Analysis of the Diffusion in Pseudobinary Systems: Applications of Gouy Interferometry Parameters to Polydisperse Systems

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The theory of diffusion in *n*-component systems has been applied to study the mutual diffusion of polydisperse polymeric systems. General relations for *n*-component systems have been obtained for the experimental Gouy parameters, D_A and Q_0. Through the use of the Flory equation for diffusion coefficients of monodisperse polymers, the expressions of D_A and Q_0 at infinite dilution, D_A^∞ and Q_0^∞, for a general molecular weight distribution have been obtained. These relations have been used to analyze the effect of polydispersity on Gouy diffusion parameters, and the relative information content of Q_0^∞ is stressed. A procedure is suggested to determine the molecular weight and to estimate the results of the fractionation through the Gouy interferometry. The results of this analysis have been applied to polyethyleneglycol, polyacrylic acid, and sodium polyacrylate diffusion data.

Introduction

All synthetic polymers show a distribution of molecular weights. The mechanism of polymerization and the subsequent modifications that the polymer undergoes (fractionation, degradation, etc.) determine its distribution function. The relative composition of polymer solutions does not depend on the total concentration or on the chemical−physical properties of the environment. Different is the case of the polydispersity of· microemulsions,[1] vescicles,[2] and various proteins,[3−6] due to association equilibria.[7] This case is dependent on chemical−physical properties of the system such as temperature, solvent modification,[8] pH, ionic strength,[9] and total concentration. However, in both cases, because it is not possible to change the relative compositions of each component independently, the solutions of polydisperse samples must be considered as pseudobinary systems.

Any method capable of distinguishing molecules of different sizes can in principle be used for polydipersity analysis. Therefore, transport properties, such as mutual, self, and thermal diffusion,[10] sedimentation,[11] viscosity, etc., are useful for this aim.

There have been previous theoretical developments for the study of polydispersity from diffusion data. Sundelof[12] developed a theory for obtaining information about the distribution function of molecular size parameters, using a general deconvolution procedure on the interferometric parameters.[13] Cussler[14−16] studied multicomponent diffusion of monodisperse and polydisperse samples of polystyrene with Gouy interferometry, but without an experimental comparison of the assumed distribution functions. Daune[17] and Ambrosone[1] studied the effect of polydispersity on self-diffusion; Ambrosone formulated a general procedure based on generating functions for restricted diffusion in droplets.

For several years some of us have been interested in diffusion of pseudobinary and multicomponent systems containing polymers[18−20] and associating solutes.[21,22] In the last few years

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the diffusion properties of aqueous solutions of oligomers[23,24] and polydisperse samples[25] of polyethylene glycol (PEG) were studied extensively. In the present paper, we focused our attention on the following points: (1) the effect of polydispersity on the experimental Gouy parameters, (2) the effect of fractionation on the Gouy parameters, (3) the possibility of obtaining an average molecular weight from Gouy parameters, and (4) the limit of the Gouy technique in polydispersity analysis. The results of this analysis have been applied to experimental data.

In a future paper this analysis will be extended to the polydispersity due to omo-association phenomena, such as dimerization, micellization, and nucleation.

Theory

Many papers have been dedicated to the analysis of ternary[26,27] and quaternary[28,29] systems in the last few decades, providing the tools to describe mutual diffusion in an *n*-component system. We report here the basic equations of multicomponent diffusion according to Fujita and Gosting[26,27] notation.

The transport properties for an *n*-component system in one single direction, *x*, are described by Fick's laws:

$$J_i = -\sum_{j=1}^{n-1} D_{ij}\left(\frac{\partial C_j}{\partial x}\right)_{T,p} \tag{1}$$

$$\frac{\partial C_i}{\partial t} = \sum_{j=1}^{n-1}\frac{\partial}{\partial x}D_{ij}\left(\frac{\partial C_j}{\partial x}\right) \tag{2}$$

where J_i is the flux of the *i* component, C_j is the concentration of component *j*, and D_{ij} are the cross-diffusion coefficients. Therefore, $(n - 1)^2$ independent mutual diffusion coefficients are necessary to define the diffusive flows. The flow of component *n* (generally the solvent) is related to that of the other $n - 1$ components through the continuity equation. Under the hypothesis of free and differential diffusion and ΔC_i small enough to assure constant D_{ij} through the diffusion boundary,

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eq 2 becomes

$$\frac{\partial C_i}{\partial t} = \sum_{j=1}^{n-1} D_{ij}\left(\frac{\partial^2 C_j}{\partial x^2}\right) \tag{3}$$

and can be integrated to give for the *i*th component

$$C_i = \bar{C}_i + \sum_{j=1}^{n-1} K_{ij}\, \mathrm{erf}(\sqrt{\sigma_j}\, y) \tag{4}$$

where $\bar{C}_i$ is the mean concentration of component *i*, K_{ij} are constants dependent on the $(n-1)^2$ diffusion coefficients and on ΔC_i, erf is the error function operator, σ_j are the reciprocals of eigenvalues of the diffusion coefficient matrix, and *y* is the reduced coordinate $x/2\sqrt{t}$ in the diffusion cell.[30,31]

Any detectable quantity related to concentration can be used for measuring mutual diffusion coefficients. Optical techniques, such as Rayleigh and Gouy interferometry, are recognized to be the most precise techniques to measure the diffusion coefficients.[32] They follow the refractive index n_λ or its gradient through the diffusion boundary as a function of time. If the refractive index is a linear function of concentration

$$n_\lambda = \bar{n}_\lambda + \sum_{i=1}^{n-1} R_i(C_i - \bar{C}_i) \tag{5}$$

we obtain

$$n_\lambda = \bar{n}_\lambda + \frac{\Delta n_\lambda}{2}\left[\sum_{i=1}^{n-1} \Gamma_i\, \mathrm{erf}(\sqrt{\sigma_i}\, y)\right] \tag{6}$$

$$\frac{\partial n_\lambda}{\partial y} = \frac{\Delta n_\lambda}{\sqrt{\pi}}\sum_{i=1}^{n-1} \Gamma_i \sqrt{\sigma_i}\, \exp(-\sigma_i y^2) \tag{7}$$

where Δn_λ is the total difference of refractive index across the diffusion boundary and Γ_i are dependent on the K_{ij} and R_i, with the condition

$$\sum_{i=1}^{n-1} \Gamma_i = 1 \tag{8}$$

For a binary system eq 7 reduces to a Gaussian curve, while for *n*-component systems it is the sum of $n-1$ Gaussian curves.

The experimental quantities detectable by the Gouy technique are D_A and Q_0. D_A is the "area/reduced height ratio":

$$D_A = \frac{(\Delta n_\lambda)^2}{4\pi t[(\partial n_\lambda/\partial x)_t]_{\max}^2} \tag{9}$$

Q_0 represents the "area under the fringe deviation graph" and is defined by the expression

$$Q_0 = \int_0^1 \Omega(\zeta)\, \mathrm{d}f(\zeta) \tag{10}$$

where

$$\zeta = x/\sqrt{4\pi D_A t} \tag{11}$$

is a generalized coordinate for multicomponent systems,[26,29,31]

$f(\zeta)$ is defined as

$$f(\zeta) = \mathrm{erf}(\zeta) - (2/\sqrt{\pi})\exp(-\zeta^2) \tag{12}$$

$$\Omega(\zeta) = \exp(-\zeta^2) - \frac{(\partial n_\lambda/\partial \zeta)}{(\partial n_\lambda/\partial \zeta)_{\max}} \tag{13}$$

and Q_0 represents the deviation of the refractive index gradient curve from a Gaussian function.[27]

For ideal binary systems D_A corresponds to the mutual diffusion coefficient D_1 of the solute, and the Q_0 value is zero. A single run is then sufficient to measure the diffusion coefficient at a given mean concentration. For real binary systems Q_0 is often different from zero. The value of Q_0 depends on various factors: (1) imperfections in the original boundary, causing a random contribution, (2) optical imperfections, with a constant contribution, (3) concentration dependence of the diffusion coefficient, with a contribution depending on the specific system.

Good siphoning technique and extrapolation of Q_0 at infinite time reduce the effect of perturbation with respect to the ideal planar initial boundary.[33] The control of instrumentation minimizes the second factor.[34] The effect of the concentration gradient size was analyzed for several systems,[35] and the *D* concentration dependence can be minimized, reducing the concentration difference ΔC_i. In binary systems the Q_0 values are not involved in the diffusion coefficient calculation. They are only used as a test of the quality of the run and generally are not reported in the literature.

For ternary systems the two experimental quantities detectable with a single run, D_A and Q_0, are insufficient for the computation of the four diffusion coefficients. At least two independent runs taken at the same mean concentrations but at different refractive index fractions, α_i, are necessary to calculate the four D_{ij}. The refractive index fraction is defined as

$$\alpha_i = (R_i \Delta C_i)/\left(\sum_{j=1}^{n-1} R_j \Delta C_j\right) \tag{14}$$

In general for an *n*-component system, at least $n-1$ independent runs, taken at the same mean concentrations, with different α_i values, are necessary to calculate the $(n-1)^2$ diffusion coefficients.

For an *n*-component system the following relations hold for D_A[36] and Q_0; see the Appendix:

$$1/\sqrt{D_A} = \sum_i \Gamma_i \sqrt{\sigma_i} \tag{15}$$

$$Q_0 = \left[(1/2)\sum_{i=1}^{n-1}\sum_{j=1}^{n-1} \Gamma_i \Gamma_j g_{ij}\right]/\left[\sum_{i=1}^{n-1} \Gamma_i \sqrt{\sigma_i}\right] \tag{16}$$

where

$$g_{ij} = \frac{\sqrt{\sigma_i} + \sqrt{\sigma_j}}{2\sqrt{2}} - \frac{\sqrt{\sigma_i \sigma_j}}{\sqrt{\sigma_i + \sigma_j}} = g_{ji} \tag{17}$$

However, in some *n*-component systems it is not possible to perform the $n-1$ runs necessary to obtain the $(n-1)^2$ diffusion coefficients. If different components are present in the same sample at a fixed molar ratio, namely, at a single defined α_i array, only a single run can be performed at each mean concentration. In this case the system behaves as a pseudobinary and can be described only by the two experimental quantities

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D_A and Q_0. Impure solutes and polydisperse samples are examples of this case. D_A and Q_0 are dependent on the diffusion coefficients and refractive fractions of all the components present in solution. Thus, in principle, their values could give information on the sample composition. It is useful to consider eqs 15 and 16 at infinite dilution. In fact for nonelectrolytes in these conditions all the cross-diffusion coefficients are zero, the main terms are equal to the limiting values of the corresponding binary systems D_i^∞, and the Γ_i values coincide with the α_i values. The following equations hold:

$$\frac{1}{\sqrt{D_A^\infty}} = \sum_{i=1}^{n-1} \frac{\alpha_i}{\sqrt{D_{ii}^\infty}} = \sum_{i=1}^{n-1} \frac{\alpha_i}{\sqrt{D_i^\infty}} \tag{18}$$

$$Q_0^\infty = \frac{\dfrac{1}{2}\sum_{i=1}^{n-1}\sum_{j=1}^{n-1}\alpha_i\alpha_j\left(\dfrac{1/\sqrt{D_i^\infty} + 1/\sqrt{D_j^\infty}}{2\sqrt{2}} - \dfrac{1}{\sqrt{D_i^\infty + D_j^\infty}}\right)}{\sum_{i=1}^{n-1}\alpha_i/\sqrt{D_i^\infty}} \tag{19}$$

These equations include the limiting case of a binary system ($n = 2$), where $D_A = D_1$ and $Q_0 = 0$. Equation 19 shows that Q_0 is positive as defined for pseudobinary systems, as discussed in the Appendix. Indeed this is confirmed by literature data[15,37] and our unpublished results on polymers and aggregated solutes.

Application

In the case of polymers the main goal is to obtain the molecular weight and the molecular weight distribution of the sample. To analyze in detail the information that can be obtained from D_A^∞ and Q_0^∞ for a polydisperse sample, we considered the dependence of these two quantities on the number-average chain length for two molecular weight distributions. In particular we considered the Schulz−Zimm,[38] SZ, and Poisson,[38] P, distributions. If i is the polymerization degree, the weight fraction distributions, $w(i)$, and the number-average, $\bar{i}_n$, and weight-average, $\bar{i}_w$, chain lengths are, respectively

$$\text{SZ:} \quad w(i) = \left(\frac{b^{a+1}}{a!}\right)i^a \exp(-bi) \tag{20}$$

$$\bar{i}_n = \frac{a}{b}, \quad \bar{i}_w = \frac{a+1}{b}$$

$$\text{P:} \quad w(i) = \frac{i}{\nu+1}\frac{\nu^{i-1}}{(i-1)!}\exp(-\nu) \tag{21}$$

$$\bar{i}_n = 1+\nu, \quad \bar{i}_w = 1+\nu+\frac{\nu}{\nu+1}$$

The SZ distribution width decreases as a increases. The SZ is a two-parameter distribution expected for a steady-state linear radical-chain polymerization, where the a value depends on the reaction conditions. It can be applied to polyacrylic acid (PAA) and sodium polyacrylate (NaPA) samples. P is a monoparameter distribution which describes ionic polymerizations with instantaneous initiation and no termination, typical of polyethylene glycol (PEG) synthesis. While SZ is used to represent fairly wide distributions, P can be applied to narrow distributions.

For the dependence of the diffusion coefficient on the molecular weight of the pure oligomers we used the Flory

equation:[39]

$$D_i^\infty = K_F M_i^\gamma \tag{22}$$

where K_F and γ are two parameters dependent on the solvent−polymer pair. Even if diffusion data are not available for oligomers or fractioned polymers, viscosity or sedimentation measurements could be used to provide γ, through the so-called exponent rule:[40]

$$a_\eta = 2 - 3a_S = -(1 + 3\gamma) \tag{23}$$

where a_η and a_S are the exponent of the scaling laws corresponding to viscosity and sedimentation

$$[\eta] = K_\eta M^{a_\eta} \qquad s = K_S M^{a_S} \tag{24}$$

If the refractive index increment expressed in the weight fraction scale does not depend on the degree of polymerization, it is preferable to use this concentration scale, because the refractive fractions coincide with the weight fraction, $\alpha_i = w(i)$. Then, using $M_i = iM_u$ where M_u is the weight of the monomeric unit, eq 18 and 19 become

$$\frac{1}{\sqrt{D_A^\infty}} = \sum_{i=1}^{n-1} \frac{w(i)}{\sqrt{K_F M_i^\gamma}} \tag{25}$$

$$Q_0^\infty = \frac{\dfrac{1}{2}\sum_{i=1}^{n-1}\sum_{j=1}^{n-1}w(i)\,w(j)\left(\dfrac{1/\sqrt{i^\gamma} + 1/\sqrt{j^\gamma}}{2\sqrt{2}} - \dfrac{1}{\sqrt{i^\gamma + j^\gamma}}\right)}{\sum_{i=1}^{n-1}\dfrac{w(i)}{\sqrt{i^\gamma}}} \tag{26}$$

We note from eq 26 that the Q_0^∞ values do not depend on K_F, and from eq 25 that the optical average molecular weight is an exponent average.[40] In fact substituting the Flory equation, eq 22, into eq 25, we obtain

$$\bar{M}_G = \left[\sum_{i=1}^{n-1} w(i)M_i^{-\gamma}/2\right]^{-2/\gamma} \tag{27}$$

that is, smaller than a numerical average[41] because γ assumes values typically in the range -0.2 to -0.8. Cussler[15] observed that this average is useful in describing diffusive properties and chemical potentials.

To underline the effect of different distribution functions on D_A^∞, we used the following expression:

$$\frac{D_A^\infty - D_i^\infty}{K_F M_u} = \bar{i}_n^\gamma - i^\gamma \tag{28}$$

The left term of eq 28 depends only on γ and on the specific distribution as does Q_0^∞. The quantity defined in eq 28 is shown in Figure 1 as a function of the number-average chain length, $\bar{i}_n$, for the two distributions. In this figure the corresponding quantity for oligomers is zero since $\bar{i}_n = i$. As can be seen, $\bar{i}_n^\gamma - i^\gamma$ increases as the distribution width increases. Q_0^∞
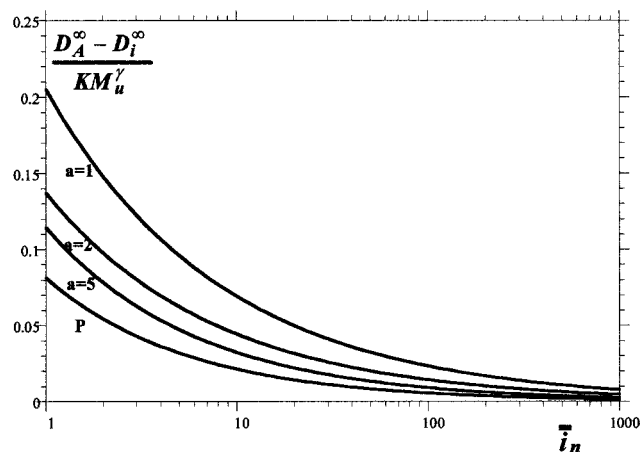
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Figure 1. Difference between generalized D_A^∞ and D_i^∞ of oligomers for different distribution functions vs $\bar{i}_n$, calculated with $\gamma = -0.5$.
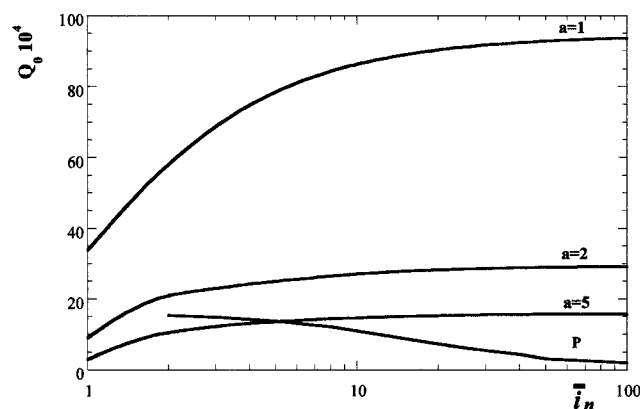

Figure 2. Q_0^∞ calculated for different distribution functions vs $\bar{i}_n$.

Figure 3. Effect of fractionation on D_A^∞ and Q_0^∞ for a hypothetical polymer with $\bar{i}_n = 10$ in a θ solvent in the case of a Poisson distribution.
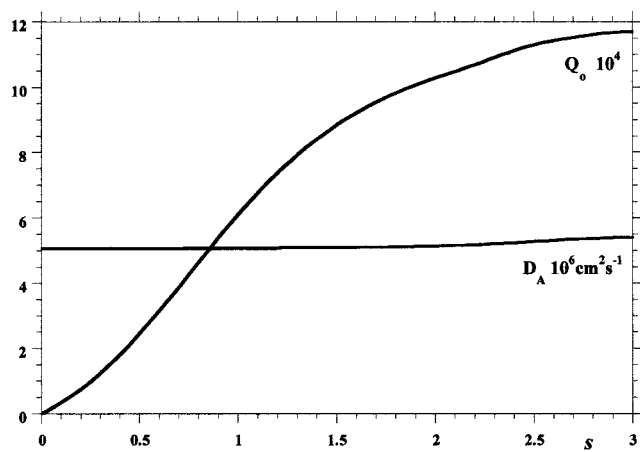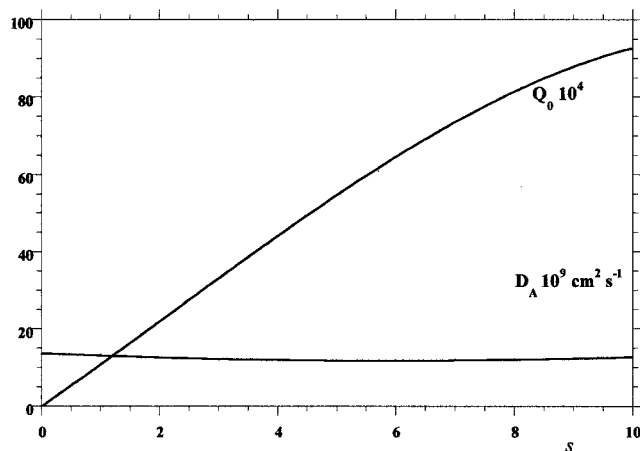

Figure 4. Effect of fractionation on D_A^∞ and Q_0^∞ for a hypothetical polymer with $\bar{i}_n = 100$ in a θ solvent in the case of a Schulz distribution.

(Figure 2) shows a very different trend for the two examined distribution functions. For the P distribution Q_0^∞ is a decreasing function of $\bar{i}_n$ and approaches zero as the polymerization degree increases. For the SZ distribution, Q_0^∞ is an increasing function of $\bar{i}_n$ and approaches a plateau or a large maximum, the value of which depends on a.

The D_A^∞ and Q_0^∞ trends suggest the following comments: (a) If the distribution function is unknown, the knowledge of both D_A^∞ and Q_0^∞ trends vs $\bar{i}_n$ allows determination of the kind of distribution. (b) If the distribution function is known, the knowledge of D_A^∞ or Q_0^∞ values allows the number-average chain length to be obtained.

The error in determining $\bar{i}_n$, $\Delta\bar{i}_n$, is related to the experimental errors ΔD_A^∞ or ΔQ_0^∞, and to the derivative of D_A^∞ or Q_0^∞ with respect to $\bar{i}_n$. These derivatives decrease, in absolute value, as the number-average chain length increases, and then the $\Delta\bar{i}_n$ increases as $\bar{i}_n$ increases. Since the relative error in D_A^∞ is usually much smaller then the corresponding error in Q_0^∞, it is preferable to use D_A^∞ to evaluate $\bar{i}_n$.

Considering eqs 22 and 25, the relative error in $\bar{i}_n$ is given by

$$\frac{\Delta\bar{i}_n}{\bar{i}_n} = \frac{1}{\gamma}\frac{\Delta D_A^\infty}{K_F(\bar{i}_n M_u)^\gamma} \tag{29}$$

The maximum $\bar{i}_n$ detectable with a fixed relative error $e_{r,i}$ is given by the equation

$$(\bar{i}_n)_{max} = \left(\left|\frac{\Delta D_A^\infty}{e_{r,i}\gamma K_F(M_u)^\gamma}\right|\right)^{1/\gamma} \tag{30}$$

The use of Q_0^∞ is also more convenient with respect to D_A^∞, in analyzing the effect of fractionation of a polydisperse sample.

To simulate a fractionation, we considered, for both SZ and P distributions, a sample with a fixed $\bar{i}_n$ and different distribution widths, obtained by truncating the original distribution at different multiples s of its numerical standard deviation, ϵ_n. In Figures 3 and 4 the D_A^∞ and Q_0^∞, computed using the same parameters as in Figures 1 and 2, are reported as a function of s. As can be observed D_A^∞ is almost independent of s, the change being of the same order of magnitude as the experimental errors, whereas the correspondent change in Q_0^∞ is very drastic and it should allow, in principle, the cut position of a fractionation to be deduced.

It is worth pointing out that the polydispersity cannot be detected from diffusion data beyond a limit $\bar{i}_n$ value, $\bar{i}_{n,l}$. This limit corresponds to the number-average chain length for which all components of the distribution in the range $\bar{i}_{n,l} \pm s\epsilon_n$ have a diffusion coefficient in the range $D_A^\infty(\bar{i}_{n,l}) \pm \Delta D_A^\infty$. The s value is a number of standard deviation sufficient to include all components present in significant amounts. The above limit

TABLE 1: Data of PEG Samples

PEG sample	$D_A^\infty \times 10^5$, cm^2 s^{-1}	$Q_0 \times 10^4$	$R^\infty h/\lambda$	M_G	M_n
200	0.629	18.3 ± 4	46.52	145 ± 25	$190-210$
300	0.505	14.1 ± 3	48.45	250 ± 35	$285-315$
400	0.438	16.4 ± 4	49.53	350 ± 40	$380-420$
600	0.352	8.4 ± 4	50.46	560 ± 80	$570-630$
1000	0.269	8.0 ± 3	51.00	991 ± 140	$950-1050$
1500	0.219	6.2 ± 3	51.57	1499 ± 200	$1400-1600$
2000	0.196	7.3 ± 3	51.42	1874 ± 250	
3400	0.138	6.7 ± 3	51.95	3700 ± 500	
10000	0.075	4.8 ± 3	52.30		

corresponds to

$$\bar{t}_{n,l} = \frac{s\epsilon_n}{1 - [1 - \Delta D_A^\infty / D_A^\infty(\bar{t}_{n,l})]^{1/\gamma}} \tag{31}$$

From eq 28 it follows that the $\bar{t}_{n,l}$ value does not depend on the molecular weight of the monomeric unit, nor on K_F, and it is only a function of γ and ϵ_n.

Experimental Section

Chemicals. The polyethyleneglycol samples at different molecular weights from 200 to 10000 have been purchased from Aldrich and used without further purification. The polyacrylic acid, PAA, has been prepared by radical polymerization in methyl ethyl ketone at 60 °C for 10 h starting from acrylic acid and diazobisisobutyronitrile as initiator. The fractionation of the product has been performed in alcoholic solution using, at controlled temperature, ethyl ether as precipitant. From the unfractionated sample, A, three fractions were obtained, A1, A2, and A3 at increasing average molecular weights. A2 was then fractionated again, obtaining the fractions A21, A22, and A23. All samples were characterized by determination of the average viscosimetric molecular weight.[42] The unfractionated polymer A and the central fractions A2 and A22 were used for the diffusion experiments. Sodium salt samples, NaPA, were obtained by neutralization at 99.99 % of the PAA with NaOH. All the PAA and NaPA data are unpublished data coming from samples used in the past for some diffusion research on polyacrylate aqueous solution.[18,19]

Solution Preparation. All solutions were prepared by weight using double-distilled water. To obtain the concentration on the molarity scale, the density of each solution was determined using an ANTOR PAAR densimeter model 602.

Diffusion Experiment. All diffusion experiments were performed, at 25.00 ± 0.01 °C, with the Gouy diffusiometer located at the Dipartimento di Chimica, Università degli Studi Federico II di Napoli, with the usual procedure described elsewhere.[30] The limiting diffusion coefficients of the PEG samples, D_A^∞, and their limiting refractive properties, $R_\%^\infty$, were obtained by extrapolation of data collected at finite concentration.[37] The Q_0^∞ values are average values because no significant trend of Q_0 as a function of polymer concentration was observed. The PEG data at finite concentration will be given and discussed in a future paper.[37] The PEG sample data used in this paper are reported in Table 1. The PAA and NaPA data are reported in Table 3.

Viscosity Experiments. All viscosity experiments were performed, at 25.00 °C, with a Ubbelhode viscometer using double-distilled water.

Results and Discussion

PEG−H₂O Systems. Figures 5 and 6 show the $R_\%^\infty$ and D_A^∞

TABLE 2: Literature Data of PEG Diffusion Coefficients at Infinite Dilution

M_W	$D_A^\infty \times 10^5$, cm^2 s^{-1}	ref	M_W	$D_A^\infty \times 10^5$, cm^2 s^{-1}	ref
106.12	0.897	23	1080	0.272	42
150.17	0.762	23	1090	0.271	42
194.23	0.669	23	1450	0.234	42
238.28	0.598	23	1588	0.221	42
282	0.530	42	2960	0.157	42
326	0.495	42	7770	0.090	42
732	0.325	42	320000	0.010	43
780	0.310	42			

TABLE 3: Experimental Results on Polyacrylic Acid and Sodium Polyacrylate Samples at $\bar{C} = 0.6$ mol L^{-1}

		PAA		NaPA	
sample	$\bar{t}_\nu$	$D_A \times 10^6$, cm^2 s^{-1}	$Q_0 \times 10^4$	$D_A \times 10^5$, cm^2 s^{-1}	$Q_0 \times 10^4$
A	970	0.814	114.2	0.392	82.1
A2	1030	0.740	35.7	0.387	19.3
A22	830	0.763	29.7	0.392	≈ 0

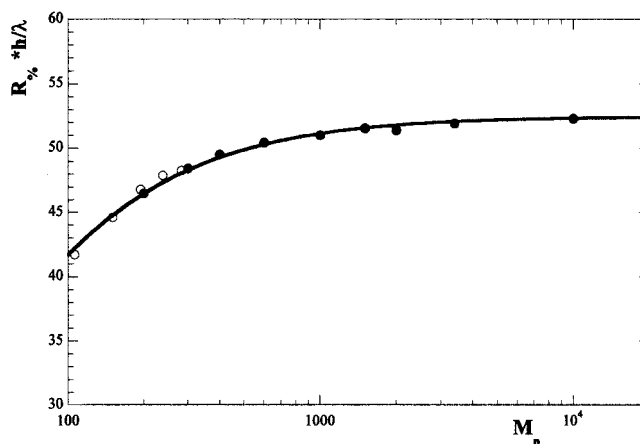**Figure 5.** Experimental infinite dilution refractive increment, $R_\%^\infty$, vs molecular weight of oligomers (○) and polydisperse samples (●).
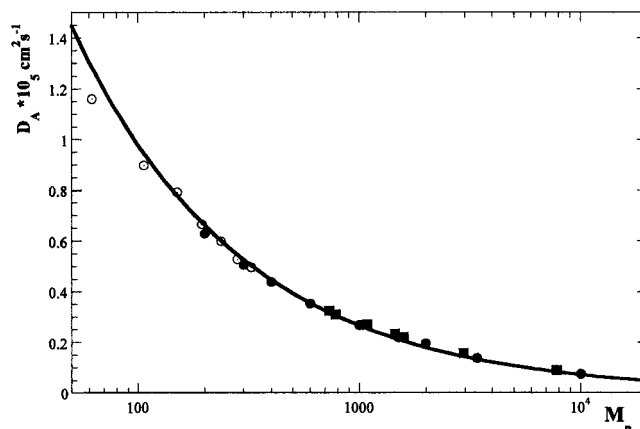

Figure 6. Experimental infinite dilution diffusion coefficients, D_A^∞, for oligomers (○), fractionated samples (■), and polydisperse samples (●) vs molecular weight.

values of polydisperse systems as a function of the molecular weight given by Aldrich; the data of oligomers from dimer to hexamer have been added. The Q_0 for the polydisperse systems are reported in Figure 7 as a function of the Aldrich molecular weight.

Equations 25 and 26 were obtained assuming $R_\%^\infty$ independent of molecular weight. This approximation seems reasonable from the inspection of Figure 5 where just a small variation on

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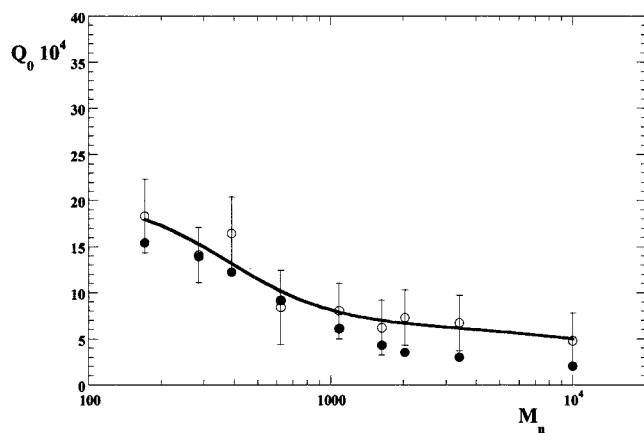
Figure 7. Experimental (○) and calculated (●) Q_0^∞ values *vs* the molecular weight of PEG samples.

$R_\%^\infty$ is observed for molecular weights larger than 1000. Equations 25 and 26 are then rigorous for high molecular weight PEG samples. Probably the same assumption can be extended to any polymer. However, for calculating D_A^∞ and Q_0^∞ from eqs 18 and 19, we considered the $R_\%^\infty$ variation on molecular weight.

To compute the average molecular weight of PEG samples from the D_A^∞ values, the parameters of the Flory equation are required. These parameters cannot be accurately determined by fitting the D_i^∞ of the first oligomers.[23] To have a good estimation of the diffusive behavior in a large range of $\bar{i}_n$, it is necessary to use diffusion data of heavy samples which behave as monodisperse from a diffusive point of view. For this reason we used the data relative to some sharply fractionated samples,[43] and of a polydisperse sample with molecular weight 320 000. To use this datum,[44] we verified, using eq 31, that this sample has an $\bar{i}_n$ value larger than $\bar{i}_{n,l}$, which corresponds to a molecular weight of 100 000 for $s = 2$.

The parameters of the Flory equation, eq 22, obtained by fitting the diffusion data given in Table 2 are $K_F = (10.6 \pm 0.3) \times 10^{-5}$ cm^2 s^{-1} and $\gamma = -0.527 \pm 0.006$. Using these constants in eq 25, the Gouy average molecular weights, $\bar{M}_G$, were evaluated. We note that the difference between $\bar{M}_G$ and M_n increases with the distribution width. The results shown in Table 1 indicate the good agreement between the calculated $\bar{M}_G$ and the Aldrich number-average M_n, on the basis of the determination of the hydroxyl content using the phthalic anhydride–pyridine method.[45]

Using eq 26 and the above K_F and γ values in the Flory equation, we calculated the Q_0^∞ for our polydisperse samples. These values are reported in Figure 7. The reasonable quantitative agreement between the experimental and predicted values confirms that the Q_0^∞ values are essentially due to the diffusive polydispersity of the samples.

PAA–H$_2$O and NaPA–H$_2$O Systems. The role of Q_0 is emphasized by the analysis of the data relative to the PAA and NaPA aqueous pseudobinary systems. The D_A and Q_0 values for three analyzed samples are reported in Table 3. Inspection of this table does show that the D_A values do not change very much, while the Q_0 value drops dramatically as the distribution width decreases on fractionation. It is worth pointing out the differences between the PAA and NaPA diffusive properties. D_A values are systematically larger for NaPA, while Q_0 values are larger for the acid samples. This behavior is due to different K_F and γ values of the Flory equation for the two com-

pounds,[16,36] which reflects the different diffusion mechanism for a weak polyacid and its salt.[16,17] An attempt to evaluate the fractionation results was done by analyzing the Q_0 values, assuming a Schulz distribution and using the γ values reported in the literature.[18,39] We obtained the γ value of polyacrylate using eq 23 together with the data of ref 42. This analysis suggested that, with respect to the complete Schulz distribution of sample A, fractions A2 and A22 have a distribution width equal to 2 and 0.5 standard deviation.

Conclusions

In this paper we generalize the definitions of interferometric parameters, D_A and Q_0, for an n-component system. Analytical expressions for D_A and Q_0 are obtained as a function of the refractive fraction and of the binary oligomer data, D_i, in the case of zero cross-diffusion coefficients. D_A^∞ appears as a general powerful tool to determine molecular weights. In the case of PEG samples we obtained results in good agreement with those yielded by Aldrich.

In general the analysis of D_A^∞ provides a new average molecular weight, the Gouy average, lower than the numerical average. Q_0 seems to be very sensitive to the diffusive polydispersity, in a generic n-component system, as in synthetic polymers in association equilibria. In particular the Q_0^∞ analysis can distinguish among different distribution functions and can estimate the fractionation results.

We emphasize that the procedures used to evaluate the average molecular weight and the efficiency of the fractionation process can be generalized to any polymers.

Appendix

According to Kim,[28] in eq 7 introducing the expression of the refractive index and its maximum and applying the interference condition in a Gouy fringe pattern arising from any symmetrical refractive index gradient curve[28,30,31] give

$$Q_0 = \int_0^\infty e^{-\zeta^2} \frac{df(\zeta)}{d\zeta} d\zeta - \int_0^\infty \frac{\sum_{i=1}^{n-1} \Gamma_i \sqrt{\sigma_i} e^{-\sigma_i y^2}}{\sum_{i=1}^{n-1} \Gamma_i \sqrt{\sigma_i}} \frac{df(\zeta)}{dz} dz$$

(A1)

where

$$z = \sqrt{\sigma_1} y \qquad \frac{df(\zeta)}{d\zeta} = \frac{4}{\sqrt{\pi}} \zeta^2 e^{-\zeta} \qquad \text{(A2)}$$

$$\frac{df(\zeta)}{dz} = \frac{4}{\sqrt{\pi}} \sum_{i=1}^{n-1} \Gamma_i \left(\frac{\sigma_i}{\sigma_1}\right)^{3/2} z^2 e^{-(\sigma_i/\sigma_1)z^2} \qquad \text{(A3)}$$

Substituting eqs A2 and A3 in eq A1 and after integrating, we obtain

$$Q_0 = [(1/2)\sum_{i=1}^{n-1}\sum_{j=1}^{n-1}\Gamma_i\Gamma_j g_{ij}]/[\sum_{i=1}^{n}\Gamma_i\sqrt{\sigma_i}]$$

with

$$g_{ij} = \frac{\sqrt{\sigma_i} + \sqrt{\sigma_j}}{2\sqrt{2}} - \frac{\sqrt{\sigma_i\sigma_j}}{\sqrt{\sigma_i + \sigma_j}} = g_{ji}$$

At infinite dilution, using eq 18

$$Q_0^\infty = 2^{-3/2} - \frac{1}{2}\sum_{i=1}^{n-1}\sum_{j=1}^{n-1}\frac{\alpha_i\alpha_j\sqrt{D_A}}{\sqrt{D_i + D_j}} \qquad (A4)$$

The refractive fraction a_i is positive for each component for definition of a pseudobinary system; hence, Q_0^∞ could not be negative.

Abbreviations and Symbols

a	parameter of SZ (eq 20)
a_S, a_η	exponent of sedimentation and viscosity coefficient dependence on the molecular weight (eq 24)
b	parameter of SZ (eq 20)
$C_i, \bar{C}_i$	concentration and mean concentration of component i (eq 5)
$D_A, D_i, D_{ij},$	mutual diffusion coefficients (apparent, of the component with polymerization degree i) and cross-diffusion coefficient (eqs 9, 18, and 1)
e_r	relative error of a specific technique (eq 30)
$f(\zeta)$	function defining the interference condition (eq 12)
g_{ij}	combination of mutual diffusion coefficients (eq 16)
h	thickness of the diffusion cell in the direction of the optical axis
$i, \bar{i}_{n,l}, \bar{i}_n, \bar{i}_{n,max}, \bar{i}_w$	polymerization degree, limit of diffusive polydispersity, number average, limit at a fixed relative error, weight average (eqs 20, 31, 20, 30, and 20)
K_F, K_S, K_h	preexponential terms of diffusion, sedimentation, and viscosity dependence on the molecular weight (eqs 22, 24, and 24)
K_{ij}	constants in the integration of the Fick equation (eq 4)
M_i, M_G, M_u	molecular weight relative to oligomer, number average, limit of diffusive polydispersity, Gouy average, and monomeric unit (eqs 22, 27, and 28)
$n_\lambda, \bar{n}_\lambda$	refractive index, mean refractive index (eq 5)
NaPA	sodium polyacrylate
P	Poisson distribution
PAA	polyacrylic acid
PEG	polyethylene glycol
Q_0	area under the deviation graph (eq 10)
$R_i, R_i^\%$	refractive increment index of component i in a generic scale and weight fraction scale (eq 14)
s	number of standard deviation (eq 31)
SZ	Schulz–Zimm distribution
t	time of diffusion phenomena (eq 2)
x	position along the diffusion cell (eq 1)
$w(i)$	distribution function in weight fraction (eq 20)
y	Boltzmann reduced coordinate (eq 4)
α_i	refractive fraction of component i (eq 14)
ϵ_n	deviation standard of a distribution (eq 31)
γ	exponent of the Flory equation (eq 22)
Γ_i	constants in the integration of the Fick equation (eq 6)
ν	average polymerization degree minus a unit for the Poisson distribution (eq 21)
Ω_j	deviation function from the Gaussian curve of the refractive index gradient (eq 10)
ζ	generalized coordinate for multicomponent systems (eq 10)

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