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DIFFUSING-PARTICLE TRAPPING KINETICS FOR A ONE-DIMENSIONAL SOLUTION

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Solvent components that prevent reagent diffusion lead to a proportion of particles that do not react, which affects the decay in the reagent concentrations. The A + B → B reaction occurring in a one-dimensional system may be accelerated or retarded in accordance with the solvent concentration. Experiments are indicated in which it is predicted that one can observe effects from fluctuations in the concentrations of the B particles and solvent components.

Reagent concentration fluctuations affect bimolecular-reaction kinetics at large times [1–7]. These fluctuation effects are particularly prominent in one-dimensional A + B → B reactions (which involve mobile particles A diffusing between immobile B trapping centers), where there are substantial deviations in the A concentration as a function of time $c_A(t)$ from the predictions made without allowance for the fluctuations, i.e., in the average-field approximation. In [1], a solution was obtained for particle random walks along a chain having randomly distributed traps, and the concentration law for large times was found as $c_A(t) \sim \exp[-\mathrm{const}(c^2 t)^{1/3}]$ ($c^2 t \gg 1$, with c the trap concentration), whereas the average-field approximation gives $c_A(t) \sim \exp(-\mathrm{const}\, c t^{\nu})$, where ν is 1/2 or 1 in accordance with the assumptions made. More detailed research on bimolecular-reaction kinetics in one dimension has shown that fluctuation effects are dependent on the relation between the particle migration and absorption rates [8]. For slow reactions (low absorption rates), there is an intermediate asymptote $c_A(t) \sim \exp[-\mathrm{const}(c t)^{1/2}]$* in the time dependence, which describes the concentration in the accessible range, while $\exp[-(c^2 t)^{1/3}]$ applies when the concentrations are too low to be measured. In [9, 10], one-dimensional A + B → B reactions were considered without using the constraint that the concentrations are small applied in [1, 8].

These kinetic features apply to binary randomly disordered chains consisting for example of nodes type A_1 (free from traps) and type A_2 (containing B traps), whose mutual disposition is random. It is assumed that the motion of the A particles before trapping is by random jumps between the A_1 nodes. Here we examine the reaction kinetics on the basis of a finite lifetime for the A particles in a three-component chain, which contains not only the above two components but also inert nodes A_3, which act as the solvent.

Averaging Formula. We consider a chain consisting of N nodes, with N_1, N_2, and N_3 of types A_1, A_2, and A_3 correspondingly, while the mutual disposition is random, so the probability of observing a node of $A_{1(2,3)}$ type at any point in the chain is $c_{1(2,3)} = N_{1(2,3)}/N$, $c_1 + c_2 + c_3 = 1$. The A_1 and A_3 nodes constitute traps and barriers for the particles migrating

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*The agreement between the relationship obtained in [8] and one of the average-field predictions is purely accidental. The dependence on the trap concentration is qualitatively different, as is the characteristic time scale [8].

via the A_1 nodes, and they divide the chain into clusters: segments composed of A_1 nodes with various boundaries $A_3A_1...A_1A_3 - b$, $A_2A_1...A_1A_2 - c$, $A_{2(3)}A_1...A_1A_{3(2)} - 0$, with the clusters belonging to the chain ends of the form $A_1...A_1A_{2(3)} - 0(b)$ and $A_{2(3)}A_1...A_1 - 0(b)$. The b, c, and o indicate the cluster types; the number of A_1 nodes in a cluster is called the length. A particle moves by random jumps between adjacent A_1 nodes with a speed w, the motion being independent in the various clusters. It is also assumed that the particles do not interact (low concentration). Particles are lost from the chain because of their finite inherent life-times βA^{-1} and due to trapping at a rate w', which occurs when a particle is at a node adjacent to a trap. It is assumed that the traps cannot be saturated and that the particles have finite lifetimes β_B^{-1} there. The reflection from the barriers is characterized by the same rate as for motion over the A_1 nodes. Then the kinetic scheme for transport in a typical cluster is
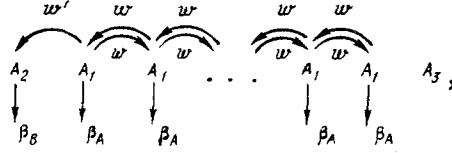
and one determines $c_A(t)$ by deriving the survival probability $\rho_n^{b(c,o)}(t)$ up to time t in these types of cluster for any length n and then averaging over all $n \in [1, N_1]$. In [11], we we considered such reduction of configuration averaging to averaging over cluster lengths for two-component systems. In [12], there is an extension to multicomponent systems.

We use these results to represent the total number of clusters (including ones at the chain ends) of types b, c, and o having length n realized in all nonequivalent configurations such as $A_1A_3A_2A_2...A_1A_2$, as

$$P^j(n) = \frac{N_1N!}{N_1!N_2!N_3!} P(n) \begin{cases} c_3(c_3 + N^{-1})/(c_2 + c_3), & j = b, & \text{(1a)} \\ c_2(c_2 - N^{-1})/(c_2 + c_3), & j = c, & \text{(1b)} \\ 2c_2(c_3 + N^{-1})/(c_2 + c_3), & j = o, & \text{(1c)} \end{cases}$$

where

$$P(n) = (N_2 + N_3)(N_1 - 1)!(N - n - 1)!/(N - 1)!(N_1 - n)! \tag{2}$$

denotes the probability that a randomly selected cluster from a set containing a three-component chain in all nonequivalent configurations has length n (no matter what the type or position in the chain).

The mean survival probability here in this randomly disordered chain is evidently equal to the ratio of the sum of the contributions from the cluster values $\rho_n^{b(c,o)}(t)$ in all $N!/N_1!N_2!N_3!$ nonequivalent configurations to the total number:

$$c_A(t) = (c_2 + c_3)^{-1} \sum_{n=1}^{N_1} P(n) [c_3(c_3 + N^{-1})\rho_n^b(t) + \tag{3}$$
$$c_2(c_2 - N^{-1})\rho_n^c(t) + 2c_2(c_3 + N^{-1})\rho_n^o(t)].$$

In (3) we have used the uniformity of the initial distribution over the A_1 nodes, which per node is taken as N_1^{-1}, so $c_A(0) = 1$. With $c_3 = 0$, (3) coincides with the expression for the averaged survival probability in a chain having randomly distributed traps [11]. This averaging formula is exact for a three-component randomly disordered chain having any length N. In what follows, we consider only an infinite chain, for which with $N \to \infty$ and $c_{2(3)} = \text{const}$ we have from (3) that

$$c_A(t) = \sum_{n=1}^{\infty} (1 - c_2 - c_3)^{n-1} [c_3^2\rho_n^b(t) + c_2^2\rho_n^c(t) + 2c_2c_3\rho_n^o(t)]. \tag{4}$$

RESULTS AND DISCUSSION

To calculate $c_A(t)$, we use a survival probability expression for type b clusters $\rho_n^b(t) = n \exp(-\beta_A t)$, while the expression for $\rho_n^{c(o)}(t)$ at large times (see below) has been obtained in [8]:

$$\rho_n^{c(o)}(t) = A_n^{c(o)} \exp [- (K_n^{c(o)} + \beta_A)t], \tag{5}$$

$$K_n^c = \frac{5}{n} \frac{n + 3\omega^{-1}}{n^2 + 5\omega^{-1}(n + 3\omega^{-1/2})} , \quad A_n^c = K_n^c n^2 (n + 3\omega^{-1})/6, \tag{6}$$

$$K_n^o = \frac{5}{n} \frac{2n + 3\omega^{-1}}{8n^2 + 5\omega^{-1}(4n + 3\omega^{-1})} , \quad A_n^0 = K_n^0 n^2 (2n + 3\omega^{-1})/3, \tag{7}$$

where $\omega = w'/2w$. The time in (5) and everywhere subsequently is expressed in $(2w)^{-1}$ units, while the rates $\beta_{A(B)}$ are in $2w$ units (without symbol change).

The zeroth and first moments of the survival probability derived from (5) coincide with the exact ones. In [10], it has been shown to be justified to use (5)-(7) for $c_A(t)$ and that the results are almost indistinguishable from the exact ones for times such that $c_A(t) < 0.5 \, c_A(0)$.

We substitute (5)-(7) into (4) to get

$$c_A(t) = \frac{\exp(-\beta_A t)}{\ln^2(1 - c_2 - c_3)} \left\{ c_3^2 \frac{\ln^2(1 - c_2 - c_3)}{(c_2 + c_3)^2} + \right.$$
$$\left. \int_0^\infty dx \, [c_2^2 A^c(x) \exp(-K^c(x, t)) + 2c_2 c_3 A^0(x) \exp(-K^0(x, t))] \right\}, \tag{8}$$

where

$$A^c(x) = 5x(x + 3\alpha)^2/6(x^2 + 5\alpha x + 15\alpha^2/2),$$

$$K^c(x, t) = \frac{5t \ln^2(1 - c_2 - c_3)}{x} \frac{x + 3\alpha}{x^2 + 5\alpha x + 15\alpha^2/2}$$

$$A^o(x) = 5x(2x + 3\alpha)^2/3(8x^2 + 20\alpha x + 15\alpha^2),$$

$$K^o(x, t) = \frac{5t \ln^2(1 - c_2 - c_3)}{x} \frac{2x + 3\alpha}{8x^2 + 20\alpha x + 15\alpha^2} ,$$

while the parameter α in $A^{c(o)}(x)$ and $K^{c(o)}(x, t)$ is $\ln(1 - c_2 - c_3)/\omega$.

In contrast to (4), one can use (8) only in a restricted fashion because of the error due to replacing the sum by an integral, which is dependent on c_2, c_3, and t [10]. For c_2, $c_3 \ll 1$, one is justified in passing from (4) to (8) if

$$\int_0^\infty A^{c(0)}(x) \exp[-K^{c(0)}(x, t)] dx < 0,3.$$

Integration in (8) gives

$$c_A(t) = \frac{\exp(-\beta_A t)}{\ln^2(1 - c_2 - c_3)} \left[c_3^2 \frac{\ln^2(1 - c_2 - c_3)}{(c_2 + c_3)^2} + c_2^2 L_1(t) + 2c_2 c_3 L_2(t) \right], \tag{9}$$

where

$$L_1(t) = \begin{cases} \frac{5}{3} \left(\frac{\pi \tau_1}{6} \right)^{1/2} \left[1 + \frac{17}{18} \tau_1^{-1/3} + \frac{205}{248} \tau_1^{-2/3} \right] \times & \text{(10a)} \\ \exp\left(-\frac{3}{2} \tau_1^{1/3} \right), \quad \tau_1 > 1, \ \alpha \ll 1, \\ 2\tau_2 K_2(2\tau_2^{1/2}), \quad 1 < \tau_2 \ll \alpha^2, \ \alpha \gg 1; & \text{(10b)} \end{cases}$$

$$\tau_1 = 10t \ln^2(1 - c_2 - c_3), \quad \tau_2 = -2\ln(1 - c_2 - c_3)\omega t,$$

and $K_2(z)$ is a modified Bessel function. For $\tau_2 \gg \alpha^2$, the (10b) intermediate asymptote becomes (10a) [8]. $L_1(t)$ describes the concentration decrease in a chain containing traps but no barriers [8, 10], while $L_2(t)$ differs from $L_1(t)$ in that t is replaced by $t/4$ in (10a) and t by $t/2$ in (10b).

We see from (9) that the untrapped proportion is $c_3^2/(c_2 + c_3)^2$, so even a small concentration of barrier molecules can lead to marked redistribution between the trapped and untrapped proportions during the lifetime. For example, typical values for the square of the diffusion displacement for triplet excitons are $l_D^2 = 1/2 \beta_A^{-1} = 10^{10}-10^{11}$ [13], and in a molecular chain having a trap concentration of 10^{-4}, triplet exciton phosphorescence is almost suppressed, the quantum yield η_A being $(2l_D^2 c^2)^{-1}$ [8]. If the traps are accompanied by the same defect-barrier concentration, then η_A 1/4, i.e., the estimates of the quantum yield from (4) with $c_2 = 10^{-4}$ and $c_3 = 0$ and 10^{-4} differ by a factor 50-500. It has been found that inherent phosphorescence for quasi-one-dimensional molecular crystals is greatly affected by minor components acting as barriers [14, 15].

The barriers alter the concentration time dependence as well as resulting in a certain proportion of A particles avoiding trapping. The final stage may be retarded or accelerated in accordance with the value of c_3. For example, for c_2, $c_3 \ll 1$ in $A + B \rightarrow B$ in an inert solvent, the reagent concentrations fall more slowly if $c_3 < c_2$, but more rapidly if $c_3 > c_2$ (by comparison with $c_3 = 0$). In fact, the defect barriers hinder motion to the traps, and contributions to the averaged survival probability come essentially only from clusters in which there is a trap at the boundary, and in which on average the particle lifetime for fast reactions is four times that in a cluster containing two traps at the boundary, or by a factor two for slow reactions. This retardation factor competes with the reduction in mean cluster length as c_3 increases, which accelerates the reaction, and thus governs the resultant effect. The retardation (acceleration) in the $c_A(t)$ decline is more pronounced for fast reactions ($\alpha \ll 1$) than for slow ones.

The phosphorescence intensity has been measured as a function of time in doped quasi-one-dimensional crystals with δ-pulse excitation (A triplet excitons, radiative free-exciton decay time β_A^{-1}, lifetime for a trapped exciton β_B^{-1}), which enables one to check the theoretical predictions on trapping in a one-dimensional solution. We first consider a crystal containing one defect type, namely traps, and consider only fast reactions. Trap-density fluctuations influence the kinetics, particularly via the characteristic $c_A(t) \sim L_1(t)$ dependence, and can be observed if $\tau_1 > 1$, $\tau_1 \gg (\beta_A t)^3$), which define the upper and lower bounds to the time interval in which $c_A(t) \sim L_1(t)$. The exciton phosphorescence will decay on that law, and the interval is quite large ($t \gg 1$) if $c_2 l_D \gg 1$. However, the latter inequality is the condition for heavy exciton phosphorescence quenching by the traps, and when it is obeyed, $\eta_A \approx 0$, so there is only very restricted scope for observing it. The quantum yield from the traps η_B is here close to one, so the intensity $\Phi_B(t) = \beta_B c_B(t)$ may be the only quantity accessible to measurement. In [9], there was a discussion of a random walk over traps in discrete time, where it was concluded that the features in $c_A(t)$ due to trap density fluctuations occur for $c_A(t)$ less than 0.15 (this applies only for $c_2 \ll 1$ [10]) and can be observed. We consider that the $L_1(t)$ dependence and an appreciable difference between $c_A(t)$ and zero are necessary but not sufficient conditions for fluctuation effects to make themselves felt.

The mean trap population $c_B(t)$ is

$$dc_B/dt = -(\beta_A c_A + \beta_B c_B + dc_A/dt),$$ (11)

the solution being

$$c_B(t) = \exp(-\beta_B t)\left[1 - c_A(t)\exp(\beta_B t) - (\beta_A - \beta_B)\int_0^t c_A(\tau)\exp(\beta_B \tau)\,d\tau\right].$$ (12)

For simplicity, we put $\beta_A = \beta_B$ in (12), the more so because this condition corresponds for example to a quasi-one-dimensional crystal of 1,2,4,5-tetrachlorobenzene, where β_A and β_B are similar [13]. At low trap concentrations, the effects from density fluctuations on the trapping kinetics are the most pronounced [8, 10], and then (9) and (12) give

$$c_B(t) = \exp(-\beta_B t)[1 - L_1(t)]_{c_s=0}.$$ (13)

Then the theoretical relationships $c_A(t) \sim \exp(-3\tau_1^{1/3}/2)$ for fast reactions and $c_A(t) \sim \exp(-2\tau_2^{1/2})$ for slow ones may make themselves felt in the positions and shapes of the trap emission intensity peaks. This still applies for unequal radiative decay rates for free and trapped excitons, apart from the case of large β_B, where the maximum in $\Phi_B(t)$ occurs in the initial stage of the $A + B \rightarrow B$ reaction, which is not described by $L_1(t)$.

It is evident that (11) retains its form when we incorporate the effects from barriers on exciton trapping, so defect density fluctuations (for traps and barriers) produce effects qualitatively the same as before, but the form of $\Phi_B(t)$ will now be dependent on c_3. This quantity can be varied [13], and thus one can improve considerably the reliability in fitting the observed and theoretical curves, and also obtain more reliable parameters from comparing theory with experiment. The barrier concentrations should satisfy $c_3 \lesssim c_2$ in order that the proportion of excitons avoiding capture should be comparatively low.

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