

Novel Method for Calculating the Diffusion Coefficients of a Ternary System Containing a Polydisperse Component. Applications to the Gouy Interferometry

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The common approach of neglecting the effect of polydispersity on matter transport leads, in multicomponent systems, to thermodynamic inconsistency at infinite dilution of all of the solutes. Furthermore such an approximation could cause an incorrect determination of the diffusion coefficients if the standard calculation procedures are applied. We present a novel approach to correct for the effect of the polydispersity of a solute on the values of the basic Gouy parameters D_A "the reduced height-area ratio" and Q_0 "the area under the Ω graph" used in the Fujita-Gosting procedure to compute the four diffusion coefficients of a ternary system containing a polydisperse component. The proposed procedure satisfies the thermodynamic requirements at infinite solute dilution. To verify the reliability of our method, a series of simulations on the ternary aqueous system containing poly(ethyleneglicol) 200 and poly(ethyleneglicol) 400 in the presence of a monodisperse solute have been performed. For the polymeric sample, Poisson and Zimm–Schultz distributions have been considered. In both cases, our procedure has been applied successfully up to dilute concentration of components present in the system.

I. Introduction

The polydispersity is a characteristic shown by most biological macromolecules and synthetic polymers. In the latter case, it takes origin from the nature of the industrial processes used in their production. Polydispersity depends on several parameters including temperature,¹ pH,² concentration of reagents,³ and nature of catalysts used, and it affects both thermodynamic and transport properties of solutions containing a polydisperse solute.^{4–7}

In principle, polydispersity affects any property that is able to distinguish molecules according to size. Diffusive properties are very sensitive to the size of particles, and for this reason, it is important to understand how the polydispersity influences them. Furthermore, in recent years, increasing interest has been devoted to systems containing at least one polydisperse component: recently, for example, multicomponent diffusion in solutions containing proteins and polymers has received increasing attention in order to understand the mechanisms regulating the nucleation and the growth of protein crystals.^{8,9} Any theory or model used to explain these mechanisms should take in to account the effect of polydispersity on the diffusion coefficients.

Over the years, several authors have examined the issue of the effect component polydispersity on diffusion processes. Sundelöf¹⁰ presented a method to determine the distribution function of molecular size parameters through a deconvolution of the interferometric parameters. Cussler and Lightfoot^{11,12} studied polydisperse systems although with no experimental comparison of the assumed distribution function. Further Comper,¹³ Leaist,¹⁴ and some of us¹⁵ performed experiments on systems containing polydisperse species. In all cases, no attention has been devoted on the effect of polydispersity on the actual data analysis, and the polydisperse component has

been considered as a pure one: this assumption is due to the experimental impossibility of analyzing polydisperse samples as if they were single solutes because the results will depend on the weight distribution.

In this paper, we will show that, without a correct analysis of experimental data, the assumption that considers the polydisperse component as a single pure component leads to incorrect conclusions because of inconsistent values of the diffusion coefficient matrix. Further, we will present a procedure that takes polydispersity into account.

Because of the mathematical complexity of the problem, our discussion is limited to the pseudoternary systems composed of one pure solute (monodisperse) and a second solute that is actually polydisperse. Such systems are only apparently ternary. If N is the number of distinct species constituting the polydisperse component, a pseudoternary system is actually a $N + 2$ component system. In this paper, the polymeric components will be identified by the subscripts 1, 2, ..., N , the monodisperse component with the subscript $N + 1$, and the solvent with the subscript 0.

For a correct description of such a system, from a diffusive point of view, it would be necessary to know the whole diffusion coefficient matrix \mathbf{D} containing $(N + 1)^2$ diffusion coefficients. Unfortunately, it is impossible to have access at this matrix experimentally, because it is impossible to change arbitrarily the ratio among the concentrations of the components constituting the polydisperse solute; thus, we can only treat the system just as a ternary one. It is therefore important to study the effects of this assumption on the meaning of the diffusion coefficients: this is the main purpose of this methodological paper.

II. Diffusion in Multicomponent Systems

The inter diffusive matter transport in a generic $N + 2$ component system, in which there are small concentration

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gradients and in absence of any chemical reaction, is fully described by the Fick's laws¹⁶

$$\mathbf{J}_i = -\sum_{j=1}^{N+1} D_{ij} \nabla c_j \quad (1)$$

$$\frac{\partial c_i}{\partial t} = \sum_{j=1}^{N+1} D_{ij} \nabla^2 c_j \quad (2)$$

where \mathbf{J}_i and c_i are, respectively, the flux and the molar concentration of the i th component, and D_{ij} is the (ij) element of the diffusion coefficient matrix \mathbf{D} . In this paper, fluxes and diffusion coefficients will be both expressed in the *volume fixed reference frame*.¹⁷ Equation 2 requires constant D_{ij} 's: this is usually a good approximation for experiments in which solute concentration changes from one side of the diffusion boundary to the other are small. The most common experimental boundary conditions used for precision diffusion coefficient measurement are the free-diffusion boundary conditions, where two solutions ("top" and "bottom") differing slightly in concentration and initially separated by a sharp boundary are allowed to diffuse into each other.¹⁸ The solution of eq 2 for free-diffusion boundary conditions can be written as follows:^{19a,b}

$$c_i(x,t) = \bar{c}_i + \sum_{j=1}^{N+1} \sum_{k=1}^{N+1} \frac{T_{i,k} T_{k,j}^{-1} \Delta c_j}{2} \operatorname{erf}\left(\frac{x}{2\sqrt{\Lambda_k t}}\right) \quad (3)$$

where \bar{c}_i is the mean concentration of the i th component, erf is the error function operator, and the Λ_k 's and the $T_{i,k}$'s are respectively the eigenvalues and the eigenvector components of the diffusion coefficient matrix \mathbf{D} according to the eigenvalue equation

$$\mathbf{D}\mathbf{T} = \mathbf{T}\mathbf{\Lambda} \quad (4)$$

In eq 3, Δc_j are the initial concentrations across the initial boundary which was formed at $x = 0$. The elapsed time, t , is the time that the diffusion process has progressed from initial step-function c_j distributions.

Diffusimeters that use Gouy and/or Rayleigh interferometric optics are the most accurate instruments for measuring multi-component diffusion coefficients. These instruments are based directly on refractive index profiles as a function of time as diffusion occurs in a diffusion cell. Because experimental concentration differences of solutes across the initial boundary are usually small in interferometric diffusimeters, the assumption that the refractive index, n_λ at wavelength λ , is linearly proportional to solute concentrations is usually valid within experimental error. Thus, the following relation is assumed:

$$n_\lambda \cong \bar{n}_\lambda + \sum_{i=1}^{N+1} \frac{\partial n_\lambda}{\partial c_i} (c_i - \bar{c}_i) = \bar{n}_\lambda + \sum_{i=1}^{N+1} R_i (c_i - \bar{c}_i) \quad (5)$$

Expressions for the refractive index and its derivative $\partial n/\partial x$ can be obtained from eqs 5 and 3

$$n_\lambda(x,t) = \bar{n}_\lambda + \frac{\Delta n_\lambda}{2} \sum_{k=1}^{N+1} \Gamma_k \operatorname{erf}\left(\frac{x}{2\sqrt{\Lambda_k t}}\right) \quad (6)$$

$$\frac{\partial n_\lambda(x,t)}{\partial x} = \frac{\Delta n_\lambda}{2\sqrt{\pi t}} \sum_{k=1}^{N+1} \frac{\Gamma_k}{\sqrt{\Lambda_k}} \exp\left(-\frac{x^2}{4\Lambda_k t}\right) \quad (7)$$

where Δn_λ is the difference of refractive index between "top" and "bottom" solutions, whereas the Γ_k 's parameters are defined by the following equation:

$$\Gamma_k = \sum_{i=1}^{N+1} \sum_{j=1}^{N+1} \frac{R_i \Delta c_j}{\Delta n_\lambda} T_{i,k} T_{k,j}^{-1} \quad (8)$$

In Gouy interferometry, monochromatic radiation passes through a cell containing the solution in which free-diffusion is occurring, which produces an interference pattern whose intensity profile represents the Fourier transform of the refractive index profile inside the diffusion cell.

The position of the j th minimum of the pattern, Y_j , can be expressed as^{20–22}

$$\frac{Y_j}{C_t} = \frac{\sum_{i=1}^{N+1} \frac{\Gamma_i}{\sqrt{\Lambda_i}} \exp\left(-\frac{y_j^2}{\Lambda_i}\right)}{\sum_{i=1}^{N+1} \frac{\Gamma_i}{\sqrt{\Lambda_i}}} \quad (9)$$

where C_t is the maximum displacement of light, and the y_j parameters are implicitly defined by equation

$$\frac{Z(j)}{J_m} = \sum_{i=1}^{N+1} \Gamma_i \left[\operatorname{erf}\left(\frac{y_j}{\sqrt{\Lambda_i}}\right) - \frac{2y_j}{\sqrt{\Lambda_i \pi}} \exp\left(-\frac{y_j^2}{\Lambda_i}\right) \right] \quad (10)$$

where $Z(j)$ is a complicated function of the fringe order j . For high values of j , it is possible to show that $Z(j) \cong j + 3/4$. In eq 10, J_m is the total fringe number

$$J_m = \frac{a \Delta n_\lambda}{\lambda} \quad (11)$$

where a is the width of the channel in the diffusion cell. In each experiment to improve the accuracy of the measurement, several exposures of the interferometric pattern are taken during the run time.

The minima positions Y_j are used to calculate the two characteristic quantities obtained by the Gouy interferometric method. The first one is the apparent diffusion coefficient D_A which would be the actual diffusion coefficient of the solute in a binary system

$$D_A = \frac{(\Delta n_\lambda)^2}{4\pi t (\partial n_\lambda / \partial x)_{\max}^2} \quad (12)$$

The second one is the "area under the deviation graph", Q_0 , that is related to all the D_{ij} 's, and gammas, and thus to initial solute concentration differences between the top and bottom solutions

$$Q_0 = \int_0^1 \Omega_j df(z_j) \quad (13)$$

where

$$z_j = \frac{x}{2\sqrt{D_A t}} \quad (14)$$

$$\Omega_j = \exp(-z_j^2) - \frac{Y_j}{C_t} \quad (15)$$

$$f(z_j) = \operatorname{erf}(z_j) - \frac{2}{\sqrt{\pi}} \exp(-z_j^2) \quad (16)$$

Because of their physical meaning, it is evident that D_A and Q_0 contain valuable information about the polydispersity in a polydisperse system.

D_A may be experimentally evaluated by first calculating φ values defined in the following equation where t' is the practical experimental elapsed time and then obtaining φ as a linear function of $1/t'$ by the method of least squares

$$\varphi = \frac{J_m^2 \lambda^2 b^2}{4C_t^2 \pi t'} = D_A + D_A t_c' \frac{1}{t'} \quad (17)$$

In eq 17, b is the distance between the center of the diffusion cell and the image plane where the fringe pattern is recorded. The ray-optics-theory maximum displacement of the light C_t can be calculated by using measured fringe minimum positions of the fringe pattern.²³ Regarding J_m , the integer part of it can be determined by counting the fringes while the fractional part through the use of a special optical mask. The quantity t_c represents the correction that must be added to the practical experimental elapsed time due to an imperfect initial boundary at the practical starting time $t' = 0$ of an actual experiment.

Once D_A is known, the Q_0 value is calculated through a graphical quadrature, plotting Ω_j vs $f(z_j)$.

The procedures for evaluation of experimental D_A and Q_0 values from the minima positions, Y_j , are hence independent of the system analyzed and do not require any hypothesis neither on the number of the components nor on their nature.

The complexity of the diffusive description of a system increases when the number of components rises.

For a binary system, D_A is equal to the binary diffusion coefficient D of the system and Q_0 is null. For a $N + 2$ component systems, D_A and Q_0 depend on the $(N + 1) \times (N + 1)$ diffusion coefficient matrix and by the refractive index ratio α_i defined as

$$\alpha_i = \frac{R_i \Delta c_i}{\Delta n_\lambda} = \frac{R_i \Delta c_i}{\sum_{j=1}^{N+1} R_j \Delta c_j} \quad (18)$$

To measure all of the diffusion coefficients for the solute components in the $(N + 1)^2$ diffusion coefficient matrix, it is necessary to perform at least $(N + 1)$ experiments at the same mean compositions, varying independently each of the solute concentration differences across the initial boundary.

The quantities D_A and Q_0 depend on the α_i 's and Λ_i 's ones through the following relations³³

$$\frac{1}{\sqrt{D_A}} = \sum_{i=1}^{N+1} \frac{\Gamma_i}{\sqrt{\Lambda_i}} \quad (19)$$

$$\frac{Q_0}{\sqrt{D_A}} = \frac{1}{2} \sum_{i=1}^{N+1} \sum_{j=1}^{N+1} \Gamma_i \Gamma_j G_{ij} = \sum_{i=1}^N \sum_{j=i+1}^{N+1} \Gamma_i \Gamma_j G_{ij} \quad (20)$$

where

$$G_{ij} = \frac{1}{2\sqrt{2}} \frac{\sqrt{\Lambda_i} + \sqrt{\Lambda_j}}{\sqrt{\Lambda_i \Lambda_j}} - \frac{1}{\sqrt{\Lambda_i + \Lambda_j}} \quad (21)$$

It is easy to show that $G_{ij} = G_{ji}$ and that $G_{ii} = 0$.

For ternary systems, the pairs (D_A, Q_0) obtained by at least two experiments are sufficient to evaluate the (2×2) diffusion matrix coefficient according to Fujita and Gosting's procedure.^{24,25} For systems with more than three components, there is no good procedure to obtain the diffusion coefficient matrix with the Gouy interferometry, except a method elaborated by Miller.²⁶ This method was used to compute the nine diffusion coefficients for the α -cyclodextrin-L-phenylalanine-mono-butylurea-water system.²⁷ Earlier, Kim^{28,29} was unsuccessful in finding a suitable third quantity needed for a 4-component Fujita-Gosting analysis, and his alternative suggestion to combine Gouy with other data was never tested.

If it is not possible to vary independently the concentration ratios of some components, we are forced to analyze the system as though it had a smaller number of components. For example, in a $N + 2$ component system, if we have $N + 1$ correlations between the solute concentrations, we can only analyze it as a binary. Instead, if the number of correlations among the solute concentrations is N , we are forced to analyze our system as a ternary.

On this basis, a pseudobinary system (a binary system in which one of the two components is polydisperse) is experimentally characterized by a single diffusion coefficient that coincides with the apparent diffusion coefficient D_A . Although this coefficient is insufficient to describe completely the diffusion of all of the species present in solution, its physical meaning is well defined. In fact its value will be in principle be in the midrange of the binary diffusion coefficients of each of the components that are in the polydisperse sample. Hence, to obtain the pseudobinary diffusion coefficient, it is only necessary to extrapolate fringe minima positions to C_t (the maximum fringe displacement based ray optics theory²⁰) and from these obtain D_A .

A pseudoternary system can be described only by four diffusion coefficients, and their determination requires at least two pairs of (D_A, Q_0) , measured at the same average concentration but at different values of the refractive index ratio. The pairs (D_A, Q_0) are used in computing the four pseudoternary diffusion coefficients according to the Fujita-Gosting's procedure. However, this procedure assumes the presence of three (and only three) components. Thus, this procedure leads to incorrect values of the diffusion coefficients if there is polydispersity of one of the components, as we will see in the next section. We will also present a way to correct the values of the experimental pairs (D_A, Q_0) in order to obtain meaningful diffusion coefficients.

III. Diffusion Coefficient Matrix in Pseudoternary Systems at Infinite Dilution

As mentioned above, if we wanted to determine the $(N + 1)^2$ diffusion coefficients in a $(N + 2)$ component system, we should perform at least $(N + 1)$ experiments at different values of the refractive fractions α_i . For systems containing polydisperse solutes, we cannot satisfy these requirements because

the concentrations of components of polydisperse solutes are correlated by molecular weight distribution functions, although these distributions will change within a diffusion boundary because of the diffusion process. We can only prepare solutions for a system that contains a pure solute and a polydisperse solute as if it were a ternary system and thus must perform the experiments as if the system were ternary. We identify such systems as pseudoternary systems.

To show the implications of this assumption we may consider a pseudoternary system and to perform a theoretical analysis at infinite dilution of all of the solutes. In these conditions, there are no interactions between the solutes composing the system. In this case, we may write

$$\lim_{X_0 \rightarrow 1} D_{ij} = D_i^\infty \delta_{ij} \quad (22)$$

where X_0 is the solvent molar fraction, δ_{ij} is the Kronecker delta, and D_i^∞ is the infinite dilution diffusion coefficient of the relative binary system solvent– i th component.

We will choose to analyze the pseudoternary system water–poly(ethylene glycol) 200–sodium chloride, whose respective experimental mutual diffusion coefficients at infinite dilution have been measured.^{30,31} PEG samples $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_k\text{H}$, with k polymerization degree, exhibit a Poisson molecular weight distribution function typical of living polymers.³² Denoting f_k as the mole fractions of each component of the polydisperse solute having a polymerization degree equal to k , we have

$$f_k = \frac{\nu^{k-1}}{(k-1)!} \exp(-\nu) \quad (23)$$

where the ν parameter is related to the average chain length \bar{l} by the relation

$$\bar{l} = \nu + 1 \quad (24)$$

From eq 24 for PEG 200, $\nu = 4.14$. For simplicity, we have truncated the Poisson distribution at a value of the polymerization degree corresponding to a residual fraction smaller than 1 (for PEG 200 that means neglecting all of the species for which $k \geq 14$).

To evaluate all of the first 13 PEG's D_i^∞ values, a fit and an extrapolation of the Flory equation³² has been made with available experimental data^{30,33}

$$\frac{D_i^\infty}{\text{cm}^2 \text{ s}^{-1}} = (1.05 \pm 0.04) \cdot 10^{-4} \cdot \left(\frac{M_i}{\text{g mol}^{-1}} \right)^{-(0.527 \pm 0.007)} \quad (25)$$

The R_i have been obtained through a linear least-squares

$$\frac{R_i}{\text{dm}^3 \text{ mol}^{-1}} = (-40 \pm 12) + (231.32 \pm 0.15)i \quad (26)$$

According to our subscript convention, we will label the PEG oligomers with the numbers 1, 2, ..., 13; thus, in this case, they represent also the polymerization degree.

For sodium chloride (the 14 component), the following data are known

$$D_{14}^\infty = 1.612 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}; \quad R_{14} = 456.8 \text{ dm}^3 \text{ mol}^{-1}$$

By using these parameters, we have obtained the (14×14) diffusion coefficient matrix in condition of infinite dilution (in this case the matrix is diagonal according to eq 22), from which it has been possible to calculate the values of D_A^∞ and Q_0^∞

(through eqs 19, 20, and 25) for some sets of the refractive index fractions α_i with $1 \leq i \leq 14$ where the first 13 α_i 's values are correlated through the molecular weight distribution function

$$\frac{\alpha_i}{\alpha_j} = \frac{R_j f_j}{R_i f_i} \quad 1 \leq i \leq 13 \quad (27)$$

Using the values of D_A^∞ and Q_0^∞ calculated as described above and applying the Fujita and Gosting procedure, the coefficients in the 2×2 diffusion coefficient matrix are obtained which describes this hypothetical pseudo ternary system. We have considered only two refractive index fractions α_1^{PT} and α_2^{PT} that are correlated to the “true” α_i 's by the following relations:

$$\alpha_1^{\text{PT}} = \sum_{i=1}^N \alpha_i \quad (28)$$

$$\alpha_2^{\text{PT}} = \alpha_{N+1} \quad (29)$$

The pseudoternary diffusion coefficients obtained with this procedure are the following:

$$\mathbf{D}^\infty = \begin{bmatrix} 0.5831 & 0.0003 \\ 0.0960 & 1.6106 \end{bmatrix} \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$$

It is apparent that all of the pseudoternary diffusion coefficients do not follow the physical requirements expressed by eq 22 and the significant nonzero value of the $D_{2,1}$ cross-term implies, erroneously, a significant interaction between the solutes at infinite dilution. Even the main diffusion coefficients do not approach to the correct values. In fact, $D_{2,2}$ should converge to the infinite dilution diffusion coefficient of sodium chloride D_{14}^∞ , whereas $D_{1,1}$ should approach to D_A of the pseudobinary system water–PEG 200 (that is equal to $0.621 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$). Peculiar diffusion coefficients values have been also obtained experimentally, by studying the ternary systems with a polydisperse solute.

The above analysis shows that the pseudoternary diffusion coefficient matrix, determined by the standard Fujita and Gosting procedure, violates the thermodynamic conditions and shows also that the analysis of a pseudoternary system neglecting completely the polydispersity can lead to seriously incorrect conclusions. In principle, to avoid this problem, we need to be able to obtain experimentally the whole diffusion coefficient matrix. On the other hand, as we have noted, this is essentially impossible to do, so the best that we can do is to be satisfied with a (2×2) matrix in which the polydisperse component is considered as a pure component having hydrodynamic properties equal to the mean ones of the polydisperse component.

We want to obtain D_A and Q_0 values for a system that will yield zero value of $D_{1,2}$ and $D_{2,1}$ and have $D_{1,1}$ and $D_{2,2}$ that match corresponding binary values at infinite dilution. This may be done by correcting the measured values of D_A and Q_0 taking into account the polydispersity of solute in a logical and meaningful way.

IV. Corrective Procedure

We will find that the pseudo ternary treatment of data does not change the effective meaning of D_A . However, for Q_0 , there are serious problems. In a pure ternary system, Q_0 is a “measurement” of the difference of the diffusivity between the two diffusing components. In a pseudoternary system, besides the contribution due to the different diffusivity among all of the polymeric constituents and the nonpolymeric solute, there

is also a contribution due to the different diffusivity of the constituents of the polymeric mixture.

To develop the corrective procedure, we will first consider the case that all of the solute components are at infinite dilution. We will then obtain the characteristics of a hypothetical pure component that best approximates the behavior of the actual polydisperse component. As stated previously, the subscript 0 identifies the solvent, 1, 2, ..., N identify the species forming the polydisperse component, and $(N + 1)$ identifies the nonpolydisperse component. An over-bar will be used to indicate the mean quantities. Reasonable values of \bar{D}_A^∞ and \bar{R} for the polydisperse component are obtained from

$$\bar{R} = \sum_{i=1}^N R f_i \quad (30)$$

$$\frac{1}{\sqrt{\bar{D}_A^\infty}} = \frac{1}{\bar{R}} \sum_{i=1}^N \frac{R f_i}{\sqrt{D_i^\infty}} \quad (31)$$

where f_i is the molar fraction of the i th solute inside the polydisperse component. The average refractive index gradient has been taken equal to the arithmetic mean of the refractive index gradients of the oligomers. The infinite dilution diffusion coefficient of the polydisperse solute is set equal to the infinite dilution diffusion coefficient of polydisperse solute in the corresponding binary case.

Starting from eqs 19 and 20 at infinite dilution where the Γ_i 's parameters coincide with the α_i 's, we write

$$\frac{1}{\sqrt{D_A^\infty}} = \sum_{i=1}^{N+1} \frac{\alpha_i}{\sqrt{D_i^\infty}} \quad (32)$$

$$\frac{Q_0^\infty}{\sqrt{D_A^\infty}} = \frac{1}{2} \sum_{i=1}^{N+1} \sum_{j=1}^{N+1} \alpha_i \alpha_j G_{ij}^\infty = \sum_{i=1}^N \sum_{j=i+1}^{N+1} \alpha_i \alpha_j G_{ij}^\infty \quad (33)$$

where D_A^∞ and Q_0^∞ should be the experimental values for a set of hypothetical measurements at infinite dilution.

Now we must express the D_A^∞ and Q_0^∞ values for hypothetical ternary systems in which the polydisperse component is replaced by a pure substance having diffusive properties defined by eqs 31 and 30. We will use the "corr" subscript to indicate that the value refers to this hypothetical system. From eqs 19 and 31, we obtain

$$\frac{1}{\sqrt{(D_A^\infty)_{\text{corr}}}} = \frac{1 - \alpha_{N+1}}{\sqrt{\bar{D}_A^\infty}} + \frac{\alpha_{N+1}}{\sqrt{D_{N+1}^\infty}} = \frac{(1 - \alpha_{N+1})}{\bar{R}} \sum_{i=1}^N \frac{R f_i}{\sqrt{D_i^\infty}} + \frac{\alpha_{N+1}}{\sqrt{D_{N+1}^\infty}} \quad (34)$$

Using eqs 18 and 27, it easy to show that

$$\frac{R f_i}{\bar{R}} = \frac{\alpha_i}{1 - \alpha_{N+1}} \quad 1 \leq i \leq N \quad (35)$$

and eliminating the $R f_i / \bar{R}$ quantities between eqs 34 and 35, we have

$$\frac{1}{\sqrt{(D_A^\infty)_{\text{corr}}}} = \sum_{i=1}^N \frac{\alpha_i}{\sqrt{D_i^\infty}} + \frac{\alpha_{N+1}}{\sqrt{D_{N+1}^\infty}} = \frac{1}{\sqrt{D_A^\infty}} \quad (36)$$

Equation 36 shows that the apparent diffusion coefficient for the hypothetical system in which the polydisperse component is replaced by a pure component has the same value of the experimental one and indicates that, at least at infinite dilution, it is not affected by polydispersity. It should be noted that eq 36 requires only the infinite dilution hypothesis.

From eqs 20 and 21 for a ternary system, we now obtain the following expression:

$$\frac{(Q_0^\infty)_{\text{corr}}}{\sqrt{(D_A^\infty)_{\text{corr}}}} = \alpha_{N+1}(1 - \alpha_{N+1}) \left[\frac{1}{2\sqrt{2}} \frac{\sqrt{\bar{D}_A^\infty} + \sqrt{D_{N+1}^\infty}}{\sqrt{\bar{D}_A^\infty} D_{N+1}^\infty} - \frac{1}{\sqrt{\bar{D}_A^\infty} + D_{N+1}^\infty}} \right] \quad (37)$$

that takes into account the effect of the polydispersity. Equation 37 requires the knowledge of the apparent diffusion coefficient of the system under study, $D_A^\infty = (D_A^\infty)_{\text{corr}}$, of the apparent diffusion coefficient of the pseudobinary system containing the solvent and the polydisperse solute $(D_A)_{\text{PB}} = \bar{D}_A^\infty$, and of the diffusion coefficient of the monodisperse component. Often these kinds of data are not available; thus, it is preferable to have an equation containing more useful parameters. That is possible when the diffusion coefficients for infinite dilution of the polydisperse components, D_i^∞ , and the apparent diffusion coefficients of the pseudobinary system, $(D_A)_{\text{PB}} = \bar{D}_A^\infty$, are smaller with respect to diffusion coefficient of non polydisperse component D_{N+1}^∞ . With these hypotheses, eq 37 becomes

$$\frac{(Q_0^\infty)_{\text{corr}}}{\sqrt{(D_A^\infty)_{\text{corr}}}} = \frac{(Q_0^\infty)_{\text{corr}}}{\sqrt{D_A^\infty}} \cong \frac{\alpha_{N+1}(1 - \alpha_{N+1})}{2\sqrt{2\bar{D}_A^\infty}} \quad (38)$$

To compare eq 38 with eq 33, we write the latter in the limiting form when $\bar{D}_A^\infty \ll D_{N+1}^\infty$

$$\frac{Q_0^\infty}{\sqrt{D_A^\infty}} = \frac{Q_0^\infty}{\sqrt{(D_A^\infty)_{\text{corr}}}} = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \alpha_i \alpha_j G_{ij}^\infty + \sum_{i=1}^N \alpha_i \alpha_{N+1} G_{i,N+1}^\infty \cong \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \alpha_i \alpha_j G_{ij}^\infty + \sum_{i=1}^N \alpha_i \alpha_{N+1} \frac{1}{2\sqrt{2\bar{D}_A^\infty}} \quad (39)$$

Analyzing eq 39 the double summation, containing only terms referring to the polydisperse solute, can be easily related to the ratio $Q_0^\infty / \sqrt{D_A^\infty}$ for a pseudobinary system composed of the solvent and the polydisperse solute. In fact for this kind of system, according to eq 20, we have

$$\frac{(Q_0^\infty)_{\text{PB}}}{\sqrt{\bar{D}_A^\infty}} = \frac{1}{2\bar{R}^2} \sum_{i=1}^{N+1} \sum_{j=1}^{N+1} R_i R_j f_i f_j G_{ij}^\infty \quad (40)$$

and using eq 35 we obtain

$$\frac{(Q_0^\infty)_{\text{PB}}}{\sqrt{\bar{D}_A^\infty}} = \frac{\sum_{i=1}^{N+1} \sum_{j=1}^{N+1} \alpha_i \alpha_j G_{ij}^\infty}{2(1 - \alpha_{N+1})^2} \quad (41)$$

From eqs 41 and 39, we conclude

$$\frac{Q_0^\infty}{\sqrt{D_A^\infty}} = (1 - \alpha_{N+1})^2 \frac{(Q_0^\infty)_{\text{PB}}}{\sqrt{\bar{D}_A^\infty}} + \sum_{i=1}^N \alpha_i \alpha_{N+1} \frac{1}{2\sqrt{2\bar{D}_A^\infty}} = (1 - \alpha_{N+1})^2 \frac{(Q_0^\infty)_{\text{PB}}}{\sqrt{\bar{D}_A^\infty}} + \frac{(1 - \alpha_{N+1})\alpha_{N+1}}{2\sqrt{2\bar{D}_A^\infty}} \quad (42)$$

Now we have just to compare eq 42 with eq 38 obtaining

$$\frac{Q_0^\infty}{\sqrt{D_A^\infty}} = (1 - \alpha_{N+1})^2 \frac{(Q_0^\infty)_{\text{PB}}}{\sqrt{\bar{D}_A^\infty}} + \frac{(Q_0^\infty)_{\text{corr}}}{\sqrt{D_A^\infty}} \quad (43)$$

Solving this equation with respect to $(Q_0^\infty)_{\text{corr}}$, we have

$$(Q_0^\infty)_{\text{corr}} = Q_0^\infty - (1 - \alpha_{N+1})^2 \sqrt{\frac{D_A^\infty}{\bar{D}_A^\infty}} (Q_0^\infty)_{\text{PB}} \quad (44)$$

Substituting eqs 31, 32, and 35 in the last equation, we obtain

$$(Q_0^\infty)_{\text{corr}} = Q_0^\infty - (1 - \alpha_{N+1})^2 \frac{(Q_0^\infty)_{\text{PB}}}{1 - \alpha_{N+1}} \frac{\sum_{i=1}^N \frac{\alpha_i}{\sqrt{D_i^\infty}}}{\sum_{i=1}^N \frac{\alpha_i}{\sqrt{D_i^\infty}} + \frac{\alpha_{N+1}}{\sqrt{D_{N+1}^\infty}}} \quad (45)$$

and under condition $D_i^\infty \ll D_{N+1}^\infty$ we have:

$$(Q_0^\infty)_{\text{corr}} = Q_0^\infty - (1 - \alpha_{N+1})(Q_0^\infty)_{\text{PB}} \quad (46)$$

Equation 46 shows that $(Q_0)_{\text{PB}}$, appropriately weighted by the $(1 - \alpha_{N+1})$ factor, must be subtracted from the experimental Q_0^∞ to have thermodynamically correct diffusion coefficients.

It can also be said, from another point of view, that the position of j th interference minimum Y_j is shifted to another position $(Y_j)_{\text{corr}}$ with respect to the same minimum of the experimental system containing the polydisperse solute. The effect of the polydispersity causes a displacement of the position of the interference minima: this displacement can be easily evaluated starting from eqs 46 and 13, 14, 15, and 16. In fact, according to these equations, we have

$$\left(\frac{Y_j}{C_t}\right)_{\text{corr}} = \frac{Y_j}{C_t} - (1 - \alpha_{N+1}) \left[\left(\frac{Y_j}{C_t}\right)_{\text{PB}} - \left(\frac{Y_j}{C_t}\right)_{\text{B}} \right] \quad (47)$$

where the subscript B refers to an hypothetical binary system containing the solvent and a hypothetical nonpolydisperse component having hydrodynamic properties equal to the mean ones of the polydisperse component. It is important to remember that eq 37 is correct with just the hypothesis of infinite dilution of the solutes, whereas eqs 46 and 47 are valid with the

additional hypothesis that the infinite dilution diffusion coefficients of the polydisperse components D_i^∞ as well as the infinite dilution apparent diffusion coefficient of the pseudo-binary system containing a polydisperse solute are smaller with respect to the diffusion coefficient of non polydisperse component D_{N+1}^∞ .

Once the experimental set of Q_0 values have been corrected through eq 46, it is possible to use the Fujita and Gosting's procedure to obtain a consistent (2×2) matrix containing the four diffusion coefficients.

V. Simulations of Pseudoternary Systems

Equations 6 and 47 work well at infinite dilution and under the conditions $D_i^\infty \ll D_{N+1}^\infty \forall 1 \leq i \leq N$. To explore their validity outside the conditions where our hypotheses directly apply, we may compare the correct diffusion coefficient matrix to a matrix of an hypothetical system in which the polydisperse component has been replaced with a nonpolydisperse one having physical chemical properties equal to the averages ones of the polydisperse solute. However, it is obviously experimentally impossible to do this and for this reason we have performed a series of numerical simulations using predictive equations to evaluate the $D_{i,j}$ for non ionic systems constituted of hard spheres, developed by some of us and described elsewhere.³⁴ According to this model, for a $(N + 2)$ component system, the diffusion coefficients are given by the following equations:

$$D_{i,i} = D_i^\infty (1 - 0.898c_i v_i) \frac{1 + 2.5c_i v_i}{1 + 2.5 \sum_{h=1}^{N+1} c_h v_h} \quad (48)$$

$$D_{i,j} = D_{i,i} \frac{c_i v_j}{[1 - \sum_{h=1}^{N+1} c_h v_h (1 - \delta_{i,h})]^2} \quad (49)$$

where v_i is the "hydrodynamic" molar volume of the i th component.

In the tests, we have used the PEG 200 to simulate a polydisperse component. To avoid a large number of simulations, we again note that the parameters D_{N+1}^∞ , v_{N+1}^∞ , and R_{N+1}^∞ are not completely independent of each other; in fact, if a molecules has a large hydrodynamic volume v , its diffusion coefficient D^∞ will have a small value and vice versa. There is also a very rough relation between the R values and v 's: in fact, R is proportional to the electron number present in the molecule. So there is, in first approximation, a linear relation between the "hydrodynamic" molar volume and the derivative $(\partial n_\lambda / \partial c)$.

To analyze the effect of different size distributions, we have also performed simulations using PEG 400 as the polydisperse component (shifting the molecular weigh distribution to higher values) and a simulation using a hypothetical PEG 200 having a larger molecular weigh distribution than the Poisson one (specifically the Zimm-Schultz distribution).

All PEG parameters except the "hydrodynamic" molar volume have been reported in section III. For the molar volume trend, we have used the following relation where k is the polymerization degree

$$\frac{v_k}{\text{cm}^3 \text{ mol}^{-1}} = (14.9 \pm 8.9) + (52.7 \pm 2.1)k \quad (50)$$

TABLE 1: Parameters Used in the Simulation on the Pseudoternary Systems in Section V

component	$10^5 D^\infty / \text{cm}^2 \text{ s}^{-1}$	$v / \text{cm}^3 \text{ mol}^{-1}$	$R / \text{dm}^3 \text{ mol}^{-1}$
X	1.158	100	900
Y	0.430	200	850
Z	0.100	15 000	100 000

obtained by fitting a straight line to the experimental effective volumes of the first six oligomers. The effective “hydrodynamic” volumes have been obtained by performing a fit of the Carter and Phillies equation³⁵ on the experimental diffusimetric data

$$D_i = D_i^\infty (1 - 0.898 c_i v_i) \quad (51)$$

For the non polydisperse component, we have chosen three possible sets of values for the D^∞ , v , and R parameters, as shown in Table 1.

To show these results in a format that more clearly demonstrates how the corrections influence the results, we present graphs containing the ratio $Q_0/\sqrt{D_A}$ instead of the (2×2) diffusion coefficient matrix. This quantity has been plotted vs the refractive index fraction α_{N+1} for three different situations:

(1) The uncorrected data. They correspond to the experimental data obtained from an hypothetical diffusion measurement, without any manipulation. In the graphs, these data are represented by a solid square ■.

(2) The data obtained from a system in which the polydisperse component has been replaced by a fictitious non polydisperse one having hydrodynamic properties equal to the mean values of the polydisperse solute. They correspond to the data obtained by eq 37. In the graphs, these data are represented by an empty triangle △.

(3) The data corrected with eq 46. They correspond to the experimental data obtained from an hypothetical diffusion measurement, elaborated according to eq 46. In the graphs, these data are represented by a cross-star ✱.

It is seen from these figures that the proposed correction is able to take into proper account the effect of the polydispersity at infinite dilution as well as at moderate concentrations of the two solutes (Figures 1a,b and 2). Unfortunately, when the concentration of at least one of the solutes becomes high, the corrections become unsatisfactory. This is illustrated by the case shown in Figure 1c.

Good results are obtained if the ratio D_A/D_{N+1} is small as well as if it is near the unity. According to our hypothesis, eq 46 is fairly accurate if the ratio D_A/D_{N+1} is greater than the unity. From this point of view, it is possible to analyze the simulations in which we have varied the average molecular weight of PEG and the molecular weight distribution. If the average molecular weight increases, the ratio D_A/D_{N+1} decreases, so that the correction is better (Figure 3).

The Zimm–Schultz molecular weight distribution has the following general equation^{36,37}

$$f_i = \frac{i^{a-1} \exp(-bi)}{\text{polylog}_{1-a}[\exp(-b)]} \quad (52)$$

where polylog is the polylogarithm function operator, whereas $a \in \mathbb{N}$ and $b \in \mathbb{R}$ are two parameters that depends on nature of the reactions through which polymer is produced. However, these two parameters are related to the average chain length $\langle i \rangle$

$$\langle i \rangle = \sum_{i=1}^{+\infty} i f_i = \frac{\text{polylog}_{-a}[\exp(-b)]}{\text{polylog}_{1-a}[\exp(-b)]} \quad (53)$$

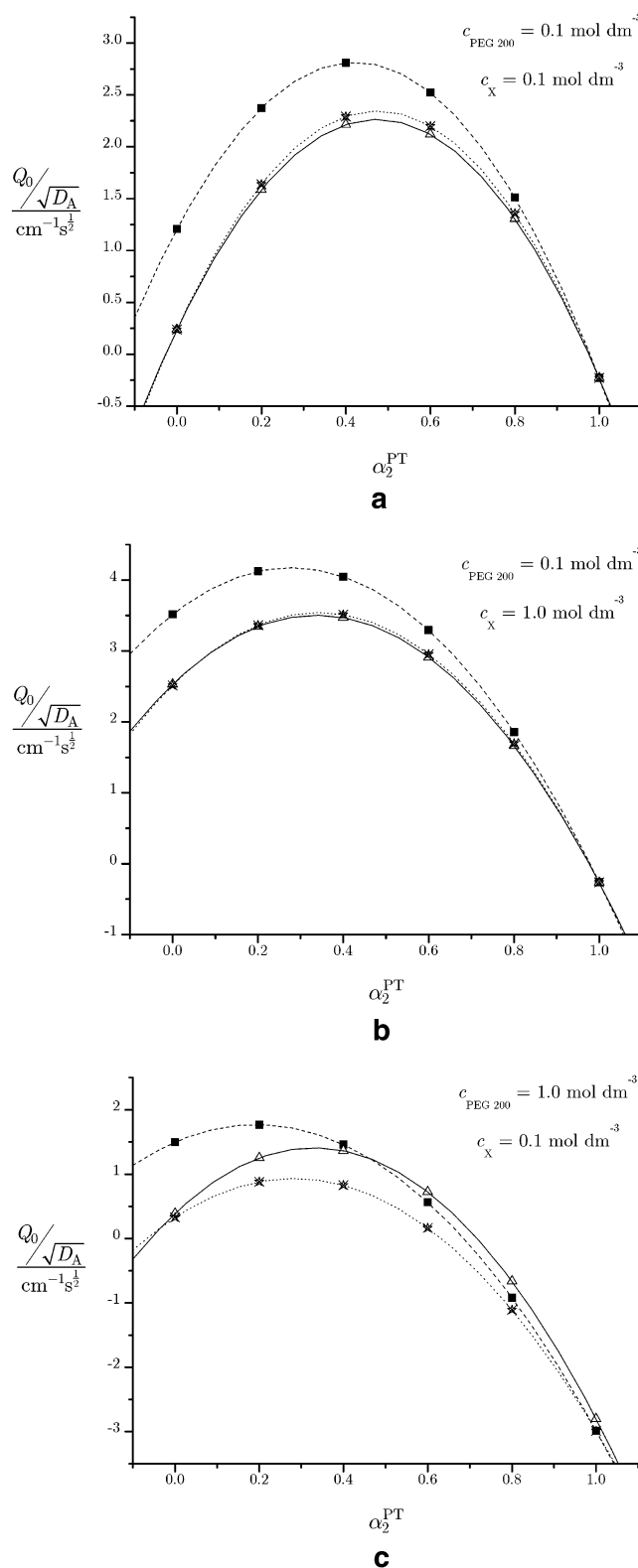


Figure 1. Values of $Q_0/\sqrt{D_A}$ vs α_2^{PT} for the pseudoternary system X–PEG 200–water.

Figure 5 shows examples of the Zimm–Schultz distribution for an hypothetical polymer having an average chain length of 100 units for a selection of values of a ; also shown in the figure is the Poisson distribution for the same value of the average chain length.

In the simulations, we have used the widest Zimm–Schultz distribution possible ($a = 1$) considering the first 34 oligomers, and it can be seen that for PEG 200 the ratio D_A/D_{N+1} is a little

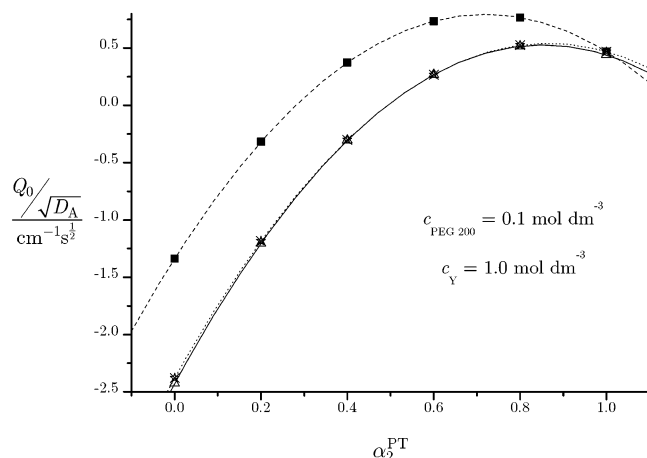


Figure 2. Values of $Q_0/\sqrt{D_A}$ vs α_2^{PT} for the pseudoternary system Y-PEG 200-water.

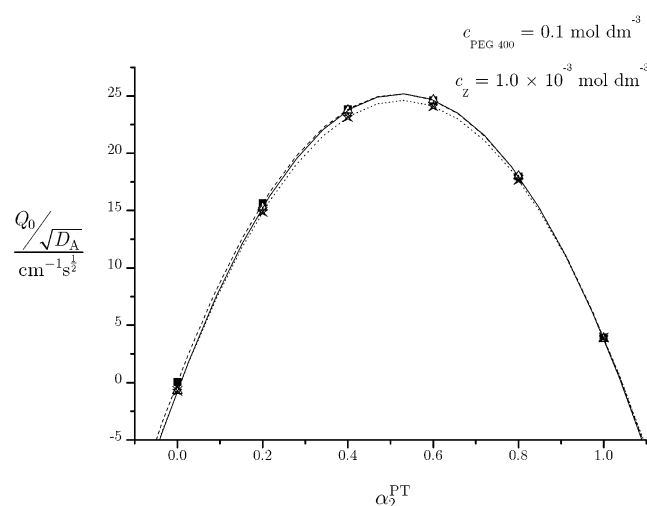


Figure 3. Values of $Q_0/\sqrt{D_A}$ vs α_2^{PT} for the pseudoternary system Z-PEG 400-water.

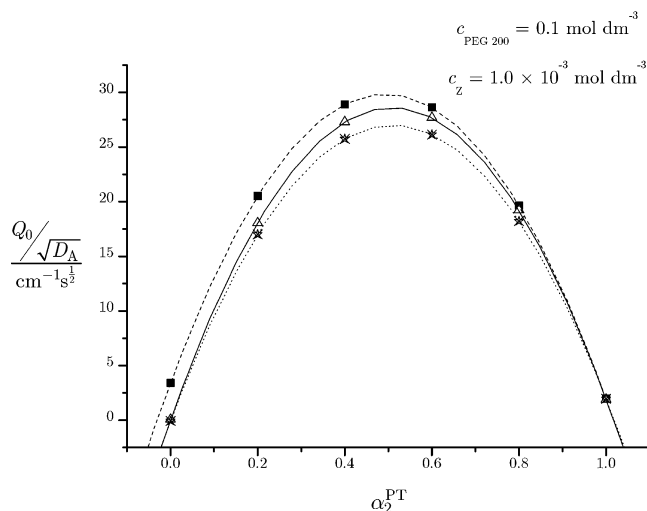


Figure 4. Values of $Q_0/\sqrt{D_A}$ vs α_2^{PT} for the pseudoternary system Z-PEG 200-water. The PEG 200 has been considered a Schultz function for the molecular weight distribution function.

greater than the same ratio for the Poisson distribution with a worsening of the results (Figure 4). Lowering of the ratio D_A/D_{N+1} for the Zimm-Schultz distribution is due to a complex combination of eqs 52 and 26.

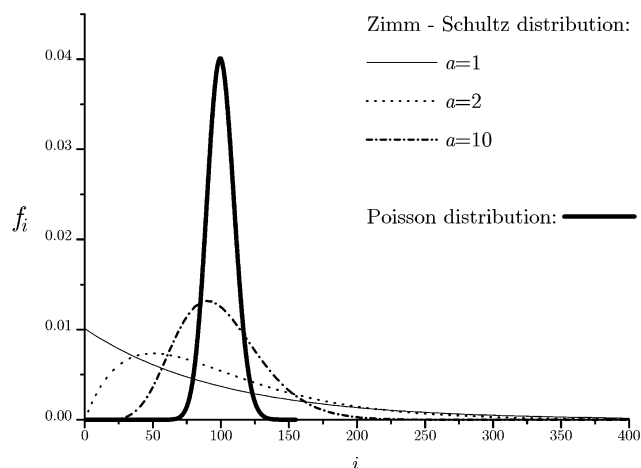


Figure 5. Some molecular weight distributions for an hypothetical polymer having an average chain length of one hundred units.

VI. Conclusions

In this report, we have presented a novel method to take into account the effect of polydispersity on the values of the basic parameters D_A , Q_0 used in the original Fujita-Gosting procedure to compute the four diffusion coefficients from Gouy interferometric data for a ternary system in which one of the solute is polydisperse. This is necessary because of the violation of the requirement that the cross-term diffusion coefficients must be zero in the absence of chemical reaction when both solutes are at infinite dilution. This inconsistency is eliminated once our corrective method is applied. Although the proposed method is theoretically correct at infinite dilution, it permits a correct computation of the diffusion coefficients of a ternary system containing a polydisperse solute even at moderate concentration of the solutes. Finally, our procedure is independent of the molecular weight distribution of the polydisperse solute and leads to a better correction of the diffusion coefficient values when the diffusivity ratio between the polydisperse and monodisperse solute is small.

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References and Notes

- (1) Bergström, M.; Eriksson, J. C. *Langmuir* **1998**, *14*, 288.
- (2) Kadima, W.; McPherson, A.; Dunn, M. F.; Jurnak, F. A. *Biophys. J.* **1990**, *57*, 125.
- (3) Wennerström, H.; Lindmann, B. *Phys. Rep.* **1979**, *52*, 1.
- (4) Mennen, M. G.; Smit, J. A. M. *Polym. Bull.* **1990**, *23*, 67.
- (5) Gujrati, P. D. *J. Chem. Phys.* **1998**, *108*, 6952.
- (6) Kang, C. H.; Sandler, S. I. *Macromolecules* **1988**, *21*, 3088.
- (7) Yuste, S. B.; Santos, A.; Lopez de Haro, M. *J. Chem. Phys.* **1998**, *108*, 3683.
- (8) Castagnolo, D.; Carotenuto, L.; Vergara, A.; Paduano, L.; Sartorio, R. *J. Cryst. Growth* **2001**, *232*, 138.
- (9) Vergara, A.; Paduano, L.; Sartorio, R. *Macromolecules* **2002**, *35*, 1389.
- (10) Sundelöf, L. O. *Ark. Kemi.* **1965**, *25*, 1.
- (11) Cussler, E. L., Jr.; Lightfoot, E. N. *J. Phys. Chem.* **1965**, *69*, 2875.
- (12) Cussler, E. L., Jr. *J. Phys. Chem.* **1965**, *69*, 1144.
- (13) Comper, W. D.; Van Damme, M. P. I.; Checkley, G. J.; Preston, B. N. *J. Phys. Chem.* **1985**, *89*, 128.

- (14) Leaist, D. G. *J. Solution Chem.* **1989**, *18*, 421.
- (15) Sartorio, R.; Vitagliano, V.; Ortona, O.; Costantino, L. *J. Solution Chem.* **1982**, *11*, 875.
- (16) Fick, A. *Pogg. Ann.* **1855**, *94*, 59.
- (17) Haase, R. *Thermodynamics of Irreversible Processes*; Academic Press: New York, 1966.
- (18) Crank, J. *The Mathematics of diffusion*; Oxford at the Clarendon Press: Oxford, U.K., 1956.
- (19) (a) IUPAC—Commission on Thermodynamics, *Measurement of the transport properties of fluids*; Blackwell Scientific Publications: Cambridge, MA, 1991. (b) Miller, D. G. Equal eigenvalues in multicomponent diffusion: the extraction of diffusion coefficients from experimental data in ternary systems in *Fundamental and Applications of Ternary Diffusion. Proceedings of the International Symposium, 29th Annual Conference of Metallurgists of CIM*, Hamilton, Ontario, August 27–28, 1990; Purdy, G. R., Ed.; Pergamon Press: New York, 1990; pp 101–108.
- (20) Kegeles, G.; Gosting, L. *J. Am. Chem. Soc.* **1947**, *69*, 2516.
- (21) Gosting, L.; Onsager, L. *J. Am. Chem. Soc.* **1952**, *74*, 6066.
- (22) Gosting, L. J.; Morris, M. S. *J. Am. Chem. Soc.* **1949**, *71*, 1998.
- (23) Akeley, D. F.; Gosting, L. *J. Am. Chem. Soc.* **1953**, *75*, 5685.
- (24) Fujita, H.; Gosting, L. *J. Am. Chem. Soc.* **1956**, *78*, 1099.
- (25) Fujita, H.; Gosting, L. *J. Phys. Chem.* **1960**, *64*, 1256.
- (26) Miller, D. G. *J. Phys. Chem.* **1988**, *92*, 4222.
- (27) Miller, D. G.; Albright, J. G.; Paduano, L.; Sartorio, R.; Vitagliano, V. *J. Phys. Chem.* **1992**, *96*, 7478.
- (28) Kim, H. *J. Phys. Chem.* **1966**, *70*, 562.
- (29) Kim, H. *J. Phys. Chem.* **1969**, *73*, 1716.
- (30) Vergara, A.; Vitagliano, V.; Paduano, L.; Sartorio, R. *Phys. Chem. Chem. Phys.* **1999**, *1*, 5377.
- (31) Vitagliano, V.; Lyons, P. A. *J. Am. Chem. Soc.* **1956**, *78*, 1549.
- (32) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
- (33) Vergara, A.; Paduano, L.; Vitagliano, V.; Sartorio, R. *J. Phys. Chem. B* **1999**, *102*, 8756.
- (34) Vergara, A.; Paduano, L.; Mangiapia, G.; Sartorio, R. *J. Phys. Chem. B* **2001**, *105*, 11044.
- (35) Carter, J. M.; Phillies, G. D. J. *J. Phys. Chem.* **1985**, *89*, 5118.
- (36) Zimm, B. H. *J. Chem. Phys.* **1948**, *16*, 1099.
- (37) Schultz, G. V. *Z. Phys. Chem., Abt. (B)* **1939**, *43*, 25.