χ_F Interaction Parameter and Single-Chain Diffusion Coefficients of Dextran/Poly(vinylpyrrolidone)/Water: Dynamic Light Scattering Experiments

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ABSTRACT: Quasi elastic light scattering (QELS) experiments have been performed on poly(vinylpyrrolidone) (PVP)/dextran mixtures in water. The experiments were made at several total polymer concentrations C_T, in the semidilute range ($C_T > C^*$ where C^* is the overlap concentration): in the homogeneous and disordered state from about C^* to $10C^*$. At relatively higher concentration, three relaxation modes have been found in the whole range of composition $x = C_{PVP}/C_T$, namely, $0 < x < 1$. The slowest one has been interpreted as being the consequence of aggregate formation. The two other frequencies are interpreted in the framework of a model describing the dynamic behavior of ternary polymer mixtures using the random phase approximation (RPA) allowing the determination of the χ_F interaction parameter and the single-chain diffusion coefficients $D_{s,i} = kT/N_i\zeta_i$, $i = 1, 2$, as well as their polymer concentration dependence. The results show that χ_F increases rather sharply with the polymer concentration, whereas D_s decreases. As the concentration increases the variation of D_s with the concentration is expected and that of χ_F is interpreted as strong interactions occurring between chains.

Introduction

The phase separation of two polymers (1 and 2) in organic solvents is relatively well understood and is usually due to repulsive interactions between chain segments of species 1 and 2. Polymer/polymer behavior in aqueous solution is less well understood, although phase-separated polymer solutions have been widely studied and used to separate biological materials.[1] The mixing of polymers in aqueous solution is important and deserves particular attention for several reasons. Besides the fundamental aspect, the knowledge of the factors (for instance, the χ_F interaction parameter) which control polymer mixing in aqueous solutions is of great interest in many industrial applications (cosmetics, food, etc., ...). The measurement of the interaction parameter for ternary polymer mixtures in organic solvents was reported first by Fukuda et al.[2] and followed by Ould-Kaddour and Strazielle[3] using static light scattering under "optical theta condition". Most of these experiments were done on very dilute systems. In this work a mixture of polymers in aqueous solution (e.g., poly(vinylpyrrolidone) (PVP)/dextran/water) is investigated using dynamic light scattering experiments where the χ_F interaction parameter and the single-chain diffusion coefficients $D_{s,i} = kT/N_i\zeta_i$ are deduced as functions of concentration in the semidilute regime ($C_T > C^*$). In previous papers, it has been shown theoretically,[4-11] and experimentally,[12-22] that the dynamic behavior of ternary polymer mixtures in a good solvent (two polymers and a solvent) is characterized by two relaxation modes. These two dynamical processes are interpreted as follows: The first one represents the total polymer concentration fluctuations and is referred to as the cooperative mode. It has an amplitude A_C and a diffusion coefficient D_C such that the corresponding frequency $\Gamma_C = q^2D_C$ where $q = (4\pi n/\lambda)\sin(\theta/2)$, λ being the wavelength of the incident radiation, θ the scattering angle, and n the refractive index of the medium. The second one describes the relaxation of the composition fluctuations and is known as the interdiffusive mode. It is the only relaxation mode which exists in the melt state.[23-25] It is characterized by the amplitude A_I and the diffusion coefficient D_I. The variations of the amplitudes (A_C, A_I) and the diffusion coefficients (D_C, D_I) with total polymer concentration C_T and composition $x = C_1/C_T$ were found to be in good agreement with theoretical predictions.[4-11] One notes that, regarding the physical meaning attributed to these modes, Akcasu[7,9,10] pointed out that this interpretation is more rigorous only under specific conditions (same molecular weight, $x = 1/2$, etc., ...). Recently,[17] it has been shown that, besides the fact that two relaxation modes describe the dynamic behavior of ternary mixtures, it is possible to extract values of important parameters such as the χ_F interaction parameter. The determination of this parameter with a good accuracy using dynamic light scattering was first suggested by Benmouna and Borsali[17,26,27] to be possible under "zero average contrast" (ZAC) conditions expressed by the equation:

$$x(\partial n/\partial c)_1 + (1-x)(\partial n/\partial c)_2 = 0 \qquad (1)$$

where x is the composition of polymer 1. $(\partial n/\partial c)_i$ ($i = 1$ or 2) is the increment of refractive index of species i. Relation (1) means that the average refractive index of the two polymers matches exactly the refractive index of the solvent. Under such a condition the interpretation of the dynamics is easier than it is in the case of an arbitrary good solvent. Moreover, at $x = 1/2$, the situation becomes even more simple since only one relaxation mode should be observed. The second mode (cooperative) disappears because its amplitude is zero ($A_C = 0$). This behavior has already been observed on PS-D/PS-H/(benzene-H + benzene-D)[15] and a poly(methyl methacrylate) (PMMA)/poly(dimethylsiloxane) (PDMS)/chloroform system[26] using neutron spin-echo (NSE) and dynamic light scattering (DLS) experiments, respectively, and confirms the usefulness of the ZAC condition.

Very recently,[22] complementary experiments using DLS on PDMS/PMMA mixtures in different solvents, where obviously the ZAC is not fulfilled, suggests that one can also have direct access, with a good accuracy, to the χ_F interaction parameter when simply analyzing the variation of the cooperative and interdiffusive diffusion coefficients as a function of composition. The determination of χ_F

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under these conditions was found to be in good agreement with that obtained using static light scattering under "optical theta condition".[3b] This result confirms the nondependency of the frequencies from the optical properties of the system and allows the determination, with a good accuracy, of important parameters such as χ_F in arbitrary solvents.

Consequently, whatever are the optical properties of the system in terms of the increment of refractive indices provided that the solvent is good, it is possible to have direct access to the concentration dependence of the χ_F interaction parameter and that of the single-chain diffusion coefficients $D_{s,i} = kT/N_i\zeta_i$ for both species. In this paper, we present for the first time the investigation of χ_F and D_s in aqueous solutions as a function of concentration in the semidilute range, using dynamic light scattering. For this purpose, we have chosen the PVP/dextran/water mixture because it constitutes a "bridge" between synthetic and natural polymers and having in mind an extension of this choice to polysaccharide mixtures where little information is available in terms of compatibility.

The model we have used for the interpretation of the relaxation modes in ternary mixtures has been developed by Akcasu, Benmouna, and Benoît and is well described in refs 4–11. Using the RPA, this model has explained several experimental results: two homopolymers in solution[12-18] and diblock copolymer/solvent[15,19,20] systems. For convenience, it is useful to recall some relations that are of interest for this work. In any ternary mixtures of two polymers in solvent, the total dynamic scattering function $S_T(q,t)$, where t is the time, is a sum of two exponentials:

$$S_T(q,t) = A_C e^{-q^2 D_C t} + A_I e^{-q^2 D_I t} \qquad (2)$$

Let us consider a system where the two polymers have different degrees of polymerization ($N_1 \neq N_2$) and different excluded volume parameters v_{ij} and are slightly incompatible ($\chi_F \neq 0$). In this case and since we are essentially interested in the determination of χ_F and $D_{s,i}$ from the variation of the diffusion coefficients as a function of the total polymer concentration C_T and the composition x, the expressions of D_C and D_I, after straightforward manipulations, can be expressed as follows:[4,5,11]

$$D_{C,I}(q) = D_{av}(q) \pm [D_{av}^{\;2}(q) - \Delta(D)]^{1/2} \qquad (3a)$$

where

$$D_{av}(q) = \frac{D_{11}(q) + D_{22}(q)}{2} \qquad (3b)$$

$$\Delta(D) = D_{11}(q)\, D_{22}(q) - D_{12}(q)\, D_{21}(q) \qquad (3c)$$

and

$$D_{11} = D_{s,1}(c)\,\frac{1}{P_1(q)}[1 + xC_T 2A_{2,1}M_{w,1}P_1(q)] \qquad (4a)$$

$$D_{22} = D_{s,2}(c)\frac{1}{P_2(q)}[1 + (1-x)C_T 2A_{2,2}M_{w,2}P_2(q)] \qquad (4b)$$

$$D_{12} = D_{s,1}(c)\; xC_T 2A_{2,12}M_{w,1}(m_2/m_1) \qquad (4c)$$

$$D_{21} = D_{s,2}(c)\; (1-x)C_T 2A_{2,12}M_{w,2}(m_1/m_2) \qquad (4d)$$

$D_{s,i}(c) = kT/N_i\zeta_i(c)$ (i = 1, 2), where ζ_i is the friction coefficient per monomer i which may depend on the concentration, $x = C_1/C_T$, and $P_i(q)$ the form factor of polymer species i. The second virial coefficients $A_{2,ij}$ (i, j = 1, 2) have been introduced via the excluded-volume parameters v_{ij} such as:

Table I. Properties of Polymer Samples

sample	$10^{-3}M_w$	$I = M_w/M_n$	R_g (Å)	A_2 (mol cm^3 g^{-2})	$\chi_{i,s}$[a]
dextran DT500	485	1.95	260	4.6×10^{-4}	0.4803
PVP K90	310	1.5	216	4.2×10^{-4}	0.4874

[a] Values deduced from those of A_2 according to relation (6a).

$$v_{ij} = 2A_{2,ij}\frac{m_i m_j}{N_{av}} \; (i, j = 1, 2) \qquad (5)$$

m_i and N_{av} are the monomer molecular weights (m_{PVP} = 111; $m_{dextran}$ = 162) and Avogadro's number. In terms of Flory's interaction parameters $\chi_{i,s}$ (interaction between the solvent and monomer of species i; i = 1 or 2) and $\chi_{F,ij}$ (interaction between monomers of species i and j; i = 1 and j = 2), the Flory–Huggins theory allows us to write:

$$A_{2,ii} = \frac{\bar{v}_i^{\,2}}{2V_s}[1/\Phi_s - 2\chi_{i,s}] \qquad i = 1, 2 \qquad (6a)$$

$$A_{2,12} = \frac{\bar{v}_1\bar{v}_2}{2V_s}[1/\Phi_s - \chi_{1,s} - \chi_{2,s} + \chi_F] \qquad (6b)$$

where Φ_s is the volume fraction of the solvent $\Phi_s = 1 - \Phi_T$. $\bar{v}_1$ and $\bar{v}_2$ are the specific volumes of both polymers ($\bar{v}_{PVP}$ = 0.776 cm^3/g; $\bar{v}_{dextran}$ = 0.65 cm^3/g), and V_s is the molar volume of the solvent (V_{water} = 18.053 cm^3/mol). Inspecting relations (3)–(6), it is clear that for a given concentration the only adjustable parameters are the χ_F interaction parameter and the single-chain diffusion coefficients $D_{s,i}$. We have investigated the PVP/dextran/water system at several total polymer concentrations and compositions, and after analyzing the results in the framework of the model described above we have obtained values of χ_F and those of $D_{s,i}$ of both polymers and their variation with the polymer concentration. The results are discussed after the Experimental Section.

Experimental Section

Materials and Sample Preparation. PVP was supplied by Fluka AG, and dextran was obtained from Pharmacia fine chemical AB Uppsala (Sweden). The characteristics of these polymers are given in Table I. The weight-average molecular weights M_W, the radii of gyration R_g, and the second virial coefficients $A_{2,i}$ of these polymers were determined by static light scattering measurements in water. Several PVP/dextran/water solutions were prepared at different total polymer concentrations (namely, $2.33 \times 10^{-2} < C_T$ (g/cm^3) $< 8.01 \times 10^{-2}$) in the range of composition $x = C_{PVP}/C_T$ ($0.05 < x < 0.95$), including the binary systems (dextran/water → x = 0 and PVP/water → x = 1). One notes that the overlap concentrations are $C^*_{PVP} \cong 1.2210^{-2}$ g/cm^3 and $C^*_{dextran} \cong 1.0910^{-2}$ g/cm^3, assuming the polymer chains are flexible and in a good solvent: $C^* = M_w/(N_{av}4\pi R_g^{\,3}/3)$. The phase separation or the concentration at the cloud point in the ternary mixture is approximately $C_{cp} \cong 8.110^{-2}$ g/cm^3 at x = 0.5. The solutions were allowed to mix for 3 days. They were filtered with 0.45-μm Millipore filters and allowed to equilibrate for a few hours following filtration and prior to measurements.

Equipment and Data Analysis. The full homodyne correlation function of the scattered intensity defined on 256 channels was obtained by using the ALV-5000 multi-τ autocorrelator from ALV (Langen, FRG). The scattered light of a vertically polarized 4880-Å argon laser (Spectra-Physics 2020) was measured at several angles in the range 30–150° at the temperature t = 25.0 ± 0.1 °C. The total intermediate scattering function $S_T(q,t)$ is related to the measured homodyne intensity

Table II. Values of $D_{C,I}$ as a Function of Concentration and Composition

x	$D_{C,I}$ for C_1 = 0.0233 g/cm^3 (10^{-7} cm^2/s)		$D_{C,I}$ for C_2 = 0.030 g/cm^3 (10^{-7} cm^2/s)		$D_{C,I}$ for C_3 = 0.040 g/cm^3 (10^{-7} cm^2/s)		D_C for C_4 = 0.05 g/cm^3 (10^{-7} cm^2/s)	D_C for C_5 = 0.060 g/cm^3 (10^{-7} cm^2/s)	D_C for C_6 = 0.080 g/cm^3 (10^{-7} cm^2/s)
0	3.00		3.25		3.80		4.11	4.44	5.03
0.06	3.11	0.44	3.41	0.32	3.87	0.26	4.23	4.59	5.21
0.11	3.23	0.40							
0.23	3.25	0.33	3.60	0.232	4.26	0.19	4.62	5.03	5.68
0.42	3.51	0.28							
0.54	3.50	0.25	3.93	0.19	4.74	0.12	5.20	5.75	phase separation
0.62	3.85	0.27							
0.83	3.74	0.31	4.15	0.20	4.93	0.138	5.49	6.04	6.90
0.91	3.76	0.32							
0.958	3.77	0.335	4.21	0.22	5.08	0.142	5.61	6.21	7.12
1.00	3.83		4.24		5.14		5.58	6.18	7.08

autocorrelation function $G^{(2)}(q,t)$ by the Siegert relation.[28]

$$G^{(2)}(q,t) = B(1 + \alpha|S_T(q,t)|^2) \qquad (7)$$

where B is the base line and α is the spatial coherence factor depending upon the geometry of the detection. The constrained regularization method (CONTIN) developed by Provencher[29] was used to obtain the distribution $A(t)$ of decay times. A statistical parameter "probability to reject" (P) is calculated for each solution, and the suggested one is that for P closest to 0.5.

$$\left[\frac{G^{(2)}(q,t)}{B} - 1\right]^{1/2} = \int_0^\infty A(t)\, e^{-(t/\tau)}\, dt = S_T(q,t) \qquad (8)$$

The analysis of the autocorrelation functions was made with a HP computer.

Results and Discussion

The experiments were performed at the angles between 30° and 150°, for several total polymer concentrations in the semidilute solution from around C^* to $10C^*$ (i.e., $2.33 \times 10^{-2} < C_T$ (g/cm^3) $< 8 \times 10^{-2}$) in the range $0 \leq x \leq 1$ and at the temperature $t = 25 \pm 0.1$ °C.

Around C^*, two relaxation modes describe the dynamics of the ternary mixture, whereas one frequency is observed in the corresponding binary systems. At relatively higher concentrations, both binary and ternary systems show the existence of a slow relaxation process which has been interpreted as being the consequence of aggregate formation. There are many reasons for that. Preparing a sample using different Millipore-filter diameters gives different results regarding the magnitude and the relaxation time of the slowest mode. Its amplitude and frequency grow with time and are very sensitive, depending on the range of concentration, to the temperature. On the other hand, the fast "legitimate" mode called cooperative (in binary systems) and the two other modes (in ternary systems) called cooperative and interdiffusive do not show any alteration of their variations with the concentration or the composition with respect to the sample preparation or to the reproducibility of the results. In all our experiments, it was always possible to separate the aggregate mode from those of interest, except for higher concentrations, namely, $C_T > 4.0 \times 10^{-2}$ g/cm^3 regarding the interdiffusion mode (see Table II and Figure 2b).

In Figure 1, we plotted the variation of the cooperative diffusion coefficients of both binary systems, $D_C = [\Gamma_C/q^2]_{q\to 0}$. They increase with the concentration as expected and present the following scaling laws with the concentration:

$$\text{for PVP/water:} \qquad D_C \approx C^{0.5} \qquad (9a)$$

$$\text{for dextran/water:} \qquad D_C \approx C^{0.43} \qquad (9b)$$

Even though these values are lower than the predicted one[30] (namely, 0.75, in a good solvent), the results support

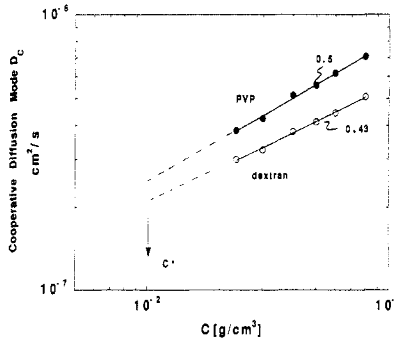

Figure 1. Logarithmic plots of the cooperative modes D_C measured in binary mixtures: (○) dextran/water and (●) PVP/water.

the interpretation of this mode as a cooperative frequency reflecting the relaxation of the pseudophysical network formed by the chains. The difference in the exponent values is probably due to the low range of molecular weights of the PVP and dextran used in these experiments. One may also explain this difference in the exponent by the fact that the water is not a very good solvent.

Parts a and b of Figure 2 represent respectively the variation of the fast (cooperative) and slow (interdiffusive) diffusion coefficients measured on the ternary PVP/dextran/water system for different total polymer concentrations as a function of the composition $0 < x < 1$ of PVP in the mixture. For completeness, the values of the cooperative modes measured in the binary systems (x = 0 and x = 1) are also reported. As has already been observed in other systems,[12-22] the fast mode increases with the polymer concentration and the slow mode decreases. In Figure 2b only three concentrations have been reported regarding the variation of the interdiffusion mode as a function of the composition. Indeed, above $C_T = 4.0 \times 10^{-2}$ g/cm^3, it was impossible to separate the interdiffusion mode from that of aggregate formation because the amplitude of the latter is dominant. This is not the case for the cooperative relaxation time since as the concentration increases the ratio D_C/D_{Aggr} increases and therefore the two modes are easily separable. The symbols represent the experimental values, and the solid lines represent the best fit according to relations (3)–(6), where $P_i(q) = P_i(0) = 1$ (i = 1, 2) since $D_{C,I} = [\Gamma_{C,I}/q^2]_{q\to 0}$. At this stage we would like to mention that in the fit procedure the interaction parameters $\chi_{i,s}$ (see Table I) deduced from the second virial coefficients $A_{2,ii}$ [see relation (6a)] have been considered independent of the concentration and the composition even though this is may be not true. But, as a first approximation, the error should not be important.

The results obtained from this fit allow us to have direct access to χ_F and $D_{s,i}$ for each concentration independently

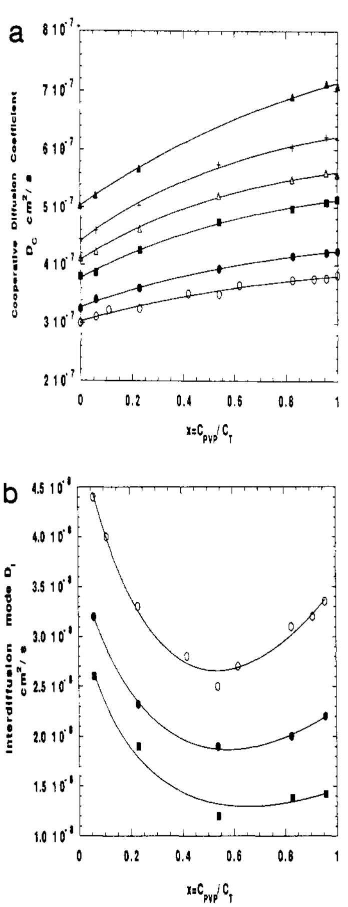

Figure 2. (a) Variation of the cooperative diffusion mode D_C measured in ternary polymer mixture PVP/dextran/water as a function of the composition $x = C_{PVP}/C_T$, for different concentrations: (○) 2.33×10^{-2} g/cm³; (●) 3.0×10^{-2} g/cm³; (■) 4.0×10^{-2} g/cm³; (△) 5.0×10^{-2} g/cm³; (+) 6.0×10^{-2} g/cm³; (▲) 8.0×10^{-2} g/cm³. The symbols represent the experimental data and the solid lines the best fits according to relations (3)–(6). (b) The same as in Figure 2a except for the interdiffusion mode.

Table III. Values of the Single-Chain Diffusion Coefficients $D_{s,i}$ and Those of the Interaction Parameter as a Function of Concentration

concn (10^{-2} g/cm³)	D_s (10^{-8} cm/s)		χ_F interaction param
	PVP	dextran	
0	5.94[a]	2.89[a]	
2.33	5.34, 5.08[b]	2.61, 2.83[b]	0.0012, 0.009[b] ± 10^{-4}
3.00	4.81, 4.19[b]	2.23, 2.33[b]	0.0016, 0.014[b] ± 10^{-4}
4.00	4.49, 3.82[b]	1.93, 1.71[b]	0.0023, 0.022[b] ± 10^{-4}
5.00	4.01	1.70	0.0027 ± 10^{-4}
6.00	3.73	1.54	0.0031 ± 10^{-4}
8.00	2.26	1.32	phase separation

[a] Extrapolated values. [b] Values obtained from the interdiffusion mode.

from the cooperative and interdiffusive relaxation modes. The results are listed on Table III. A first observation can be made: the values of $D_{s,i}$ and those of χ_F obtained independently from both relaxation modes are close to each other. Qualitatively, this result and the comparison of the fit parameters obtained from both relaxation frequencies are comforting and imply very important consequences in some situations. For instance, this would mean that the interaction parameter and the single-chain diffusion coefficients can be obtained even when one of the relaxation modes is difficult to observe (i.e., weak amplitude, very fast or very slow relaxation). Quantitatively, the fit reveals that the single-chain diffusion coefficients decrease whereas the interaction parameter increases with the total polymer concentration. These behaviors are illustrated in parts a and b of Figure 3, respectively.

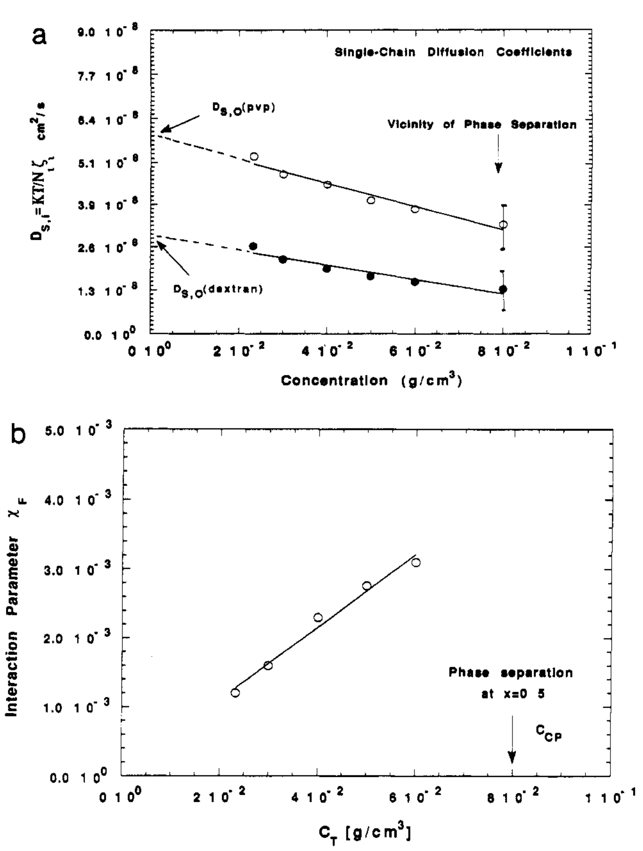

Figure 3. (a) Variation of the single-chain diffusion coefficients $D_{s,i}$ of (○) PVP and (●) dextran as a function of the concentration. (b) Variation of the interaction parameter χ_F in the ternary mixture PVP and dextran in water as a function of the concentration.

In earlier papers,[4–22] it has been assumed, for the sake of simplicity, that the single-chain diffusion coefficient is independent of the concentration even though this is not true. In these experiments this dependence is clearly observed and confirms the physical meaning attributed to this motion. Namely, $D_{s,i}$ corresponds to the value that would have the diffusion coefficient of a labeled chain i in a matrix of polymer j/solvent at the corresponding concentration of polymer j. This result could be compared to that one would obtain using forced Rayleigh scattering (FRS), pulsed-field-gradient NMR, fluorescence recovery after photobleaching (FRAP), or neutron spin-echo techniques). As the concentration increases, one understands easily that the single-chain motion becomes slower due to the presence of supplementary chains in the system. This is what Figure 3a means. One notes, however, that the $D_{s,i}$ values extracted at $C_T = 8.010^{-2}$ g/cm³ (in the vicinity of phase separation) present a nonnegligible error and may be questionable.

The model we have used in this paper in its static property version[31] has explained several static ternary mixture experiments in the semidilute and also the dilute properties by means of extrapolation at $C = 0$. This is very surprising since it shows that the RPA is capable of going beyond the border of the model itself and is somewhat contradictory. In the dynamic version one is tempted to do the same extrapolation as in the static case and therefore one may try to compare the values of the single-chain diffusion coefficients ($D_s°$) to those obtained at infinite dilution in the corresponding binary systems: One obtains for PVP/water $D° = 1.3 \times 10^{-7}$ cm²/s and for dextran/water $D° = 1.2 \times 10^{-7}$ cm²/s. The extrapolation to zero concentration, as shown in Figure 3a, gives $D_s° = 5.94 \times 10^{-8}$ and 2.89×10^{-8} cm^2/s for PVP and dextran, respectively. As one can see, these values ($D°$, $D_s°$) are different and the agreement is rather bad. Consequently this comparison or this type of extrapolation is very hazardous and risky contrary to the static case where the extrapolation gives correct results. Indeed, the model as described in this paper is valid in the semidilute system ($C > C^*$) and therefore does not take into account the bulk flow effects[23-25] (hydrodynamic interactions) which are very important in the dilute system. To go further in our analysis, the $D°$ were converted to the equivalent hydrodynamic radii (R_H) using Stokes–Einstein relation $D° = kT/(6\pi\eta_s R_H)$ where k is Boltzmann's constant, η_s the viscosity of the solvent, and T the absolute temperature. This gives $R_{H,PVP} = 186$ Å and $R_{H,dextran} = 201$ Å and allows the determination of the ratios R_G/R_H, namely, 1.16 and 1.29 for PVP and dextran, respectively. These values are less than the predicted one (1.862 in good solvent and 1.054 in Θ solvent). The polydispersity of the samples or/and the quality of the solvent are probably at the origin of this difference. More experimental investigations and the analysis of the ratio in terms of quality of the solvent and rigidity of the chains are under study and will be discussed in a forthcoming paper.[32]

As far as the interaction parameter χ_F is concerned, it increases rather sharply with the concentration. This behavior could be understood as reflecting how much the chains interact to each other. Indeed, for semidilute systems, when only single contacts between monomers are assumed to ensure the thermodynamics of the system, χ_F should be independent of the concentration as it is, and has been observed, in dilute solutions.[2] This is not the case for our system, and this increase seems to indicate that as the concentration increases the PVP and dextran chains are strongly interacting. This increase of χ_F is proportional the number of contacts between chains which is probably at the origin of aggregate formation. It is however interesting to note that the determination of χ_F using static light scattering is, of course, possible, but the accuracy would be questionable since this system does not satisfy the "optical theta condition".

Conclusion

In this paper we have investigated the dynamic behavior of a PVP/dextran mixture in water using quasi elastic light scattering experiments. Around C^*, two relaxation modes describe the dynamics of the mixture. At relatively higher concentrations, three relaxation modes have been observed at several concentrations in the whole range of composition ($0 < x < 1$). The slowest one has been interpreted as reflecting the motion of associations or aggregate formation. The analysis of the two other modes in the framework of a model developed by Akcasu, Benmouna, and Benoît based on the RPA allows the determination of the interaction parameter χ_F and that of the single-chain diffusion coefficients $D_{s,i}$ for both species as a function of the total polymer concentration. The results show that $D_{s,i}$ decreases with the concentration whereas χ_F increases. The variation of $D_{s,i}$ with the concentration is expected and confirms the slowing down of the motion of a single labeled chain i in a matrix of unlabeled j polymer. The dependence of χ_F with the concentration may be understood as the consequence of strong interactions between chains as the concentration increases.

This work shows that using dynamic light scattering experiments it is possible to have direct access to two important parameters, namely, the single-chain diffusion coefficients (mobility) and the interaction parameter χ_F (compatibility) in ternary polymer systems consisting of polymer 1/polymer 2/solvent in the homogeneous and disordered state.

Other systems involving mixtures of polysaccharides in aqueous solution are considered in the framework of similar investigations where little information is available in terms of mobilities and compatibility.

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