 \text{ mol dm}^{-3}$,⁸ and PEG6(6)–PEG2(2)–H₂O at four compositions with a total molar concentration equal to $C_t = C_6 + C_2 = 0.3000 \text{ mol dm}^{-3}$.¹⁰

PEG is a class of chemicals that are of considerable interest from theoretical and technological points of view. Because of its geometrical structure, PEG is largely soluble in water.^{28,29} Because of the good PEG–water interactions, only weak nonbonding solute–solute interactions are present in these solutions. These interactions can then be neglected in dilute solutions. Hence, mixtures of PEG oligomers at low total concentrations are then a good test for eqs 11 and 15. The agreement between the experimental, $(D_{ij})_{\text{exp}}$, and the predicted, $(D_{ij})_{\text{calc}}$, diffusion coefficients is good for the systems that have been examined.

An excluded-volume effect was also recognized as an important factor for predicting the concentration dependence of the D_{ij} values for the system lysozyme–NaCl–H₂O.^{8,11,12} In this system, because of the electrolytic nature of both of the components, the volume effect adds to other chemical potential effects in the determination of the diffusion coefficients. Actually, because of the low concentration of the protein and its large effective volume, only the main- and cross-term diffusion coefficients of NaCl are significantly affected by the excluded-volume effect. Equations 11 and 15 when applied to the lysozyme–sodium chloride–water system worked well for the prediction of the concentration dependence of the cross-term diffusion coefficient for the flow of the salt because of a gradient of the protein and worked well for predicting the main-term coefficient for the salt itself.⁸

In the present paper, we want to test the accuracy of eqs 11 and 15 in estimating the diffusion coefficients up to moderately high concentrated solutions. At increasing total solute concen-

TABLE 1: Density Parameters, Eqs 17 and 18, for the Ternary System PEG4(4)–PEG2(2)–H₂O

C_4 , mol dm ⁻³	C_2 , mol dm ⁻³	d , g cm ⁻³	H_4 , 1000 g mol ⁻¹	H_2 , 1000 g mol ⁻¹
0.132 92	0.666 99	1.010 505 ± 0.000 011	0.0291 ± 0.0005	0.0147 ± 0.0003
0.265 95	0.534 07	1.012 442 ± 0.000 004	0.0293 ± 0.0002	0.0147 ± 0.0001
0.534 10	0.265 97	1.016 361 ± 0.000 004	0.0295 ± 0.0001	0.0146 ± 0.0001
0.667 33	0.133 06	1.018 336 ± 0.000 002	0.0297 ± 0.0001	0.0148 ± 0.0001
0.120 00	1.079 95	1.016 196 ± 0.000 004	0.0299 ± 0.0005	0.0149 ± 0.0002
0.300 03	0.900 07	1.018 890 ± 0.000 001	0.0296 ± 0.0001	0.0147 ± 0.0001
0.899 99	0.300 00	1.027 714 ± 0.000 005	0.0294 ± 0.0002	0.0148 ± 0.0001
1.079 99	0.120 02	1.030 355 ± 0.000 008	0.0293 ± 0.0003	0.0150 ± 0.0004

trations, the number of solute–solute nonbonding interactions increases, and this effect can become important in determining the experimental values of the diffusion coefficients.

We present here the diffusion coefficients of the ternary system PEG4(4)–PEG2(2)–H₂O(0) at eight compositions. Four compositions are at $C_t = C_4 + C_2 = 0.8000$ mol dm⁻³ and four at $C_t = C_4 + C_2 = 1.2000$ mol dm⁻³.

As done for the data at $C_t = C_4 + C_2 = 0.4500$ mol dm⁻³, the data have been analyzed as a function of the parameter β_4 :

$$\beta_4 = \frac{\bar{C}_4}{\bar{C}_4 + \bar{C}_2} \quad (16)$$

which represents the fraction of PEG4 with respect to the total solute concentration. The diffusion and viscosity data of the systems PEG4(4)–H₂O(0) and PEG2(2)–H₂O(0) have been analyzed using eqs 8 and 7, respectively, where the deviation from hard-sphere theory is also applied to the binary systems.

Experimental Section

Chemicals. Tetra(ethylene glycol) (PEG4), purity 99% and molecular weight (MW) = 194.23 g mol⁻¹, and di(ethylene glycol) (PEG2), purity 99% and MW = 106.12 g mol⁻¹, were purchased from Aldrich and used without further purification.

Solution Preparation. The solutions for diffusion, density, and viscosity measurements were prepared by weight with double-distilled water, MW = 18.016 g mol⁻¹, using a Mettler balance, model AT 400.

Density Measurements. The densities of all solutions were measured in order to calculate the molar concentration of all solutions from their values of molality. The density measurements have been performed at 25.00 ± 0.01 °C using an Anton PAAR densimeter, model 602. The instrument was calibrated with double-distilled water and with air, whose density was based on the ambient humidity and pressure, where the humidity was corrected to 25.00 °C. The following linear expression has been fitted to the density data of the solution at each mean concentration that were prepared for the diffusion experiments:

$$d(C_4, C_2) = d(\bar{C}_4, \bar{C}_2) + H_4(C_4 - \bar{C}_4) + H_2(C_2 - \bar{C}_2) \quad (17)$$

where \bar{C}_i is the mean concentration of component i and H_i is defined by the relation

$$H_i = \left(\frac{\partial d}{\partial C_i} \right)_{C_j} \quad (18)$$

The values of $d(\bar{C}_4, \bar{C}_2)$, H_4 , and H_2 for the examined compositions are reported in Table 1.

Viscosity Measurements. The viscosity measurements on the binary systems PEG4–H₂O and PEG2–H₂O, as function of the concentration, have been performed at 25.00 ± 0.01 °C,

TABLE 2: Relative Viscosities of the Binary Systems PEG4(4)–H₂O(0) and PEG2(2)–H₂O

system PEG2(2)–H ₂ O		system PEG4(4)–H ₂ O	
C_2 , mol dm ⁻³	$\eta_{2,rel}$	C_4 , mol dm ⁻³	$\eta_{4,rel}$
0.0000	1.000	0.0000	1.000
0.0449	1.013	0.0494	1.031
0.0988	1.029	0.1039	1.066
0.1958	1.058	0.2586	1.172
0.2911	1.088	0.5212	1.377
0.5671	1.181	0.8558	1.719
0.7432	1.244	1.6131	2.926
0.8290	1.275		
1.6029	1.611		
2.8105	2.332		

TABLE 3: System PEG4(4)–PEG2(2)–H₂O^a

ΔC_4 , mol dm ⁻³	ΔC_2 , mol dm ⁻³	J	$D_A \times 10^5$, cm ² s ⁻¹	$Q_0 \times 10^4$	α_4
$C_4 = 0.132\ 92$ mol dm ⁻³ ; $C_2 = 0.666\ 99$ mol dm ⁻³					
-0.000 88	0.073 00	31.60	0.8010	-9.95	-0.025 37
0.013 71	0.115 04	64.92	0.7473	7.67	0.196 52
0.029 19	0.084 16	65.11	0.6980	18.40	0.415 83
0.077 78	0.000 01	71.97	0.5834	12.34	1.000 06
$C_4 = 0.265\ 5$ mol dm ⁻³ ; $C_2 = 0.534\ 07$ mol dm ⁻³					
0.000 18	0.155 92	71.12	0.7866	-11.22	0.002 29
0.015 73	0.124 87	71.84	0.7380	5.19	0.212 35
0.062 34	0.031 34	70.73	0.6115	13.01	0.798 18
0.077 89	0.000 20	71.02	0.5766	8.57	0.998 71
$C_4 = 0.534\ 10$ mol dm ⁻³ ; $C_2 = 0.265\ 97$ mol dm ⁻³					
0.000 57	0.155 83	70.87	0.7760	-33.46	0.007 49
0.016 10	0.124 70	71.22	0.7200	-15.38	0.210 29
0.062 70	0.031 36	72.35	0.6030	5.50	0.804 83
0.078 24	0.000 20	73.00	0.5772	6.08	0.998 76
$C_4 = 0.667\ 33$ mol dm ⁻³ ; $C_2 = 0.133\ 06$ mol dm ⁻³					
0.001 18	0.155 79	72.55	0.7727	-38.21	0.015 15
0.016 55	0.124 66	72.52	0.7180	-19.94	0.212 35
0.062 62	0.031 19	72.22	0.5921	6.62	0.803 03
0.078 00	0.000 05	72.87	0.5557	4.71	0.999 68

^a Interferometric data for the experiments at $C_t = 0.8000$ mol dm⁻³. ΔC_i : concentration difference of component i across the initial diffusion boundary. J : total number of Gouy interference fringes. D_A : apparent diffusion coefficient (ref 24). Q_0 : "area under the deviation function" (ref 24). α_4 : refractive index fraction of PEG4.

using an Ubbelohde viscometer and double-distilled water as the reference liquid. The experimental data are reported in Table 2.

Diffusion Measurements and Data Analysis. The diffusion experiments have been performed with the Gouy diffusimeter³⁰ located at the Chemistry Department of the University "Federico II" of Naples. A description of this apparatus and the usual procedure of running are reported elsewhere.³¹ The interferometric data have been analyzed using the computer programs described in the literature.^{32,33} The most relevant data for determining the four diffusion coefficients are reported in Tables 3 and 4. The D_{ij} values relative to the volume fixed frame of reference³⁴ are collected in Table 5.

TABLE 4: System PEG4(4)–PEG2(2)–H₂O^a

ΔC_4 , mol dm ⁻³	ΔC_2 , mol dm ⁻³	J	$D_A \times 10^5$, cm ² s ⁻¹	$Q_0 \times 10^4$	α_4
$C_4 = 0.120\ 00\ \text{mol dm}^{-3}$; $C_2 = 1.079\ 95\ \text{mol dm}^{-3}$					
0.000 00	0.155 54	71.34	0.7506	-17.34	0.000 00
0.015 56	0.124 48	70.80	0.7080	8.46	0.203 24
0.062 22	0.031 16	72.07	0.5929	26.76	0.802 95
0.077 78	0.000 04	72.57	0.5573	23.20	0.999 75
$C_4 = 0.300\ 03\ \text{mol dm}^{-3}$; $C_2 = 0.900\ 07\ \text{mol dm}^{-3}$					
-0.000 01	0.199 99	91.26	0.7554	-18.36	-0.000 10
0.020 01	0.160 01	91.63	0.7049	-3.14	0.203 39
0.050 00	0.099 83	92.20	0.6434	14.88	0.505 58
0.100 00	0.000 04	93.17	0.5517	17.14	0.999 80
$C_4 = 0.899\ 99\ \text{mol dm}^{-3}$; $C_2 = 0.300\ 00\ \text{mol dm}^{-3}$					
0.000 04	0.123 90	57.02	0.7219	-48.18	0.000 65
0.013 48	0.108 11	62.02	0.6775	-26.48	0.200 80
0.052 71	0.026 66	61.02	0.5598	7.95	0.799 36
0.053 66	0.026 93	61.95	0.5613	6.98	0.800 60
0.067 43	0.000 00	62.45	0.5264	1.64	1.000 00
$C_4 = 1.079\ 99\ \text{mol dm}^{-3}$; $C_2 = 0.120\ 02\ \text{mol dm}^{-3}$					
0.000 00	0.155 49	70.10	0.7059	-79.69	0.000 00
0.015 60	0.124 48	72.00	0.6608	-42.38	0.205 07
0.062 17	0.031 11	71.59	0.5514	-2.06	0.804 44
0.077 75	-0.000 01	73.09	0.5208	3.09	1.000 06

^a Gouy data for the experiments at $C_1 = 1.2000\ \text{mol dm}^{-3}$. ΔC_i : concentration difference of component i across the initial diffusion boundary. J : total number of Gouy interference fringes. D_A : apparent diffusion coefficient (ref 24). Q_0 : "area under the deviation function" (ref 24). α_4 : refractive index fraction of PEG4.

Results and Discussion

Binary Systems. The diffusion data of the binary systems PEG2(2)–H₂O(0) and PEG4(4)–H₂O(0), reported elsewhere,³⁵ have been reanalyzed in this paper according to eq 8 to obtain the D_i^∞ and V_i values. To analyze the possible deviation from the Carter and Phillies equation, a polynomial of a suitable degree has been fitted to the experimental data. We found that eq 8 is verified for the system PEG2(2)–H₂O(0) up to $C_2 \cong 2.8\ \text{mol dm}^{-3}$, whereas for the system PEG4(4)–H₂O(0), systematic deviations are observed for concentrations larger than $C_4 \cong 0.9\ \text{mol dm}^{-3}$. The following equations were obtained:

Systems PEG2(2)–H₂O(0)

$$C_2 \leq 2.8105\ \text{mol dm}^{-3}$$

$$D_2 \times 10^5 = (0.895 \pm 0.002)[1 - 0.898C_2(122.4 \pm 1.9) \times 10^{-3}] \pm 0.004\ \text{cm}^2\ \text{s}^{-1} \quad (19)$$

$$D_2 \times 10^5 = (0.898 \pm 0.001) - (0.106 \pm 0.002)C_2 + (0.0027 \pm 0.0008)C_2^2 \pm 0.002\ \text{cm}^2\ \text{s}^{-1} \quad (20)$$

Systems PEG4(4)–H₂O(0)

$$C_4 \leq 0.8558\ \text{mol dm}^{-3}$$

$$D_4 \times 10^5 = (0.668 \pm 0.003)[1 - 0.898C_4(223.8 \pm 8.5) \times 10^{-3}] \pm 0.004\ \text{cm}^2\ \text{s}^{-1} \quad (21)$$

$$C_4 \leq 1.6131\ \text{mol dm}^{-3}$$

$$D_4 \times 10^5 = (0.670 \pm 0.003) - (0.153 \pm 0.010)C_4 + (0.0022 \pm 0.0006)C_4^2 \pm 0.003\ \text{cm}^2\ \text{s}^{-1} \quad (22)$$

In Figure 1, the experimental D_i data are reported as a function of C_i . In this figure, dotted lines represent the trends of eq 8,

whereas full lines represent the trends of the polynomials. As can be observed for the system PEG2(2)–H₂O(0), the two fitting curves nearly overlap. For the system PEG4(4)–H₂O(0), the difference between the calculated and experimental D_4 value at $C_4 = 1.2000\ \text{mol dm}^{-3}$ is about 2% of the experimental one. Particularly, the D_4 experimental values are larger than those predicted by the hard-sphere theory. It should be pointed out that the use of the Carter and Phillies equation (8), in a larger concentration range, leads to a fit of the experimental D_4 data that is worse than that of the linear equation.

The difference between the experimental D_i and those predicted by the hard-sphere model can be attributed to the presence of solute–solute interactions, whose number increases as the total concentration increases. The presence of these interactions can affect both the mobility and the thermodynamic factor of the species. Usually, nonbonding interactions are supposed to happen through a partial overlapping of the hydration cospheres of two or more hydrated solute molecules with a release of solvent molecules to the bulk.³⁶ As a consequence, a decrease of the hydrodynamic volume per molecule and the possibility of the local motion of a couple, or a triplet, of molecules could be expected. Then, with respect to the values predicted by the hard-sphere model, the presence of solute–solute interactions should imply larger values of the solute mobility. On the contrary, it is reasonable to presume that the thermodynamic factor is, in the presence of solute–solute interactions among spheres, always lower than that predicted by the hard-sphere model. The experimental D_4 values for C_4 larger than $0.9\ \text{mol dm}^{-3}$ seems to indicate a prevalent effect of the mobility factor in determining the values of the diffusion coefficients.

We analyzed the viscosity data for the binary systems in a similar way. Using the V_i values which were previously obtained, we computed the relative viscosity, η_{rel} , as a function of the concentration using the Einstein equation (7). Then we fitted a polynomial of a suitable degree to the experimental η_{rel} data to analyze the difference between the predicted and the experimental values. The equations that were obtained are

Systems PEG2(2)–H₂O(0)

$$C_2 \leq 2.8105\ \text{mol dm}^{-3}$$

$$\eta_{2,\text{rel}} = 1.000 + (0.271 \pm 0.003)C_2 + (0.072 \pm 0.001)C_2^2 \pm 0.004 \quad (23)$$

Systems PEG4(4)–H₂O(0)

$$C_4 \leq 1.6131\ \text{mol dm}^{-3}$$

$$\eta_{4,\text{rel}} = 1.000 + (0.486 \pm 0.022)C_4 + (0.438 \pm 0.015)C_4^2 \pm 0.012 \quad (24)$$

The experimental data and the trends of the fitted equations are reported in Figure 2. In this figure, dotted lines represent eq 7, and full lines are the trends of the polynomials reported above, eqs 23 and 24.

As can be seen, the agreement between the predicted and the experimental data is limited to a concentration range smaller than that found for the diffusion coefficients through the Carter and Phillies equation (8). In fact, for the system PEG2–H₂O, eq 7 can represent the experimental data only for $C_2 \leq 0.9\ \text{mol dm}^{-3}$ and for the system PEG4–H₂O only for $C_4 \leq 0.4\ \text{mol dm}^{-3}$.

TABLE 5: System PEG4(4)–PEG2(2)–H₂O^a

β_4	$(D_{44})_{\text{exp}}$	$(D_{44})_{\text{calc}}$	$(D_{42})_{\text{exp}}$	$(D_{42})_{\text{calc}}$	$(D_{24})_{\text{exp}}$	$(D_{24})_{\text{calc}}$	$(D_{22})_{\text{exp}}$	$(D_{22})_{\text{calc}}$
$C_t = 0.4500 \text{ mol dm}^{-3}$								
0.0000		0.587	0.000	0.000			0.851	0.851
0.1667	0.592 ± 0.002	0.593	0.005 ± 0.002	0.008	0.084 ± 0.009	0.072	0.829 ± 0.006	0.827
0.3333	0.587 ± 0.002	0.597	0.002 ± 0.002	0.016	0.054 ± 0.010	0.058	0.827 ± 0.007	0.804
0.6666	0.598 ± 0.001	0.604	0.019 ± 0.001	0.028	0.030 ± 0.004	0.029	0.786 ± 0.003	0.759
0.8333	0.593 ± 0.001	0.606	0.037 ± 0.001	0.033	0.017 ± 0.004	0.015	0.732 ± 0.004	0.737
1.0000	0.606	0.608			0.000	0.000		0.715
$C_t = 0.8000 \text{ mol dm}^{-3}$								
0.0000		0.537	0.000	0.000			0.815	0.816
0.1662	0.549 ± 0.003	0.546	0.010 ± 0.001	0.015	0.091 ± 0.006	0.124	0.771 ± 0.003	0.781
0.3324	0.556 ± 0.003	0.554	0.016 ± 0.002	0.027	0.053 ± 0.006	0.101	0.749 ± 0.004	0.747
0.6676	0.561 ± 0.004	0.561	0.046 ± 0.002	0.043	0.035 ± 0.006	0.052	0.651 ± 0.004	0.681
0.8338	0.547 ± 0.003	0.562	0.051 ± 0.001	0.049	0.026 ± 0.006	0.027	0.643 ± 0.004	0.649
1.0000	0.562	0.561			0.000	0.000		0.618
$C_t = 1.2000 \text{ mol dm}^{-3}$								
0.0000		0.489	0.000	0.000			0.775	0.777
0.1000	0.496 ± 0.007	0.498	0.019 ± 0.004	0.014	0.163 ± 0.017	0.192	0.704 ± 0.011	0.751
0.2500	0.512 ± 0.004	0.508	0.026 ± 0.002	0.031	0.105 ± 0.009	0.165	0.688 ± 0.005	0.713
0.7500	0.516 ± 0.004	0.516	0.057 ± 0.004	0.057	0.029 ± 0.008	0.062	0.577 ± 0.006	0.593
0.9000	0.513 ± 0.007	0.511	0.084 ± 0.002	0.059	0.020 ± 0.018	0.026	0.487 ± 0.008	0.558
1.0000	0.518	0.507			0.000	0.000		0.536

^a Experimental and predicted D_{ij} values at $C_t = 0.4500$ (ref 8), 0.8000, and 1.2000 mol dm⁻³.

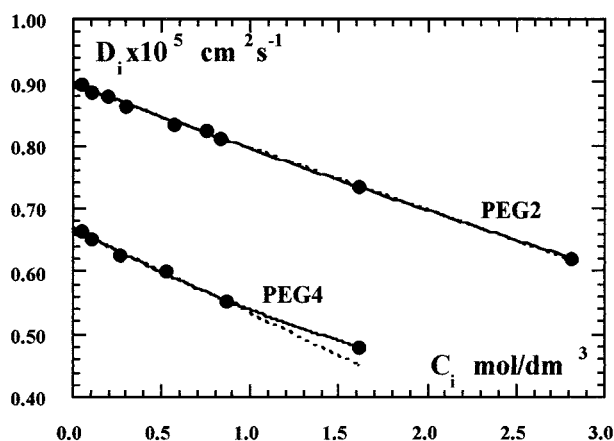


Figure 1. Diffusion coefficients of the systems PEG2(2)–H₂O and PEG4(4)–H₂O as a function of the PEG molar concentration. Full lines represent eqs 20 and 22. Dotted lines represent eqs 19 and 21 (see text).

Ternary Systems. The experimental diffusion coefficients, $(D_{ij})_{\text{exp}}$, are reported in Figure 3, main terms, and Figure 4, cross terms, as a function of β_4 . In these figures, full lines represent the linear fitting of the experimental data.

As can be seen in Figure 3, the experimental D_{ii} values are a linear ascending function of β_i with a very different slope for the two oligomers. As the total concentration increases, the values of the main-term diffusion coefficients decrease as expected. D_{ij} with $i \neq j$ must be zero at $\beta_i = 0$ and show a linear ascending trend as a function of β_i , with different slopes for the two oligomers, larger for D_{24} than for D_{42} . At increasing C_t , an increase of the slopes is observed.

Using the D_i^∞ and the V_i values obtained by the analysis of the binary systems and eqs 11 and 15, we computed the values of the ternary diffusion coefficients at all of the compositions experimentally investigated. The results are reported in Table 5 and shown in Figure 5, where the calculated values $(D_{ij})_{\text{calc}}$ are drawn as a function of the experimental ones, $(D_{ij})_{\text{exp}}$. As can be seen in the figure, the overall prediction is pretty good, the fitting leads to the correlation $(D_{ij})_{\text{calc}} = (1.009 \pm 0.005)(D_{ij})_{\text{exp}}$, rather than $(D_{ij})_{\text{calc}} = (D_{ij})_{\text{exp}}$ for a perfect prediction.

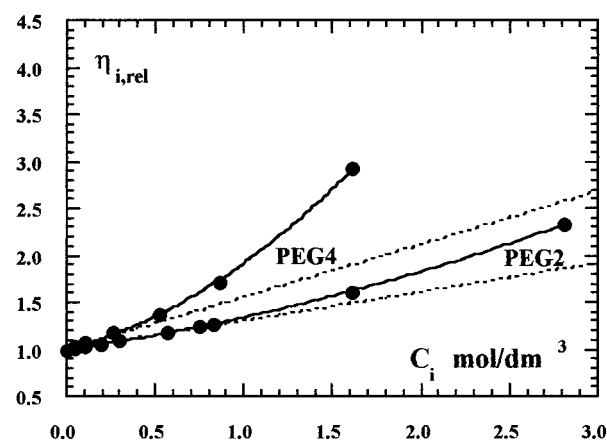


Figure 2. Relative viscosity of the systems PEG2(2)–H₂O and PEG4(4)–H₂O as a function of the PEG molar concentration. Full lines represent eqs 23 and 24. Dotted lines represent the trends of Einstein equation (7) using the effective volume obtained by eqs 19 and 21 (see text).

However, the residual distribution is not statistical. In particular, a good agreement between the predicted and the experimental values is found at $C_t = 0.4500 \text{ mol dm}^{-3}$, whereas systematic differences between these two values are observed at $C_t = 0.8000$ and $1.2000 \text{ mol dm}^{-3}$. This behavior is not strange because the predictive equations we proposed are expected to be more accurate in dilute solutions.

With regard to the main-term diffusion coefficients, whereas eq 8 seems to supply a fairly good prediction of the binary diffusion coefficients, eqs 7 and 10 do not supply a good prediction of the binary and ternary viscosities at high solute concentrations (see also the Binary Systems section).

Obviously, we could use the experimental values η_i and η_{ij} to test the validity of eq 11, but the objective of a prediction is to reduce the number of quantities that have to be experimentally determined. For this reason, we explored the possibility of predicting the ternary η_{ij} values using the experimental η_i ones.³⁷ However, also in this case, the prediction is quite good for the main diffusion coefficients at $C_t = 0.4500 \text{ mol dm}^{-3}$ but is not as good as the total solute concentration increase.

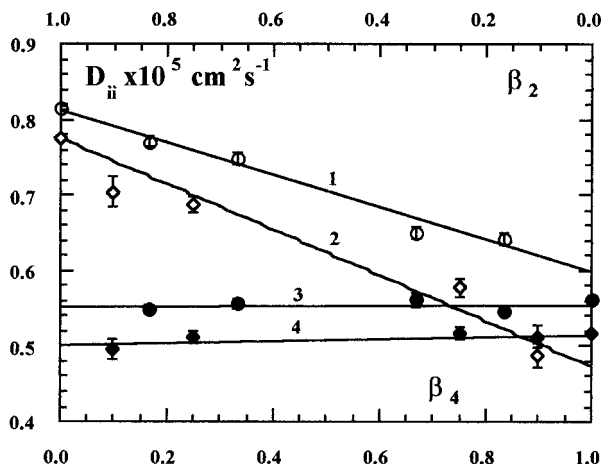


Figure 3. Main-term diffusion coefficients of the system PEG4(4)–PEG2(2)–H₂O. The lines reported represent the result of a linear fitting of the experimental data. Line 1: D_{22} at $C_t = 0.8000 \text{ mol dm}^{-3}$. Line 2: D_{22} at $C_t = 1.2000 \text{ mol dm}^{-3}$. Line 3: D_{44} at $C_t = 0.8000 \text{ mol dm}^{-3}$. Line 4: D_{44} at $C_t = 1.2000 \text{ mol dm}^{-3}$.

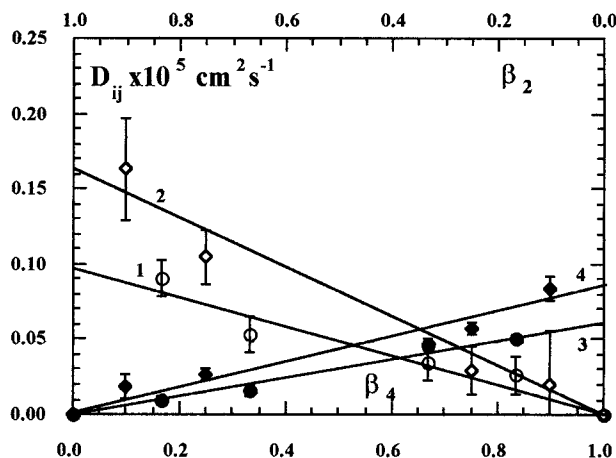


Figure 4. Cross-term diffusion coefficients of the system PEG4(4)–PEG2(2)–H₂O. The lines reported represent the result of a linear fitting of the experimental data. Line 1: D_{24} at $C_t = 0.8000 \text{ mol dm}^{-3}$. Line 2: D_{24} at $C_t = 1.2000 \text{ mol dm}^{-3}$. Line 3: D_{42} at $C_t = 0.8000 \text{ mol dm}^{-3}$. Line 4: D_{42} at $C_t = 1.2000 \text{ mol dm}^{-3}$.

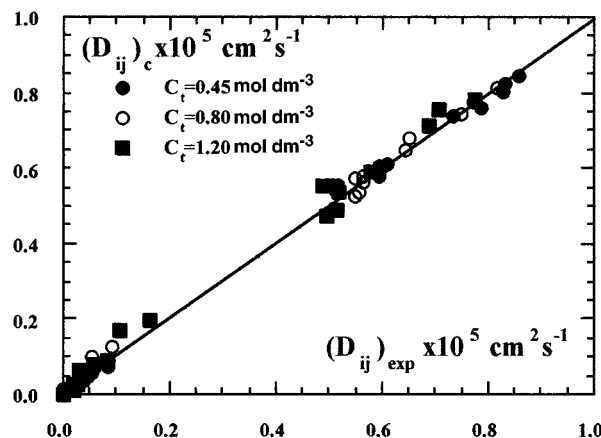


Figure 5. $(D_{ij})_{\text{calc}}$ VS $(D_{ij})_{\text{exp}}$ for the system PEG4(4)–PEG2(2)–H₂O: $C_t = 0.4500 \text{ mol dm}^{-3}$ (●); $C_t = 0.8000 \text{ mol dm}^{-3}$ (○); $C_t = 1.2000 \text{ mol dm}^{-3}$ (■).

This implies that eq 11 itself is critical in more concentrated solutions. Even if eq 11 shows discrepancies in the prediction of coefficient D_{22} at high concentrations, it still can explain a very peculiar behavior of this coefficient at $\beta_4 = 1$. As can be

seen from Table 5, the limit main-term diffusion coefficient of PEG2 at $\beta_4 = 1$, D_{22}^∞ , in a solution of PEG4 at $C_t = 1.2000 \text{ mol dm}^{-3}$, is smaller than the corresponding main value relative to PEG4, $D_{44} \equiv D_4$. This can be qualitatively justified by the proposed equation. In fact, the equations for D_{22}^∞ and D_4 are given by

$$D_{22}^\infty = D_2^\infty \frac{1}{1 + 2.5C_4V_4} = D_2^\infty \frac{1}{1 + 2.5C_tV_4} \quad (25)$$

$$D_4 = D_4^\infty (1 - 0.898C_4V_4) = D_4^\infty (1 - 0.898C_tV_4) \quad (26)$$

Using the values obtained for D_i^∞ and V_i , it is found that D_{22}^∞ and D_4 have very close values in the concentration range $C_t = 1.0$ – 1.6 mol dm^{-3} . The possibility of obtaining in a ternary system D_{ii}^∞ values smaller than the D_j values even if D_i^∞ is larger than D_j^∞ is a general issue that comes out of the different impact of the solute volume fraction on the main-term diffusion coefficients (see eq 12).

With regard to the cross-term diffusion coefficients, the systematic differences observed at high total solute concentration between the predicted and the experimental values can be due to a wrong evaluation of the ternary main-term diffusion coefficients (see eq 15) or to the presence of other contributions beyond the excluded volume in determining the D_{ij} values.

Because in eq 15 the D_{ij} values depend on the values of the corresponding D_{ii} , whose estimation was poor at the highest concentrations, we also computed the cross-term diffusion coefficients using the experimental main-term diffusion coefficients. Even if the differences between the experimental and predicted values decrease, there is not a significant improvement in the prediction. Then also the use of eq 15 is critical in the concentrated solutions. Finally it is interesting to note that the differences between the experimental and predicted diffusion coefficients at high concentration are larger for the diffusion coefficients relative to PEG2, D_{22} and D_{24} , with respect to those relative to PEG4, D_{44} and D_{42} . For these coefficients, the prediction is also reasonably good in the most concentrated solutions.

We will show, in the following, that the differences between the experimental D_{ii} values and those predicted by our extension of the current hard-sphere theory can be explained in terms of a mobility variation due to solute–solute interactions.

In concentrated solutions, solute–solute interactions can significantly contribute to the value of the diffusion coefficients. If a chemical equilibrium is present between the solutes, a simple correlation between the diffusion coefficients, the equilibrium constant, the stoichiometric concentrations, and the diffusivity of the real species present in solution can be found. In the case of weak solute–solute nonbonding interactions, only a qualitative discussion on the effect of these interactions on the diffusion coefficients can be made.

As said before, solute–solute nonbonding interactions are supposed to happen for a partial overlapping of the hydration cospheres and the release of water molecules to the bulk. In ternary systems, self- and cross-interactions are present. These interactions are supposed to be statistical, and then their number is simply dependent on the solute concentrations. In this analysis, we will only consider pair interactions. As a function of β_4 , the number of PEG2–PEG2 interactions decreases, vanishing at $\beta_4 = 1.0$, and the number of PEG4–PEG4 interactions has an opposite trend, whereas the number of PEG2–PEG4 interactions is zero at $\beta_4 = 0$, increases to reach a maximum at $\beta_4 = 0.5$, and then decreases to vanish at $\beta_4 = 1.0$.

At increasing β_4 values, the progressive substitution of PEG2–PEG2 interactions, between two “small and fast” molecules, with PEG2–PEG4 interactions, between a small and fast molecule and a “big and slow” one, implies (a) an increase of the effective volume per PEG2 molecule and (b) a lowering of the probability of PEG2 diffusing as a couple PEG2–PEG2.

Both of these two phenomena yield to a decrease of the mobility of the lighter oligomer PEG2. This, in principle, should imply D_{22} values smaller than those predicted by a simple viscosity correction; this issue is confirmed by the experimental data.

For PEG4 at increasing β_2 values, and then at decreasing β_4 values, we have an analogy of the previous statements: (a) a decrease of the effective volume per PEG4 molecule and (b) a lowering probability of PEG4 diffusing as a couple PEG4–PEG4.

In this case, a and b have an opposite effect on the mobility of PEG4, and the overall effect depends on their relative weight. In this case, we do not expect a significant contribution of the solute–solute interactions to the D_{44} values. This expectation is confirmed by the experimental values that are in good agreement with those obtained by using the proposed predictive equation.

Then the mobility variation seems, by itself, to be able to explain the experimental values of the main-term diffusion coefficients. Regarding the cross-term diffusion coefficients, we obtained a good qualitative agreement between the experimental and predicted D_{ij} values, but the quantitative discrepancy cannot be attributed unambiguously to the solute–solute interactions.

Conclusion

We have analyzed the excluded-volume contribution to the diffusion coefficient in some binary systems. We also proposed semiempirical predictive equations for main- and cross-term diffusion coefficients of a three-component system and tested the validity of these equations for several nonelectrolytic ternary systems at moderate solute concentrations. In this paper, we have discussed the applicability of these equations in more concentrated solutions. We verified that even if the prediction is fairly good systematic differences between the predicted and experimental values can be found as the total solute concentration increases. The proposed predictive equations will be useful in evaluating the diffusion coefficients matrix for the polydisperse system, which was never completely described.

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- (37) For a mixture of two liquids of viscosity η_1 and η_2 , the following equation provides a good estimation of the ternary viscosity η_{12} (ref 38)

$$\frac{1}{\eta_{12}} = x_1 \frac{1}{\eta_1} + x_2 \frac{1}{\eta_2}$$

where x_i is the molar fraction of component i in solution. Extending this equation to a mixture of solutions containing different solutes, we obtain the following expression for the viscosity of our ternary system at the total concentration C_t :

$$\frac{1}{\eta_{42}} = \beta_4 \frac{1}{\eta_4(C_4 = C_t)} + (1 - \beta_4) \frac{1}{\eta_2(C_2 = C_t)}$$

This equation appears to estimate the viscosity of the ternary system much better.

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