Cross-Diffusion in a Water-in-Oil Microemulsion Loaded with Malonic Acid or Ferroin. Taylor Dispersion Method for Four-Component Systems

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We describe an improved Taylor dispersion method for four-component systems, which we apply to measure the main- and cross-diffusion coefficients in an Aerosol OT water-in-oil microemulsion loaded with one of the reactants of the Belousov–Zhabotinsky (BZ) reaction, water(1)/AOT(2)/R(3)/octane(4) system, where R is malonic acid or ferroin. With [H2O]/[AOT] = 11.8 and volume droplet fraction φd = 0.18, when the microemulsion is below the percolation transition, the cross-diffusion coefficients D13 and D23 are large and positive (D13/D33 ≈ 14, D23/D33 ≈ 3) for malonic acid and large and negative for ferroin (D13/D33 ≈ −112, D23/D33 ≈ −30) while coefficients D11 and D22 are small and negative for malonic acid (D11/D33 ≈ −0.01, D22/D33 ≈ −0.14) and small and positive for ferroin (D11/D33 ≈ 5 × 10−4, D22/D33 ≈ 8 × 10−3). These data represent the first direct determination of cross-diffusion effects in a pattern-forming system and of the full matrix of diffusion coefficients for a four-component system. The results should provide a basis for modeling pattern formation in the BZ–AOT system.

1. Introduction
Understanding the mechanism of nonequilibrium pattern formation in dissipative physical, chemical, and biological systems is one of the most important challenges of nonlinear science. Most patterns in reaction–diffusion systems are thought to arise from either the Turing or the wave instability.1 The Turing instability generates patterns that are stationary in space and time and possess an intrinsic wavelength. The wave instability (sometimes referred to as the finite wavelength instability) produces wavelike patterns, e.g., standing or packet waves, with a characteristic temporal period and spatial wavelength.

For two-variable systems, the Turing instability requires sufficiently different diffusion coefficients for the activator and inhibitor species, Dactiv > Dinhib, a relationship often referred to as long-range inhibition and short-range activation. Localized stationary patterns can also emerge under this condition.2,3

The wave instability, which requires at least three variables, typically involves an additional fast-diffusing activator or a large diffusion coefficient for a third species that is coupled to the activator.4–6 Both the Turing and wave instabilities generally require unequal self-diffusion (or intradiffusion) coefficients, i.e., the coefficients of proportionality between the flux of a species and its concentration gradient, with the single exception7 of subcritical Turing instability under inhomogeneous initial conditions. On the other hand, there are several theoretical papers on systems with cross-diffusion,8–12 whereby gradients in the concentration of one species affect the flux of another species, or with flow or convective terms,13 which are analogous to cross-diffusion, that exhibit dissipative patterns even with equal self- or main-diffusion coefficients. Cross-diffusion terms are always present in biological chemotactic systems and are thought to be responsible for many patterns in bacterial colonies.14–17

An n-species reaction–diffusion system with cross-diffusion can be described by the partial differential equations

\[
\frac{\partial c_i}{\partial t} = R(c_i, c_j) + \text{div}(D_{ii} \nabla c_i) + \sum_{j \neq i} \text{div}(D_{ij} \nabla c_j)
\]

where the reactive, or chemical, term \(R(c_i, c_j)\) depends in general on all the concentrations \(c_i\); \(D_{ii}\) are the main-diffusion coefficients; and the cross-diffusion term, \(\text{div}(D_{ij} \nabla c_j)\), links the gradient of species \(c_j\) to the flux of species \(c_i\). If \(D_{ij} > 0\), then the \(i\)th species diffuses from larger to smaller concentrations of the \(j\)th species, analogous to the case of ordinary self-diffusion.18

If \(D_{ij} < 0\), then the \(i\)th species diffuses in the opposite direction, against the gradient \(\nabla c_j\). Unlike the main- (or diagonal) diffusion coefficients, \(D_{ii}\), the cross-diffusion (or off-diagonal) coefficients \(D_{ij}\) must approach zero as \(c_i\) tends to zero, since there cannot be a flux of \(c_i\) if \(c_j = 0\).

Finding a model that gives patterns similar to those observed experimentally is not sufficient to provide an understanding of reaction–diffusion systems, since quite different models can exhibit very similar patterns. To our knowledge, cross-diffusion coefficients have not previously been determined experimentally in any reaction–diffusion system that gives rise to pattern formation. The Belousov–Zhabotinsky reaction dispersed in Aerosol OT water-in-oil microemulsion (BZ–AOT system)19,20 gives rise to perhaps the richest array of patterns of any reaction–diffusion system characterized to date. While we have been able to model most of these patterns using only self-diffusion terms, preliminary calculations suggest that the introduction of even small values of cross-diffusion coefficients can affect the system behavior dramatically.

Measurements of cross-diffusion coefficients in pure ternary AOT microemulsions (without BZ reactants) reveal that the
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To improve the results of fitting, a moment analysis procedure was developed. In this method, three experimentally obtained values (combinations of the normalized peak height, and normalized first and second moments of dispersion profile) coupled by three linear equations are linearly linked to nine parameters that are combined to yield the nine diffusion coefficients. Although this method gives better results, the main drawback of the least-squares method remains, i.e., the uncertainty due to the existence of local minima. As a result, the error in some cross-diffusion coefficients can exceed 100%. 

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The Taylor dispersion technique is based on the diffusive spreading of a drop of solution injected into a laminarly flowing stream of the same mixture but with slightly different concentrations. A small volume of the perturbing solution is injected into the flowing eluent at the entrance of a long capillary tube. As it moves along the tube, the injected sample is deformed by the flow, the rate of which has a parabolic shape across the capillary, and by radial diffusion. The drop spreads out into a shape that can be fitted by a combination of Gaussian functions for an \( (n+1) \)-component system. The eluted peak, sometimes called the Taylor peak, is monitored by a suitable detector such as a flow-through spectrophotometer or a refractive index detector (RID). The diffusion coefficients are calculated from the parameters of the Gaussian functions that fit the eluted peak.

In three-component systems, there are direct relations between the fitting parameters (four parameters taken from the two Taylor peaks) and the four diffusion coefficients. However, in quaternary systems there are no such relations for finding the nine diffusion coefficients. Usually, an experimentalist has six equations available to find nine unknown coefficients either in the Taylor method or in the interferometry technique. One procedure employs simultaneous least-squares fitting of all experimental curves by a set of nine parameters. The precision of the least-squares fitting depends on the quality of the Taylor peaks. If the Taylor peaks can be unambiguously fitted by a set of three Gaussian curves, then the result of fitting procedure should be satisfactory. In most cases, however, the Taylor peaks can be satisfactorily fitted by more than one set of Gaussians, and it is difficult to choose the best fit. In some cases, the fitting procedure does not converge or it yields several local minima. As a result, the error in some cross-diffusion coefficients can exceed 100%.

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In this paper, we introduce two new methods that directly link experimental data to the nine diffusion coefficients. In the first method, we employ the four ternary diffusion coefficients of the pure AOT microemulsion (obtained in additional experiments that are assumed not to change significantly upon adding the fourth component (a reactant of the BZ reaction). This assumption is certainly not correct for a general four-component system, but for AOT microemulsion loaded with a species, e.g., malonic acid, at relatively small concentration, it may be a reasonably accurate approximation. The second method employs data obtained from two different detectors, e.g., a refractive index detector and a flow-through spectrophotometer. This method is useful if a BZ reactant (ferroin in our case) has a large extinction coefficient in an accessible spectral range.

In section 2, we present the main ideas of the Taylor method for quaternary systems. In section 3 we develop the method for calculating diffusion coefficients from experimental data. Section 4 outlines the experimental procedures. As an illustration of our methods, we present in section 5 results on cross-diffusion coefficients in the water(1)/AOT(2)/malonic acid (or ferroin)(3)/octane system. We conclude with section 6. Derivations of many important formulas can be found in the Appendices and the Supporting Information.

2. Skeleton of the Theory. In this paper, we describe a Taylor dispersion method for obtaining cross-diffusion coefficients in quaternary systems based in part on the ideas of Price, who developed the Taylor method for three-component systems. We apply our technique to obtain the cross-diffusion coefficients of malonic acid, sodium malonate, and ferroin (reactants of the BZ reaction) in an AOT water-in-oil microemulsion.

The procedure is computationally complex, and we sketch here the general outline before presenting the details. In Table 1, we define a set of vectors and matrices used in the calculations. Our ultimate goal is to find the 3 × 3 diffusion matrix \( D \) for the full 4-component system. We do this by defining an effective diffusion matrix \( E \) for the radially averaged concentrations in the flow system, which can be inverted to yield \( D \). By fitting the detector response observed when the injected droplet reaches the detector(s) to a sum of three Gaussians, we obtain a set of equations that relate the experimentally observed amplitudes and dispersions to the elements of \( E \). It turns out that the maximal amount of information that can be derived from experiments with different droplet compositions yields only six independent equations for the nine elements of \( F \). By utilizing data from experiments on the three-component subsystem water/AOT/octane, we can find four of the elements of the diffusion matrix \( D \) and determine the remaining unknown elements of \( D \) using data for the quaternary system. In general, experiments on a three-component subsystem provide four independent equations for the four elements of \( D \) or, equivalently, \( E \) (see Table 1). An alternative way to obtain three additional equations is to use data from a different detector, e.g., a spectrophotometer that is sensitive only to one component of the four-component system.

Consider a long, narrow, cylindrical tube with radius \( R_0 \) and impermeable walls, in which a homogeneous liquid mixture of four components flows under laminar conditions. The velocity profile for laminar flow in such a tube is parabolic:

\[
u(r) = 2u_0(1 - r^2)
\]  
where \( r = R/R_0 \), \( R \) is the radial distance from the tube axis, and \( u_0 \) is the mean velocity of the fluid mixture.

At time \( t = 0 \), a small drop containing the same four components, but with slightly different concentrations, is injected into the tube at axial coordinate \( z = 0 \) (\( z \) increases along the
TABLE 1: Vectors and Matrices Used in the Taylor Dispersion Method

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flow direction. Since the volume of the sample introduced is small, we treat this injection as a δ-function perturbation. It is convenient to consider the evolution of the perturbation in a frame that moves along the z axis with velocity $u_0$. In this frame, the flow velocity $u(r)$ becomes

$$u(r) = u(r) - u_0 = u_0(1 - 2r^2)$$  \(3\)

The concentrations of the four components obey the relation:

$$\phi_1 + \phi_2 + \phi_3 + \phi_4 = 1$$  \(4\)

where $\phi_i$ is the volume fraction of the $i$th component, and $c_i$ is related to the concentration $c_i$ by

$$c_i = ϕ_i M_i / d_i$$  \(5\)

where $M_i$ is the molecular weight and $d_i$ is the density of the $i$th component. Equation 4 implies that only three of the components are independent. We denote the concentration of the solvent (in our case, the oil, octane) as $c_4$ and write equations for the fluxes of the other three components in the moving frame for the $z$ direction and for the radial direction:

$$J_z = c_i u_0 (1 - 2r^2) - \sum_{j=1}^{3} D_j \frac{∂c_j}{∂z}$$  \(6\)

$$J_{ir} = -\sum_{j=1}^{3} D_j \frac{∂c_j}{∂r}$$  \(7\)

$i = 1, 2, 3$. Using the continuity equation, we obtain three partial differential equations for our three independent species:

$$\frac{∂c_i}{∂t} = \frac{∂J_z}{∂z} - \frac{∂J_{ir}}{∂r}$$  \(8\)

Our first goal is to reduce eqs 8 to a simpler set of equations independent of $R$, taking the form

$$\frac{∂c_i}{∂t} = \sum_{j=1}^{3} F_{ij} \frac{∂^2 c_j}{∂z^2}$$  \(9\)

In Appendix 1, we show how to do this and find that

$$F_{ij} = \frac{R_{ij}^2}{48\text{det}(D)} \text{det}(M_{ij})(-1)^{(i+j)}$$  \(10\)

where $\text{det}(D)$ is the determinant of the 3 × 3 diffusion matrix $D$ and $\text{det}(M_{ij})$ is the determinant of the minor associated with element $D_{ij}$ of $D$, for example, $\text{det}(M_{ij}) = (D_{12}D_{33} - D_{13}D_{23})$. The coefficients $F_{ij}$ have the same dimensions as the diffusion coefficients $D_{ij}$ (cm²/s), but they are inversely proportional to $D_{ij}$. In the simplest case, when all the off-diagonal elements of $D$ are zero, eq 10 reduces to $F_{ij} = K_{ij}/D_{ij}$, where $K_{ij} = -R_{ij}u_0^2/48$. Note that in eq 8 we consider $c_i$ as a function of all three spatial coordinates, while in eq 9 $c_i$ depends only on $z$, i.e., $c_i$ in eq 9 is averaged over the cross section of the tube. One condition for the validity of the Taylor method is that measurements be made at “long times”, at which the radial variation of $c_i$ is small relative to the axial variation. Equations 9 have the same form as the equations for a one-dimensional diffusive process, and they can be solved analytically.

In the next section, we describe a procedure for finding the matrix $F$ experimentally using the Taylor dispersion method. Knowing the elements of $F$, we can solve our main problem, i.e., finding the elements of $D$, by inverting eq 10:

$$D_{ij} = K_{ij}\text{det}(M_{ij})^{-1}(-1)^{(i+j)}/\text{det}(F)$$  \(11\)

where $\text{det}(M_{ij})$ is the determinant of the minor associated with element $D_{ij}$ of matrix $F$.

**Matrices $F$ and $D$.** Equation 9 can be solved analytically. We note that eq 9 takes the same form for either the absolute concentrations $c_i$ or the differential concentrations $Δc_i = c_i - c_{i,t}$, where $c_{i,t}$ is the concentration in the flow solution and $c_i$ is the corresponding concentration in the injected sample. In the following we consider $c_i$ as the differential concentration, omitting “Δ”. We seek a solution of (9) of the form

$$c_i = \sum_{j=1}^{3} B_{ij} G_j \quad i = 1, 2, 3$$  \(12\)

where $G_i$ is the Gaussian function

$$G_i = \frac{1}{2\sqrt{πσ_i}} \exp \left[ -\frac{(z_0 - z)^2}{4σ_i^2} \right] \quad i = 1, 2, 3$$  \(13\)

Substituting eqs 12 and 13 into eq 9, we obtain

$$σ_i B_{ij} = \sum_{k=1}^{3} F_{ik} B_{kj} \quad i = 1, 2, 3; j = 1, 2, 3$$  \(14\)

from which it follows that the $σ_i$ are the eigenvalues of $F$:
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which also implies (Vieta’s equations) that

\[
\sigma_1 + \sigma_2 + \sigma_3 = F_{11} + F_{22} + F_{33} \tag{16}
\]

\[
\sigma_1 \sigma_2 + \sigma_2 \sigma_3 + \sigma_3 \sigma_1 = \text{det}(M_{F11}) + \text{det}(M_{F22}) + \text{det}(M_{F33}) \tag{17}
\]

\[
\sigma_1 \sigma_2 \sigma_3 = \text{det}(F) \tag{18}
\]

Therefore, only six of the nine equations in eq 14 are independent. To find the nine \(B_{ij}\) we must take into account three additional equations from the initial conditions for the three concentrations \(c_i\):

\[
P_j/(\pi R_0^2) = \sum_{j=1}^{3} B_{ij} \quad i = 1, 2, 3 \tag{19}
\]

where \(P_i\) is the excess (in mol) of the \(i\)th component injected at \(t = 0\) and \(z = 0\). We use this rather straightforward but cumbersome method of calculating \(B_{ij}\) from \(F_{ij}\) (see Supporting Information) for building the \(c_i\) through eq 12 and then reconstructing the signal \(S\) of our detector through eq 20 (see next paragraph). Comparing the reconstructed and experimentally found signals for different initial concentrations \(c_{i0}\) (or \(P_i\)) in the injected samples helps us to improve the reliability of the calculated coefficients \(D_{ij}\), as we discuss in section 5.

Determining \(F_{ij}\) requires a detector that measures the dispersion (Taylor) peak at the end of our long narrow tube. When a refractive index detector is used, the signal \(S\) of the RID (measured in volts) is directly proportional to small changes in the concentrations of all the components of the flow mixture, i.e., to the \(c_i\), and in the case of three independent concentrations (four components) can be fitted by a sum of three Gaussians:

\[
S = \sum_{j=1}^{4} K_{i,j} \exp[1] = \sum_{i=1}^{3} P_{i,\text{exp}} G_i \tag{20}
\]

where the coefficients \(P_{i,\text{exp}}\) and the dispersions \(\sigma_i\) in \(G_i\) (eq 13) are found by fitting the experimental peaks. Using eqs 4 and 5, eq 20 can be rewritten as

\[
\sum_{i=1}^{3} P_{i,\text{exp}} G_i = \Delta \phi_1(K_{i1}d_1/M_1 - K_{i4}d_4/M_4) + \Delta \phi_2(K_{i2}d_2/M_2 - K_{i4}d_4/M_4) + \Delta \phi_3(K_{i3}d_3/M_3 - K_{i4}d_4/M_4) \tag{21}
\]

Replacing \(\Delta \phi_i\) by \(c_i M_i/d_i\), eq 21 transforms further to

\[
\sum_{i=1}^{3} P_{i,\text{exp}} G_i = \sum_{i=1}^{3} K_{i} c_i \tag{22}
\]

where \(K_i = K_{i0} - K_{i4} d_4 / (M_4 d_4)\), \(i = 1, 2, 3\).

Using eq 12 and equating the coefficients of each of the \(G_i\), we have

\[
\sum_{j=1}^{3} K_{j} B_{ij} = P_{i,\text{exp}} \quad i = 1, 2, 3 \tag{23}
\]

Equations 14 and 19 enable us to replace the \(B_{ij}\) by the \(F_{ij}\) in eq 23. In Appendix 2, we derive the fundamental relations between the experimental data \((P_{i,\text{exp}}, \sigma_i)\) and the theoretical values \((F_{ij}, K_1, K_2, K_3)\). Here, we simply write the final eqs 24 and 26 used for finding \(K_1, K_2, K_3\), and finally the \(F_{ij}\).

The general equation for the sensitivity coefficients \(K_i\) in eq 22 may be written as:

\[
\left(\sum_{i=1}^{3} P_{i,\text{exp}}\right)\pi R_0^2/V_0 = \sum_{i=1}^{3} K_i c_{i0} \tag{24}
\]

where \(V_0\) is the injected volume. By analyzing three experiments involving injections with only \(c_{i0} \neq 0\) or \(c_{20} = 0\) or \(c_{30} = 0\), we find from eq 24:

\[
K_i = l_0^{-1} \left(\sum_{j=1}^{3} P_{i,\text{exp},j} \right) c_{i0} \quad i = 1, 2, 3 \tag{25}
\]

where \(l_0^{-1} = \pi R_0^2/V_0\) and \(P_{i,\text{exp},j}\) is the amplitude obtained for the \(j\)th Gaussian by fitting the experiment in which only \(c_{i0} \neq 0\). To find the \(F_{ij}\), we employ the following fundamental relation:

\[
\sum_{j=1}^{3} K_{i,j} F_{ij} = l_0^{-1} \left(\sum_{j=1}^{3} \sigma_j P_{i,\text{exp},j} \right) c_{i0} = W_i \quad i = 1, 2, 3 \tag{27}
\]

Equations 16–18 and eq 27 relate the \(F_{ij}\) to experimentally measurable quantities, but these six equations are insufficient to determine the nine \(F_{ij}\). Additional experiments with initial injections having other compositions \(c_{i0}\) do not provide independent information, since the new equations, analogous to eq 26, are simply linear combinations of eq 27. Exactly this circumstance explains the relatively low precision of previous methods based on least-squares fitting. From a practical point of view, however, different combinations of the \(c_{i0}\) may make possible a more precise determination of the \(\sigma_i\). To obtain enough equations to determine the \(F_{ij}\), we must utilize additional information. If the fourth component cannot be detected spectrophotometrically and if this component does not affect significantly the interaction between the other three components (the structure of the AOT microemulsion in our case), then we may use the values of the cross- and main-diffusion coefficients found for a three-component subsystem under the assumption that these quantities remain unchanged on addition of the fourth component.

In Appendix 3, we summarize the key equations for the three-component system, including the equations analogous to our basic eqs 24 and 26. In the AOT microemulsion studied here, the natural choice for the three-component subsystem is water/AOT/octane, a system in which nanometer-size water droplets diffuse in the continuous oil (octane) phase. The fourth component can then be chosen as any of the reactants of the BZ reaction. We assume that the four diffusion coefficients of the pure AOT microemulsion (three-component system) remain nearly unchanged in the four-component system, e.g., when malonic acid or ferroin are added. We discuss the validity of this assumption in section 5.

We denote the components as water (1), AOT (2), and BZ reactant (3), with octane as the solvent. For the three-component system, we can measure \(D_{11}, D_{12}, D_{21},\) and \(D_{22}\), the main and cross-diffusion coefficients for water (1) and AOT (2). We define the matrix \(D_2\) with elements \(D_{11}, D_{12}, D_{21},\) and \(D_{22}\). The required additional equations for finding the \(F_{ij}\) can be obtained from eq 11, written for \(D_{11}, D_{12}, D_{21},\) and \(D_{22}\):

\[
D_{11} = K_{F10}(F_{22} F_{33} - F_{23} F_{32})/(\sigma_1 \sigma_2 \sigma_3) \tag{28}
\]

\[
D_{22} = K_{F10}(F_{11} F_{33} - F_{13} F_{31})/(\sigma_1 \sigma_2 \sigma_3) \tag{29}
\]
Three-component subsystem, are related by 

\[ D_{12} = K_{FP}(F_{13}F_{32} - F_{12}F_{33})/\sigma_{12}\sigma_{3} \]  
\[ D_{21} = K_{FP}(F_{23}F_{31} - F_{21}F_{33})/\sigma_{21}\sigma_{3} \]  

Equations 10 and 11 imply that 

\[ \text{det}(F)\text{det}(D) = K_{FD}^3 \]  

An analogous equation can be obtained for the matrices \( E \) and \( D_2 \) for the three-component system (see Appendix 3): 

\[ \text{det}(E)\text{det}(D_2) = K_{FD}^2 \]  

The eigenvalues of \( E \), \( s_1 \) and \( s_2 \), found experimentally for the three-component subsystem, are related by \( s_1s_2 = \text{det}(E) \); eq 18 gives \( \sigma_{12}\sigma_{3} = \text{det}(F) \). Also, \( \text{det}(D_2) = D_{11}D_{22} - D_{12}D_{21} = \text{det}(D_{23}) \), and eq 10 for \( F_{33} \) may be written as \( F_{33} = K_{FP}\text{det}(D_{33})/\text{det}(D) \). These results can be combined with eqs 32 and 33 to yield 

\[ F_{33} = \sigma_{12}\sigma_{3}/s_1s_2 \]  

Using eqs 17 and 28–31, we have 

\[ D_{11} + D_{22} + D_{33} = K_{FP}(1/\sigma_{1} + 1/\sigma_{2} + 1/\sigma_{3}) \]  

An analogous expression can be written for the three-component system: 

\[ D_{11} + D_{22} = K_{FP}(1/\sigma_{1} + 1/\sigma_{2}) \]  

Combining eqs 35 and 36, we have 

\[ D_{33} = K_{FP}(1/\sigma_{1} + 1/\sigma_{2} + 1/\sigma_{3} - 1/s_1 - 1/s_2) \]  

Thus we can find \( F_{33} \) and \( D_{33} \) directly from the results of fitting the experimental peaks, independent of the other elements of \( F \) and \( D \). There are many ways to obtain the remaining elements of \( F \) and \( D \) from the equations at our disposal. For example, from eqs 29, 31, and 27, we have 

\[ (\sigma_{12}\sigma_{3}D_{22}/K_{FD} + F_{13}F_{31} = F_{11}F_{33}) \]  
\[ -(\sigma_{12}\sigma_{3}D_{21}/K_{FD} + F_{23}F_{31} = F_{21}F_{33}) \]  
\[ K_{F1}F_{13} + K_{F2}F_{23} + K_{F3}F_{33} = W_{1}F_{33} \]  

which can be combined to give 

\[ K_{1}(\sigma_{12}\sigma_{3}D_{22}/K_{FD} - K_{2}(\sigma_{12}\sigma_{3})D_{21}/K_{FD} + \]  
\[ (K_{F1} + K_{F2})F_{31} + K_{F3}F_{33} = W_{1}F_{33} \]  

Using eq 27 with \( i = 3 \), we finally obtain an expression for \( F_{31} \) 

\[ F_{31} = (F_{Fd}W_{1}F_{13} + K_{2}D_{21}\sigma_{12}\sigma_{3} - K_{2}D_{22}\sigma_{12}\sigma_{3})/(K_{FD}W_{3}) \]  

An equation for \( F_{32} \) can be found in the same fashion. Combining eqs 28, 30, and 27 gives 

\[ -K_{1}D_{12}(\sigma_{12}\sigma_{3})/K_{FD} + K_{2}D_{11}(\sigma_{12}\sigma_{3})/K_{FD} + (K_{F1} + \]  
\[ K_{F2} + K_{F3}F_{32} = W_{2}F_{33} \]  

Again using eq 27, we obtain 

\[ F_{32} = (F_{Fd}W_{2}F_{23} + K_{1}D_{12}\sigma_{12}\sigma_{3} - K_{2}D_{11}\sigma_{12}\sigma_{3})/(K_{FD}W_{3}) \]  

Utilizing eqs 10 and 11, eqs 42 and 44 give us equations for \( D_{31} \) and \( D_{32} \) in terms of the known \( F_{ij} \), 

\[ D_{31} = -(D_{11}F_{31} + D_{12}F_{12})/F_{33} \]  
\[ D_{32} = -(D_{12}F_{31} + D_{22}F_{12})/F_{33} \]  

Now only two elements of \( D \) remain to be found, namely \( D_{13} \) and \( D_{23} \), along with the corresponding elements of \( F \) and \( F_{33} \) as well as the elements \( F_{11}, F_{12}, F_{21} \), and \( F_{22} \), which differ from the elements \( E_{11}, E_{12}, E_{21} \), and \( E_{22} \) of the three-component subsystem. 

We can again use eqs 27–29 and the additional eq 16 to find \( F_{13} \) and \( F_{23} \). Omitting some algebra, we finally obtain: 

\[ F_{13} = [F_{33}K_{1}(\sigma_{1} + \sigma_{2} + \sigma_{3} - F_{33}) - K_{2}(1/s_1 + \]  
\[ 1/s_2\sigma_{12}\sigma_{3} + (K_{F3}F_{33} - W_{3})F_{32}]/(K_{F2}F_{33} - K_{F3}F_{32}) \]  
\[ F_{23} = [F_{33}K_{1}(\sigma_{1} + \sigma_{2} + \sigma_{3} - F_{33}) - K_{1}(1/s_1 + \]  
\[ 1/s_2\sigma_{12}\sigma_{3} + (K_{F3}F_{33} - W_{3})F_{32}]/(K_{F2}F_{33} - K_{F3}F_{32}) \]  

where the expressions for \( F_{31} \) and \( F_{32} \) in eqs 47 and 48 are taken from eqs 42 and 44, respectively. Knowing \( F_{13} \) and \( F_{23} \), we can write equations for \( D_{13} \) and \( D_{23} \): 

\[ D_{13} = -(D_{11}F_{13} + D_{12}F_{23})/F_{33} \]  
\[ D_{23} = -(D_{21}F_{13} + D_{22}F_{23})/F_{33} \]  

Now, we know all the \( D_{ij} \) and can calculate \( F_{11}, F_{12}, F_{21} \), and \( F_{22} \) using eq 10. The equations for \( F_{1}, F_{12}, F_{21}, \) and \( F_{22} \) can be written as: 

\[ F_{11} = (D_{22}\sigma_{12}\sigma_{3}/K_{FD} + F_{13}F_{33})/F_{33} \]  
\[ F_{22} = \sigma_{1} + \sigma_{2} + \sigma_{3} - F_{1} - F_{3} \]  
\[ F_{21} = (W_{1} - K_{F1} - K_{F3})/K_{2} \]  
\[ F_{12} = (W_{2} - K_{F2} - K_{F3})/K_{1} \]  

The resulting values of \( D_{ij} \) are quite sensitive to the experimental data, \( \sigma_{i}, P_{i,exp}, \) and \( W_{i} \), as well as to the values of \( K_{1}, K_{2}, \) and \( K_{3} \). Therefore independent determination of the \( D_{ij} \) is desirable if feasible. 

If the detector is sensitive to only a single component, more accurate determination of diffusion coefficients \( D_{ij} \) is possible. For example, neither water nor AOT absorbs in the visible range. If we can detect component 3 optically, as in the case of ferroin, we can set \( K_{1} = K_{2} = 0 \) in eq 22 and simplify the subsequent equations. Equation 24, for example, takes the form 

\[ (P_{i,exp} + P_{2,exp} + P_{3,exp})\pi R_{i}^2/V_{0} = K_{5}c_{3} \]  

and eqs 27 transform into 

\[ K_{5}F_{3i} = W_{i} \]  
\[ i = 1, 2, 3 \]  

Equations 24a and 27a allow us to determine \( F_{3i} \) with greater accuracy, and eqs 45 and 46 can in turn be used to calculate \( D_{31} \) and \( D_{32} \). In general, three eqs 27a obtained from optical detection, three eqs 27 obtained from refractive index detection, and three eqs 16–18 are sufficient to find all nine diffusion coefficients. 

If it is possible to find another wavelength of light at which \( K_{2} = K_{3} = 0 \) (for example, in the IR), then eq 27 would yield more accurate expressions for the \( F_{ij} = W/K_{1} \). 

3. Experimental Section

Our experimental setup for the measurement of diffusion coefficients (see Supporting Information) is built around a high pressure liquid chromatography apparatus, which ensures suit-
Cross-Diffusion in a Water-in-Oil Microemulsion

The length of Teflon capillary tubing used in most experiments was about 30 m between the injector and the spectrophotometer cell (Shimadzu UV-1650PC) and 32 m between the injector and the cell of the differential flow-through refraction index detector, RID (Agilent 1100 series), though for some experiments we employed a 60 (62) m tube. The inner radius \( R_0 \) (= 0.42 mm) of the tubing was determined by gravimetry, i.e., from the mass of water required to fill the tube, and also by direct observation through a microscope of a thin slice of the tubing. The tubing was coiled in a 50 cm diameter helix. In experiments with malonic acid or sodium malonate, the Teflon capillary tubing is directly connected to the RID (the spectrophotometer was not used). An isocratic pump (Agilent G1310A), which maintained a steady flow, was placed between the eluent reservoir and the injector. Sample loops of volumes 10 and 20 \( \mu \)L were used for injection. Taylor peaks were detected at \( \lambda = 510 \) nm (ferroin molar extinction coefficient, \( \epsilon = 1.1 \times 10^4 \) M\(^{-1}\)cm\(^{-1}\)). The HPLC flow-thru cell (Shimadzu) has 1 mm internal diameter and path length \( l_c = 1 \) cm (8 \( \mu \)L inner volume). Both detectors were connected to a personal computer for data acquisition.

The eluent reservoir was also connected to a vacuum pump to degas the flowing solution. The injector and capillary tubing were kept at 23 °C in a thermostatted incubator (Fisher Scientific). All experiments with AOT microemulsions were run at a flow rate between 0.1 mL/min and 0.15 mL/min.

We also used a dynamic light scattering apparatus (DynaPro, Protein Solutions, High Wycombe, U.K.) to monitor the size of water droplets in the AOT microemulsion loaded with a reactant of the BZ reaction.

Water-in-oil microemulsions were prepared using bidistilled water, AOT (sodium bis(2-ethylhexyl)sulfosuccinate Aerosol OT, Aldrich) and octane (Sigma analytical grade). Octane was further purified by mixing with concentrated \( \text{H}_2\text{SO}_4 \) for two days; a stock solution of AOT in octane ([AOT] = 1.5 M) was prepared and filtered through a 0.45 \( \mu \)m Teflon filter to remove possible impurities.

The radius of the droplet of water core in nanometers is roughly given by \( R_w = 0.17 \omega \)\(^{25,41,42} \) where \( \omega = [\text{H}_2\text{O}]/[\text{AOT}] \); \( R_w \) is independent of the octane volume fraction in the microemulsion. The total radius of the droplet plus the surrounding AOT monolayer (hydrodynamic radius), \( R_d \), exceeds \( R_w \) by the length of an AOT molecule (∼1.1 nm). Many physical properties of microemulsions show a threshold-like dependence on \( \phi_d \); the volume fraction of the dispersed phase \( (\phi_d = \phi_{\text{H}_2\text{O}} + \phi_{\text{AOT}}) \). This dependence is due to percolation. If \( \phi_d \ll \phi_{cr} \) (percolation threshold, \( \phi_{cr} \approx 0.5 - 0.6 \)), the microemulsion can be accurately characterized as a medium in which water droplets float freely.

Malonic acid (MA, Aldrich) and its disodium salt (Na\(_2\)MA, Fluka), were used as received. Ferroin was prepared by mixing \( 1,10\)-phenanthroline (Sigma) and FeSO\(_4\)·7H\(_2\)O (Fisher) in stoichiometric proportions (3:1) to get a 0.125 M stock solution.

In the following, we specify concentrations of \( \text{H}_2\text{O} \), AOT, MA, Na\(_2\)MA, ferroin, and octane with respect to the total volume of the microemulsion. Samples were injected every 3 h to avoid overlapping of the broad (up to 2 h wide) peaks. Experimental peaks generated with different injections were simultaneously fitted, using the Levenberg–Marquardt algorithm,\(^{43} \) to the following equation:

\[
\nu(t) = \sum_{i=1}^{3} \frac{P_{i,\text{exp}}}{4\pi \sigma_i^2} \exp \left[ -\frac{u_0^2(t-t_0)^2}{4\sigma_i^2} \right]
\]

where \( P_{i,\text{exp}}, \sigma_i, \) and the retention time \( t_0 \) were chosen as fitting parameters. The expression \( (z_0 - z)^2 \) in eq (13) is replaced here by \( u_0^2(t-t_0)^2 \). A baseline of the form \((a + bt)\) was previously subtracted from the recorded signals with the help of suitable software.

4. Results

Two-Component Systems. In order to verify the condition of laminar flow, the flow rate was checked with a binary system of octane in hexane. Figure 1 shows that the diffusion coefficient is independent of eluent flow rate at \( u_0 < 0.5 \text{ mL/min} \). The value of \( D \) at the plateau (where \( u_0 < 0.5 \text{ mL/min} \), \( 3.4 \times 10^{-5} \text{ cm}^2/\text{s} \), agrees well with earlier determinations.\(^{44} \) At larger flow rates, turbulence apparently begins to affect diffusion in the tube. For a further check on the operation of the equipment, we measured the diffusion coefficient of an aqueous mannitol solution \((D = 0.656 \times 10^{-5} \text{ cm}^2/\text{s})\),\(^{45} \) and the result was in agreement with the literature value to within the experimental error.

Water/AOT/Octane System. In order to calculate main- and cross-diffusion coefficients for the quaternary system, \( \text{H}_2\text{O}/\text{AOT}/\text{BZ}-\text{reactant/octane} \), we determined the diffusivities in the ternary system, to which the fourth component (MA, Na\(_2\)MA, or ferroin) was later added. Microemulsions with several compositions below the percolation limit were investigated, and the results were used in our analysis of the quaternary system.

Several experiments were performed by injecting samples with an excess of one (\( \text{H}_2\text{O} \) or AOT) or two components. All Taylor dispersion peaks obtained were then simultaneously fitted using eq 55 with \( i = 1, 2 \) to extract the experimental parameters \((P_{i,\text{exp}}, \sigma_i)\). Figure 2 shows the peaks obtained by injecting samples with an excess of only AOT (dashed line) or only \( \text{H}_2\text{O} \) (solid line) into a carrier stream of microemulsion with \( \omega = 11.84 \) and \( \phi_d = 0.18 \). These peaks were used to calculate the instrumental sensitivity coefficients \( K_i \) using eq A3.11. We found that \( K_1 = -2.07 \text{ V/M} \) and \( K_2 = 42.3 \text{ V/M} \). Note that these \( K_i \) are different between \( K_{\text{AOT}} \) and \( K_{\text{AOT}}M_d(M_d/\text{M}_d) \) (eq 22). Therefore, under some conditions, it is possible to obtain “negative” Taylor peaks.

Using eq A3.17 for \( E_{11} \) and eqs A3.12–A3.15, we found the \( E_{10} \), and then using eq A3.3, we transformed these results to diffusion coefficients \( D_i \). Then, using eqs A3.5–A3.8, we built analytical solutions of eq A3.1, the \( c_i \) given by eq A3.9, for many different injections and compared the analytical signals.

**Figure 1.** (A) Taylor dispersion profile for the 2-component system hexane-octane at \( u_0 = 0.3 \text{ mL/min} \approx 0.9022 \text{ cm/s} \) for \( R_0 = 0.042 \text{ cm} \). The total length of capillary tubing used is \( L_0 \approx 60 \text{ m} \). The injected sample is octane; the eluent is hexane. The experimental curve is fitted by a single Gaussian with \( P_{\text{exp}} = 119.65 \text{ V x cm} \) and \( \sigma = 0.88 \text{ cm/s} \). \( D = R_0^2u_0^2/(480) \). (B) Dependence of the diffusion coefficient of octane in hexane on the average flow rate \( u_0 \) in the capillary. Error bars in (B) are smaller than the size of the symbols.
Gaussian curves with ∆ radii for pure and loaded ME suggests that MA and Na₂MA in pure AOT-ME (without additives). The coincidence of the (with concentrations as in our Taylor experiments) show a single 

Then we can replace one or two of the peaks with peaks obtained typically in the range of 3 deviations. The standard deviations found in this manner were

\[ \Delta = 3.552 \text{ M, [AOT]} \times 9.4 \text{ cm, and } \Delta = 0.032 \text{ M, [H}_2\text{O}] = \Delta = 0 \text{ M, [MA]} = 0 \text{ M, [octane]} = 5.046 \text{ M ( } \omega = 11.84 \text{ and } \varphi_4 = 0.18) \text{, } T = 23 \text{ °C. Experimental peaks are fitted by a sum of two Gaussian curves with } P_{1,\text{exp}} = 3.51 \text{ V } \times \text{ cm, } s_1 = 7.5 \text{ cm/s, } P_{2,\text{exp}} = 7.94 \text{ V } \times \text{ cm, and } s_2 = 9.15 \text{ cm/s for dashed line and } P_{1,\text{exp}} = -4.78 \text{ V } \times \text{ cm, } s_1 = 7.5 \text{ cm/s, } P_{2,\text{exp}} = -18.44 \text{ V } \times \text{ cm, and } s_2 = 9.15 \text{ cm/s for solid line.}

**TABLE 2: Ternary Diffusion Coefficients and Sensitivity Coefficients \( K_i \) for Water (1) and AOT (2) in Water/AOT/Octane Microemulsions with \( \omega = 11.84 \text{ and } \varphi_4 = 0.18 \)**

<table>
<thead>
<tr>
<th>( D_{11} )</th>
<th>( D_{12} )</th>
<th>( D_{21} )</th>
<th>( D_{22} )</th>
<th>( K_1 )</th>
<th>( K_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6 ± 0.04</td>
<td>7.8 ± 2</td>
<td>-0.01 ± 0.002</td>
<td>1.3 ± 0.04</td>
<td>-2.07</td>
<td>42.3</td>
</tr>
</tbody>
</table>

\( ^a \) Coefficients \( D_{ij} \) are reported in units of \( 10^{-6} \text{ cm²/sec} \), \( K_1 \) and \( K_2 \) in V/M.

(Taylor peaks) \( S = K_1 c_1 + K_2 c_2 \) to the corresponding experimental peaks. By tuning slightly the \( D_{ij} \) to minimize the difference between the analytical and corresponding experimental peaks, we were able to adjust all analytical peaks to the experimental ones. The resulting \( D_{ij} \) are reported in Table 2. The standard deviation associated with the fitting procedure itself is relatively small, but other factors, particularly the baseline subtraction, contribute larger sources of error. To estimate the uncertainty in our results, we can choose any two experimental peaks (like those shown in Figure 2) and find \( E_{ij} \) and then \( D_{ij} \). Then we can replace one or two of the peaks with peaks obtained with different initial concentrations and find new values of \( E_{ij} \) and \( D_{ij} \). From several sets of \( D_{ij} \) obtained in this fashion, we can obtain the mean \( \langle D_{ij} \rangle \) and the corresponding standard deviations. The standard deviations found in this manner were typically in the range of \( 3-22\% \).

**Water/AOT/MA/Octane and Water/AOT/Na₂MA/Octane Systems.** Dynamic light scattering (DLS) experiments on the AOT microemulsion loaded with malonic acid or with Na₂MA (with concentrations as in our Taylor experiments) show a single narrow peak corresponding to the radius of the water droplets in pure AOT-ME (without additives). The coincidence of the radii for pure and loaded ME suggests that MA and Na₂MA probably have only a very small effect on the physical structure of the microemulsion, and consequently, it is reasonable to assume that the diffusion coefficients \( D_{11}, D_{12}, D_{21}, \text{ and } D_{22} \) found for the ternary system are substantially unchanged in the quaternary system. The diffusion coefficient of water droplets, \( D_0 \), found in our DLS experiments is about \( 6.3 \times 10^{-7} \text{ cm/s} \) for \( \omega = 11.8 \).

Figure 3 shows Taylor dispersion peaks generated by injection of samples in which the concentration of a single component differs from that in the carrier solution with \( \omega = 11.84, \varphi_4 = 0.18, \) and \( [\text{MA}] = 0.032 \text{ M} \) and \( T = 23 \text{ °C} \).

**TABLE 3: Preliminary Quaternary Diffusion Coefficients and Sensitivity Coefficients \( K_i \) for Water(1)/AOT(2)/MA(3)/Octane System at \( \omega = 11.84, \varphi_4 = 0.18, [\text{MA}] = 0.032 \text{ M} \) and \( T = 23 \text{ °C} \)**

<table>
<thead>
<tr>
<th>( D_{13} )</th>
<th>( D_{23} )</th>
<th>( D_{31} )</th>
<th>( D_{32} )</th>
<th>( D_{33} )</th>
<th>( K_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.0</td>
<td>1.7</td>
<td>-0.004</td>
<td>-0.09</td>
<td>0.5</td>
<td>-12.3</td>
</tr>
</tbody>
</table>

\( ^a \) Coefficients \( D_{ij} \) are reported in units of \( 10^{-6} \text{ cm²/s} \), \( K_3 \) in V/M. Coefficients \( D_{11}, D_{12}, D_{21}, D_{22}, K_1, \) and \( K_2 \) are the same as in Table 2.
Cross-Diffusion in a Water-in-Oil Microemulsion

In addition to estimation of standard deviations, we also tested the robustness of our results by other methods. For example, we analyzed the effect on the analytical solution shown in Figure 5B of changes in the very small negative diffusion coefficients \(D_{31}\) and \(D_{32}\). Panels C and D in Figure 5 report, respectively, the analytical solutions with \(D_{31} = D_{32} = 0\) and with small positive values of \(D_{31}\) and \(D_{32}\). Comparing Figure 5A with Figure 5C,D, it is evident that the curves in panels C and D in Figure 5 deviate significantly from the corresponding experimental curves shown in Figure 5A.

Of course, this simple test is not sufficient to demonstrate the validity of the calculated diffusion coefficients. Concerted variations of several of the \(D_{ij}\) may lead to negligible changes in the analytical solutions. Such small concerted deviations can be generated by small changes in the fitting parameters \(\sigma_i\) and \(P_{\text{exp}}\). Analysis shows, however, that small variations in the \(\sigma_i\) and \(P_{\text{exp}}\) do not significantly affect the \(D_{ij}\). We have calculated approximate variations in the derivatives \(\partial D_{ij}/\partial \sigma_i\) (see Table 5) by changing \(\sigma_i\) and calculating the resulting values of \(D_{ij}\). Analogous values were obtained for \(\partial D_{ij}/\partial P_{\text{exp}}\) by varying \(P_{\text{exp}}\). The error in \(D_{ij}\) can be estimated as \((\partial D_{ij}/\partial \sigma_i)\Delta \sigma_i/D_{ij}\) or \((\partial D_{ij}/\partial P_{\text{exp}})\Delta P_{\text{exp}}/D_{ij}\), where \(\Delta \sigma_i\) and \(\Delta P_{\text{exp}}\) are the errors in \(\sigma_i\) and \(P_{\text{exp}}\), respectively. We estimate \(\Delta \sigma_i\) and \(\Delta P_{\text{exp}}\) to be 10–20% due to uncertainties in baseline subtraction and/or small errors in sample preparation, which cause slightly different values of \(K\). These evaluations yield errors in the \(D_{ij}\) comparable to those shown in Table 4, i.e., 5–50% for the various \(D_{ij}\). Such accuracy is more than sufficient for our ultimate purpose of modeling of dissipative patterns in the BZ–AOT system. We thus have some confidence that the \(D_{ij}\) obtained by this method are reasonably accurate.

A possible problem with the use of malonic acid as the fourth component may arise from the lack of a common ion between MA and AOT. Interdroplet collisions may cause an exchange between the hydrogen ions of malonic acid (\(pK_{a1} = 2.83, pK_{a2} = 5.69\) in bulk water) and the sodium ions of AOT, generating a flux of the fifth component, making our system pseudoquaternary. The possibility of such a scenario is rather low, since dissociation of MA inside water droplets, where the dielectric constant \(\epsilon\) is about 5–10 (instead of \(\approx 80\) in the bulk water),\(^{46-48}\) should be small. Nevertheless this possibility is not zero, and we therefore investigated the contribution of these counterion fluxes (in the form of fluxes of Na2MA or protonated AOT molecules, \(\text{HSO}_3^\text{-}/\text{AOT}\)) to our system by performing experiments with disodium malonate (Na2MA) as the fourth component. The solubility of Na2MA is smaller than that of MA, which resulted in the lower [Na2MA] used in our experiments. The values of the main- and cross-diffusion coefficients (cf. Tables 4 and 6) are almost the same as in the case of malonic acid.

Comparing the diffusion coefficient of water droplets, \(D_{ij}\) found in the DLS experiments (\(D_{ij} \approx 6.3 \times 10^{-7}\) cm\(^2\)/s) to the \(D_{ij}\) values found in the Taylor experiments, we see that \(D_{ij}\) is very close to \(D_{11}\) and \(D_{33}\).
Water/AOT/Ferroin/Octane system. Measurement of $D_\eta$ for this system is more complex. The problem is that the DLS spectrum has a second peak corresponding to ferroin, its concentration in the injected solution. The spectrophotometric peak with an amplitude of this peak, which probably indicates the presence of clusters of water droplets. To see clearly the RID signal corresponding to ferroin, its concentration in the injected solution must be relatively large; at such a concentration, the DLS spectrum is bimodal with two pronounced peaks. The use of a spectrophotometer as a second detector is very helpful in this situation.

Figure 6A–C shows the RID output for the Taylor dispersion peaks generated by the injection of samples in which the concentration of water, AOT, or ferroin, respectively, exceeds that in the carrier solution. The spectrophotometric peak corresponding to the RID peak in Figure 6C is shown in Figure 6D. The peak in Figure 6D is very well fitted by a single Gaussian curve, providing us with the dispersion of one of the three Gaussian functions, let say $\sigma_3$. Using eq 27a for $i = 3$ and the coefficient $K_{3,spec}$ ($K_{3,spec}$ coincides with the product $\epsilon_0\epsilon_{SIO}$, where $\epsilon_{SIO}$ is the extinction coefficient of ferroin at $\lambda = 510$ nm), we can calculate element $F_{33}$ of the matrix $F$. Unfortunately, we were not able to use eq 27a to determine $F_{31}$ and $F_{32}$, because the ferroin flux induced by the water and AOT gradients was too low to be detected spectrophotometrically. Since the accuracy of our spectrophotometric detection is about 0.001 au (au = absorption units), the minimal detectable concentration of ferroin is about 0.001/(510 mV) = 0.2 µM. Note that the minimal concentration of ferroin detectable by the RID and determined as $V_{noise}K_{3,RID}$ is also about 0.2 µM, since $V_{noise} \approx 0.1$ mV and $K_{3,RID} \approx 500$ m/V (see Table 7).

Knowing $\sigma_3$, we can accurately determine the other two dispersions, $\sigma_1$ and $\sigma_2$, by fitting the peaks shown in Figures 6A–C. Knowing the value of $F_{33}$ and the product $\sigma_1\sigma_2\sigma_3$, we can evaluate the product $s_1s_3$ using eq 34 and compare this value to the $s_1s_3$ found in pure AOT microemulsion (water/AOT/octane system). The good agreement between the two $s_1s_3$ values suggests that the diffusion coefficients $D_{11}$, $D_{12}$, $D_{21}$, and $D_{22}$ do not change significantly in the quaternary system upon adding ferroin.

The shape of the peak in Figure 6C suggests the presence of coupled fluxes of water and AOT associated with the gradient of [ferroin]. Comparing the Taylor peaks in Figures 6C (for ferroin) and 3C (for malonic acid), we see that they lie in opposite directions. This fact is reflected in the opposite signs of all the cross-diffusion coefficients for ferroin and MA.

From our analysis of the Taylor peaks, we find that the values of $K_1$ and $K_2$ are the same as in the water/AOT/octane ternary system. Applying the same data analysis as employed for malonic acid, we obtain the main- and cross-diffusion coefficients reported in Table 7.

### 6. Discussion

In this paper, we have adapted the Taylor dispersion method to four-component systems by using data either from a three-component subsystem or from a second detector sensitive to the concentration of a single component. We showed that data from fitting the experimental Taylor peaks by three Gaussians can be transformed into the nine elements of the matrix $F$ and then into the nine elements of the diffusion matrix $D$ composed of the main- and cross-diffusion coefficients.

In principle, this theory can be extended to an arbitrary multicomponent system, which seems difficult, if not impossible, with previous methods. In general, in an $(n+1)$-component system with an $n \times n$ D-matrix, to find the $n^2$ elements of the corresponding F-matrix, we have $n$ equations obtained from $n$ independent RID-experiments with only $\Delta C_i \neq 0$ (cf. eq 25), $n$ Vieta’s equations (cf. eqs 16–18) relating the elements of $F$ and the $\sigma_n$, and $(n-1)^2$ elements of $D_{n+1}$ from a suitable n-component subsystem measured in another set of experiments. The constraint $\text{det}(F)\text{det}(D) = K_{n+1}$ reduces the number of independent equations from $n+n+(n-1)^2$ to $n^2+1$ to $n^2$. The eqs 24 and 26 generalize to

$$I_0^n \sum_{i=1}^{n} P_{\exp} = \sum_{i=1}^{n} K_{n+1}$$

$$I_0^n \sum_{i=1}^{n} \sigma P_{\exp} = \sum_{i=1}^{n} \sum_{j=1}^{n} K_{F_{ij}}$$

For a three-component system, we can determine all four elements of $D_2$ in just two experiments without performing experiments on a two-component subsystem. For more complex systems, however, beginning with the quaternary $(n=4)$ system, we have to perform experiments to determine the $D_1$ for an $(n-1)$ component subsystem. This makes our theory matchless-like. However, by using different detectors, e.g., an RID and a spectrophotometer (or Raman spectrometer), it may be possible to find some of the $D_{ij}$ directly from experiments only on the n-component system.

There are several potential pitfalls in our method. First, when we use coefficients $D_1$ found in an $(n-1)$-component subsystem for determining $D_0$ in the n-component system, we must be sure that they are the same, i.e., that addition of the $n^\text{th}$ component does not significantly alter the physical structure of the $(n-1)$-component system or the interactions between these $(n-1)$-components. In the case of AOT microemulsions, the fourth component can in general change the radius (or structure) of the water nanodroplets, if either the concentration or the linear extent of the fourth component is too large. We probably create such a situation when we use ferroin as the fourth component. One of the consequences of these changes might be the unusual shape of the Taylor peak shown in Figure 6C. This peak has two maxima, and the amplitude of the maximum at longer time is larger than the amplitude of the maximum at shorter time. This very reproducible shape cannot be well fitted by any combination of Gaussian curves with the same retention time $t_0$. At present, we do not have a satisfactory explanation for this phenomenon.

Second, in the case of AOT microemulsions, the sensitivity constant $K_1$ (for water) may depend on the radius of the water droplet core. This dependence originates from the dependence of the refractive index $n$ on the dielectric permittivity and magnetic permeability, $\epsilon$ and $\mu$, respectively:

$$n = (\epsilon_0 / \epsilon_0 \mu_0)$$

where $\epsilon_0$ and $\mu_0$ are the values in vacuum, and in turn on the dependence of $\epsilon$ on $\omega = [\text{H}_2\text{O}]/[\text{AOT}])$. In experiments
Injected samples contain (A) an excess of H2O, (signal of spectrophotometer). Dotted lines show experimental peaks, and solid lines show analytical signals built using values from Table 7.

\[ \omega \text{ and with } k \text{ its value in the eluent, we actually change the radius } \]

in the eluent microemulsion; consequently all \( D_{ki}^* \) are equal; \( c_j \) is the concentration of solute \( k \) (1 = H2O, 2 = AOT, and 3 corresponds to one of the BZ reactants, MA or ferroin).

Table 7: Quaternary Diffusion Coefficients (in cm²/s) for Water(1)/AOT(2)/Ferroin(3)/Octane System at \( \omega = 11.84, q_A = 0.18, [\text{ferroin}] = 1.61 \times 10^{-5} \text{ M}, \text{ and } T = 23 \text{°C} \times \text{cm/s),} \]

<table>
<thead>
<tr>
<th>( j )</th>
<th>( D_{12} )</th>
<th>( D_{23} )</th>
<th>( D_{31} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>((5 \pm 0.3) \times 10^{-7})</td>
<td>((5.2 \pm 2) \times 10^{-6})</td>
<td>((-4.5 \pm 1) \times 10^{-5})</td>
</tr>
<tr>
<td>2</td>
<td>((-1.2 \pm 0.2) \times 10^{-6})</td>
<td>((1.2 \pm 0.3) \times 10^{-6})</td>
<td>((-1.2 \pm 0.1) \times 10^{-5})</td>
</tr>
<tr>
<td>3</td>
<td>((2.2 \pm 3) \times 10^{-30})</td>
<td>((3.2 \pm 1) \times 10^{-9})</td>
<td>((4 \pm 0.7) \times 10^{-7})</td>
</tr>
</tbody>
</table>

* Averaged values were found using the same procedure as for the system water(1)/AOT(2)/MA(3)/octane: \( K_{1,\text{RID}} = -2.05 \text{ V/M, } K_{2,\text{RID}} = 42.3 \text{ V/M, } K_{3,\text{RD}} = 554 \text{ V/M, } K_{3,\text{spec}} \equiv K_{\text{E10}} = 1.0 \times 10^{4} \text{ M}^{-1}. \)

Consider first the coefficients \( D_{12} \) and \( D_{21} \). If we increase \( c_2 \), the radius of a droplet \( R_w \) decreases and consequently (due to the Stokes–Einstein relation) \( D_{23} \) increases. Hence \( \partial D_{23}/\partial c_2 \) is positive and \( D_{12} \) should be positive. If we increase \( c_1 \), the radius of a droplet increases, \( D_{23} \) decreases, \( \partial D_{23}/\partial c_1 < 0 \) and \( D_{21} \) should be negative. The actual values of \( D_{12} \) and \( D_{21} \) follow from the dependences of the droplet radius on \( c_1 \) and \( c_2 \).²⁶

With ferroin as the fourth component (\( c_3 \)), we do not have an analytical expression for the dependence of \( R_w \) on [ferroin]. However, the DLS experiments indicate the emergence of clusters as [ferroin] increases. If ferroin is located in the surfactant layer (since phenanthroline is hydrophobic), it may deform the spherical droplets, leading to clustering or enlarging of \( R_w \). Clustering implies that \( \partial D_{23}/\partial c_3 \) should be negative and consequently \( D_{13} \) and \( D_{23} \) also should be negative. Very large negative values of \( D_{13} \) and \( D_{23} \) may arise with large clusters (radius ca. 20 nm) or droplets containing ferroin.

In the case of malonic acid, we did not observe noticeable changes in the size of water droplets, and therefore the most plausible mechanism appears to be “excluded volume”;²²,5² The larger concentration of MA induces a larger effective concentration of water in the droplet, since the volume available for motion of water inside the droplets, or more precisely, in the aqueous pseudophase, becomes smaller. In the “excluded volume” mechanism, the cross-diffusion coefficients can be expressed as \( D_{ik} \equiv D_i V_{C_i} / (1 - q_{iA})^2 \), where \( V_i \) is the molar volume and \( q_{iA} = V_{iC_i} \) is the volume fraction of malonic acid in the aqueous phase. This hypothesis, however, does not explain the cross-diffusion between MA and AOT, \( D_{23} \). Perhaps a small decrease of the droplet radius with increasing [MA] also plays a role. More data, and especially the dependence of \( D_{13} \) and \( D_{23} \) on [MA], are needed.

It is difficult to characterize at this stage, without knowing the cross-diffusion coefficients for the other BZ reactants (especially Br⁻, Br₂, and HBrO₂), what precise role cross-diffusion plays in pattern formation in the BZ–AOT system. It does seem clear, though, both from the experiments presented here and from preliminary calculations, that introduction of nonreactive neutral molecules like AOT and H2O into the
reaction–diffusion equations can change the diffusion fluxes of reactive molecules through cross-diffusion and can consequently contribute significantly to the observed patterns.

If the large negative cross-diffusion coefficients $D_{13}$ and $D_{23}$ for ferroin are explained by an increase in the droplet radius or by clustering of small droplets promoted by ferroin molecules, then it seems plausible that in the BZ–AOT system all other molecules present inside water droplets have countercurrents induced by the gradient of [ferroin] or [ferriin] (oxidized form of ferroin), i.e., negative cross-diffusion coefficients. This hypothesis can be used in simulating, for example, Turing patterns in the BZ–AOT system with the classical Oregonator model with only three species (HBrO$_2$, Br$^-$, and catalyst) possessing nonzero cross-diffusion coefficients and nearly equal main diffusion coefficients.

Acknowledgment. We are grateful to Derek Leaist for practical advice and encouragement. This work was supported in part by the Chemistry Division of the National Science Foundation through grants CHE-0615507 and CHE-0625866 and by the donors of the American Chemical Society Petroleum Research Fund through grant 42222-AC6.

Appendix I. Derivation of eq 9
If we replace $R$ by $R_0$, $\partial t$ by $\partial z$, $\partial c_i/\partial t$ by $\hat{c}_i/\partial z$, and $D_i$ by $\hat{D}_i$, eqs 6–8 give

$$
\hat{D}_i \hat{c}_i/\partial z = \hat{R}_i \hat{D}_i \hat{c}_i/\partial z^2 + \hat{R}_0 \hat{D}_i \hat{c}_i/\partial z^2 + (\partial \hat{c}_i/\partial z) \hat{R}_0 \hat{D}_i \hat{c}_i/\partial z + r^{-1} \partial c_i/\partial r + D_i \hat{\hat{c}}_i/\partial z^2 + r^{-1} \partial c_i/\partial r + D_i \hat{\hat{c}}_i/\partial z^2 +
$$

We assume that the terms $\hat{\hat{c}}_i/\partial z^2$ are small, i.e., $R_0 \hat{\hat{c}}_i/\partial z^2 \ll \hat{\hat{c}}_i/\partial z^2 + r^{-1} \partial c_i/\partial r$ and $D_i \hat{\hat{c}}_i/\partial z^2 \ll (\partial \hat{c}_i/\partial z) \hat{R}_0 \hat{D}_i \hat{c}_i/\partial z$, so that the first three terms on the right-hand side of eq A1.1 can be neglected. In effect, we ignore axial diffusion and take into account only radial diffusion in the flowing mixture. We further assume that at long times, i.e., far down the tube, the mixture has reached a steady state, so that $\partial \hat{c}_i/\partial t = 0$. These two assumptions are independent of the number of components and were first introduced by Taylor for two-component systems and then used by Price for three-component systems. Price showed that these assumptions are valid if $L/\hat{D}_i > 2R_0^2/(3.82D_i)$, where $L$ is the distance from the injector to the detector. In general, the diagonal elements $D_i$ should be replaced by the eigenvalues of matrix $D$, which are always real and positive, while $D_i$ can be negative. The validity of these assumptions is also justified by accurate (1–5%) measurements of binary diffusion coefficients. Under these assumptions, eq A1.1 can be written as

$$
r_u \hat{c}_i/\partial z = D_{11} (\hat{\hat{c}}_i/\partial z^2 + r^{-1} \partial \hat{c}_i/\partial r) + D_{12} (\hat{\hat{c}}_i/\partial z^2 + r^{-1} \partial \hat{c}_i/\partial r) + D_{13} (\hat{\hat{c}}_i/\partial z^2 + r^{-1} \partial \hat{c}_i/\partial r) + D_{14} (\hat{\hat{c}}_i/\partial z^2 + r^{-1} \partial \hat{c}_i/\partial r) (A1.2)
$$

and

$$
r_u \hat{c}_i/\partial z = D_{21} (\hat{\hat{c}}_i/\partial z^2 + r^{-1} \partial \hat{c}_i/\partial r) + D_{22} (\hat{\hat{c}}_i/\partial z^2 + r^{-1} \partial \hat{c}_i/\partial r) + D_{23} (\hat{\hat{c}}_i/\partial z^2 + r^{-1} \partial \hat{c}_i/\partial r) + D_{24} (\hat{\hat{c}}_i/\partial z^2 + r^{-1} \partial \hat{c}_i/\partial r) (A1.3)
$$

where $D_{ij} = R_0 \hat{D}_i \hat{D}_j (1 - 2r^2)$. Solving eq A1.4 for $\hat{\hat{c}}_i/\partial z^2 + r^{-1} \partial \hat{c}_i/\partial r$ and substituting the result into eqs A1.2 and A1.3 gives

$$
r_u \hat{c}_i/\partial z = (D_{11} - D_{13} D_{31}/D_{33}) (\hat{\hat{c}}_i/\partial z^2 + r^{-1} \partial \hat{c}_i/\partial r) + (D_{12} - D_{13} D_{32}/D_{33}) (\hat{\hat{c}}_i/\partial z^2 + r^{-1} \partial \hat{c}_i/\partial r) (A1.5)
$$

and

$$
r_u \hat{c}_i/\partial z = (D_{21} - D_{23} D_{31}/D_{33}) (\hat{\hat{c}}_i/\partial z^2 + r^{-1} \partial \hat{c}_i/\partial r) + (D_{22} - D_{23} D_{32}/D_{33}) (\hat{\hat{c}}_i/\partial z^2 + r^{-1} \partial \hat{c}_i/\partial r) (A1.6)
$$

Then, we can eliminate ($\hat{\hat{c}}_i/\partial z^2 + r^{-1} \partial \hat{c}_i/\partial r$) from eqs A1.5 and A1.6 to obtain

$$
R_0^2 \hat{c}_i/\partial z - (\det(M_{D11}) \partial \hat{c}_i/\partial z - \det(M_{D21}) \partial \hat{c}_i/\partial z + \det(M_{D12}) \partial \hat{c}_i/\partial z - \det(M_{D22}) \partial \hat{c}_i/\partial z) (A1.7)
$$

Assuming that $\hat{c}_i/\partial z$ is independent of $r$, eq A1.7 has the solution:

$$
c_i = c_{1c} + T_1 (r^2 - r^2/2) (A1.8)
$$

where

$$
T_1 = \frac{R_0 \hat{c}_i/\partial z}{(\det(M_{D11}) \partial \hat{c}_i/\partial z - \det(M_{D21}) \partial \hat{c}_i/\partial z + \det(M_{D12}) \partial \hat{c}_i/\partial z - \det(M_{D22}) \partial \hat{c}_i/\partial z)} (A1.9)
$$

The rate of transfer of $c_1$ across the cross-section of the tube is

$$
Q_1 = 2\pi R_0^2 \hat{c}_i/\partial z (1 - r^2) \partial \hat{c}_i/\partial z (A1.10)
$$

Substituting $c_1$ from (A1.8) into (A1.10), we have

$$
Q_1 = \text{constant} - 2\pi R_0^2 T_1 \partial \hat{c}_i/\partial z (A1.11)
$$

Applying the continuity equation, we can write that

$$
\partial \hat{Q}_i/\partial z = -\pi R_0^2 \partial \hat{c}_i/\partial t (A1.12)
$$

where $\hat{c}_i$ is the average concentration $c_i$ over the cross-section of the tube. The condition of long time implies that the radial variation of $c_i$ is small, so that $\hat{c}_i(\hat{c}_i)/\partial t \approx \hat{c}_i(\hat{c}_i)/\partial t$ at a fixed $\hat{c}_i$. Then, eqs A1.9, A1.11, and A1.12 give

$$
R_0^2 \hat{c}_i/\partial z - (\det(M_{D11}) \partial \hat{c}_i/\partial z - \det(M_{D21}) \partial \hat{c}_i/\partial z + \det(M_{D12}) \partial \hat{c}_i/\partial z - \det(M_{D22}) \partial \hat{c}_i/\partial z) (A1.13)
$$

since $D_{ij} \partial \hat{c}_i/\partial z - \det(M_{D21}) \partial \hat{c}_i/\partial z + \det(M_{D22}) \partial \hat{c}_i/\partial z) = 1/\det(D)$ and $[D_{ij} \partial \hat{c}_i/\partial z - \det(M_{D21}) \partial \hat{c}_i/\partial z + \det(M_{D22}) \partial \hat{c}_i/\partial z) = D_{ij} \partial \hat{c}_i/\partial z$. The coefficients in front of $\hat{\hat{c}}_i/\partial z^2$, $\hat{\hat{c}}_i/\partial z^2$, and $\hat{\hat{c}}_i/\partial z^2$ in (A1.13) are equal respectively to $F_{11}$, $F_{12}$, and $F_{13}$. Equations analogous to A1.13 can be deduced from eqs A1.2–A1.4 for the concentrations $c_2$ and $c_3$, with respective coefficients $F_{2j}$ and $F_{3j}$.

Appendix II. Derivation of eqs 24 and 26
Starting from eq 23, we can sum the experimental pre-exponential terms to get
\[ \sum_{i=1}^{3} P_{i, \text{exp}} = \sum_{i=1}^{3} K_i \sum_{j=1}^{3} B_{ij} \]  
(A2.1)

Substituting eq 19, we have
\[ \sum_{i=1}^{3} P_{i, \text{exp}} = (\pi R_0^2)^{-1} \sum_{i=1}^{3} K_i P_i \]  
(A2.2)

Using eqs \( P_i = c_0 V_0 \) and \( \pi R_0^2 V_0 = l_0^{-1} \), A2.2 transforms to:
\[ \Gamma_0^{-1} \sum_{i=1}^{3} P_{i, \text{exp}} = \sum_{i=1}^{3} K_i c_0 \]  
(A2.3)

which is eq 24.

To find a relation between the coefficients \( F_{ij} \) and the data obtained by fitting the experimental peaks \( (\sigma_i \) and \( P_{i, \text{exp}} \), we start again from eq 23. Multiplying \( P_{i, \text{exp}} \) by \( \sigma_i \), we get
\[ \sigma_i P_{i, \text{exp}} = \sigma_i \sum_{j=1}^{3} K_j B_{ij} \]  
(A2.4)

Summing over \( i \) in eq A2.4:
\[ \sum_{i=1}^{3} \sigma_i P_{i, \text{exp}} = \sum_{i=1}^{3} K_i \sum_{j=1}^{3} \sigma_i B_{ij} \]  
(A2.5)

Inserting eq 14 into eq A2.5, we have
\[ \sum_{i=1}^{3} \sigma_i P_{i, \text{exp}} = \sum_{i=1}^{3} K_i \sum_{j=1}^{3} F_{ij} \sum_{k=1}^{3} B_{jk} \]  
(A2.6)

Using eq 19 gives
\[ (\pi R_0^2) \sum_{i=1}^{3} \sigma_i P_{i, \text{exp}} = \sum_{i=1}^{3} K_i \sum_{j=1}^{3} P_i F_{ij} \]  
(A2.7)

Finally, replacing \( P_j \) with \( c_0 V_0 \), we have:
\[ \Gamma_0^{-1} \sum_{i=1}^{3} \sigma_i P_{i, \text{exp}} = \sum_{i=1}^{3} c_0 \sum_{j=1}^{3} K_i F_{ij} \]  
(A2.8)

which is eq 26.

### Appendix III. Equations for the three-component system

The equations derived for the four-component system are applicable to the three-component system after appropriate modification. Equation 9 now becomes
\[ \frac{\partial c_i}{\partial t} = \sum_{j=1}^{2} E_{ij} \frac{\partial^2 c_j}{\partial z^2} \]  
(A3.1)

where the matrix \( \mathbf{E} \) is the counterpart of \( \mathbf{F} \) for the three-component system. Equation 10 now becomes
\[ E_{11} = K_{FP} D_{20}/\text{det}(\mathbf{D}_2), \quad E_{12} = -K_{FP} D_{21}/\text{det}(\mathbf{D}_2), \]  
\[ E_{21} = -K_{FD} D_{12}/\text{det}(\mathbf{D}_2), \quad E_{22} = K_{FP} D_{11}/\text{det}(\mathbf{D}_2) \]  
(A3.2)

where \( K_{FD} \equiv R_0^2 c_0^2/48 \) and \( \text{det}(\mathbf{D}_2) = D_{11} D_{22} - D_{12} D_{21} \).

The transformation from the coefficients \( E_{ij} \) to the coefficients \( D_{ij} \) (cf. eq 11) assumes the form
\[ D_{11} = K_{FP} E_{22}/\text{det}(\mathbf{E}), \quad D_{12} = -K_{FP} E_{21}/\text{det}(\mathbf{E}), \]  
\[ D_{21} = -K_{FD} E_{22}/\text{det}(\mathbf{E}), \quad D_{22} = K_{FP} E_{11}/\text{det}(\mathbf{E}) \]  
(A3.3)

where \( \text{det}(\mathbf{E}) = E_{11} E_{22} - E_{12} E_{21} \).

Equation 14 transforms into
\[ sA_{ij} = \sum_{k=1}^{2} E_{ik} A_{kj} \quad i = 1, 2; j = 1, 2 \]  
(A3.4)

where the \( s_i \) are the eigenvalues of \( \mathbf{E} \) and the \( A_{ij} \) are the counterparts of the \( B_{ij} \) for the three-component system.

The equations for the \( A_{ij} \) can be easily written, since they are much less cumbersome than the equations for the \( B_{ij} \):
\[ A_{11} = (\pi R_0^2)^{-1}[P_1(E_{11} - s_2) + P_2 E_{22}]/(s_2 - s_1) \]  
(A3.5)
\[ A_{12} = (\pi R_0^2)^{-1}[P_1 E_{12} E_{21}/(s_2 - E_{22}) - P_2 E_{12}]/(s_1 - s_2) \]  
(A3.6)
\[ A_{21} = (\pi R_0^2)^{-1}[P_2 E_{22} E_{21}]/(s_1 - E_{22}) - P_2 E_{21}]/(s_2 - s_1) \]  
(A3.7)
\[ A_{22} = (\pi R_0^2)^{-1}[P_2 (E_{22} - s_1) + P_1 E_{21}]/(s_2 - s_1) \]  
(A3.8)

and the concentrations \( c_i \) are expressed as
\[ c_i = A_{i1} G_1 + A_{i2} G_2 \quad i = 1, 2 \]  
(A3.9)

The general expression analogous to eq 24 for determining the sensitivity coefficients \( K_1 \) and \( K_2 \) (cf. eq 22) is
\[ \Gamma_0^{-1} (P_{1, \text{exp}} + P_{2, \text{exp}}) = K_1 c_{i1} + K_2 c_{i2} \]  
(A3.10)

From experiments involving injections with only \( c_{i0} = 0 \), we have
\[ K_i = l_0^{-1} (P_{1, \text{exp}, i} + P_{2, \text{exp}, j})/c_{i0} \quad i = 1, 2 \]  
(A3.11)

Knowing \( K_1 \) and \( K_2 \), we can find the \( E_{ij} \) from the following four equations:
\[ K_1 E_{11} + K_2 E_{21} = C_1 \]  
(A3.12)
\[ K_1 E_{12} + K_2 E_{22} = C_2 \]  
(A3.13)
\[ E_{11} + E_{22} = s_1 + s_2 \]  
(A3.14)
\[ E_{11} E_{22} - E_{12} E_{21} = s_1 s_2 \]  
(A3.15)

where \( C_i = l_0^{-1} (P_{1, \text{exp}, i} + P_{2, \text{exp}, j})/c_{i0} \), \( i = 1, 2 \). Equations A3.12–A3.15 are analogous to eqs 27–29 and follow from eq A3.16, which is analogous to the fundamental eq 26.
\[ \Gamma_0^{-1} [P_{1, \text{exp}, i} + P_{2, \text{exp}, j}] = (K_1 E_{11} + K_2 E_{21}) c_{i1} + \]  
\[ (K_1 E_{12} + K_2 E_{22}) c_{i2} \]  
(A3.16)

Solving eqs A3.12–A3.15 for \( E_{11} \), we find
\[ E_{11} = [s_1 s_2 + C_1 C_2/(K_1 K_2) - (s_1 + s_2) C_1/K_1]/(C_2/K_2 - C_1/K_1) \]  
(A3.17)

The expressions for \( E_{12}, E_{21}, \) and \( E_{22} \) are straightforward.

In general, to determine the four \( E_{ij} \) it is sufficient to perform only two experiments, with \( c_{i0} = 0 \) and \( c_{i0} = 0 \). The measured dispersions \( s_i \) should be identical, i.e., \( s_{1,1} = s_{1,2} \) and \( s_{2,1} = s_{2,2} \), where the second subindex indicates the number of the experiment.

**Supporting Information Available:** Details of the calculation of the \( \mathbf{B}_{ij} \) from the \( \mathbf{F}_{ij} \) and a schematic drawing of the apparatus for the Taylor dispersion experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

**References and Notes**
