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ORIGINAL CONTRIBUTION

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Control of reactions between surfactant reagents in miniemulsions. Surface nanoreactors

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Abstract Emulsions may be used to speed up reactions of surface-active reagents. In this paper, a theoretical analysis of a simple catalytic reaction (**A** + **B** → **P** + **B**) is performed, where the substrate **A** in the presence of the catalyst **B** in an emulsion is converted into the product **P**, and both the substrate **A** and the catalyst **B** are surfactants. It was shown that, because molecules **A** and **B** are concentrated in surface layers of the emulsion, these layers act as nanoreactors ensuring a significant acceleration of the catalytic reaction within a certain range of emulsion droplet sizes. The reaction rate depends significantly on the emulsion droplet's size and there exists an optimal droplet size at which the reaction acceleration is maximal. If the product of the reaction is not surface-active, the reaction rate can remain practically unchanged up to virtually complete substrate conversion. Besides, it was shown that the Michaelis–Menten-type dependence of the reaction rate on the substrate concentration (i.e., the increase in the rate with subsequent saturation) can be observed in the system under consideration.

Keywords Nanoreactors · Surfactant reagent · Emulsions

Introduction

The control of the rate of chemical reactions is of significant fundamental interest. One of the possible ways of speeding up a simple binary reaction is to assemble the reagents in a part of a system, the reactor, or in a set of microreactors distributed uniformly in the whole volume of the system. To concentrate reagents in limited volume, different heterogeneous systems can be used [1], such as polymer gels having catalytic sites attached to gel chains [2], structured polymer gels [3], dendrimers [4], micellar solutions, and dilute emulsions [1, 5–11].

The speeding up of the reactions rate in micellar solutions can reach 100 of times [1, 5–7]. This acceleration is caused by the concentration of reagents within micelles and depends on the volume fraction occupied by the micelles in the solutions [5–7].

The micellar solutions are effective in the case when reagents have high affinity to the non-polar interior of micelles. In case of surface-active reagents, they would be concentrated at the interface rather than in bulk volumes. Therefore, the possible way to speed up chemical reactions between such compounds is to use emulsions as the reaction media. The basic theory describing this effect is developed in the present paper.

It is worthwhile to mention that the processes when the compounds involved have high surface activities play a significant role in many biological systems also. A good illustration for this statement is given by the recent work [12], which considered DNA renaturation at the water–phenol interface. It was experimentally proved (see [12] and references herein) that complimentary single-stranded DNA chains are very intensively adsorbed at the surfaces of phenol droplets immersed in water, and therefore a rapid reassociation reaction between them takes place mainly at the water–phenol interface. Due to the concentration of single-stranded DNA in the interface layers, the rate of the reaction is many times higher than it would be in homogeneous water solution. Interestingly in this case, the ‘‘reagents’’ (single-stranded DNA chains) have high surface activity, while the ‘‘product’’ of their reaction (double-stranded DNA) is not surface active and tends to go to the bulk of the water phase.

Generally speaking, we have recently shown that not only base pairs of nucleic acids but almost all hydrophilic monomer units—both of synthetic and biological molecules—demonstrate some properties of surface-active molecules [13]. This happens because they normally contain hydrophobic groups, in addition to hydrophilic ones, therefore they are not ‘‘hydrophilic in all respects‘‘. As a result, such monomer units, being immersed into the mixture of water and organic solvent (e.g., emulsion), are preferentially absorbed at the interfaces (the corresponding partition coefficients between water, organic solvent and their interface were measured in Ref. [13]).

In Refs. [14 and 15], we proposed a new amphiphilic side-chain model of polymer chain in which the dualistic character of hydrophilic monomer unit is explicitly incorporated by representing each monomer units as ‘‘dumbbell’’ consisting of hydrophobic (**H**) and hydrophilic (**P**) parts linked by rigid bonds of a fixed length. We have found that for side-chain model of polymer chain, a variety of novel structures are possible in a poor solvent depending on the interaction between hydrophobic (**H**) and hydrophilic (**P**) sites. In particular, thermodynamically stable anisometric structures have been observed including disk-like, stretched necklace-like conformations, sausage-like objects, and cylindrical-shaped conformations. All these microstructures are formed due to the surface activity of ‘‘dumbbell’’ amphiphilic monomer units.

One can expect that this fact—amphiphilic structure of monomeric units—can influence other properties of polymer systems, in particular, the kinetic of chemical reactions in such systems. It is known that the interface layers often provide certain features that are favorable for chemical reactions [9–11, 16]. A binary reaction rate constant can be higher at the droplet surfaces than in the outer solution or inside the droplets [9]. Moreover, some reactions take place only at the surface and are impossible in the bulk phase [10, 11, 16].

However, in the present paper, our target is to describe a somewhat different effect. We will show that the use of emulsion solution could lead to a significant growth of reaction rate between amphiphilic—surface active—compounds exclusively due to their concentrating at the interfaces. Indeed, if reagents are surface active, they are preferentially adsorbed at the surface of the emulsion droplets rather than dissolved in either the outer phase or inside the droplets (see Fig. 1). So, the reaction proceeds mainly in the surface layers of emulsion droplets, which therefore play the role of effective surface nanoreactors. Here we use the term nano in order to stress that the thickness of adsorbed layer (which is a spatial size of these reactors) is around 1–2 nm.

We will show that in this case, there is an optimum emulsion droplet size at which the acceleration of reaction is maximal. Indeed, if the droplets are small, the reagents are distributed over a large surface area, so their surface concentrations are low, and therefore the reaction rate in the surface layers is small. With an increase in the droplet size (as the surface layer size decreases in comparison with the emulsion volume), the concentrations of the substrate and the catalyst at the surface increase. In turn, this induces the increase of reaction rate. However, on the other hand, if the droplets are very large, then the surface layers occupy too small a fraction of the overall volume. Thus, the amount of the substrate and the catalyst in the surface layers is small, and they make insignificant contribution to the reaction rate, which occurs mainly in the bulk phases. It is worthwhile to mention here that, in our consideration, we do not take into account possible dependence of emulsion droplets on reactant concentrations.

In this paper, we propose a simple theory of the kinetics of the catalytic reaction $\mathbf{A} + \mathbf{B} \rightarrow \mathbf{P} + \mathbf{B}$, where the substrate **A** in the presence of the catalyst **B** in an emulsion is converted into the product **P**. We will assume that both the substrate **A** and the catalyst **B** are surfactants. In this case, because molecules **A** and **B** are concentrated in the surface layers of the emulsion, these layers act as nanoreactors ensuring a significant acceleration of the catalytic reaction within a certain range of emulsion droplet sizes.

The model

Let us consider the simple catalytic reaction ($\mathbf{A} + \mathbf{B} \rightarrow \mathbf{P} + \mathbf{B}$), where the substrate **A** in the presence of the catalyst **B** is converted into the product **P**. The reaction occurs in an emulsion involving monodisperse droplets of radius R. According to the main purpose of the study, we assume that substances **A**, **B**, and **P** are distributed somehow between the outer phase, inner phase, and interfacial layers of the emulsion droplets. In order to develop a statistical theory, we need to define the thickness d of the interfacial layers. We will assume here that d is of the order of several Angstroms, and that the volume of all the molecules involved in the reaction (**A**, **B**, and **P**) is of order d^3. In other words d is the parameter characterizing all microscopic sizes in the system under consideration.

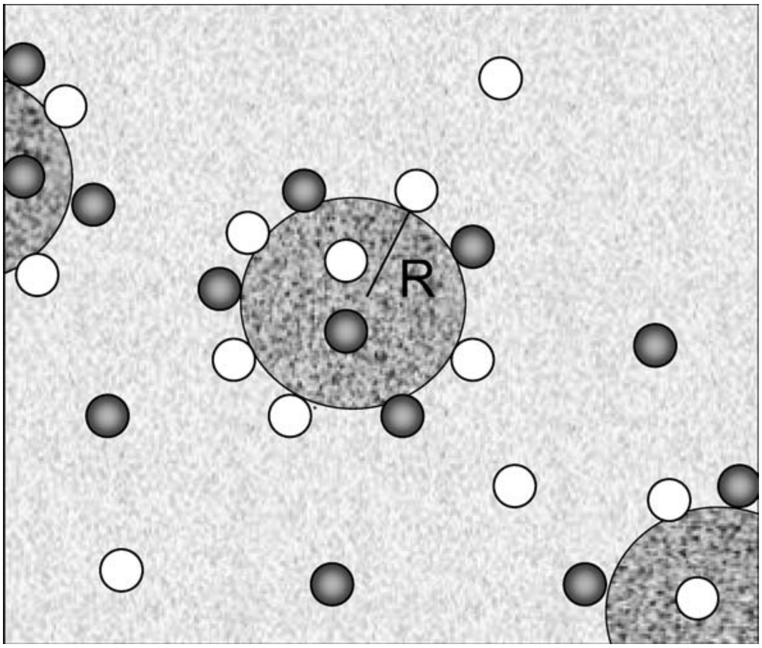

Fig. 1 Schematic representation of emulsion with the molecules of substrate and catalyst. *open circle* are substrate molecules, *closed circle* are molecules of the catalyst. *R* radius of emulsion droplets

Let us denote the volume fraction of the molecules in the inner and outer phases and in the surface layer as $\varphi_i^{\rm in}$, $\varphi_i^{\rm out}$, φ_i^b (i = **A**, **B** and **P**), respectively. Let $f_i^{\rm in}$, $f_i^{\rm out}$, f_i^b (i= **A**, **B** and **P**) be the free energies per molecule corresponding to the molecular interactions with the interior of emulsion droplet, with the outer solution, and with the emulsion surface respectively. The energies are normalized to kT, where T is the temperature and k is the Boltzmann constant.

At low concentrations of the substrate **A** and the catalyst **B** in solution, the free energies $F^{\rm in}$ of the inner phase and the free energy $F^{\rm out}$ of the outer phase can be represented as the sum of two contributions, namely, the translational entropy of molecules **A**, **B**, and **P**, and the contribution describing the interaction of these molecules with the environment [17]:

$$\begin{aligned}\frac{F^{\rm in}d^3}{V^{\rm in}kT} &= \sum_{i=A,B,P}\varphi_i^{\rm in}\ln\varphi_i^{\rm in} + \sum_{i=A,B,P}\varphi_i^{\rm in}f_i^{\rm in},\\ \frac{F^{\rm out}d^3}{V^{\rm out}kT} &= \sum_{i=A,B,P}\varphi_i^{\rm out}\ln\varphi_i^{\rm out} + \sum_{i=A,B,P}\varphi_i^{\rm out}f_i^{\rm out},\end{aligned}\tag{1}$$

where $V^{\rm in}$ and $V^{\rm out}$ are the volumes of the inner and the outer phase respectively. The sum of these volumes is equal to the total volume V of system: $V^{\rm in} + V^{\rm out} = V$.

If the surface activity of molecules **A**, **B**, and **P** is high, even at low concentrations of **A**, **B** and **P** molecules in the system, they can tightly cover the surface of the droplet ($\varphi_A^b + \varphi_B^b + \varphi_P^b \approx 1$); therefore the free energy $F^b$of the surface layer is the sum of mixing free energy (for which we use the Flory–Huggins approximation [18]) and free energy of interaction. The mixing free energy is composed of translational entropies of **A**, **B**, and **P** molecules and the entropic factor accounting for excluded volume [18]:

$$\begin{aligned}\frac{F^b d^3}{V^b kT} = &\sum_{i=A,B,P}\varphi_i^b\ln\varphi_i^b\\ &+\left(1-\sum_{i=A,B,P}\varphi_i^b\right)\ln\left(1-\sum_{i=A,B,P}\varphi_i^b\right)\\ &+\sum_{i=A,B,P}\varphi_i^b f_i^b,\end{aligned}\tag{2}$$

where V^b is the total volume of the interface layers. It is the sum of the volume of all interfacial regions of all emulsions droplets (for each droplet such volume is equal to $4\pi R^2 d$). This volume V^b is directly connected with the volume $V^{\rm in}$ of inner phase and radius R of emulsion droplets: $V^b = 3V^{\rm in}d\big/R$.

Thus if the fraction of oil in the system is constant ($V^{\rm in}$=const), the volume of interface V^b available for absorption of **A**, **B** and **P** molecules scales as $1/R$, i.e. it decreases with the increase of the size of emulsion droplets or, equivalently, with the decrease of the number of emulsion droplets in solution.

The equilibrium values of $\varphi_i^{\rm in}$, $\varphi_i^{\rm out}$, φ_i^b (i = **A**, **B** and **P**) are determined from the conditions that the chemical potentials of these compounds in all the coexisting phases are equal:

$$\frac{\partial(F^b/V^b)}{\partial\varphi_i^b} = \frac{\partial(F^{\rm in}/V^{\rm in})}{\partial\varphi_i^{\rm in}} = \frac{\partial(F^{\rm out}/V^{\rm out})}{\partial\varphi_i^{\rm out}}\tag{3}$$

As the reaction proceeds, the substrate amount in the system decreases while the amount of product increases. This causes the redistribution of the catalyst, the substrate, and the product between phases. Generally speaking, this redistribution depends in a complex way on the conversion of the reaction, which in its turn is determined by the local concentrations of the substances **A** and **B** in all the parts of the reaction volume. All this implies quite complex time dependence of the reaction rate.

In the present paper, we adopt some simplifying assumptions, which, on one hand, permit to describe the main novel physical aspects for the system under consideration and, on the other hand, allow to perform numerical calculations up to the end at reasonable time. Namely, we assume that the mass transfer rate between the phases is much higher than the reaction rate and that the reaction rate in each phase is equal to the product of reactant concentrations with the reaction rate constant K which was taken as equal in all phases. In this case, the average reaction rate M in the system (per unit reactor volume) at a given moment of time **t** can be described by the expression [17]:

$$M(t) = K\sum_{j} \frac{V^j(t)}{V} \varphi_A^j(t)\varphi_B^j(t), \tag{4}$$

where the summation is over all the phases j (j= in, out, b); and $\varphi_A^j(t)$, $\varphi_B^j(t)$ are the current values of the volume fractions of the compounds **A** and **B** in the phase j, respectively.

At any moment of time t, the values of $\varphi_i^{\text{in}}(t)$, $\varphi_i^{\text{out}}(t)$, $\varphi_i^{b}(t)$ (i = **A**, **B** and **P**) are related by the expressions:

$$\frac{\varphi_i^{\text{in}}(t)V^{\text{in}} + \varphi_i^{b}(t)V^{b} + \varphi_i^{\text{out}}(t)V^{\text{out}}}{V} = \varphi_i(t), \tag{5}$$

where $\varphi_i(t)$ (i = **A**, **B** and **P)** is the average volume fraction of the compound i in the whole volume V. Generally speaking, the volumes of inner and outer phases vary during the reaction. However, at low concentrations of the reagents, this variation can be ignored. The system of Eqs. 1–5 completely determines the dependence of the reaction rate $M(t)$ on the parameters of the system at any given moment of time t. In particular, using the system of Eqs.1—5, we can easily determine reaction rate $M_0 = M(0)$ at zero time when the average concentration of the product in the reactor is equal to zero and the average concentrations of the substrate and the catalyst are equal to the fixed initial values.

When we investigate the dependence of M on time t, we should take into account that the average concentration of the catalyst **B** is constant and the average concentrations of the substrate **A** and the product **P** alter in the course of time according to the following equation:

$$\frac{\mathrm{d}\overline{\varphi_A}(t)}{\mathrm{d}t} = -\frac{\mathrm{d}\overline{\varphi_P}(t)}{\mathrm{d}t} = -M(t). \tag{6}$$

Therefore, in order to investigate the kinetics of the reaction, we have to solve simultaneously the system of non-linear Eqs. 1–5 and the differential equation (6).

This system of equations was solved numerically at different values of the parameters: we varied the ratio V^{in}/V, the average catalyst concentration ϕ_B, and the average initial substrate concentration $\phi_A(0)$, the energy parameters $\varepsilon_i^{\text{in-out}} = f_i^{\text{in}} - f_i^{\text{out}}$ (i = **A**, **B** and **P**) characterizing the advantage of preferential dissolution in the inner phase as compared to the outer phase, and also the energy parameters $\varepsilon_i^{b\text{-out}} = f_i^{b} - f_i^{\text{out}}$ (i = **A**, **B** and **P**) characterizing the surface activity of the corresponding compounds. Results are presented in the next section.

Results and discussion

The results of the calculations are presented in Figs. 2–7. Figure 2 shows the curves for the initial reaction rate M_0 at zero time normalized to the reaction rate M^* (here and below M^* is the reaction rate that would be in homogeneous bulk solution with the same initial concentrations of reagents: $M^* = K\varphi_A(0)\varphi_B$) as a function of the emulsion droplet radius R for the case when both the substrate **A** and the catalyst **B** do not preferentially dissolve in the inner or the outer phases $\varepsilon_A^{\text{in-out}} = \varepsilon_B^{\text{in-out}} = 0$, but both substances are surface active and are adsorbed in the surface layers of emulsion droplets. For the case of Fig. 2, we assume that the energy gains from interfacial adsorption for the substrate **A** and the catalyst **B** are equal: $\varepsilon_A^{b\text{-out}} = \varepsilon_B^{b\text{-out}} = \varepsilon_s < 0$.

If the surface activity is low ($\varepsilon_s = -2$), the effect of concentrating at the surfaces of emulsion droplets is weak. In this case, the rate M_0 increases slightly with the decrease in the emulsion droplet radius R (here and below droplet radius R is normalized by interface thickness d). With an increase in the surface activity ε_s plot $M_0(R)/M_*$ becomes non-monotonic. A pronounced maximum emerges, and with the increase of the parameter ε_s, the height of the maximum increases and the peak is shifted towards larger values of R [19] .

Finally, at $|\varepsilon_s| \geq 14$, the maximum value of the rate M_0 is 10,000 times higher than that in the bulk of a homogeneous system and the rate can be decreased or increased thousands of times by means of changing the emulsion droplet size. At $|\varepsilon_s| = 14$ all molecules of A and B tend to adsorb at the surface of emulsion droplet. And one can find molecules A and B dissolved in inner and outer parts of emulsion only if all the available sites in absorbed layers are occupied. Similar effect is observed in the case of higher values of $|\varepsilon_s|$ as well. Calculations show that beginning with value of the energy parameter $|\varepsilon_s| = 14$, the function $M_0(R)$ remains virtually constant with further increase in $|\varepsilon_s|$.

At $|\varepsilon_s| \geq 14$ and when the total volume occupied by the molecules **A** and **B** is smaller than the total volume of interfacial regions (i.e., in case of relatively small emulsion droplets), practically all the catalyst and substrate molecules are adsorbed at the surfaces of the droplets and the reaction occurs only there. In this regime, all molecules **A** and **B** are in the interfacial layers and the volume V_b of these layers decreases inversely proportionally to R. Thus the volume fractions φ_A^b and φ_B^b of the molecules **A** and **B** in the surface layers increase proportionally to R and the reaction rate $M_0\tilde{\varphi}_A^b(0)\varphi_B^b V_b/V$ also increases proportionally to R as seen in Fig. 2. This increase continues up to the value of radius equal to R^m, when the molecules **A** and **B** occupy all the interfacial regions but still practically no molecules **A** and **B** float in bulk phases, i.e.,

$$\begin{aligned} &\varphi_A^b + \varphi_B^b = 1, \\ &\varphi_A^{\text{in}} = \varphi_B^{\text{in}} = \varphi_A^{\text{out}} = \varphi_B^{\text{out}} = 0. \end{aligned} \tag{7}$$

This means that at $R = R^m$ the following equation is fulfilled: $1 = \frac{\varphi_A(0)+\varphi_B}{V_b^{\max}} V$, where $V_b^{\max} = 3V^{\text{in}} d / R^m$.

After simple transformations this equation can be written as:

$$\frac{R^m}{d} = \frac{3V^{\text{in}}}{V} \frac{1}{\varphi_A(0) + \varphi_B}$$

Because of the symmetry of chosen values of the parameters the volume fractions of the substrate and the catalyst are everywhere equal to each other and thus:

$$\frac{R^m}{d} = \frac{3V^{\text{in}}}{V} \frac{1}{2\varphi_A(0)} \tag{8}$$

When R is equal to R^m the reaction rate is maximal and equal to $M_0^{\max} = K\varphi_A(0)/2$. Correspondingly, the ratio $M_0^{\max}/M^*$ of reaction rate $M_0^{\max}$ at this point to the reaction rate M^* in homogeneous solution with the same concentration is $M_0^{\max}/M^* = \frac{\varphi_A(0)}{2\varphi_A(0)\varphi_B} = \frac{1}{2\varphi_B}$. Thus, the lower are the concentrations of the reagents the higher is the increase of reaction rate due to their concentrating in surface layer at $R = R^m$.

As R exceeds R^m and increases further, not all of the molecules **A** and **B** find room in the surface layers. Thus, they have to be dissolved in other phases. Nevertheless, their concentrations in the droplet cores and in the outer solution remain low and, therefore, the reaction rate outside the surface layers can be neglected. For the most part, only the reaction in the surface layers contributes to the general reaction rate. The volume fractions φ_A^b and φ_B^b of catalyst and substrate molecules in the surface layer remain close to the maximum possible values (in the case under consideration, because of the symmetry they are equal to 1/2). But the volume of surface layers V_b decreases inversely proportionally to R. Thus, in this region the reaction rate M_0 decreases inversely proportionally to R as well: $M_0\tilde{\varphi}_A^b\ (0)\varphi_B^b V_b/V\tilde{1}/R$; this formula explains the decrease of M_0 with R seen in Fig. 2 at large values of R.

If the surface activities of substrate and catalyst are not extremely large ($\varepsilon_s > -14$), then the surface layers

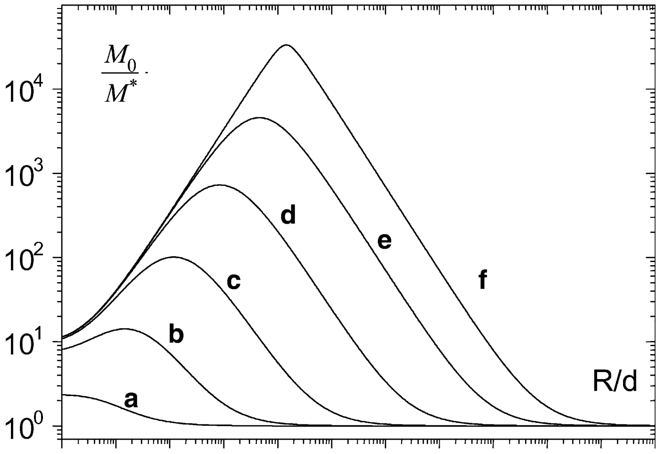

Fig. 2 The initial rate of reaction M_0 versus emulsion droplet size R at $V^{\text{in}}\ /V = .1$, $\varepsilon_A^{\text{in-out}} = \varepsilon_B^{\text{in-out}} = 0$, $\varphi_A(0) = \varphi_B = 10^{-5}$ and $\varepsilon_s = -2$(**a**), -4(**b**), -6(**c**), -8(**d**), -10, (**e**), -14(**f**)

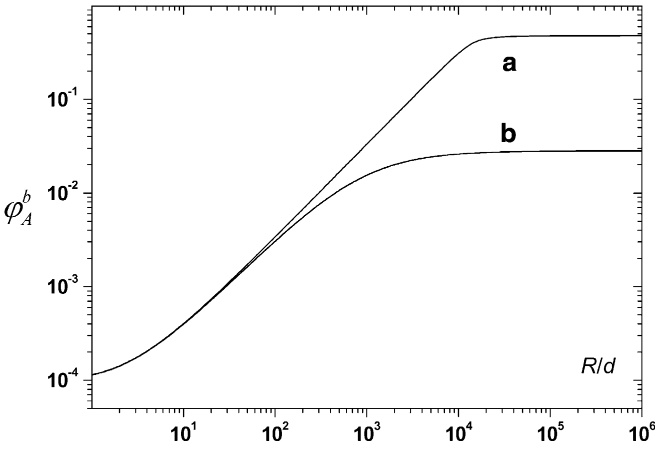

Fig. 3 The initial volume fraction of substrate in the surface layers $\varphi_A^b(0)$ versus emulsion droplet size R at $V^{\text{in}}\ /V = .1$, $\varepsilon_A^{\text{in-out}} = \varepsilon_B^{\text{in-out}} = 0$, $\varphi_A(0) = \varphi_B = 10^{-5}$, and $\varepsilon\ _s = -14$ (**a**) and -8 (**b**)

of emulsion are filled up only partly even at high values of radius R (Fig. 3): our calculations show that the less is the absolute value of ε_s the lower are the limiting values of φ_A^b and φ_B^b and the smaller are the emulsion droplets R at which these limiting values of φ_A^b and φ_B^b and the maximum rate $M_0^{\max}$of reaction are reached (see the shift of maxima of the curves in Fig. 2 with the decrease of ε_s).

At very large values of R, the volume fraction of surface layers is very small and the contribution of the reaction in the layers to the general reaction rate in all the phases is negligible, therefore the ratio M_0/M^* is equal to unity.

Here it should be mentioned that since the value of the thickness of surface layers d is never smaller than 0.1 nm and the radius of emulsion droplets is never larger than 1 mm, the ratio R/d cannot exceed 10^7. Although very small and very large values of R/d are meaningless, we have plotted the curves in the range of the ratio R/d from 1 to 10^{10} in order to give a general idea of the limiting behavior of these curves. (This remark also concerns Fig. 4.)

Figure 4 presents the $M_0(R)/M^*$ curves for the case when surface activities of both the substrate and the catalyst are high and the surface activity of the substrate is higher than the surface activity of the catalyst: $\varepsilon_A^{b-\text{out}}<\varepsilon_B^{b-\text{out}}<0$. In this case, the shape of the curve M_0/M^* versus R depends significantly on the ratio between the average concentrations of the substrate and the catalyst. One can see that if the substrate's average concentration is much higher than the catalyst's average concentration (curve *a* in Fig. 4), then the curve has a pronounced maximum at a certain value $R=R^*$. It is of interest that as R increases further three times only, the reaction rate decreases hundreds of times. This is because at $R=R^*$ the total volume of the surface layers is virtually equal to the total volume of the substrate and the catalyst molecules, i.e., the layers are fully occupied. When the droplet radius exceeds R^* and increases further, the total volume of the surface layers decreases. This causes the replacement of the catalyst in the surface layers by the more surface-active substrate. As the reaction takes place mainly in the surface layers, this leads to a sharp drop in the reaction rate. The sharp change in the reaction rate at only slight variation of the size of emulsion droplets means that the reaction can be easily controlled by changing the droplet size.

Conversely, when the substrate concentration is much lower than the catalyst concentration (case b in Fig. 4), the curve M_0/M^* versus R has quite a long plateau near the maximal reaction rate. It means that the reaction rate in such systems remains close to the maximal rate as the emulsion droplet radius R is varied several 100s of times. The explanation is simple: for a large range of variation of R all more surface-active substrate molecules are accommodated in the interfacial layers, and the concentration of much more numerous catalyst molecules in these layers is practically constant. It should also be stated that, because of the symmetry of the problem, curves similar to that shown in Fig. 4 can also be observed for the case when, on the contrary, the surface activity of the catalyst exceeds the surface activity of the substrate.

Figure 5 presents the kinetics of the reaction for the case $\varphi_A(0)=10^{-4}$, $\varphi_B=10^{-5}$, $\varepsilon_A^{\text{in}-\text{out}}=\varepsilon_B^{\text{in}-\text{out}}=\varepsilon_P^{\text{in}-\text{out}}=0$, when surface activities of both the substrate and the catalyst are high $\varepsilon_A^{\text{in}-b}=\varepsilon_B^{\text{in}-b}=-14$ and the product is not surface active $\varepsilon_P^{\text{in}-b}=0$. Curve a presents the reaction rate M as a function of time t (in the plot, time t is normalized by the characteristic time of reaction $1/K$). Curve b presents the time dependence of the average substrate volume fraction $\phi_A(t)$.

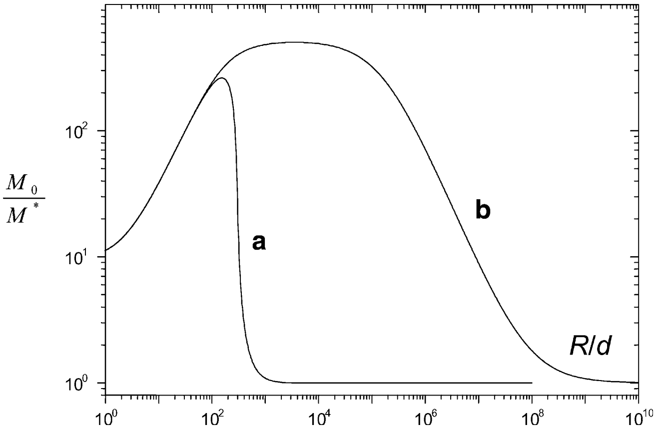

Fig. 4 The initial reaction rate M_0 vresus emulsion droplet size R at $\varepsilon_A^{b-\text{out}}=-14$, $\varepsilon_B^{b-\text{out}}=-7$, $V^{\text{in}}/V=.1$, and various average volume fractions of the catalyst and substrate in the solution: $\varphi_A(0)=10^{-3}$ and $\varphi_B=10^{-7}$ (**a**); $\varphi_A(0)=10^{-7}$ and $\varphi_B=10^{-3}$ (**b**)

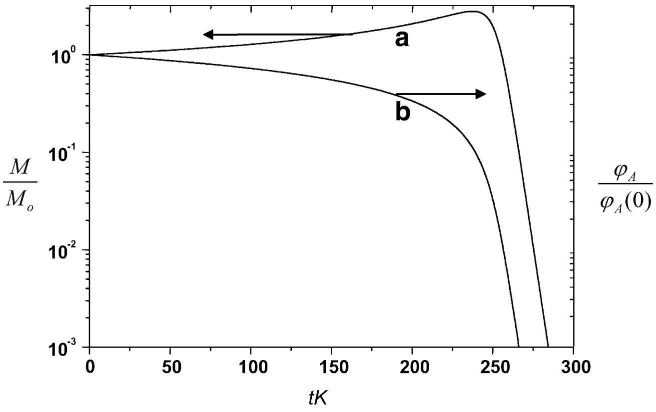

Fig. 5 Reaction rate M (**a**) and the average volume fraction ϕ_A (**b**) vs time t (multiplied by the reaction rate constant K) at $R/d=10^4$, $\varepsilon_A^{b-\text{out}}=\varepsilon_B^{b-\text{out}}=-14$, $\varepsilon_A^{\text{in}-\text{out}}=\varepsilon_B^{\text{in}-\text{out}}=\varepsilon_P^{\text{in}-\text{out}}=0$, $V^{in}/V=.01$, and $\varepsilon_B^{b-\text{out}}=0$

One can see that starting from zero time till the moment t^*, the reaction rate M varies only slightly. In this period of time, the reaction rate M is never smaller than the reaction rate M_0 at zero time and does not exceed the value M_0 by more than 2.5 times (M t) $/M_0 < 2.5$). On the other hand, during this period of time, the average substrate concentration decreases significantly. For example, at the time t^* (t^* $K{\sim}250$) $M{\sim}M_0$ while $\varphi_A(t^*)$ is hundreds of times lower than the average substrate concentration at zero time ϕ_A (0). Thus, up to virtually complete substrate conversion, the reaction rate remains close to the reaction rate at the initial moment of time.

Such a behavior can be again explained by the fact that the reaction occurs only in the surface layers. In the course of the reaction, the substrate in the surface layers turns into product. The product is not surface active; therefore it leaves the surface layers and goes to other locations of the system and gives room to new portions of surface-active substrate to be adsorbed on the surface layers. Thus, the reaction rate does not change significantly until virtually all the substrate in the bulk of the mixture is run out. And thereafter, the reaction rate decreases sharply.

If the product **P** is also surface active, the reaction kinetics is different. Fig 6 presents the kinetics of the reaction for the case that differs from the one presented in Fig. 5 only in the surface activity of the product. For the case of Fig. 6 the surface activity of the product is higher than that of the substrate and the catalyst: $\varepsilon_P^{b-\text{out}} = -17$. One can see that the reaction rate decreases sharply in the very beginning of the process (Fig. 6b) while the substrate average volume fraction ϕ_A (t) remains practically invariable (Fig. 6a). At the same time the volume fraction of the product $\varphi_P^b(t)$ in the surface layers increases sharply in the very beginning of the process and thereafter it tends to unity (Fig. 6.1).

This behavior of the reaction kinetics is explained by the fact that the product is more surface-active than

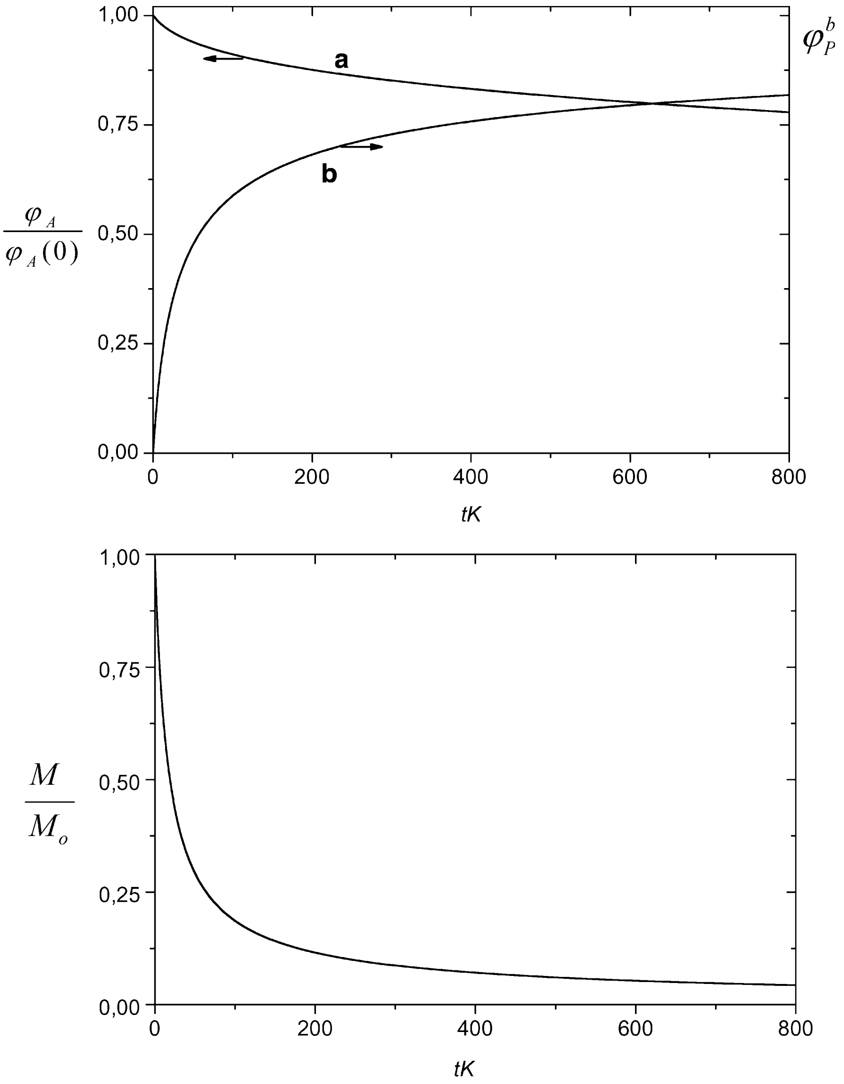

Fig. 6 Reaction rate M (**a**), the average volume fraction ϕ_A (**b**) (1), and the volume fraction of the product in the surface layers φ_p^b (2) versus time t (multiplied by the reaction rate constant K) at $R/d = 10^4$, $\varepsilon_A^{b-\text{out}} = \varepsilon_B^{b-\text{out}} = -14$, $\varepsilon_A^{\text{in-out}} = \varepsilon_B^{\text{in-out}} = \varepsilon_P^{\text{in-out}} = 0$, $V^{in}/V = .01$, and $\varepsilon_P^{b-\text{out}} = -17$

both the substrate and the catalyst. Therefore, virtually all the product that appears in the course of the reaction adsorbs on the droplet surfaces and forces out the reagents from the surface layers. Since the reaction takes place mainly in the surface layers, this "poisoning effect" causes a sharp decrease in the reaction rate in the very beginning of the process.

Figure 7 presents the curves of the reaction rate M_0 as a function of the substrate average volume fraction ϕ_A (0) for the case of the catalyst with high surface activity ($\varepsilon_B^{b\text{-out}} = -14$) and various substrate surface activities $\varepsilon_A^{b\text{-out}}$. The reaction rate M_0 is normalized to the reaction rate M^* in the bulk of a homogeneous system where $\varphi_A(0) = 10^{-3}$ and the concentration of the catalyst is the same as in the case under consideration. One can see that the function $M_0/M^*(\varphi_A)$ depends in a complex way on $\varepsilon_A^{b\text{-out}}$. This function can be both monotonic (curve **a**) and non-monotonic with a pronounced maximum (curve **b**).

In the case presented by curve **b**, the reaction rate attains maximum when the volume fractions of the substrate and the catalyst in the surface layers are equal to 1/2: $\varphi_A^b = \varphi_B^b \approx 1/2$. This is due to the fact that the reaction takes place mainly in the surface layers. Because of high surface activities of the substrate and the catalyst, they densely cover the droplets surfaces (i.e., the sum of their volume fractions in the surface layers is virtually equal to unity: $\varphi_A^b + \varphi_B^b \approx 1$). As the average concentration of the substrate in the reactor increases, its volume fraction in the surface layers also increases, hence the catalyst is forced out of the surface layers and its concentration in the layers drops. The reaction rate is roughly equal to the product of the substrate and the catalyst concentrations in the surface layers. Therefore, it attains the maximum when $\varphi_A^b = \varphi_B^b \approx 1/2$.

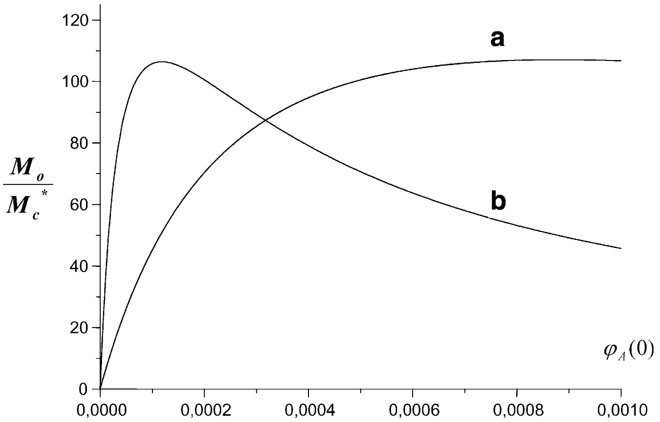

Fig. 7 The initial reaction rate M_0 versus average volume fraction ϕ_A (0) of the substrate in the reactor at $R/d = 10^4$, $\varphi_B = 6 \cdot 10^{-6}$, $V^{in}/V = .01$, $\varepsilon_A^{\text{in-out}} = \varepsilon_B^{\text{in-out}} = 0$, $\varepsilon_B^{b\text{-out}} = -14$, and $\varepsilon_A^{b\text{-out}} = -9$ (**a**); $\varepsilon_A^{b\text{-out}} = -11$ (**b**)

In the case when surface activity of the catalyst is much higher than surface the activity of the substrate, the function $M_0/M^*(\varphi_A)$ shows monotonic increase with subsequent saturation. This dependence is similar to the so-called Michaelis–Menten kinetics dependence.

It is known that many reactions catalyzed by natural enzymes are described by the Michaelis–Menten kinetics [20, 21]. This is explained by the fact that such reaction is a two-step process: the enzyme and the substrate first form a complex; after that, with a certain probability, either the reaction can proceed, so that the substrate **A** is converted into the product **P** or the complex is decomposed. Our calculations show that the Michaelis–Menten-type dependence of the reaction rate on the substrate concentration (i.e., the increase in the rate with the subsequent saturation) can also be observed for a simple catalytic reaction occurring in emulsions (see curve **a** in Fig. 7) in the case when catalytic molecules have high surface activity.

Conclusion

In this paper, we propose a simple theory of the kinetics of the catalytic reaction **A** + **B** → **P** + **B**, where the substrate **A** in the presence of the catalyst **B** in an emulsion is converted into the product **P**, and both the substrate **A** and the catalyst **B** are surface active. It was shown that because molecules **A** and **B** are concentrated in surface layers of the emulsion, these layers act as surface nanoreactors ensuring a significant acceleration of the catalytic reaction within a certain range of emulsion droplet sizes. Generally speaking, in experiment, this acceleration can be even more significant since in many cases the reaction constant at the interface is higher that that in bulk phases [9–11, 16].

The great advantage of using such surface nanoreactor is that the emulsion droplet volume (and therefore, the rate of reaction) can be easily and reversibly altered in the course of the reaction. For example, let us imagine that there exists an unstable emulsion maintained by the effect of ultrasound. If the ultrasound effect becomes more intense, the droplets of emulsion break up rapidly and their total surface increases. On the contrary, if the ultrasound effect weakens, the droplets merge and their total surface decreases. Thus, the reaction rate control by means of ultrasound effect is possible.

Our calculations showed that the Michaelis–Menten-type dependence of the reaction rate on the substrate concentration (i.e., the increase in the rate with the subsequent saturation) can be observed in such systems for the case when surface activity of the catalyst exceeds significantly the surface activity of the substrate.

One can expect that in the case of polymer systems the effects described above can be stronger than that for low-molecular substances. First, the tendency for amphiphilic macromolecules to adsorb at the interfaces should be very pronounced. In addition to this, such macromolecules should stabilize the emulsions. This gives rise to interesting possibilities in the context of this paper, in particular to the possibility of catalysis of reactions in emulsions by catalytically active groups attached to amphiphilic macromolecules. These possibilities will be the subject of another paper.

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