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Retarded transfers of an emulsified two-component oil phase

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We study oil evaporation from oil in water emulsions, whose oil phases are mixtures of two alkanes of different solubilities in water. The aqueous phase is a colloidal clay suspension that exhibits a yield stress, in which the oil droplets are immobilized. A surfactant-free emulsion is thus formed, providing a convenient model system in which the oil transfer solely occurs through the aqueous phase. When the emulsion is left in contact with the atmosphere, oil evaporation results in the formation of a droplet-free region in the emulsion, and that region grows diffusively with time. We show that the transfer of the more soluble alkane is dramatically retarded when the mixture ratio of the less soluble alkane is increased, as a consequence of entropy loss associated with oil demixing. Using a simple transfer model, which captures well the experimental trends, we study the alkane concentrations both within the oil droplets and within the aqueous phase of the emulsion. We report overshoots in the concentration profiles of the less soluble alkane both in the emulsion and in the droplets, and explain their formation using a qualitative argument.

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I. INTRODUCTION

Emulsions and foams are examples of kinetically stable multiphase systems. Long-term stability is needed in many applications involving these systems. For instance, stable monomer emulsions are required to prepare polymer dispersions [1]; stability is also a concern for foams used in the food industry [2]. One of the destabilizing mechanisms results from the transfer of the emulsified (or gas) phase in the continuous phase. In the case of emulsions, such a mechanism is known as Ostwald ripening and is generally responsible for the increase in the polydispersity of the droplets of the dispersed phase [3]. It is now well known that one method to retard the Ostwald ripening process consists of adding a compound that is miscible with the dispersed phase. If the two compounds of the dispersed phase have very different solubilities in the continuous phase, entropic effects result in a decrease of the rate of transfer of the more soluble compound to the continuous phase [4,5]. The addition of a less soluble compound thus has a stabilizing effect for the dispersion of the more soluble one, and has proved to be very efficient in systems in which Ostwald ripening is a major concern, such as nanoemulsions [6].

Characterizing the resulting kinetics stabilization can, however, be difficult because other destabilizing mechanisms—such as droplet coalescence—may concomitantly occur. The presence of other compounds added to stabilize the emulsions, such as solid particles, is also likely to induce effects that interfere with the mechanisms at stake [7]. Those difficulties can be avoided by using model oil in water emulsions, which are free from any other compounds, and in which the only possible oil transfer occurs through the aqueous phase. Such emulsions can be obtained by mixing oil with a yield stress aging fluid, an aqueous suspension of nanometric clay particles, Laponite [8]. When dispersed in water, the clay

particles can form gels that present physical aging: After a strong shear has been applied to them, they evolve from low viscosity fluids to pastes with large apparent yield stress within several minutes [9]. If mixed with oil, they form oil-in-water emulsions in which the oil droplets remain mechanically immobilized as the aqueous phase recovers its yield stress. The coalescence and creaming of the oil droplets are therefore avoided. The stabilization is of purely mechanical origin and does not require any added compound; in particular, it does not involve adsorption of the clay particles at the oil-water interface [8].

We have shown in a previous work that if an emulsion of a volatile oil in a Laponite suspension is left in contact with the atmosphere, the evaporation proceeds in an original fashion: An oil-droplet-free region appears in the emulsion in contact with the atmosphere, and a very sharp front separates that region from the emulsion, as illustrated in Fig. 1(a) [8]. The evaporation is limited by the diffusion of dissolved oil through that region. We have shown that the size of the droplet-free region grows diffusively with time and we have successfully modeled the oil transfers at stake; we have, in particular, determined the effective diffusion coefficient characterizing the growth of the droplet-free region. In addition, we have explained the formation of a self-sharpening front between the emulsion and the droplet-free zone, that the self-sharpening process is associated with the decrease of the front diffusion coefficient with the oil volume fraction. Since it is the transfer through the aqueous phase, and not through the emulsion-atmosphere interface or within the atmosphere, that controls the evaporation rate, the emulsions we consider constitute appropriate systems to easily study oil transfers.

Herein we consider the case of an emulsified phase which is a mixture of two different oils; we show that evaporation of the oil phase then proceeds similarly as in the case of a single oil emulsion. We have focused on oil mixtures in which the oil that has the larger solubility in the aqueous phase also has a larger molecular diffusion coefficient in that

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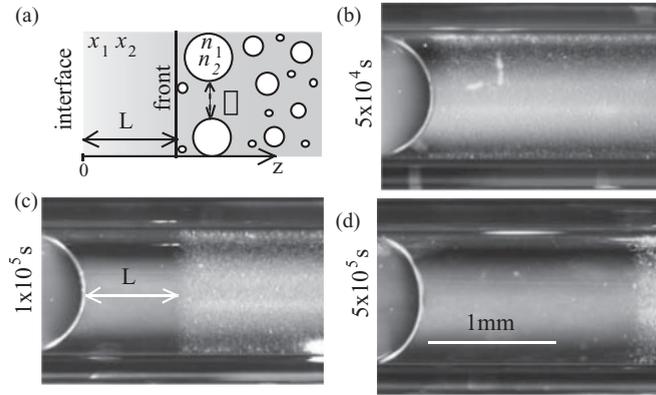


FIG. 1. (a) Schematic representation of the emulsion as it evaporates, and introduction of the notations used: A droplet-free region, of length L , develops between the interface with the atmosphere (taken as the origin of spatial coordinate z) and the emulsion. x_1 and x_2 are the concentrations (in mol/mol) of each alkane dissolved in the aqueous phase; n_1 and n_2 are the molar quantities of each alkane in a droplet. The droplets' mean separation distance is denoted as ξ . (b), (c), and (d) show photographs of an emulsion at successive times of the evaporation process. In (b) a small droplet-free region has developed from the emulsion-atmosphere interface (meniscus on the left-hand side); in (c) and (d) that region has grown. The length of the droplet-free region L is measured along the capillary tube centerline.

phase. We report that the rate of transfer of the more soluble oil can then be substantially decreased. We have experimentally studied the growth of the droplet-free region that forms in those emulsions in contact with the atmosphere. The effective diffusion coefficient that characterizes that growth varies with the mixture ratio of the emulsified oils, as well as with the total oil volume fraction. Using a simple transfer model, we successfully describe the variations of the effective diffusion coefficient. In addition, we have numerically studied the variations in the oil concentrations both within the emulsified droplets and in the aqueous phase. We show that for the more soluble alkane the concentration profiles quickly become self-similar, whereas the less soluble alkane slowly accumulates in the vicinity of the front in both the aqueous phase and the droplets.

II. MATERIALS AND METHODS

The aqueous phase is a Laponite suspension of concentration 2.5% wt/wt. It is prepared by mixing Laponite powder

(Rockwood, quality RD) with de-ionized water whose pH is set to 10 by adding sodium hydroxide (concentration $10^{-4}M$). The suspensions are stirred for 1 week and further kept at rest for 1 week more in order to ensure full hydration of the clay platelets. Oil is then emulsified by ultrasonication of the Laponite and oil mixture. After emulsification, the Laponite recovers its yield stress and oil droplets of diameter close to $10 \mu m$ are immobilized in the Laponite; they therefore do not further cream nor coalesce. We have shown in a previous work that the clay particles do not adsorb at the water-oil interfaces, therefore the emulsions are not Pickering emulsions [8].

We have used linear alkanes as oil phases: Pentane is mixed with either hexane or heptane. The physical data of the different alkanes is gathered in Table I; the solubilities of hexane and heptane in an aqueous phase are, respectively, about 5 times and 20 times smaller than that of pentane. Reference experiments with emulsions of single alkanes have been carried out. For emulsions of oil mixtures, the total volume fraction in alkane ranges from 0.3% to 10% in the case of heptane-pentane mixtures, whereas it has been fixed at 2% for hexane-pentane mixtures. Known volumes of alkanes are mixed, and the resulting mass variation of the emulsion is measured, allowing us to determine the effective oil volume fraction within $5 \times 10^{-3}\%$. After a 12-h rest, the emulsion is made to fill a glass capillary tube (inner diam 1 mm). The tube is further immersed in silicon oil. As the alkanes are mutually miscible with silicon oil, the former is not expected to modify their evaporation process. We have checked that the evaporation process is actually identical within an emulsion in contact with the atmosphere or with silicon oil. The solubility of water in silicon oil being, on the contrary, very small, the silicon oil bath strongly limits the evaporation of water over the very long times needed for some experiments (up to 2 weeks). The tube is left at room temperature ($20 \text{ }^\circ\text{C}$) and is imaged using a binocular microscope.

III. EXPERIMENTAL RESULTS

As evaporation proceeds, a droplet-free region forms in the emulsion from the silicon oil-emulsion interface (also named atmosphere-emulsion interface in the following) and further develops, as shown in the photographs of Fig. 1.

As in the case of single alkane emulsions [8], the front separating the droplet-free region from the alkane mixture

TABLE I. Values of the useful thermodynamical properties of the used alkanes.

	Pentane	Hexane	Heptane
Molecular diffusion coefficient D_m (m^2/s) ^a	6×10^{-9}	2×10^{-9}	1.3×10^{-9}
Solubility in water x^* (mol/mol) ^b	1×10^{-5}	2.05×10^{-6}	4.56×10^{-7}
Density ρ (kg/m^3) ^c	0.630×10^3	0.659×10^3	0.683×10^3

^aReference [8].

^bReference [10].

^cReference [11].

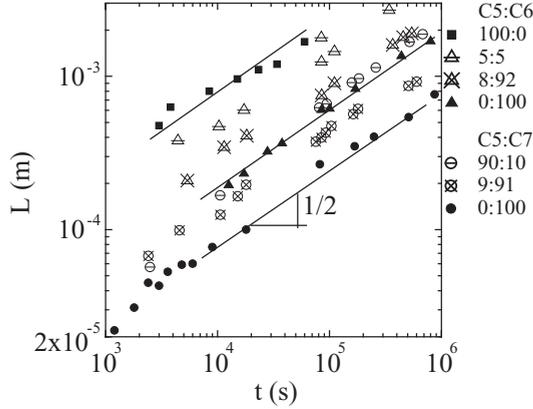


FIG. 2. Length of the droplet-free region as a function of time for single alkane emulsions (full symbols), as well as for pentane-hexane (triangles) and pentane-heptane (circles) emulsions with different mixture ratios. In each case, the total oil volume fraction in the emulsion is 2%. The full lines represent diffusive laws with effective diffusion coefficient for single alkane emulsions of, respectively, pentane, hexane, and heptane: $D = 3.2 \times 10^{-11} \text{ m}^2/\text{s}$, $D = 2.0 \times 10^{-12} \text{ m}^2/\text{s}$, and $D = 3.2 \times 10^{-13} \text{ m}^2/\text{s}$.

emulsion is very sharp. As the silicon oil-emulsion interface is curved, the length of the droplet-free region L is defined as the distance between the front and the meniscus along the capillary centerline (see Fig. 1). The measured variations of L as a function of time, for a pentane-hexane mixture emulsion, are shown in Fig. 2. After a transitory regime, L grows with the square root of time following $L = \sqrt{2Dt}$, whatever the composition of the oil phase.

The evaporation of single alkane emulsions has been detailed in a previous work [8]. Briefly, as a consequence of the very small solubility of alkanes in the aqueous phase, the rate-limiting step of alkane evaporation is the diffusion of dissolved alkane through the droplet-free region. The more droplets there are in the emulsion, the longer it takes to transfer the alkane to the atmosphere, and thus the slower is the growth of the droplet-free region. As a result, the diffusion coefficient D characterizing the growth of the droplet-free region is several orders of magnitude smaller than the molecular diffusion coefficient of the alkane, D_m ; we have shown it is given by the following:

$$D = \frac{D_m x^* \nu_{Cn}}{\nu_w \phi}, \quad (1)$$

where x^* is the alkane solubility in the aqueous phase, ν_{Cn} and ν_w are, respectively, the molar volumes of alkane and water, and ϕ is the oil volume fraction. As the evaporation is not limited by diffusion of the alkane gas in the atmosphere, the effective diffusion coefficient is independent of quantities such as the alkane vapor pressure.

In the case of the alkane mixtures we consider herein, the effective diffusion coefficient characterizing the growth of the droplet-free region analogously varies with the total oil volume fraction; in addition, it depends on the mixture ratio of the oil phase. The increase of D with the (more soluble) pentane volume ratio we have measured in

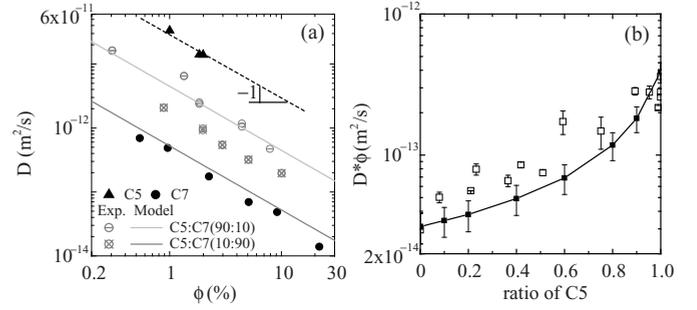


FIG. 3. (a) Effective diffusion coefficient D characterizing the growth of the droplet-free region as a function of the total oil volume fraction ϕ for pentane, heptane, and two pentane-heptane mixtures; the dotted line represents the computed value of D for emulsions of pentane alone, whereas the solid lines represent the computed values of D for the two different mixtures. (b) Product of D and ϕ as a function of the mixture ratio of pentane for pentane-hexane mixtures. The experimental data (empty squares) are shown together with the computed values (filled squares and line). The experimental error bars represent the data dispersion over three different experiments, and the ones for the computed values result from the uncertainties on the molecular diffusion coefficients (see Table I).

pentane-heptane [Fig. 3(a)] and pentane-hexane [Fig. 3(b)] mixtures is illustrated in Fig. 3. As the pentane ratio increases, the diffusion coefficient monotonically increases from its value for heptane (respectively, hexane) alone to pentane alone. The less soluble the added compound, the more spectacular is the retarding effect on the evaporation. For instance, to divide by 5 the diffusion coefficient characterizing the evaporation, one needs to add to pentane either 50% of hexane or only 10% of heptane. In addition, we have found that the front diffusion coefficient scales as $1/\phi$, where ϕ is the total oil volume fraction. That scaling is illustrated in Fig. 3(a) for a pentane-heptane mixture; it is similar to the one found with single alkane emulsions [8]. In the case of emulsions of a single alkane, the decrease with the volume fraction of D is at the origin of the formation of a sharp front between the emulsion and the droplet-free region: An oil droplet left alone in the droplet-free region would empty out faster than a droplet in the emulsion. For a two-component oil phase, the same observed scaling of D with the total volume fraction is evidence for the existence of a unique front for both alkanes. We will show below that this result is confirmed by numerical calculations. The scaling of D with ϕ has also been used in order to compare the data from different experiments in which the oil volume fraction may differ slightly, owing to the uncertainties in the preparation of the emulsions. It is thus the variations of the product $D\phi$ as a function of the mixture ratio that are displayed in Fig. 3(b).

IV. ALKANE TRANSFER MODEL

We describe the alkane transfers in the frame of a one-dimensional model. We denote as z the coordinate whose origin lies at the emulsion-atmosphere interface (see Fig. 1).

We denote as $x_i(z,t)$ ($i=1,2$) the molar fraction, as a function of both time and space, of the alkane i dissolved in the aqueous phase. We model the droplets in the emulsion by the quantity $n_i(z,t)$ ($i=1,2$) that represents the number of moles of alkane i within a droplet located at coordinate z and time t .

First, let us consider an oil droplet of radius R , containing n_i moles of each alkane i , and in equilibrium with the aqueous phase. We denote as x_i^{equ} the molar fraction of dissolved alkane i in the aqueous phase at equilibrium. Equating the chemical potentials of alkane i in the droplet and in the aqueous phase yields

$$x_i^{\text{equ}} = x_i^* \frac{n_i}{n_i + n_j} \exp\left(\frac{R_{ci}}{R}\right), \quad (2)$$

in which the exponential term reflects the capillary pressure due to alkane i in the droplet.

The capillary radius is given by $R_{ci} = \frac{2\gamma_i v_{mi}}{R_{PG} T}$, where γ_i is the interfacial tension with water of alkane i , v_{mi} its molar volume, R_{PG} the ideal gas constant, and T the absolute temperature. $R_{ci} < 5$ nm for all the alkanes considered herein; the exponential term therefore remains close to 1, and $x_i^{\text{equ}} \approx x_i^* n_i / (n_i + n_j)$, except for nanometric droplets.

Let us now consider the oil transfers within the emulsion that is in contact with the atmosphere at $z=0$. In the droplet-free region, i.e., for $0 \leq z < L$, the alkane molar fractions in the aqueous phase, x_1 and x_2 , obey simple diffusion equations:

$$\frac{\partial x_i}{\partial t} = D_{mi} \frac{\partial^2 x_i}{\partial z^2}, \quad (3)$$

with the index $i=1,2$ referring to the considered alkane, D_{mi} being the molecular diffusion coefficient of alkane i .

Within the aqueous phase containing oil droplets, i.e., for $z \geq L$, a similar diffusion process occurs. However, if the concentration of dissolved alkane i is smaller (respectively, larger) than the equilibrium value x_i^{equ} , a flux of alkane i from the droplet toward the aqueous phase (respectively, from the aqueous phase toward the droplet) occurs. The time derivative of x_i therefore writes

$$\frac{\partial x_i}{\partial t} = D_{mi} \frac{\partial^2 x_i}{\partial z^2} - \frac{D_{mi}}{\xi^2} (x_i - x_i^{\text{equ}}). \quad (4)$$

The flux from or toward the droplet is related to the variations of the number of moles of alkane i in the droplet:

$$\alpha \frac{\partial n_i}{\partial t} = \frac{D_{mi}}{\xi^2} (x_i - x_i^{\text{equ}}), \quad (5)$$

where α depends on the water molar weight M_w and density ρ_w , as well as on the distance ξ : $\alpha = M_w / (\rho_w \xi^3)$.

At $t=0$, the emulsion is supposed to be homogeneous and monodisperse, with droplets of radius $R = 5 \mu\text{m}$, whatever the value of $z \geq L$. The initial values $n_1(z,t=0)$ and $n_2(z,t=0)$ are computed using the value of R , together with the respective values of liquid alkane densities and the mixture ratio. The surface-to-surface distance between droplets is given by the initial alkane volume fraction of the emulsion, ϕ , and by R following $\xi = 2R(\phi^{-1/3} - 1)$. In the aqueous

phase, we assume that the initial values of the concentrations in dissolved alkanes, $x_1(z,t=0)$ and $x_2(z,t=0)$, are the equilibrium values; they are thus computed using Eq. (2). In practice, alkane dissolution in the aqueous phase is a fast process compared to the evaporation process; the assumption made using Eq. (2) for the initial values is therefore justified. The variations of $n_i(z,t)$ and $x_i(z,t)$ are computed iteratively using Eqs. (4) and (5). The values of time and space steps chosen for the computation are, respectively, 7.5 ms and 10 μm .

At each iteration, the computed values for $n_i(z,t)$ that are negative are set at zero, and the larger z value at which $n_i(z,t) = 0$ gives the position of the front between the emulsion and the droplet-free region. In line with the experimental findings, we have found that the front location is the same for both alkanes. In addition, the droplet-free region grows diffusively in time after a transitory regime. The duration of the transitory regime depends on both the nature of the oil phase and its mixture ratio. We have systematically fitted the numerical data in the diffusive regime in order to obtain the diffusion coefficients characterizing the growth of the droplet-free region. The coefficients are shown in Fig. 3 as a function of the oil volume fraction for a pentane-heptane mixture [Fig. 3(a)], as well as a function of the mixture ratio for a pentane-hexane mixture [Fig. 3(b)]. The numerical data well describe the experimental variations, although they slightly underestimate the diffusion coefficient. The error bars of the experimental data in Fig. 3(b) correspond to the experimental dispersion found for three different experiments made in parallel. The error bars on the computed values of D result from the uncertainties on the molecular diffusion coefficients whose values are given in Table I. The discrepancy between experimental and numerical data is larger when the ratio of the more soluble alkane is small, showing the limits of our description based on a continuous medium in those conditions.

Figure 4 shows the computed number of moles of alkane i in a droplet, n_i , and of the concentration of alkane i dissolved in the aqueous phase, x_i , as a function of the parameter $u = z/\sqrt{t}$, and at different times in an emulsion whose oil phase is a mixture of pentane (denoted as alkane 1) and hexane (denoted as alkane 2). The data for two different mixture ratios are represented in Fig. 4; the pentane ratio is, respectively, 90% on the left-hand side of Fig. 4 and 50% on the right-hand side. The adopted representation evidences that, for the more soluble oil (pentane), the concentration profiles, in the droplets as well as in the aqueous phase, quickly become self-similar. Moreover, those profiles grow monotonically with the distance from the interface with the atmosphere or, as represented in Fig. 4, with parameter $u = z/\sqrt{t}$. The concentration profiles of the less soluble alkane, either within the droplets or in the aqueous phase, are on the contrary not monotonic: In the emulsion close to the front, they exhibit overshoots.

The existence of a maximum in the concentration profiles of the less soluble (and also less mobile) compound results from the faster diffusion of molecules of the other (more soluble) compound toward the interface with the atmosphere, which leads to an increase in the concentration of the dissolved less soluble alkane. The maximum exhibited by the spatial variations of x_2 can be predicted using a simple argument:

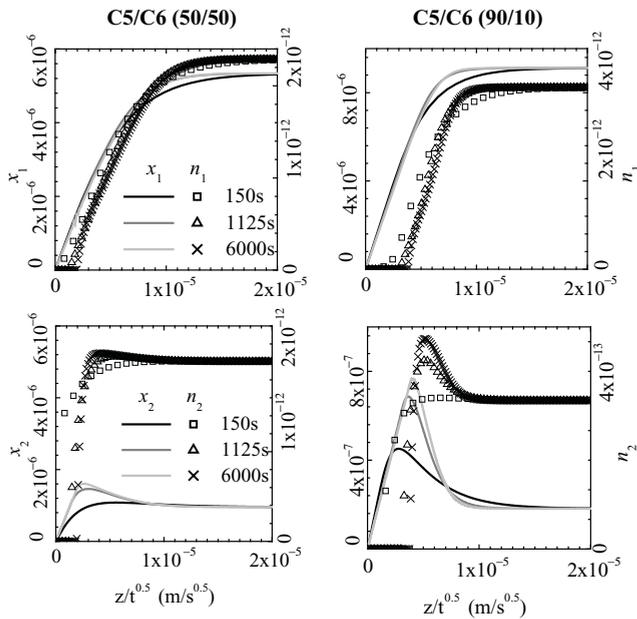


FIG. 4. Alkane concentration profiles in the oil droplets (number of moles, n_i , right axes) and dissolved in the aqueous phase (x_i in mol/mol, left-hand axes), as a function of the parameter $u = z/\sqrt{t}$. The graphs are for two different pentane-hexane mixtures, with volume ratios of pentane, respectively, of 50% (graphs on the left-hand side) and 90% (graphs on the right-hand side). The index “1” refers to pentane (top graphs) and the index “2” refers to hexane (bottom graphs). In each case, the curves obtained at three different times are plotted.

Beyond the front, i.e., within the emulsion, the concentrations in dissolved alkane are close to their equilibrium values following Eq. (2): $x_i \approx x_i^* n_i / (n_i + n_j)$. Using the relation between the molar quantities $n_1 / (n_1 + n_2) + n_2 / (n_1 + n_2) = 1$, yields the following relation between the derivatives of the concentrations in dissolved alkane:

$$x_2^* \frac{dx_1}{du} = -x_1^* \frac{dx_2}{du}. \quad (6)$$

Within the emulsion, the derivatives of the concentration of dissolved alkanes must therefore have opposite signs. That relation is indeed well verified far away from the front where $dx_1/du = dx_2/du = 0$. Closer to the front, the concentration in dissolved pentane x_1 increases with u . According to Eq. (6), the increase of x_1 must be associated with a decrease in x_2 , the concentration of dissolved hexane. Because in the droplet-free zone x_2 grows with u , if it decreases in the emulsion then it must exhibit a maximum, whose location roughly coincides with the front. As illustrated in Fig. 4, we observe such a maximum in the computed concentration profiles, whatever the mixture ratio.

The number of moles of hexane in the droplets has a maximum as well. It results from the excess concentration in dissolved hexane that leads to a flux of hexane molecules toward the droplets. More quantitatively, the equation describing the coupling between the variations of the concentrations of dissolved alkane and the number of moles within a droplet is inferred from Eqs. (4) and (5); if written according to parameter

$u = z/\sqrt{t}$, it yields

$$\alpha \frac{dn_i}{du} = -\frac{2D_{mi}}{u} \frac{\partial^2 x_i}{\partial u^2} - \frac{\partial x_i}{\partial u}. \quad (7)$$

Far from the front in the emulsion, all the terms of Eq. (7) are zero. In the region of the emulsion close to the front, however, hexane transfers mostly occur between the droplets and the aqueous phase; the term $\partial x_i / \partial u$ in Eq. (7) is therefore small compared to the other terms, and the derivative of n_2 is therefore proportional to the second derivative of x_2 . The curves for n_2 therefore exhibit a maximum that coincides with the inflection point of x_2 , in line with the computed data of Fig. 4.

In the region of the emulsion close to the front, the less soluble alkane therefore accumulates both in the droplets and in the aqueous phase. The importance of that effect indeed depends on the mixture ratio of the alkane mixture: Increasing the ratio of the more soluble alkane results in enhancing the concentration gradients of the less soluble alkane in that region, as appears from Fig. 4.

In summary, the more soluble alkane quickly migrates toward the emulsion-atmosphere interface to evaporate. As a consequence, the less soluble alkane is trapped in the droplets located in the vicinity of the droplet-free region. The relative concentration of the less soluble alkane thus increases, generating a gradient that leads to a migration of the less soluble alkane both forwards and backwards. Because of the accumulation of the less soluble alkane in the droplets, the chemical potential of the more soluble alkane decreases. The accumulation of the less soluble alkane thus slows down the migration of the more soluble alkane. As a result of these interplays, a stationary regime is reached—according to the reduced variable $u = z/\sqrt{t}$ —with a maximum in the concentration of the less soluble alkane at the front.

In conclusion, we have studied the evaporation of alkane mixtures emulsified in aqueous yield stress fluids. Those emulsions provide model systems for studying oil transfers independently from other processes, and our study more generally aims at understanding the complex transfers occurring in multicomponent systems. The evaporation results in the formation of a droplet-free region in the emulsion, starting from the interface with the atmosphere and growing diffusively with time. The diffusion of the dissolved alkanes through that region is the rate-limiting step of the evaporation process. As a result, the effective diffusion coefficient characterizing the growth of the droplet-free region depends on the alkane solubilities and diffusion coefficients, as well as on their total volume fraction and mixture ratio. We have shown that adding a less soluble alkane strongly retards the transfer of the more soluble alkane, and we have discussed the experimental data in the light of a simple transfer model. Using that model, we have moreover studied the concentration profiles of both alkanes. We have in particular demonstrated that the concentration profiles of the less soluble compound exhibit overshoots in both the aqueous phase and the droplets, and we have explained that result using a simple argument. Those findings could be of relevance for other multicomponent systems, in which the existence of regions depleted in dispersed compounds may induce the formation of large concentration gradients of the less soluble compound.

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