Quaternary Cross-Diffusion in Water-in-Oil Microemulsions Loaded with a Component of the Belousov–Zhabotinsky Reaction

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Received: March 26, 2010; Revised Manuscript Received: May 7, 2010

We obtain the diffusion matrix, \( \mathbf{D} \), consisting of the main and cross-diffusion coefficients for a loaded AOT microemulsion, a quaternary system containing water (1)/AOT (2)/species (3)/octane (4). Here “species” is a component of the Belousov–Zhabotinsky reaction: NaBr, NaBrO₃, bathoferroin, ferroin, or Br₂. The main and cross-diffusion coefficients of each species depend crucially on its solubility. For water-soluble species (the salts), \( D_{13} \) and \( D_{23} \) are large (much larger than the main diffusion coefficients) and positive. For species located mainly in the surfactant shell (bathoferroin or ferroin), \( D_{13} \) and \( D_{23} \) are large and negative. For oil-soluble Br₂, \( D_{13} \) and \( D_{23} \) are larger and more negative, whereas \( D_{33} \gg D_{11}, \ D_{22} \). The coefficients \( D_{31} \) and \( D_{32} \) are small for all species studied.

1. Introduction

The primary mechanisms of pattern formation in reaction–diffusion systems include excitability for traveling trigger waves (e.g., spirals or concentric rings), bistability for labyrinthine or localized patterns, Turing instability for temporally stationary, spatially periodic patterns, and wave instability (sometimes called the finite wavenumber Hopf instability) for standing waves. In all cases, the reacting species are assumed to obey the simple Fickian diffusion law, where “simple” in this context means that the diffusivity matrix, \( \mathbf{D} \), is diagonal. The ratios between the diagonal elements of \( \mathbf{D} \), the main diffusion coefficients, are critical in determining the mechanism of pattern formation. For example, for Turing instability, \( D_{\text{activator}} \) must be significantly larger than \( D_{\text{inhibitor}} \), where \( D_{\text{activator}} \) and \( D_{\text{inhibitor}} \) are the diffusion coefficients, respectively, of a species that grows autocatalytically and of one that inhibits the autocatalysis.

A more general treatment of reaction–diffusion systems allows for the possibility of cross-diffusion, in which a flux of one species can be induced by a gradient of another species. Cross-diffusion, if it occurs, can affect all of the above mechanisms of pattern formation and may play a significant role in many patterns previously described. Examples include patterns in a CFUR (continuously fed unstirred reactor), where the gradients of species across a feeding gel layer may be large, and the Belousov–Zhabotinsky (BZ) reaction dispersed in water-in-oil aerosol OT (AOT) microemulsion, (BZ-AOT system), where large cross-diffusion effects (for example, a flux of water molecules induced by a flux of AOT molecules) are well documented. For this reason, more detailed information about the effects of cross-diffusion in pattern-forming reaction–diffusion systems is essential for understanding the mechanism of pattern formation. In this article, we continue our investigation of cross-diffusion in the BZ-AOT system.

In a previous article, we extended the Taylor dispersion method to enable measurement of cross-diffusion in four-component systems because four is the minimum number of species for a loaded water-in-oil AOT microemulsion. Although the Taylor method is not as precise as Rayleigh interferometry on a Gosting diffusiometer, information on cross-diffusion coefficients obtained by the Taylor method is sufficient to evaluate the importance (or lack of importance) of cross-diffusion for pattern formation. In the systems of interest here, species 1 is water, 2 is AOT, 3 is a component of the BZ reaction, and 4 is oil (octane in our case). Using this improved Taylor method, we examined two BZ species, malonic acid (MA) and ferroin, and found that the off-diagonal elements of the Fickian diffusivity matrix \( \mathbf{D} \), \( D_{13} \) and \( D_{23} \), are large and positive (\( D_{33}/D_{13} \approx 14, D_{32}/D_{13} \approx 3 \)) for MA and large and negative for ferroin (\( D_{33}/D_{13} \approx -112, D_{32}/D_{13} \approx -30 \)), whereas the coefficients \( D_{31} \) and \( D_{32} \) are small and negative for MA (\( D_{33}/D_{31} \approx -0.01, D_{32}/D_{31} \approx -0.14 \)) and small and positive for ferroin (\( D_{33}/D_{31} \approx 5 \times 10^{-4}, D_{32}/D_{31} \approx 8 \times 10^{-3} \)). A positive (negative) cross-diffusion coefficient, \( D_{ij} \), implies that species \( i \) diffuses toward smaller (larger) concentrations of species \( j \). To complete the first stage of our investigation, we now determine cross-diffusion coefficients for the remaining species in the BZ reaction.

Here we present results on the main and cross-diffusion coefficients for four additional BZ species with quite different hydrophilic–hydrophobic properties. We investigate sodium bromate, which is the oxidizing agent in the BZ reaction; sodium bromide, which acts as an inhibitor and is a key species in the oscillatory behavior; a metal complex, such as bathoferroin (BF), which catalyzes the reaction; and finally, molecular bromine, which is a BZ-inhibiting intermediate formed during the reaction between bromate and bromide in acidic solution. The four species partition quite differently in the microemulsion (ME): bromate and bromide, as water-soluble salts, are located primarily in the water core of the nanodroplets. Because of the hydrophobic nature of the bathophenantroline ligand and the metal ion at its center, BF is soluble in neither water nor oil and should reside in the surfactant layer; this fact is reflected in a larger droplet radius measured in dynamic light scattering (DLS) experiments. Finally, the partition coefficients of Br₂ between octane (oil) and water (W) ([Br₂]₀/[Br₂]ₐ ≈ 20) and...
between AOT and octane ([Br2]_{0,exp}/[Br2]_{0,lat} \approx 5)^{23} indicate that this species is preferentially located in the oil phase (because the volume of octane is much greater than that of AOT) at the small droplet fraction, \( q_d \), used in our experiments.

To establish the dependence of the main and cross-diffusion coefficients on the concentration of droplets, we also measure the diffusion matrix \( D \) for one of the BZ components, ferroin, at several volume fractions and a constant droplet radius.

In Section 2, we present elements of the theory of the Taylor dispersion method used in our determinations. In Section 3 we explain our experimental methods. Our results appear in Section 4, and we conclude with a discussion in Section 5. Some cumbersome but useful equations are grouped in the Appendix.

2. Data Analysis: Theory

In quaternary systems (three solutes + solvent), the diffusion matrix \( D \) contains nine elements, namely, the three diagonal main diffusion coefficients, \( D_{ii} \), and the six off-diagonal cross diffusion coefficients \( D_{ij} \), \( i \neq j \). As the solvent in our water-in-oil microemulsion, we choose the continuous phase, the oil (component 4). In our recent article,\(^{17}\) we extended the Taylor dispersion technique, which involves the diffusive spreading of a drop of solution injected into a laminarly flowing stream containing the same components at slightly different concentrations, by developing two methods to calculate the nine diffusion coefficients in a four-component system. In the first approach, we employ only a refractive index detector (RID) to record the eluted Taylor peaks and make the assumption that the addition of the fourth (BZ) component to the three-component (ME) system does not significantly affect the interactions between the original three components. For example, we assume that the addition of bromate (component 3) to a pure AOT ME leaves the coefficients \( D_{11}, D_{12}, D_{21} \), and \( D_{22} \) essentially unchanged. For relatively low concentrations of this added component, this is likely to be a reasonably accurate approximation. However, further fitting of the Taylor peaks by a set of Gaussian curves can improve the final result, especially at higher concentrations of the BZ component. Our second method requires the use of an additional detector, for example, a spectrophotometer, to measure the concentration of at least one component (note that the RID records the total signal from all components), for example Br2 or BF.

In both methods, we first calculate the coefficients, \( F_{ij} \), of a matrix \( F \) that links the partial derivatives of the concentrations, \( c_i \), of all components in the flowing stream

\[
\frac{\partial c_i}{\partial t} = \sum_{j=1}^{3} F_{ij} \frac{\partial^2 c_j}{\partial z^2}
\]

where the concentration \( c_i \) of the \( i \)th component is related to its volume fraction \( q_i \) as

\[
q_i = c_i M_i d_i
\]

where \( M_i \) is its molecular weight and \( d_i \) is its density. The coefficients \( F_{ij} \) have the same dimensions as the diffusion coefficients \( D_{ij} \) (\( \text{cm}^2/\text{s} \)), but they are inversely proportional to \( D_{ij} \).\(^{17-19}\) The \( F_{ij} \) can be obtained from the experimentally found parameters \( P_{i,exp} \), \( K_i \), and \( \sigma_i \) through the following equations

\[
F_0^{-1} \sum_{j=1}^{n} P_{i,exp} = \sum_{j=1}^{n} K_j c_0
\]

\[
I_0^{-1} \sum_{j=1}^{n} \sigma_j P_{i,exp} = \sum_{j=1}^{n} c_j F_{ij}
\]

where \( l_0 \) is the length of the capillary occupied by the sample injected at the initial time \( (l_0)^{-1} = \pi R_0^2/\phi_0 \), \( V_0 \) is the injected volume, \( R_0 \) is the inner radius of the tubing, \( P_{i,exp} \) are the pre-exponential parts of the Gaussian functions used to fit the experimental peaks, \( \sigma_i \) are the dispersions of the Gaussian functions, which are equal to the eigenvalues of the dispersion matrix \( F \), \( c_0 \) is the difference between the concentration of component \( i \) in the injected sample and in the carrier stream, and \( K_i \) is the instrumental sensitivity with respect to that component (typically linear in the concentration). The experimentally measurable quantities \( P_{i,exp} \), \( K_i \), and \( \sigma_i \) can be found by fitting all experimental peaks \( v(t) \) (generated with injections of different compositions) according to

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

where \( u_0 \) is the mean velocity of the carrier stream and \( t_0 \) is the retention time. Roughly speaking, \( t_0 \) corresponds to the maximum or minimum of the Taylor peak. Before applying eq 5, we calculate and subtract a baseline of the form \((a + bt)\) from the measured signal.

The coefficients \( K_i \) can be found by analyzing three experiments involving injections with only \( c_{10} \neq 0, c_{20} = 0, \) or \( c_{30} \neq 0 \) as

\[
K_i = I_0^{-1} \left( \sum_{j=1}^{3} P_{j,exp} \right) c_i c_0 \quad i = 1, 2, 3
\]

and \( P_{j,exp} \) is the amplitude obtained for the \( j \)th Gaussian by fitting the experiment in which only \( c_j \neq 0 \).

Finally, the diffusion coefficients \( D_{ij} \) can be derived from the coefficients \( F_{ij} \) through the relation\(^{17}\)

\[
D_{ij} = \frac{R_0^2 l_0^2}{48 \text{det}(F)} \text{det}(M_{ij})(-1)^{(ij)}
\]

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

3. Experimental Section

Experiments were performed with a high-pressure liquid chromatography apparatus adapted with a long Teflon capillary in the place of the chromatography column to match the Taylor dispersion conditions.\(^{18,24}\) The capillary was coiled in a 50 cm diameter helix, and its length was \( \sim 30 \) 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 RID (Agilent 1100 series). The inner radius \( R_0 \) (\( 0.42 \) mm) of the tubing was determined by gravimetry. An isocratic pump (Agilent G1310A), which maintained a steady flow, was placed between the eluent reservoir and the injector (Reodine).
A sample loop of volume 20 μL (= V₀) was used for injections. In addition to the Taylor peaks recorded by RID, signals were detected spectrophotometrically at λ = 532 nm in experiments with bathoferroin (molar extinction coefficient, ε₅₃₂ = 19,270 M⁻¹ cm⁻¹) and at λ = 400 nm with bromine (ε₄₀₀ = 172 M⁻¹ cm⁻¹). The HPLC flow-thru cell (Shimadzu) had a 1 mm inner diameter and path length l₁ = 1 cm (8 μL inner volume). Both detectors were connected to a personal computer for data acquisition.

The injector and capillary Teflon tubing were kept at 23 °C in a thermostatted incubator (Fisher Scientific). The flow rate was 0.15 mL/min for all experiments.

We also used a DLS apparatus (DynaPro, Protein Solutions, High Wycombe, U.K.) to monitor the size of water droplets in the AOT microemulsion loaded with a reagent of the BZ system. The mean radius of a droplet water core in a pure AOT microemulsion is roughly given by R_w/nm = 0.17ω₂, where ω = [H₂O]/[AOT]; R_w is independent of the octane volume fraction in the microemulsion. We use ω = 11.84 in our experiments. 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), and the DLS method allows us to measure R_d.

Many physical properties of microemulsions show a threshold-like dependence on ω, the volume fraction of the dispersed phase (q_d = q_D,W + q_AOT). This dependence is due to percolation. If q_d ≪ q_w (the percolation threshold, q_w ≈ 0.5 to 0.6), then the microemulsion can be accurately characterized as a medium in which water droplets float freely. We worked at q_d = 0.18, except in the case of ferroin, where we explored a range of q_d ≈ q_w.

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 H₂SO₄ for 2 days; a stock solution of AOT in octane ([AOT] = 1.5 M) was prepared and filtered through a 0.45 μm Teflon filter to remove possible impurities.

Sodium bromate, NaBrO₃ (SIGMA), sodium bromide, NaBr (Fisher), ferroin (Fluka), and molecular bromine, Br₂ (SIGMA), were used as received. We prepared bathoferroin by dissolving the desired amount of bathophenanthrolnine (4,7-diphenyl-1,10-phenanthroline, Aldrich) in a 1.5 M solution of AOT in octane and then adding a 0.25 M FeSO₄ aqueous solution in the ratio [BP]/[Fe²⁺] = 3. In the following, we specify concentrations of H₂O, AOT, NaBrO₃, NaBr, ferroin, Br₂, BF, and octane with respect to the total volume of the microemulsion. Samples were injected every 3 h.

Using the Taylor dispersion method for a three-component system, we first measured the diffusion coefficients of the ternary AOT system (pure AOT microemulsion) at the chosen ω (= 11.84) and q_d (≈ 0.18). We obtained D₁₁ = 0.6 ± 0.04 × 10⁻⁶ cm²/s, D₁₂ = 7.8 ± 2 × 10⁻⁶ cm²/s, D₂₁ = -9.0 ± 0.002 × 10⁻⁶ cm²/s, and D₂₂ = 1.3 ± 0.04 × 10⁻⁶ cm²/s. Data for other values of q_d will be presented in Section 4.

For each BZ component, we followed the same experimental and analytical procedures. Several samples with an excess or a defect of one or more of the three solutes were injected into the flowing solution. The experimental dispersion peaks obtained for each system were simultaneously fitted using eq 5 with i = 1, 2, 3 to extract experimental parameters P_{exp} and α_i. (In all of our systems, the indices 1, 2, and 3 correspond to H₂O, AOT, and the BZ component, respectively.) The experimental parameters together with the diffusion coefficients D_{ij} (i,j = 1, 2) were used to calculate the dispersion coefficients F_j according to eqs A1–A9 in the Appendix.

The values of D_{ij} calculated from eq 7 were successively refined to get the best match between the experimental and analytical peaks, with the constraint that the eigenvalues of matrix D must be real and positive.

4. Results

4.1. NaBrO₃ and NaBr. The squares in Figure 1 represent the RID experimental signals obtained by injecting an excess of H₂O (panel A), an excess of AOT (panel B), and an excess of bromate (panel C) into the carrier stream. The fitting procedure yielded sensitivity coefficients K₁ = -2 V/M, K₂ = 42 V/M, and K₃ = -8 V/M. The K_i can be either positive or negative because they represent differences among the sensitivities of the instrument with respect to the solute and the solvent. The values for K₁ and K₂ are consistent with results obtained for the ternary system, supporting our assumption that the ME structure is not changed significantly by the addition of bromate. The solid lines in Figure 1 represent the fitted curves obtained with the aid of eq 5. The diffusion coefficients deduced from these curves are reported in Table 1. The complex shape of the peak in Figure 1C demonstrates the presence of coupled flows, that is, fluxes of H₂O or AOT induced by the gradient of NaBrO₃. In the absence of cross-diffusion, these peaks would be simple Gaussians.

If we use NaBr as the fourth component, instead of NaBrO₃, the recorded Taylor dispersion peaks have almost the same shape as those in Figure 1. The diffusion coefficients calculated for the water/AOT/NaBr/octane system with K₁ = -2.06 V/M, K₂
TABLE 2: Quaternary Diffusion Coefficients (in cm²/s) for the Water (1)/AOT (2)/NaBr (3)/Octane System at ω = 11.84, qa = 0.18, [NaBr] = 0.01 M, and T = 23 °C

<table>
<thead>
<tr>
<th>j</th>
<th>D₁₁</th>
<th>D₁₂</th>
<th>D₁₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(6.3 ± 0.3) × 10⁻⁷</td>
<td>(6.3 ± 0.2) × 10⁻⁶</td>
<td>(8 ± 1) × 10⁻⁵</td>
</tr>
<tr>
<td>2</td>
<td>(1.2 ± 0.3) × 10⁻⁸</td>
<td>(1.2 ± 0.2) × 10⁻⁶</td>
<td>(4.7 ± 0.8) × 10⁻⁶</td>
</tr>
<tr>
<td>3</td>
<td>(3.3 ± 0.3) × 10⁻⁸</td>
<td>(3.7 ± 0.2) × 10⁻⁶</td>
<td>(4.7 ± 0.7) × 10⁻⁷</td>
</tr>
</tbody>
</table>

= 52.6 V/M, and K₁ = −30 V/M are reported in Table 2. We see that for both NaBrO₃ and NaBr, the coefficients D₁₁ and D₁₃ are very small, whereas D₁₂ is large and positive.

4.2. Bathofeeroon. In experiments with the BZ catalyst BF, we experience the same problem we encountered with ferroin, namely, that the DLS measurements indicate a bimodal distribution (Figure 2) of droplet radii at the rather large concentration of BF used in the injected sample. The peak at high R₀ suggests the presence of clusters with a radius of 9 nm. Clearly, the formation of clusters shows that the added component (BF) affects the ME significantly; consequently, the diffusion coefficients D₁₁, D₁₂, D₁₃, and D₁₃ found for the pure microemulsion will almost surely be different for a microemulsion loaded with BF. Second, clusters may have their own (smaller) diffusion coefficients and may require additional equations and experiments. Fortunately, in the case of BF, we can employ a spectrophotometer as a second detector for that species. Because none of the other species present in solution absorbs in the visible range, it is feasible to detect a single Gaussian dispersion profile for BF; consequently, we can calculate c₁ with high precision. Moreover, we can also estimate F₃₃ without using data from the three-component system (pure microemulsion) because we have K₁ = K₂ = 0, and if only c₁₀ ≠ 0, eq 4 gives  F₃₃ = α₃₀exp(c₁₀dK₁).

Figure 3 shows the experimental dispersion curves for three injections with compositions different from the carrier solution. Panels A–C present the RID signal, whereas panel D shows the spectrophotometric signal recorded at λ = 532 nm for the experiment shown in panel C. Note that the concentration of BF at the maximum of the Taylor peak in Figure 3D (≈ 6.42 × 10⁻⁵ M + 0.1/19000 M ≈ 6.9 × 10⁻⁵ M) is significantly smaller than that in the injected sample. At such small concentrations of BF, the DLS spectrum has a dominant maximum at R₀ = 2 nm. Therefore, the concentration of clusters decreases over the course of our experiment, which suggests that the coefficients in the diffusivity matrix found below should be interpreted with some caution. From the fitting of the experimental Taylor peaks (solid curves in Figure 3), we calculated the RID sensitivity coefficients (K₁ = −2.4 V/M, K₂ = 43.2 V/M, and K₃ = 600 V/M) and the diffusion coefficients reported in Table 3. Note that coefficient D₂₁ is almost two times smaller than that in the pure microemulsion or the microemulsion loaded with NaBrO₃. Presumably, this change results from the effect of BF on the structure of the microemulsion (clustering).

4.3. Br₂. In the case of Br₂ as the fourth component, it is also possible to use a spectrophotometer as a second detector. The availability of a second detector is quite important here because the volatile nature of Br₂ makes the measurement of its diffusivity more challenging if we use only RID. Molecular bromine can escape from the Teflon tubing, as can be seen from the slope of the time series shown in Figure 4, where the absorbance of bromine was recorded at λ = 400 nm.

Figure 5 shows the Taylor peaks for three different injections into the flowing solution (with excesses of (A) H₂O, (B) AOT, and (C) Br₂). The calculated diffusivities are reported in Table 3, where we see that the main diffusion coefficients for Br₂, D₁₃, is two orders of magnitude larger than that for NaBrO₃ and BF. As expected from its solubility properties, the main diffusion coefficient of bromine is of the same order of magnitude as that of octane (2.63 × 10⁻⁵ cm²/s).

4.4. Cross-Diffusion at Different qa. The matrix D of diffusion coefficients in the water/AOT/ferroin/octane system calculated at three different droplet fractions qa (≈ 0.1, 0.18, and 0.25) and constant ω (≈ 11.84) is reported in Table 5 and Figure 6. The main diffusion coefficients D₁₁ and D₁₂ (the ternary subsystem) as well as D₁₃ are found to decrease at higher values of qa in parallel with the viscosity of the solution. These
of decrease significantly with droplet fraction, whereas the values where the droplets’ hydrodynamic radius \((\ell)\) diminishes when the concentration of droplets is decreased, and, as a result, the molecular volume of the catalyst decreases, and, as a result, the partial

\[D_{ij} = D_0^{ij} + C_i(\partial D_j^*/\partial C_3)\]  

\[D_{ik} = C_j(\partial D_{ij}/\partial C_i)\]  

The reduction in magnitude of the coefficients \(D_{ij}\) and \(D_{ik}\) with increasing \(q_d\) can be explained in part by the smaller effect of [ferroin] on the structure of the nanodroplets at larger \(q_d\) and in part by the smaller interaction between ferroin and AOT as well as between ferroin and water in the droplet clusters.

5. Discussion

The Taylor peaks reported in Figures 1 and 3–5 show that samples containing an excess of injected water or AOT generate curves with similar shapes for all systems analyzed. In contrast, samples containing an excess of one of the BZ reagents give a distinctive profile for each of the four species, NaBrO₃, NaBr, BF, and Br₂. The peaks for NaBrO₃ (Figure 1C) and NaBr resemble the previously obtained peaks for MA and sodium malonate under analogous conditions. The Taylor peaks for BF (Figure 3C) and for ferroin also resemble one another. Generalizing these data, we suggest that the peak shapes and consequently the sign and magnitude of the diffusion coefficients in the four-component system, water/AOT/species/octane, are largely determined by the solubility properties of the BZ species.

For water-soluble species like NaBrO₃, NaBr, MA, and sodium malonate, the species resides primarily in the water cores of the nanodroplets. The diffusion coefficient of the BZ reactant, \(D_{3i}\), is therefore of the same order of magnitude as that of \(H_2O\) \((D_{11})\). The cross-diffusion coefficients \(D_{3i}\) and \(D_{23}\), which account for the coupled flows of the BZ reactant induced, respectively, by water and AOT, are large and positive, whereas the cross-diffusion coefficients, \(D_{31}\) and \(D_{22}\), which account for the flows induced by the BZ reactant in water and AOT, are small.

In the case of BF, as well as ferroin, where most of the species can be found in the surfactant shell of the nanodroplet, the main diffusion coefficient, \(D_{3i}\), is also of the same order of magnitude as \(D_{11}\) (for \(H_2O\)), but the cross-diffusion coefficients show a very different behavior: large and negative \(D_{3i}\) and small and positive \(D_{31}\) and \(D_{32}\).

The oil-soluble Br₂ gives a peak with a positive sharp central maximum and two broad negative tails. As previously noted, the main diffusion coefficient, \(D_{3i}\), for this species, is two orders of magnitude larger than that of bromate and BF. It is also interesting to note that the signs of the (rather small) cross-diffusion coefficients \(D_{31}\) and \(D_{32}\) are opposite, in contrast with the results obtained for the other BZ species. Finally, \(D_{13}\) and \(D_{23}\) were found to be large and negative, as in the case of BF.

We attempt here to provide some insight into the above behavior. A key result is that

\[D_{ii}^{*} = \partial D_j^*/\partial C_i\]  

\[D_{ik} = C_j(\partial D_{ij}/\partial C_i)\]  

\(D_{ij}\) is the solute intradiffusion or self-diffusion coefficient of species \(i\) and \(C_i\) is the concentration of that species. Leaist has discussed the behavior of the three-component (water–AOT–oil) system, in particular, the coefficients \(D_{13}\), \(D_{12}\), \(D_{21}\), and \(D_{22}\). Increasing the concentration of water in the microemulsion at constant [AOT] leads to a larger average droplet size and a lower mobility of the droplets so that the partial derivative term in eq 8 is negative for \(i = 1\). Increasing \(C_2\), that is, [AOT], gives smaller, more mobile droplets and a positive value of \(\partial D_j^*/\partial C_i\). The self-diffusion coefficients, \(D_{ii}^{*}\), are roughly equal to the diffusion coefficient of the drops. This

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<tr>
<th>(j)</th>
<th>(D_{11})</th>
<th>(D_{12})</th>
<th>(D_{13})</th>
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<tr>
<td>1</td>
<td>((6.3 \pm 0.4) \times 10^{-7})</td>
<td>((6.6 \pm 3) \times 10^{-6})</td>
<td>((-1.3 \pm 0.2) \times 10^{-4})</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>((-1 \pm 0.2) \times 10^{-7})</td>
<td>((1.2 \pm 0.2) \times 10^{-6})</td>
<td>((-2.6 \pm 0.09) \times 10^{-6})</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>((0.6 \pm 1.5) \times 10^{-7})</td>
<td>((-9.8 \pm 3) \times 10^{-7})</td>
<td>((1.9 \pm 0.3) \times 10^{-5})</td>
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</table>

findings are in line with previously reported results for the ternary system. The counter-flows of water and AOT induced by ferroin (proportional to coefficients \(D_{13}\) and \(D_{23}\), respectively), decrease significantly with droplet fraction, whereas the values of \(D_{11}\) and \(D_{22}\) remain almost constant.

Using DLS to monitor the changes in the ME structure, we have found, as expected, that the presence of clusters (Figure 2) diminishes when the concentration of droplets is decreased, whereas the droplets’ hydrodynamic radius \((R_h)\) increases slightly. This dependence of \(R_h\) on \(q_d\) can be explained by the fact that the ratio [ferroin]/[droplets] approaches unity as \(q_d\) decreases, and, as a result, the molecular volume of the catalyst contributes significantly to the average size and the shape of
means that \( \partial D_3 \)/\( \partial C_2 \) is positive and \( \partial D_2 \)/\( \partial C_1 \) is negative. Therefore, the signs of \( \partial D_1 \)/\( \partial C_1 \) and eqs 8 and 9 predict that \( D_{11} < D_{22}, D_{12} \) is positive, and \( D_{31} \) is negative, as observed.

For BF and Br₂, the formation of aggregates appears to play a major role in determining the cross-diffusion coefficients. In the case of BF, the tendency to form clusters of droplets noted above implies that increasing [BF] lowers the mobility of the species that travel with the droplets so that \( \partial D_1 \)/\( \partial C_1 \) is negative.

TABLE 5: Diffusion Coefficients, \( D_{ij} \) (in cm²/s), and Sensitivity Coefficients, \( K_i \), for the Water (1)/AOT (2)/Ferroin (3)/Octane System at Several \( \omega_d \) with \( \omega = 11.84 \) and \( T = 23 \) °C

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<thead>
<tr>
<th>( \text{Ferroin} ) (M)</th>
<th>( D_{11} )</th>
<th>( D_{12} )</th>
<th>( D_{13} )</th>
<th>( K_1 ) (V/M)</th>
<th>( K_2 ) (V/M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.57 ( \times 10^{-3} )</td>
<td>(1.2 ( \pm 0.07 )) ( \times 10^{-6} )</td>
<td>(1.7 ( \pm 0.7 )) ( \times 10^{-6} )</td>
<td>(-1.2 ( \pm 0.2 )) ( \times 10^{-4} )</td>
<td>-1.95</td>
<td>48</td>
</tr>
<tr>
<td>1.61 ( \times 10^{-5} )</td>
<td>(5.0 ( \pm 0.3 )) ( \times 10^{-7} )</td>
<td>(5.2 ( \pm 2 )) ( \times 10^{-6} )</td>
<td>(-4.5 ( \pm 0.6 )) ( \times 10^{-5} )</td>
<td>0.18</td>
<td>42.3</td>
</tr>
<tr>
<td>2.58 ( \times 10^{-5} )</td>
<td>(3.0 ( \pm 0.2 )) ( \times 10^{-8} )</td>
<td>(4.5 ( \pm 2 )) ( \times 10^{-6} )</td>
<td>(-4.7 ( \pm 0.7 )) ( \times 10^{-6} )</td>
<td>0.25</td>
<td>46</td>
</tr>
</tbody>
</table>

where \( V_1 \) is the molar volume and \( q_k = V_k C_k \) is the volume fraction of the salt in the aqueous phase. The “excluded volume” hypothesis explains well the positive cross-diffusion coefficient \( D_{32} \). The positive value found for \( D_{32} \), that is, the tendency of AOT molecules to diffuse toward smaller concentrations of water-soluble BZ species, may result from a small decrease in the droplet radius with increasing salt concentration due to the electrical screening effect of the salt on the repulsion between the SO₃⁻ groups of the AOT. This screening can reduce the radius of the droplets, resulting in positive \( \partial D_2 \)/\( \partial C_1 \) and consequently positive \( D_{32} \).

In all of our systems, the coefficients \( D_{31} \) and \( D_{32} \) are comparable to our experimental error, that is, indistinguishable from zero in our experiments. We attribute their small magnitude to the fact that \( C_3 \ll C_1, C_2 \) and the proportionality of \( D_{3j} \) to \( C_j \).

Figure 6. Dependence of the main- and cross-diffusion coefficients for the system water/AOT/ferroin/octane on the droplet fraction \( \omega_d \). \( \omega = 11.84, T = 23 \) °C.
because the partial derivative terms in eq 9 should be comparable to the derivatives with respect to the other species present in the drops.

To evaluate the significance of the cross-diffusion coefficients found in this work for pattern formation in the BZ-AOT system, we also require the cross-diffusion coefficients between species involved in the BZ reaction, that is, cross-diffusion coefficients in five-component systems (AOT microemulsions loaded with two BZ species). We intend to attack this challenging problem in future work, in which the data obtained here for four-component systems will play a vital role.

Acknowledgment. This work was supported in part by the National Science Foundation through grant CHE-0526866. F.R. was supported by a Marie Curie International Outgoing Fellowship within the 7th European Community Framework Programme.

Appendix

We give here the equations used to calculate the quantities $F_{ij}$ from the experimentally measured quantities.

$$F_{11} = \left( D_{22} \sigma_1 \sigma_2 \sigma_3 / K_{FD} + F_{13} F_{31} \right) / F_{33}$$  (A1)

$$F_{12} = (W_2 - K_2 F_{22} - K_3 F_{32}) / K_1$$  (A2)

$$F_{13} = \left( F_{33} K_2 (\sigma_1 + \sigma_2 + \sigma_3 - F_{33}) - K_2 (1/s_1 + 1/s_2) \sigma_1 \sigma_2 \sigma_3 + (K_2 F_{33} - W_3) F_{32} / (K_2 F_{31} - K_4 F_{32}) \right) / K_1$$  (A3)

$$F_{21} = (W_4 - K_4 F_{11} - K_5 F_{51}) / K_2$$  (A4)

$$F_{22} = \sigma_1 + \sigma_2 + \sigma_3 - F_{11} - F_{33}$$  (A5)

$$F_{23} = \left( F_{33} K_4 (\sigma_1 + \sigma_2 + \sigma_3 - F_{33}) - K_4 (1/s_1 + 1/s_2) \sigma_1 \sigma_2 \sigma_3 + (K_4 F_{33} - W_3) F_{32} / (K_4 F_{31} - K_2 F_{32}) \right) / K_2$$  (A6)

$$F_{31} = (K_{FD} W_1 F_{33} + K_2 D_{21} \sigma_1 \sigma_2 \sigma_3 - K_2 D_{23} \sigma_1 \sigma_2 \sigma_3) / (K_{FD} W_3)$$  (A7)

$$F_{32} = (K_{FD} W_2 F_{33} + K_4 D_{12} \sigma_1 \sigma_2 \sigma_3 - K_4 D_{13} \sigma_1 \sigma_2 \sigma_3) / (K_{FD} W_3)$$  (A8)

$$F_{33} = \sigma_1 \sigma_2 \sigma_3 / s_1 s_2$$  (A9)

where $s_1$ and $s_2$ are the dispersion of the Gaussian functions for the three-component system, $W_i = i_0 \times (\sum_{j=1}^{3} \sigma_j P_{j,\text{exp}} \times \beta \varepsilon_{\text{FD}}$ and $K_{FD} = R_0^2 n_0^2 / 48$.

References and Notes


(9) Horváth, J.; Szalai, I.; De Kepper, P. Science 2009, 324, 772–775.


