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Description of a simple model that demonstrates that the rates of common thermally activated chemical reactions in oil-in-water emulsions are much slower than the rates of molecular diffusion

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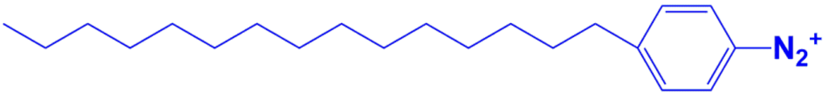
Interpreting the distribution and kinetics of reactants in compartimentalized systems such as micelles, microemulsions, vesicles, emulsions and nanoemulsions, is of major importance because they are much more relevant mimics of organized cells than bulk solution. Physical methods such as scattering and microscopy show organized media as discrete structures, e.g., droplets, providing useful knowledge on their physical properties (size, polidispersity, etc.). However, relevant information on chemical composition and medium properties of the different regions of the multiphasic systems can only be obtained by means of chemical reaction methods, in which one reactant, the so-called chemical probe molecule, is chosen for its special properties, e.g., controlled distribution, strong absorbance, etc.. These "chemical kinetic methods", based on the use of ground state chemical reactions, have been exploited for years to obtain insights into the component (e.g., reactant distributions) and medium properties of colloidal systems. When the rate of the chemical reaction is slow compared to emulsion dynamics, the chemical reactants "see" the emulsion droplets as three separate regions (oil, interfacial and aqueous) where the reactants partition thermodynamically according to their relative solubility in each region. However, when the diffusion of reactants is rate-limiting, the transport of reactants between regions is the slow step and the rate of the reaction depends on both the dynamics of the droplets and processes such as changes in the solvation of the reactant, proton transfers or monomer, solute or counterion entry and exit from the aggregates. Here we report on a simple mathematical model, based on the Smoluchowski´s diffusion theory, which allows one to predict when a particular chemical reaction is, or is not, under dynamic equilibrium in compartimentalized systems of interest to food chemistry such as oil-in-water emulsions. Predicting the relative values of the diffusion rates compared to the chemical rates is basic and very valuable to safely use of "chemical kinetic methods" to probe the composition of association colloids.

INTRODUCTION

Understanding chemical reactivity in multiphasic systems requires the use of chemical reaction methods where a chemical probe is selected because of its special physicochemical properties.[1, 2] For instance, we employed the specifically designed chemical probe 4-hexadecylbenzenediazonium,16-ArN$_2^+$, tetrafluoroborate, Scheme 1, to determine the distribution of antioxidants between the different regions of oil-in-water emulsions as well as their effective concentrations.[3, 4] Experimental results are interpreted on the basis of the pseudophase kinetic model providing insights into the composition and properties of the interfacial region of the emulsions.[1] By employing this methodology, we successfully provided a molecular explanation for the effects of the hydrophobicity of the antioxidants in relation with their efficiency (cut-off effect) and provided a valuable and robust tool to interpret and predict the effects of other important parameters on the distribution and interfacial concentrations of antioxidants, which is directly related to their efficiency[1-4].



Scheme 1. Chemical structure of the probe 16—ArN$_2^+$ used to determine the distribution of antioxidants in oil-in-water emulsions and nanoemulsions. The counterion (BF$_4^-$) is not displayed for simplicity.

Pseudophase kinetic models are commonly grounded on the assumption that the diffusivities of the reactants between the oil, interfacial and aqueous reaction regions of the emulsions are orders of magnitude faster than the rate of the chosen reaction (in our case, that between the 16ArN$_2^+$ and the antioxidant AO), so that AOs distribute between the different regions of the emulsion on the basis of their solubility in the oil, interfacial and aqueous regions, and that the reaction with the chemical probe does not perturb reactant distribution [1, 5]. Nevertheless, the kinetics of chemical reactions at the interfaces of emulsions is difficult to study because a number of processes that occur on a variety of time scales take place simultaneously. Emulsion droplets break and reform continuously, and emulsion components such

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as oil, water, surfactants, antioxidants, lipid radicals or other reactive molecules exchange between droplets. Thus, the rate chemical reactions that take place at the interfaces may depend on the rates of transport of emulsion components between the three regions of the emulsion and eventually may be rate-limiting [1, 2, 5].

It may be instructive to describe and predict the limits under which pseudophase kinetic models, commonly employed to interpret chemical reactivity in multiphasic systems, can be safely employed to get insights into the properties of multiphasic systems. We, therefore, aim to analyze the effects of molecular motion in emulsions on the chemical reactions and we will analyze here the conditions where either the diffusion or the kinetics is predominant. The resulting mathematical model should be based on experimentally measurable quantities so that the different contributions to the transport of reactants can be accurately separated and sufficiently detailed.

WHY DIFFUSION IS IMPORTANT IN COLLOIDAL (AND BULK) CHEMISTRY?

Emulsions are metastable dispersions in which molecular transport plays a central role in the various mechanisms driving the system towards its state of minimal energy.[6] Molecular diffusion in colloidal systems and, particularly, in emulsions has attracted considerable interest to control the macroscopic physicochemical properties of the system [7, 8]. Emulsions are highly dynamic systems and diffusion within droplets, exchange of material between droplets, and self-diffusion of droplets in the continuous phase are common dynamic processes having different time scales which may affect their potential use. For example, Ostwald ripening involves the transfer of oil through the aqueous phase, while coalescence involves oil transfer achieved by fusion of the emulsifier film (a droplet-droplet direct interaction). Interfacial adsorbed surfactants are also dynamic, experiencing lateral and transversal diffusion processes, undergoing continuous reorganization, and are transferred between emulsion droplets. Surfactants are able to form micelles in the water phase and they may form swollen micelles (which are several nm in size) that contain oil molecules. These swollen micelles may carry small fractions of oil from small to big droplets and may contribute to the ripening of the emulsions [9].

Diffusion in emulsions is also relevant to control the kinetic processes of the various chemical reactions that take place at the liquid-liquid interfacial boundaries because emulsion droplets are broken and reorganized constantly, and oil, surfactants and other emulsion components are (rapidly) transferred between droplets. In general, the rate of any chemical reaction depends on the properties of the reaction medium (e.g., polarity) and on the concentrations of reactants at the reaction site, which in turn may depend on the rates of flow of reactants between the three regions of the emulsion. However, mass transfers driven by the differences in droplet compositions may affect chemical reactivity, and it needs to be taken into consideration for a comprehensive understanding of the chemical reactions [1].

Diffusion of reactive molecules within or between emulsion droplets depends not only of their molecular nature but also on the particular properties of the components of the emulsions (composition, polarity and viscosity of the oil, components of the water phase, nature of the emulsifier, etc.), and can be either faster or slower than the undergoing chemical reaction. If the observed rate depends on the rate of molecular diffusion, the reactions are said to be under microscopic diffusion control, meanwhile if the observed rate depends on the rate at which solutions mix, they are said to be macroscopic diffusion control. When the reaction is slow in comparison with the emulsion dynamics, the reaction "sees" the emulsion droplets as static entities, so that the observed rate of the reaction can be computed as the summation of the rates in all regions of the emulsion. On the contrary, when the diffusion of reactants is rate-limiting, the dynamics of the droplets needs to be taken into account to explain the fate of the chemical reactions [10-13].

WORKING FRAMEWORK AND CONSTRAINTS

Most kinetic theories have been described by assuming ideal, dilute and homogeneous systems, and certainly food emulsions are complex systems containing mixtures of oils, aqueous solutions containing ionic and nonionic compounds in different extents and a emulsifier that creates an interfacial region connecting the oil and water phases [11]. Thus, they are far from ideal systems and simplifications are required. The approach we described below will be as simple as possible by considering "ideal" systems where there are no physical barriers limiting the transport of molecules between the different regions of the system. Thus, we need to be aware that some complications may arise in real systems due to deviations from simple diffusion laws, molecular mobility, partitioning and volume exclusion effects, etc.

In addition, we will limit our analyses to reactions where electrostatic forces are unimportant, i.e., reactions with neutral molecules with no steric barriers. This simplifies considerably the model because does not require consideration of electrostatic interactions, however, we will mention later which are the effects of considering ionic reactants.

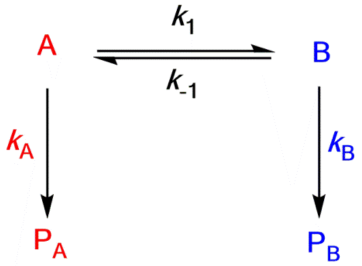
For the sake of simplicity, we will hereafter only consider closed systems where there is no mass transfer to and from the surroundings and will assume that:

1) Once bulk mixing of the components is done, the resulting solutions are ideally mixed, that is, the reactants are uniformly distributed throughout the bulk fluid and their concentration is the same everywhere and the measured rate does not depend on the rate at which the solutions are mixed, i.e., mixing effects are neglected.

2) The concentrations of reactants are low enough to neglect deviations from ideality so that the use of activity coefficients to correct deviations from ideality is not necessary.

Diffusive *vs* reactive systems and the Acree-Curtin-Hammet principle

The Acree-Curtin–Hammett principle[14, 15] is an important concept described in most physical-organic chemistry textbooks which is commonly used to explain the dependence of the product ratio, originated from a pair of reactants in equilibrium, on the relative size of the rate constants involved, Scheme 2. The reactive molecules in equilibrium can be equilibrating conformers, tautomers, or stereoisomers, etc.



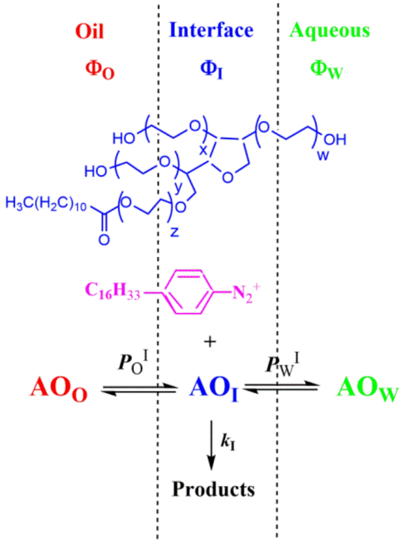
Scheme 2. Kinetic representation of the formation of different products from two reactants in equilibrium with one another. The rapidly interconverting reactants can have any relationship between themselves (stereoisomers, constitutional isomers, conformational isomers, etc.).

The principle can be, basically, formulated as follows: "*if the magnitude of the rates involving the equilibrium process of A and B (k_1, k_{-1}) are much higher those the rates of the chemical reactions leading to the formation of products (k_A, k_B), then the system is under kinetic control, and the final product ratio is equal to the ratio of the product forming rate constants, equation 1, where K is the equilibrium constant (= k_1/k_2)*". On the contrary, if the rates of diffusion are lower than the rates of the chemical reaction, then the reaction is diffusion-controlled and the product distribution depends, in a complex manner, on both the relative size of the diffusion rate constants and the chemical rate constants.

$$\frac{[\mathrm{P}_A]_\infty}{[\mathrm{P}_A]_\infty} = \frac{k_A}{k_B}\frac{1}{K} \qquad (1)$$

The Acree-Curtin-Hammett ideas can be extended to settings where the reactants partition between regions of different solvent properties.[1, 16] For example, after bulk mixing of antioxidants (reactant A) in oil-in-water emulsions, they distribute between the oil, water and interfacial regions according to their polarity. However, the 16-ArN$_2^+$ chemical probe employed to determine their distribution (reactant B) does not partition because it is water insoluble due to the long alkyl chain and, at the same time, is oil insoluble because it is a cation and the reaction between 16-ArN$_2^+$ and the AOs takes place primarily in the interfacial region of the emulsion, Scheme 3.

According to Scheme 3, the reaction between 16-ArN$_2^+$ and the antioxidants may be diffusion-controlled or kinetically-controlled. Diffusion control stands when the rate of the chemical reaction is faster than the rates of flow of the antioxidants reaching the interface and the flow of products away. Alternatively, the reaction may be under kinetic control if the rate of the chemical reaction is much slower than the diffusion rates. The reaction between 16-ArN$_2^+$ and the antioxidants is said to be under "dynamic equilibrium" when diffusion is orders of magnitude faster than the rate of the chemical reaction.

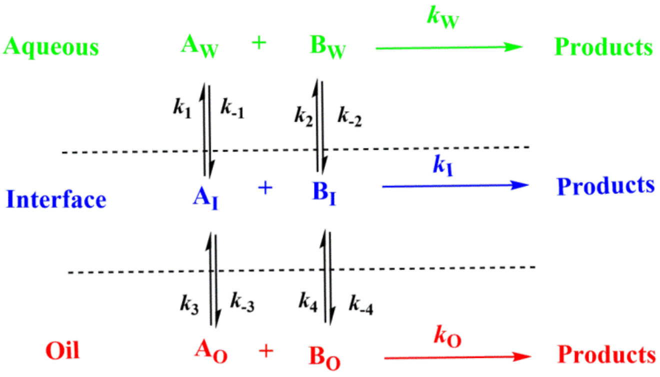


Scheme 3. Basic representation of the bimolecular reaction between the chemical probe 16-ArN$_2^+$ and an antioxidant AO that distributes between the oil, interfacial and aqueous regions. The reaction takes place exclusively in the interfacial region because 16-ArN$_2^+$ is both oil and water insoluble.

As stated by the Acree-Curtin-Hammet principle, if diffusion is much faster than the chemical reaction, then the product yields are determined by the concentration of the reactants in the interfacial region, and the observed rate constant is given by equation 2.

$$r = k_{\mathrm{I}}(\mathrm{AO_I})(16\text{-}\mathrm{ArN}_{2\mathrm{I}}^{+}) \qquad (2)$$

We note that in the case that both reactants distribute between all regions, Scheme 4, then the local concentrations in each region need to be considered and the observed rate can be expressed as the sum of the rates in each region.



Scheme 4. Basic representation of a bimolecular reaction taking place in a multiphasic system, showing the distribution of the substrate **A** and the reactant **B** between the different regions.

We, therefore, need to make sure that the dynamic equilibrium condition holds to safely use equation 2. Probably the easiest way to address this obstacle is to think in any reaction taking place in a solvent of a given viscosity. The Transition State Theory (TST) states that a bimolecular reaction between the reactants **A** and **B** is initiated when the reactants get in contact (“encounter pair”) and lead to the formation of the activated complex, that must move on to the products for the reaction to proceed, otherwise the reaction does not take place. Two limiting situations can be distinguished, A) when the reaction is under full diffusion control, i.e., when the observed rate constants, k_{obs}, of the reaction are similar to those of the diffusion of reactants, k_{D} , and B) that holds when the reaction is under *activation (or kinetic) control, that holds when* k_{obs} is equal to that of the chemical reaction, k_{chem},. For any other intermediate values, the reactions are under *partial diffusion control*.

To distinguish between those limiting conditions, we need to estimate how much slower needs to be the rate of the chemical reaction compared to the rate limiting diffusion.

Development of the model: how much slower should be the rate of the chemical reaction compared to the rates of diffusion to achieve the dynamic equilibrium condition?

Our model is based on the Smoluchowski theory for Brownian motion [17] in a viscous fluid who was first employed to interpret the rate of coagulation of uncharged, spherical, colloidal particles interacting with each other [16].

In emulsions, the oil, water and aqueous regions have different viscosities and solvent properties. To simplify the mathematical treatment, we consider that the two reactive molecules A and B are spherical having radii r_A and r_B, respectively, and if they are going to react, they first must come together in a fluid of a given viscosity (for example, that of water) with an energy enough to overcome the activation barrier. The effects of viscosity will be considered later. In practice, this means that the model assumes that:

a) the reactive molecules A and B are neutral and diffuse in water (chosen as model solvent) and have sufficient energy to react at every encounter. The effects of the activation energy E_a on the chemical reaction and the effects of viscosity on the rate of diffusion will be discussed later, once the model is set-up.

b) the observed rate does not depend on the rate at which the reactants are mixed (i.e., mixing effects are unimportant) and that reactants are uniformly distributed.

c) the orientation and steric effects are considered unimportant and therefore the estimated rate constant will be an upper limit. If either orientation or steric effects need to be considered, then the true rate constant will be a fraction of that estimated with our model; however, as we will see, the mean conclusions will still hold.

A full description of the mathematical treatment describing these two cases can be found elsewhere [10, 11, 16] and will be condensed here to show the key points.

According to the Fick´s law of diffusion of spherical molecules that moves under a gradient of concentration, the diffusive flux J of a **B** molecule towards an **A** molecule is described by equation 3, where S is the surface area given by S = 4π r_{AB}^2, D_B is the diffusion coefficient of reactant B and dc_B/dr is the concentration gradient.

$$J_B = \frac{dn_B}{dt} - D_B S \frac{dc_B}{dr} = -4\pi r_{AB}^2 D_B \frac{dc_B}{dr} \qquad (3)$$

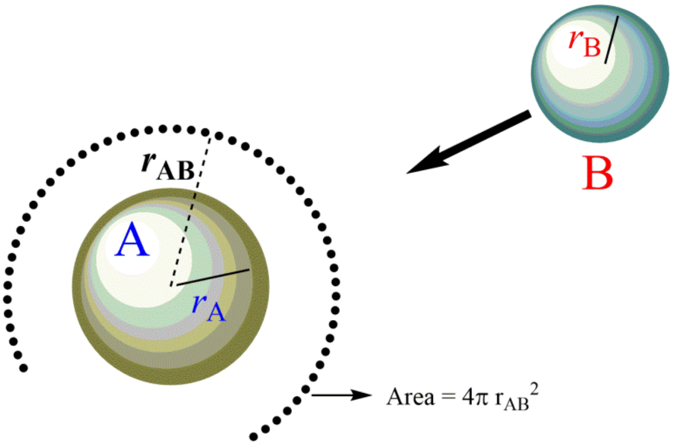


Figure 1. Diffusion of reactive molecules **A** and **B** in a bulk fluid of viscosity η. The reaction proceeds once the molecules get in contact ($r_{AB} = r_A + r_B$).

If the **B** molecule reaches the critical distance r_{AB}, Figure 1, and reacts immediately, the reaction is under diffusion control, and the concentration of **B** at r_{AB} is zero, i.e., $[\mathbf{B}]_{r(AB)} = 0$. After integration, and bearing in mind that the **A** molecules can also diffuse toward the **B** molecules, equation 4 can be derived, where D_A and D_B are the diffusion coefficients of **A** and **B**, respectively.

$$J_B = 4\pi(D_A + D_B) r_{AB} [B] \qquad (4)$$

Since we assume that there is reaction at every encounter, equation 4 stands for the rate of the reaction between **A** and **B**, equation 5, and the rate constant of diffusion is given by equation 6.

$$r = 4\pi(D_A + D_B) r_{AB} [A][B] \qquad (5)$$

$$k_D = 4\pi(D_A + D_B) r_{AB} \qquad (6)$$

Equation 6 is the plain equation for a reactive system under diffusion control. Since the reactive molecules are usually much larger in size than the solvent molecules, the Stoke´s law, equation 7, applies and the more useful approximate equations 8 can be derived.[10, 18] In equations 7-8, k_B is the Boltzmann´s constant, T is the temperature and r the hydrodynamic radius of the reactive molecules.

$$D = \frac{k_B T}{6\pi\eta r} \qquad (7)$$

$$k_D = \frac{2k_B T}{3\eta}\left(\frac{(r_A + r_B)^2}{r_A r_B}\right) \qquad (8)$$

The size of the molecules appears to have a small effect on k_D as shown by equation 8, because the ratio $(r_A + r_B)^2/ r_A r_B$ does not vary greatly with the relative size of the molecules. For instance, when $r_A = r_B$, the ratio $(r_A + r_B)^2/ r_A r_B = 4$, but if the size of one of the molecules is higher, e.g., $r_A = 2\ r_B$, the ratio is only 4.5, i.e., if the size of one of the molecule doubles, k_D only increases by ~ 11%. The relative insensitivity of k_D to the molecular size can be rationalized on the grounds of two opposite effects that roughly cancel each other: big molecules move slowly compared to the smaller ones, but at the same time increase their areas S for encounter with the other reactive molecule.[11]

If the reactive molecules would react immediately upon an encounter, the reaction is under full microscopic diffusion control and an approximate value for the rate of the reaction between neutral molecules that are can be found by employing equation 8. In water, at T = 25 ºC, the viscosity is $\eta \sim 0.9$ cP s (Table 1), and for molecules of similar size ($r_A \approx r_B$), a value of $k_D \approx 7\text{x}10^9$ dm^3 mol^{-1} s^{-1} can be estimated for the bimolecular reaction. This k_D value represents an upper limit value for diffusion-controlled reactions of neutral molecules. That is, neutral molecules cannot react faster than the rate at which the diffuse in the solvent. Obviously, if reactive ions are involved, the value is expected to be somewhat higher because the electrostatic interactions increase their diffusivity and a values of k_D ranging (3-15)x10^{10} dm^3 mol^{-1} s^{-1} have been estimated for the reaction between hydrogen ions and various anions.

When the chemical process is not fast enough to remove the reactive molecules completely as they reach the critical distance r_{AB}, then the concentration of **B** molecules at a distance r_{AB} is not zero and the overall reaction is the resultant of a reaction in series and therefore the observed rate constant, k_{obs}, depends on the relative values of k_D and k_{chem}, equation 9. Note that equation 9 reduces to equation 6 when $k_{chem} >>> 4\pi(D_A+D_B)r_{AB}$, meanwhile when $k_{chem} <<< 4\pi(D_A+D_B)r_{AB}$, $k_{obs} = k_{chem}$ (i.e., no diffusion control).

$$k_{obs} = \frac{k_{chem}}{1 + \dfrac{k_{chem}}{4\pi(D_A + D_B)r_{AB}}} = \frac{k_{chem}}{1 + \dfrac{k_{chem}}{k_D}} \qquad (9)$$

An analyses of the variation of k_{obs} with k_{chem} for a given value of k_D, equation 9, allows us to predict if the observed rate constant is, or is not, affected by the diffusion of reactants and in what extent it is. For the purpose, we can plot the variation of k_{obs} with k_{chem} for a given upper limit value of k_D.

Figure 2 displays the variation of k_{obs} with log(k_{chem}) for a bimolecular reactions in aqueous solution after setting a value for $k_D = 7\text{x}10^9$ dm^3 mol^{-1} s^{-1} (T = 25 ºC). As can be observed in Figure 2, diffusion controlled reactions ($k_{obs} \approx k_D$) are those whose rate of the chemical reaction is $k_{chem} \geq 10^{12}$ M^{-1} s^{-1}. For kinetically-controlled reactions, $k_{obs} \approx k_{chem}$, and k_{chem} should be $k_{chem} < 10^9$ dm^3 mol^{-1} s^{-1}. For intermediate k_{chem} values ($10^9 - 10^{11}$ dm^3 mol^{-1} s^{-1}), the reaction is controlled by both diffusion and activation in a different extent, depending on the particular k_{chem} value. For example, when $k_{chem} \sim k_D$ (= 7x10^9 dm^3 mol^{-1} s^{-1}), $k_{obs} \approx 3\text{x}10^9$, i.e., approximately 50% of diffusion control.

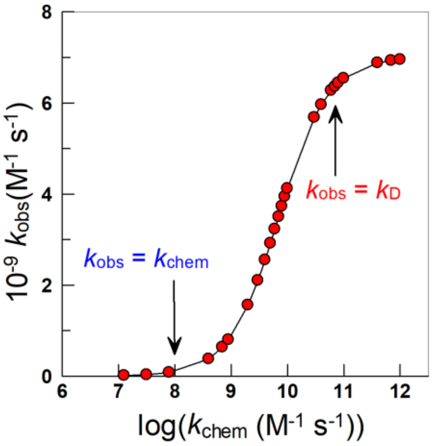


Figure 2. Changes in k_{obs} as a function of log(k_{chem}) for a bimolecular reaction in aqueous solution, according to equation 9. The rate of diffusion of reactants $k_D = 7\text{x}10^9$ M^{-1}s^{-1} has been estimated by employing equation 8 with η = 0.9 cP s at T = 25 ºC (see text for details).

Thus, it seems reasonable to assume that, after the bulk mixing of the reactants, the system remains under dynamic equilibrium because a vast majority of thermal reactions in solution are slow, minutes to hours to days, in the time scale of molecular diffusion, which is ~ 10^{-9} s. We however, still want to set the limits of what can be considered "slow" or "fast" for a thermal reaction and, for the purpose, will analyze the effects of the viscosity of the solvent and the activation energy of the chemical reaction on the relative k_D and k_{chem} values.

EFFECTS OF THE VISCOSITY OF THE SOLVENT AND THE ACTIVATION ENERGY OF THE CHEMICAL REATION

The analysis above was done for bimolecular reactions in aqueous solution assuming that the reaction proceeds immediately upon an encounter. We now may wonder what happen in the other regions of the emulsion, which have higher viscosity compared to that of water, and what would happen if the molecules do not have enough energy to overcome the activation barrier, i.e., we will analyze how the viscosity η of the solvent and the activation energy E_a of the chemical reaction affect our previous results.

If the reaction takes place in a fluid other than water (for example, the oil or interfacial region of the emulsions), then the rate of diffusion k_D is lowered because it depends on the viscosity. When considering, for instance, olive oil as a representative food oil and by employing the viscosity value given in Table 1, the upper limit rate value for the diffusion of reactive molecules is, according to equation 8, $k_D \approx 1.75\text{x}10^8$ dm^3 mol^{-1} s^{-1}

Table 1. List of some common food fluids and their estimated viscosities at 25 ºC unless otherwise indicated. The viscosity of food emulsions vary according to their particular applications, but they usually range $\eta_{emulsion} = 10^2 - 10^4\ \eta_{water}$. Data compiled from different sources.[19, 20]

Food Fluid	η (cP s)	Food Fluid	η (cP s)
Water	1	Sesame oil (35 ºC)	41
Milk (18 ºC)	2.0	Soybean oil (30 ºC)	41
Vinegar	12-15	Palm oil (37 ºC)	43
Oleic acid	40	Sunflower	49
Olive oil (30 ºC)	40	Corn oil	50-100

Thus, by setting this value in equation 9, we can plot the variation of k_{obs} with k_{chem} to estimate the relative contributions of k_{chem} and k_D to k_{obs} , Figure 3. In this case, for full diffusion controlled ($k_{obs} \approx k_D$) reactions in olive oil, k_{chem} should be greater than $\approx 10^9$ M^{-1} s^{-1}. For activation-controlled reactions, $k_{obs} = k_{chem} < 10^6$ dm^3 mol^{-1} s^{-1}.

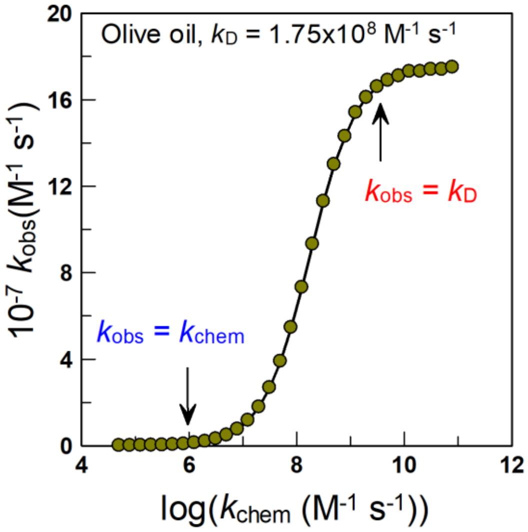


Figure 3. Changes in k_{obs} for reactions of neutral molecules in olive oil as a function of k_{chem} values according to equation 9. The viscosity of olive oil is ~ 40 times higher than that of water at T = 25 ºC and, according to equation 8, the rate of diffusion of reactants has been set as $k_D = 1.75\text{x}10^8$ M^{-1}s^{-1}.

As indicated before, the above analysis was carried out by assuming that the reactive molecules react immediately when they collide. However, when molecules encounter each other, they may not need to react immediately because of the activation energy barriers but also due to geometrical constrains, and thus the values determined before are only upper limits. We will analyze now which is the role of the activation energy of the chemical reaction that, according to the TST theory, largely affects the rate of the chemical reaction. In fact, without activation energy barriers, chemical reactions would be so fast that, for example, foods would spoilage immediately because of their chemical unstability. Table 2 shows activation energy values for bimolecular reactions in aqueous solution (T = 25 ºC) and the corresponding rate constants. The names of particular reactions are not given on purpose because the aim here is to illustrate the effect of E_a on k_{chem}, no matter the type of reaction.

Comparison of the k_{chem} values in aqueous solution, Table 2, with the diffusion rate values estimated in Figures 2-3 indicates that for any chemical reaction with E_a higher than ~ 25 KJ mol^{-1}, $k_{obs} = k_{chem}$, i.e., for most thermally activated reactions that may take pace in emulsions, the reactants are distributed according to their solubilities in the different regions of the emulsion before they react, and the rates of diffusion of the reactants are much higher than those of the chemical reactions and the system will be under dynamic equilibrium.

Table 2. Typical values of the rate constants obtained for bimolecular reactions in aqueous solution at T = 25 ºC as a function of their E_a values. Data from Van Boeckel.[11, 12]

E_a (kJ mol^{-1})	k_{chem} (dm^3 mol^{-1} s^{-1})
~ 0	~ 10^{10}
< 25	10^9 - 10^{10}
50	10^5
100	10^{-4}
> 200	< 10^{-22}

We note that for extremely rapid reactions, for example radical reactions where there is short-lived radicals, or photochemical reactions where excited-state molecules may play a significant role, the reactions may be diffusion-controlled, as their activation energies are < 10 kJ mol^{-1} , and the rate of the reaction depends on the dynamics of the fast processes (nanoseconds to microsecond) in the aggregate such as the changes in solvation of the probe, proton transfer or monomer, solute or counterion entry and exit from the aggregates. Some of these reactions, for instance the bimolecular quenching of the excited state of the probes by other molecules present in the medium, have been used to determine the mobilities of molecules, to estimate local microviscosities and encounter probabilities in the medium and to investigate ultrafast proton transfer reactions.[5]

CONCLUSIONS

We have described a simple mathematical model, grounded on simple diffusion laws, that permits an analyses of the conditions required to distinguish between kinetically-controlled or diffusion-controlled reactive systems based on molecular and solvent properties. On view of the order of magnitude of most thermally activated chemical reactions, we can conclude that in fluid oil-in-water emulsions and their rates are much smaller (10^7 – 10^{10} fold) than the diffusion of the reactants, and the system is under dynamic equilibrium. This conclusion is very important for a safe use of chemical reactions to probe and study the effects of compartimentalized systems such as emulsions to get information on the composition and locations of molecules of interest within the system. This also implies that the distribution of reactants between the different regions depends only on their relative solubility in each region and not on the size or shape of the droplet provided that the emulsions are physically stable for times longer than the kinetic experiment. The importance is enhanced when taking into account that physical methods such as light-scattering or microscopy are not responsive to the type of molecules present in the investigated system and therefore do not offer any information on their composition.

However, even if the dynamic equilibrium condition applies, unraveling reaction mechanisms such as that depicted in Scheme 4 is extremely complex because of very intricate kinetic equations obtained as a result of the huge amount of parameters needed to fully depict the partitioning of reactants and because the rates constants of the reactions in each region can vary by several orders of magnitude because the solvent properties of each region are totally different.

Simplifications to Scheme 4 can be made by a judiciously selection of the physicochemical properties of the reactants and the experimental conditions. The pseudophase kinetic method employed to calculate the distributions of antioxidants in unbroken emulsions works, among others, because the chemical probe chosen, 16-ArN_2^+, both water and oil insoluble and its reactive moiety is located in the interfacial region of the emulsion, where reacts with the antioxidant. Therefore, the complex kinetic mechanism shown in Scheme 4 can be simplified to that in Scheme 3 because the concentration of 16-ArN_2^+ in the oil or aqueous regions is negligible and the chemical reaction with the antioxidants takes place exclusively in the interfacial region.

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