

LETTERS

Stochastic Treatment of Dye Transfer between Droplets Dispersed in Water

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A theory of dye transfer dynamics between droplets in emulsion, based on the stochastic model of solubilization is presented. The model is applied to interpret recent experimental results on transfer of coumarin 540 dye molecules dissolved in nanodroplets after mixing equal volumes of dye-labeled and dye-free *n*-decane emulsion in water.

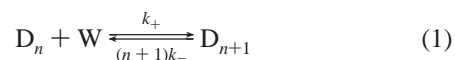
Recently, Sakai et al.¹ have studied the exchange kinetics of coumarin 540 (C540) solubilized in nanodroplets of *n*-decane emulsion in water by using a single-particle detection technique based on confocal fluorescence microscopy. In their experiments equal volumes of emulsion A containing C540-labeled droplets and emulsion B containing dye-free droplets were mixed, and the time evolution of fluorescence intensity emitted from C540 molecules was observed after the mixing. Emulsions A and B contained the same concentration of *n*-decane droplets having the same average diameter. They observed the fluorescence of C540 molecules in each single droplet passing through the focal volume of the laser beam as a spike-like signal (bunching signal) with height proportional to the number of dye molecules. The average number of C540 molecules per droplet at a given time *t* after mixing of emulsion A with emulsion B was obtained as the average height of the fluorescence bunching signals registered over the one-second intervals around the time *t*. This number was decreasing rapidly with the time elapsed after mixing of the two emulsions, which indicated that C540 molecules dissolved in droplets originating from emulsion A were transferred to dye-free droplets originating from emulsion B.

As a mechanism of the dye transfer between droplets these authors assumed the migration of C540 molecules via the aqueous phase, i.e., an exit or permeation of dye molecules from

a droplet into water, then diffusion in water, and re-entry into another (or the same) droplet. As it is known from studies on probe molecule transport in micelle solutions, this process is governed by the first-order rate constant for exit^{2,3} and is important when the solubility of a solute in water is sufficiently high. The second possible mechanism of exchange is a dye hopping from one micelle to another during the droplet collision. Sakai et al. concluded, however, from their analysis of experimental data that this mechanism is not important in their system. This mechanism^{4–11} can occur in nonionic surfactant micelles and becomes important at high micelle concentrations and at elevated temperatures. In the case of micelles theoretical models have been developed for different migration mechanisms.^{12–18}

We employ the stochastic methods used in the theory of micellar solutions to develop the model of dye transfer between droplets via the aqueous phase and we apply it to analyze the results of ref 1. As can be shown afterward, our model leads to quite different estimation of the dye transfer rate from that of Sakai and co-workers.

We describe the transfer dynamics as



where D_n is the droplet with *n* dye molecules, *W* stands for the dye molecule in the aqueous phase, and k_+ is the rate constant

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for entry of a dye molecule into a droplet. The rate constant for exit of a dye from a given droplet is proportional to the number of dye molecules in the droplet. If the droplet contains only one dye molecule, then k_- is the rate constant for exit of this molecule to the aqueous phase, but if the droplet has $(n + 1)$ dye molecules, the rate constant for exit of any one of them is equal to $(n + 1)k_-$.

In accordance with the experimental conditions the dye is initially present only in emulsion A, and its equilibrium distribution among droplets is Poissonian²

$$P_n(\bar{n}_0) = \bar{n}_0^n \exp(-\bar{n}_0)/n! \quad (2)$$

The average number of dye molecules per droplet in emulsion A is given by

$$\bar{n}_0 = k_+[W]/k_- \quad (3)$$

where $[W]$ is the concentration of dye molecules in the aqueous phase.

Immediately after mixing equal volumes of emulsion A and dye-free emulsion B, the concentrations of droplets containing n solutes, denoted as $[D_n](t)$, decrease initially to a half (for $n \neq 0$) and ultimately reach the equilibrium values $[D_n](\infty)$. The total concentration of droplets in the mixture $[D]$ remains constant and equal to the initial concentration of droplets in emulsion A. The concentration of dye molecules in water reduces to $[W]/2$ after the mixing and remains constant during the equilibration process. The last point results from the fact that, after the mixing, the total entry rate v_+ of dye molecules into the droplets is equal to the total exit rate v_- of those from the droplets to the aqueous phase. Indeed, we have $v_+ = k_+(1/2)[W][D]$ and $v_- = \sum_{n=1}^{\infty} nk_-(1/2)[D_n](0) = (1/2)k_- \bar{n}_0[D] = (1/2)k_+[W][D]$.

It is convenient to use in the following equations the time dependent normalized dye occupancy distribution $Q_n(t)$ given by

$$Q_n(t) = [D_n](t)/[D] \quad (4)$$

instead of $[D_n](t)$. Hence eq 1 corresponds to a set of linear kinetic equations for the distribution $Q_n(t)$

$$\begin{aligned} \frac{d}{dt}Q_0(t) &= -\frac{1}{2}k_+[W]Q_0(t) + k_-Q_1(t) \\ \frac{d}{dt}Q_n(t) &= \frac{1}{2}k_+[W]Q_{n-1}(t) - \left(\frac{1}{2}k_+[W] + nk_-\right)Q_n(t) + \\ &\quad (n+1)k_-Q_{n+1}(t) \quad n \geq 1 \end{aligned} \quad (5)$$

By means of generating function $F(s,t)$ defined by

$$F(s,t) = \sum_{n=0}^{\infty} s^n Q_n(t) \quad (6)$$

eqs 5 can be transformed into a partial differential equation of the form

$$\frac{\partial}{\partial t}F(s,t) = k_-(1-s)\frac{\partial}{\partial s}F + \frac{1}{2}k_+[W](s-1)F \quad (7)$$

From the initial condition for the dye distribution

$$\begin{aligned} Q_0(0) &= \frac{1}{2}\{P_0(\bar{n}_0) + 1\} \\ Q_n(0) &= \frac{1}{2}P_n(\bar{n}_0) \quad n \geq 1 \end{aligned} \quad (8)$$

we can obtain the initial condition on the generating function

$$F(s,0) = \frac{1}{2}\{\exp[k_+[W](s-1)/k_-] + 1\} \quad (9)$$

The solution of eq 7, given the initial condition of eq 9, has the form

$$\begin{aligned} F(s,t) &= \frac{1}{2} \left\{ \exp \left[\frac{k_+[W]}{2k_-} (s-1)(1 + e^{-k_-t}) \right] + \right. \\ &\quad \left. \exp \left[\frac{k_+[W]}{2k_-} (s-1)(1 - e^{-k_-t}) \right] \right\} \end{aligned} \quad (10)$$

The distribution $Q_n(t)$ is obtained from

$$Q_n(t) = \frac{1}{n!} \left[\frac{\partial^n}{\partial s^n} F(s,t) \right]_{s=0} \quad (11)$$

and can be written as

$$Q_n(t) = \frac{1}{2} [P_n(\bar{n}_A) + P_n(\bar{n}_B)] \quad (12)$$

where \bar{n}_A and \bar{n}_B are given by

$$\bar{n}_A(t) = \frac{1}{2}\bar{n}_0[1 + \exp(-k_-t)] \quad (13)$$

$$\bar{n}_B(t) = \frac{1}{2}\bar{n}_0[1 - \exp(-k_-t)] \quad (14)$$

The first term on the right-hand side of eq 12 originates from dye-labeled emulsion A with $\bar{n}_A(0) = \bar{n}_0$, whereas the second term originates from the dye-free emulsion B with $\bar{n}_B(0) = 0$. Both \bar{n}_A and \bar{n}_B tend to $(1/2)\bar{n}_0$ as $t \rightarrow \infty$. This is clearly shown in Figure 1 where the distribution (12) is plotted for several values of the normalized time k_-t , starting from $k_-t = 0$, up to $k_-t = 3$ after the mixing. In the calculation we assumed $\bar{n}_0 = 80$, which corresponds to experimental value of ref 1 for the average number of detectable dye molecules per droplet in the dye-labeled emulsion A. The curves for smaller values of k_-t have two distinct maxima: the first one describes the dye occupancy distribution originating from emulsion B, whereas the second one is related to emulsion A. At the instant of mixing the function $Q_n(0)$ is composed of the delta function at $n \equiv \bar{n}_B = 0$ and a Poisson distribution with average at $n \equiv \bar{n}_A = 80$. It is interesting to note that even for relatively short times, e.g., $k_-t = 0.3$, the droplets originating from emulsion B contain on the average as many as 10 dye molecules. The equilibration, however, takes a considerable time. Although $Q_n(t)$ shows only one maximum at $k_-t = 2$, the average dye occupancy in the droplets of emulsion A and B remains still different, $\bar{n}_A = 45$ and $\bar{n}_B = 35$.

When calculating the average number of dye molecules in droplets, we should define the ensemble of droplets over which

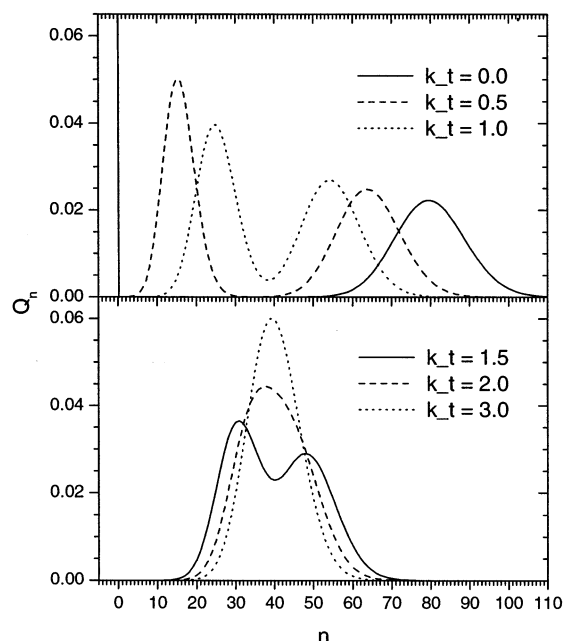


Figure 1. Distribution of dye molecules among droplets calculated from eq 12 for various values of normalized time k_-t .

the average is taken. If we include all droplets in the ensemble then the average $\bar{n}^{(0)}(t)$ is expressed as

$$\bar{n}^{(0)}(t) = \sum_{n=0}^{\infty} n Q_n(t) / \sum_{n=0}^{\infty} Q_n(t) \equiv \frac{1}{2} n_0 \quad (15)$$

and its value does not change during the whole equilibration process. This average is not relevant to the experiment of Sakai et al. because the dye-free droplets are not detected in their experiment at all. The most obvious choice is to exclude the empty droplets from the ensemble. If we assume that a droplet with at least one dye molecule can be detected as a bunching signal in their experiment, the average number of dye molecules calculated from bunching signals is given by

$$\bar{n}^{(1)}(t) = \sum_{n=1}^{\infty} n Q_n(t) / \sum_{n=1}^{\infty} Q_n(t) \quad (16)$$

which leads to a simple formula

$$\bar{n}^{(1)}(t) = \frac{\bar{n}_0}{2 - \exp[-\bar{n}_A(t)] - \exp[-\bar{n}_B(t)]} \quad (17)$$

More generally, if a droplet that contains at least m dye molecules can be detected as a bunching signal, the average number of dye molecules calculated from bunching signals is given by

$$\bar{n}^{(m)}(t) = \sum_{n=m}^{\infty} n Q_n(t) / \sum_{n=m}^{\infty} Q_n(t) \quad (18)$$

The time evolution of $\bar{n}^{(m)}(t)$ obtained from eq 18 for several values of m is presented in Figure 2. As can be expected, the larger m the longer it takes to reach the asymptotic value after mixing the dye-labeled with the dye-free emulsions. In the case when m is close to or larger than $(1/2)\bar{n}_0$ (i.e., 40 in the present calculation), the asymptotic value of $\bar{n}^{(m)}(t)$ is much higher than $(1/2)\bar{n}_0$.

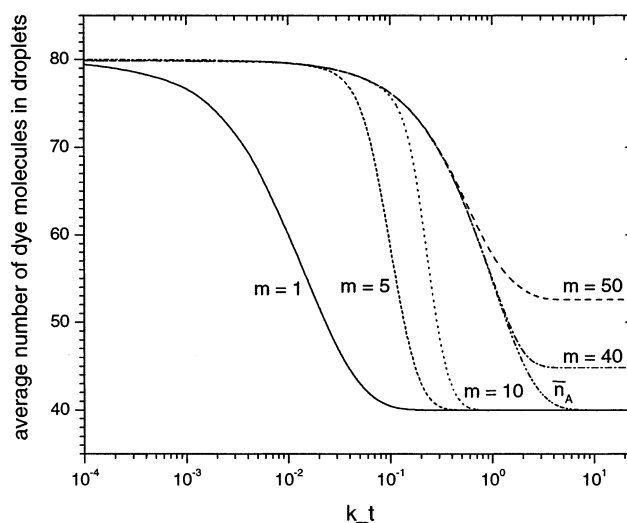


Figure 2. Average number of dye molecules in detectable droplets as a function of k_-t calculated according to the restriction that only droplets containing at least m dye molecules are detected. The average of dye molecules in a droplet originating from emulsion A is also included for comparison.

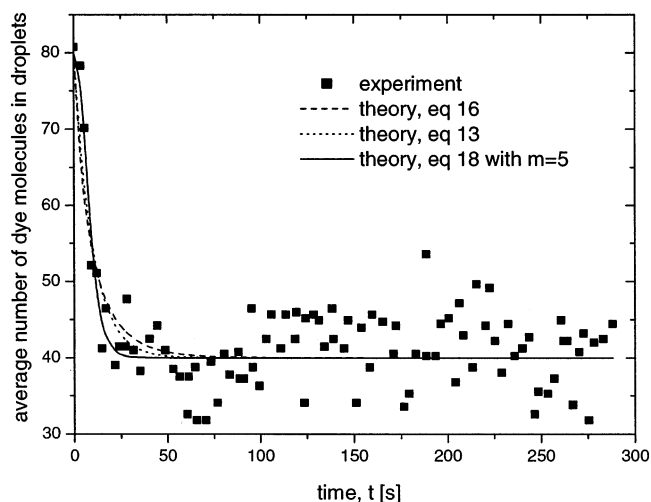


Figure 3. Average number of dye molecules per droplet as a function of time elapsed after the mixing of equal volumes of emulsions A and B. The experimental results of ref 1 (black squares) are fitted by eq 16 (dashed line), by eq 18 with $m = 5$ (full line), and by eq 13 (dotted line). The fitting parameter is the rate constant k_- .

In Figure 3 we fit $\bar{n}^{(1)}(t)$ given by eq 17 to the experimental data of ref 1 for the time evolution of the average number of C540 molecules in a droplet after mixing equal volumes of the dye-labeled and the dye-free *n*-decane emulsion in water and obtained $1.726 \times 10^{-3} \text{ s}^{-1}$ as the value of the rate constant k_- . Because of the noise level it may not be possible to detect droplets containing only a single dye molecule. If we assume that droplets containing less than 5 dye molecules cannot be detected and use eq 18 with $m = 5$ to fit experimental data, we obtain $k_- = 1.215 \times 10^{-2} \text{ s}^{-1}$. The rate constant k_- corresponds to the parameter α introduced in ref 1. Sakai et al. assumed that in the initial step of the relaxation of the average number calculated from the bunching signals, the droplets originating from emulsion B give practically no contribution and considered that it is approximated by the average number of dye molecules in a droplet originating only from dye-labeled emulsion A. The latter is given by eq 13 of the present paper and included in Figure 2 for comparison.

There are, however, three problems in the approach proposed by Sakai et al.:

1. As it was mentioned before, if a droplet contains no dye molecule, it cannot be detected as a bunching signal. Therefore the fraction of droplets, which contain no dye molecule, has to be excluded in the calculation of the average of dye molecules in a droplet. However, this has not been done in their treatment.

2. Although it takes a long time to reach the equilibrium distribution after the mixing of dye-labeled emulsion A and dye-free emulsion B, it is rather fast for a few dye molecules to migrate from one droplet to another. Therefore, if a droplet that contains dye molecules, e.g., not less than 5 can be detected as a bunching signal, it is not correct to neglect the contribution of droplets originating from emulsion B in calculation of the average of the dye molecules per droplet.

3. When they calculate the average number of dye molecules in a droplet originating from emulsion A, they made some mistake.¹⁹ The correct equation is given by our eq 13. If one fits eq 13 to the relaxation curve of the averaged number of dye molecules per droplet calculated from bunching signals, one gets $k_- = 0.1035 \text{ s}^{-1}$. However, because there are two defects described above in using eq 13 to analyze experimental data, this value has no significance. If the detection limit m happens to be close to $(1/2)n_0$, eq 13 may approximate the correct relaxation curve of the average number rather well at short times, as shown in Figure 2. Only in this case, the analysis of experimental data on the basis of eq 13 may give a correct value for the rate constant.

It is important to construct the histograms of the distribution of heights of bunching signals at different times and compare them with the distributions Q_n of dye molecules among droplets shown in Figure 1. If droplets that contain at least m molecules can be detected as bunching signals, the occupancy distribution of dye molecules in a droplet calculated from bunching signals is predicted to be truncated at $n = m$ and has no population in the region for $n < m$. In this way it would be possible to determine the detection limit m experimentally.

If the transfer of dye molecules between droplets occurs during droplet collisions, the distribution of dye molecules among droplets after the mixing of emulsions A and B is still given by eq 12 with k_- replaced by $k[D]$, where $[D]$ is the total concentration of droplets. Therefore, in this case the relaxation of the average number of dye molecules per droplet calculated from bunching signals should depend on the total concentration of droplets.

References and Notes

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- (19) In eq 7 of ref 1 it was not taken into account that in emulsion A dye molecules are present not only in droplets but also in the aqueous phase.