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RAPID COMMUNICATION

Kinetics of transport of benzoic acid in emulsions

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The rate of interphase transport of benzoic acid in sunflower oil-in-water emulsions containing SDS, Tween-80 and whey protein as surfactants was measured by a continuous flow kinetic technique. The approach allowed concentration–time data, on a millisecond timescale, to be obtained. These confirmed that the transport occurs on this timescale but the apparent size of the oil droplets was substantially greater than their actual size, interpreted as a thick diffusion layer of aqueous solvent surrounding each droplet.

INTRODUCTION

Low-molecular-weight organic food components such as flavour volatiles and preservatives owe their functional behaviour to their non-polar character. They often show significant solubility in both the aqueous and oil phases of foods and in oil–water model systems, e.g. emulsions. In some situations, the oil phase provides a better environment than the aqueous phase for food components to react with each other; transfer of reactants from an aqueous phase to an oil phase can cause an increase in rate of reaction (Massey *et al.*, 1979). On the other hand, when one reactant is ionic and the other non-ionic, the addition of oil is expected to reduce the rate of reaction in the aqueous phase by effectively separating the reactants. The rate of interphase transport may, or may not, control the rates of such reactions.

The sensory properties of flavour volatiles depend on their activity (in the chemical sense) in the aqueous phase, but the many stages of food formulation and preparation, and finally ingestion involve the mixing and dilution of dispersed food components. The rate of equilibration of flavour volatiles between aqueous and non-aqueous phases is relevant to the perceived quality of such foods.

Wedzicha (1988) estimated that, for a diffusion coefficient of a solute in oil of 5×10^{-10} m^2 s^{-1}, the transport from oil droplets in an emulsion occurs on a timescale of milliseconds. A number of different approaches have been used to measure such transport. The rate of interphase transport in stirred bulk oil and water systems (Waterbeemd *et al.*, 1981) is controlled mainly by the movement of the solute to and from the interface. Any measurement which is made on the timescale of seconds, or longer, is likely to have been limited by this diffusion process. Transport behaviour in the diffusion layer close to the oil–water interface can be studied by varying the thickness of this layer by means of the rotating disc approach (Albery *et al.*, 1976; Guy *et al.*, 1984), originally developed to study diffusion close to electrode surfaces. A specific interest in the study of interphase transport is to be able to extract, from such kinetic data, information regarding the permeability to solute molecules of any surfactant layer adsorbed at the oil–water interface. In order to acquire appropriate kinetic data it is necessary to investigate solute transport at such rates that the transport process through the interfacial layer becomes rate-limiting. This could be achieved by reducing the distance for the solute to travel in the oil, by reducing its thickness to the order of a micrometre, e.g. as in the diffusion from emulsified oil droplets.

Hey & Al-Sagheer (1994) used the different ^{1}H NMR relaxation rates of 1,4-dioxane molecules in water and in xylene solution to measure the rate of interfacial transport of dioxane in both directions, in xylene-in-water emulsions. However, there has been no direct measure of the rate of undirectional transport of a solute from the oil phase of an emulsion. In this investigation we propose to measure this rate for benzoic acid in a sunflower oil-in-water emulsion in order to obtain the timescale of the transport process and to discover whether three surfactants with somewhat different structures (SDS, Tween-80 and whey protein) exert different kinetic effects.

The approach which was adopted is to mix an emulsion containing benzoic acid with a small excess of NaOH solution, to which the acid–base indicator phenolphthalein had been added. The time taken for the alkali to be neutralised by the diffusing acid can be obtained by observing the change in colour of the indicator in a continuous flow kinetic apparatus. In order to carry out such measurements it is necessary first to establish the distribution of benzoic acid between the oil and aqueous phases of the emulsion.

MATERIALS AND METHODS

Materials

Unless otherwise stated, all reagents were obtained from BDH Chemicals Ltd, Poole. Tween-80 was obtained from Aldrich, Gillingham, whey protein 4034 (batch PSR 04199) was from the New Zealand Dairy Board, Wellington and sunflower oil was purchased from a local retailer.

Partitioning behaviour

Equal volumes of sunflower oil containing benzoic acid (10–100 mM) and acidified water (15 mM HCl, pH 2.5 ± 0.1) or solutions (2% w/v) of SDS, Tween-80 or whey protein in HCl (15 mM, pH < 2.7) were allowed to reach equilibrium at 25.00 ± 0.05°C. Oil–water mixtures were shaken whilst mixtures of oil and surfactant were stirred gently to avoid the formation of an emulsion. The benzoic acid concentration in the aqueous phase was measured at 270 nm after diluting in HCl solution (15 mM) and the concentration of benzoic acid remaining in the oil was obtained by difference. The actual (measured) pH of the aqueous phase was used in all calculations.

Kinetic measurements

Emulsions of 20% (v/v) sunflower oil (containing 200 Mm benzoic acid) in HCl solution (15 mM, pH 2.5) containing emulsifier (2% w/v) SDS, Tween-80 or whey protein were prepared using a laboratory homogeniser (model S500, Shields Instruments, York). Droplet size distribution, and the total droplet surface area per ml of oil, in the emulsions, was determined (presentation code 0405) using the Mastersizer (Malvern Instruments, Malvern).

A continuous flow appratus was set up in which the emulsion and NaOH solution (25–36 mM) containing phenolphthalein were placed in separate thermostatted (25.00 ± 0.05°C) burettes connected to a stainless steel mixing block. This was drilled with 2-mm holes such that the emulsion and the NaOH solution mixed from opposite directions and the mixture was allowed to flow down a 2-mm glass capillary tube (the observation tube) at right angles to the direction of flow of the "reactants". The two liquids were drawn through the apparatus by connecting the observation tube to a flask (2 dm^{-3}) to act as a vacuum ballast chamber which was connected to a water pump. Flow rate was controlled by the use of stop cocks attached to the burettes. A kinetic run involved evacuating the apparatus and timing the flow of the solutions for exactly 8 s during which time the colour change in the observation tube was photographed (100 ASA, no flash, 0.25 s exposure) against a calibrated scale. The flow rate was read from the burettes and the velocity in the observation tube calculated from its volume, determined gravimetrically with mercury, and length.

RESULTS AND DISCUSSION

Partitioning behaviour of benzoic acid in oil–water

When benzoic acid is added to an oil–water system, it becomes distributed between the two phases according to the partition coefficient, $\boldsymbol{P}$,

$$P = [HA]_{\mathrm{oil}}/[HA]_{\mathrm{aq}} \tag{1}$$

where $\boldsymbol{HA}$ denotes the undissociated acid. When expressed in terms of identical species in the two phases, $\boldsymbol{P}$ is independent of concentration or pH but, for a given pair of solvents, depends on temperature. Because salts of carboxylic acids are relatively insoluble in the organic phase (Rekker, 1977) and the undissociated acids undergo concentration-dependent association (dimerisation) in the organic phase, one usually measures the value of the apparent partition coefficient, $\boldsymbol{P}_{\mathrm{app}}$, which is defined by,

$$P_{\mathrm{app}} = c_{\mathrm{oil}}/c_{\mathrm{aq}} \tag{2}$$

where $c_{\mathrm{oil}} = [HA] + 2[(HA)_2]$ and $c_{\mathrm{aq}} = [HA] + [A^-]$. The effects of pH and dimerisation are separately described by,

$$P_{\mathrm{app}} = P[H^+]/([H^+] + K_a) \tag{3}$$

$$P_{\mathrm{app}} = P + 2P^2K_d[HA]_{\mathrm{aq}} \tag{4}$$

where $\boldsymbol{K}_a$ is the dissociation constant of the acid (6.46×10^{-5} mol dm^{-3} for benzoic acid) and $\boldsymbol{K}_d$ the dimerisation constant. The conditions chosen for the measurement of $\boldsymbol{K}_d$ were pH 2.5, 25 °C. A graph of $\boldsymbol{P}_{\mathrm{app}}$ vs $[\boldsymbol{HA}]$ in the aqueous phase is shown in Fig. 1, from which $\boldsymbol{P} = 4.27$ and $\boldsymbol{K}_d = 9.8$ mol^{-1} dm^3.

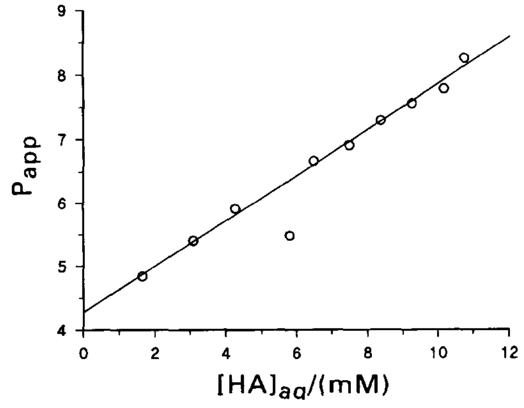

Fig. 1 The effect of benzoic acid concentration in the aqueous phase, $[HA]_{\mathrm{aq}}$ on its apparent partition coefficient, P_{app}, in the system sunflower oil–water.

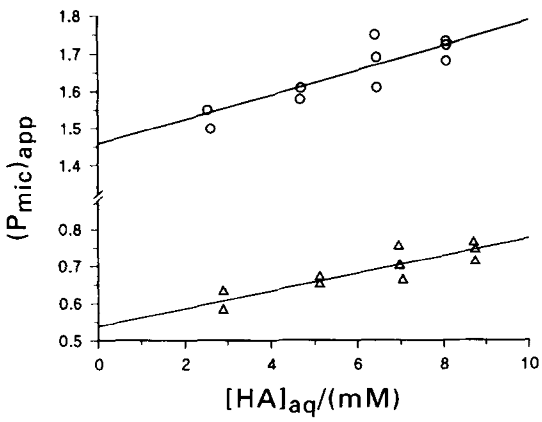

Fig. 2 The effect of free benzoic acid concentration in the aqueous phase, $[HA]_{\mathrm{free}}$, on the apparent micelle partition coefficient $(P_{\mathrm{mic}})_{\mathrm{app}}$, for SDS (○) and Tween-80 (△).

When benzoic acid is dissolved in a solution containing a micelle-forming surfactant, e.g. Tween-80 or SDS, a proportion of the acid becomes associated with the micelles. This behaviour may be described as a partitioning effect though the micelles do not constitute a separate phase. A micelle partition coefficient, P_{mic}, is defined here as,

$$P_{\mathrm{mic}} = [HA]_{\mathrm{mic}}/[HA]_{\mathrm{free}} \qquad (5)$$

where the concentration in the micellar environment, $[HA]_{\mathrm{mic}}$, and in the surrounding solution, $[HA]_{\mathrm{free}}$, is in terms of the total volume of the solution. The more conventional quantitation of this partitioning in terms of mole fractions is less useful for the present investigation.

A straightforward approach to the measurement of P_{mic} is to obtain the distribution of benzoic acid between the bulk phases of oil and a solution of surfactant, and to use the apparent partition coefficient in the simultaneous solution of equations (1), (2) and (4) to give,

$$[HA]_{\mathrm{free}} = \{-1 + (1 + 8K_{\mathrm{d}}c_{\mathrm{oil}})^{\frac{1}{2}}\}/4K_{\mathrm{d}}P \qquad (6)$$

$[HA]_{\mathrm{mic}}$ may be obtained by subtracting $[HA]_{\mathrm{free}}$ from the total concentration of HA in the aqueous phase. The value of P_{mic} obtained in this way was designated the apparent micelle partition coefficient, $(P_{\mathrm{mic}})_{\mathrm{app}}$ and its value is shown graphically for Tween-80 and SDS over a range of benzoic acid concentrations in Fig. 2. This shows the value of $(P_{\mathrm{mic}})_{\mathrm{app}}$ to be concentration-dependent. Whilst the reason for this dependence is not of importance in the present investigation, it is required to model this behaviour in order to calculate the concentration of free and bound benzoic acid at any benzoic acid concentration found in a benzoic acid-containing emulsion. It was decided to treat the data in the same way as for the oil–water partitioning and to define an association constant, K_{m}, equivalent to the dimerisation constant of the acid in the oil. Thus,

$$(P_{\mathrm{mic}})_{\mathrm{app}} = P_{\mathrm{mic}} + 2(P_{\mathrm{mic}})^2 K_{\mathrm{m}}[HA]_{\mathrm{free}} \qquad (7)$$

Table 1. Values of P_{mic} and K_{m} obtained from the partitioning of benzoic acid in the system sunflower oil–water–surfactant, at a surfactant concentration of 2% (w/v), 25 °C

Surfactant	P_{mic}	K_{m} (mol^{-1} dm^3)
SDS	1.46	8.0
Tween-80	0.535	42

and the values of P_{mic} and K_{m} are given for the two surfactants in Table 1. No evidence of any interaction between the whey protein and benzoic acid was obtained.

Theoretical distribution of benzoic acid in emulsions

Emulsions contained 20 vol % sunflower oil and their characteristics for the 3 surfactants and given in Table 2. These characteristics were checked each time a new batch of emulsion was prepared and before every set of measurements was made. To calculate the distribution of benzoic acid in each emulsion, equations (1)–(7) were solved simultaneously with the additional condition of conservation of mass of benzoic acid during the formation of the emulsion, i.e.

$$(c_{\mathrm{o}})_{\mathrm{oil}} V_{\mathrm{oil}} = c_{\mathrm{oil}} V_{\mathrm{oil}} + c_{\mathrm{aq}} V_{\mathrm{aq}} \qquad (8)$$

where $(c_{\mathrm{o}})_{\mathrm{oil}}$ is the concentration of benzoic acid dissolved in the oil, of which a volume V_{oil} was used to prepare the emulsion containing a volume V_{aq} of water. The concentration of benzoic acid in the aqueous phase is expressed as the formula for the solution of a quadratic equation,

$$[HA]_{\mathrm{aq}} = \{-B + (B^2 - 4AC)^{\frac{1}{2}}\}/2A \qquad (9)$$

where, for a 20 vol % emulsion, $A = 2K_{\mathrm{d}}P^2 + 8K_{\mathrm{m}}(P_{\mathrm{mic}})^2$, $B = P + 4 + 4P_{\mathrm{mic}}$ and $C = 0.2$. Use of equations (1), (5) and (9) allows the complete distribution of benzoic

Table 2. Characteristics of emulsions containing 20 vol % oil

Surfactant	$d_{3,2}$ (μm)	$d_{4,3}$ (μm)	Total surface (m^2 cm^{-3})
SDS	0.40	0.53	15.0
Tween-80	0.41	0.54	14.8
Whey	0.43	0.54	13.9

Table 3. Distribution of benzoic acid, HA, between the components of oil–water emulsions whose characteristics are given in Table 2. The quantities $[HA]_{\mathrm{free}}$, $[HA]_{\mathrm{oil}}$, c_{oil}, $[HA]_{\mathrm{mic}}$ are defined in equations (1), (2) and (5), whilst $c_{\mathrm{mic}} = (P_{\mathrm{mic}})_{\mathrm{app}}/[HA]_{\mathrm{free}}$ and was obtained from the constants defined by equation (7)

Surfactant	$[HA]_{\mathrm{free}}$ (mM)	$[HA]_{\mathrm{oil}}$ (mM)	c_{oil} (mM)	$[HA]_{\mathrm{mic}}$ (mM)	c_{mic} (mM)
SDS	10.4	44.5	83.3	15.1	18.7
Tween-80	12.5	53.2	109	6.7	10.3
Whey	14.8	63.0	137	0	0

acid to be calculated. The results of these calculations for the three emulsions used for kinetic work are given in Table 3. These calculations neglect any additional interaction between the surfactant at the oil–water interface and the benzoic acid.

Kinetic measurements

For kinetic measurements, a volume V_e of emulsion was mixed with a volume V_s of alkali, and the concentration of NaOH remaining in the aqueous phase at the instant of mixing is given by $\{[\mathrm{NaOH}]_0 V_s - 0.8c_{aq}V_e\}/(V_e + V_s)$ where $[\mathrm{NaOH}]_0$ is the original concentration of NaOH in the reservoir. The distance along the tube at which the indicator changed colour was converted to time of diffusion using the volume of the observation tube, 0.4828 cm^3, its length, 15.2 cm and the volume flow rate of the reactants. Typically, the mixture moved along the observation tube at a rate of 1 cm ms^{-1} and it was possible to resolve times as small as 0.2 ms. The initial concentration of benzoic acid in the aqueous phase at the instant of mixing was calculated from the data given in Table 3. It is assumed that this acid is instantly neutralised by NaOH and the concentration of NaOH remaining for a given emulsion–NaOH mixture, was obtained. Figures 3, 4 and 5 show the time taken for this excess to be neutralised as a result of the transport of benzoic acid from the oil phase. Initial rates of release of benzoic acid are the slopes of these graphs at time zero and are found to be 0.98, 0.75 and 0.85 mol dm^{-3} s^{-1} for emulsions prepared with SDS, Tween-80 and whey protein, respectively. The fact that the lines depicting initial rates do not pass through the origin is the result of uncertainty mainly in the time taken for the emulsion and NaOH to mix, and the effective time for the release of benzoic acid between the point at which the flows of emulsion and NaOH solution were combined and the start of the observation tube. The use of the change in concentration with time to obtain rate of acid release does not depend on such an error in timing, but it is open to question as to whether or not the initial rate is, in fact, being measured.

For a collection of spherical solute-containing droplets of radius r, each with number probability P_r, which are in contact with a medium whose solute concentration can be regarded as constant while diffusion is taking place, the total mass M_t of solute which has entered or left the droplets after a time t is given by,

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2}\sum_{r=0}^{\infty} P_r \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-Dn^2\pi^2 t/r} \qquad (10)$$

where M_∞ is the mass of solute contained in each droplet, D is the diffusion coefficient and n is an integer.

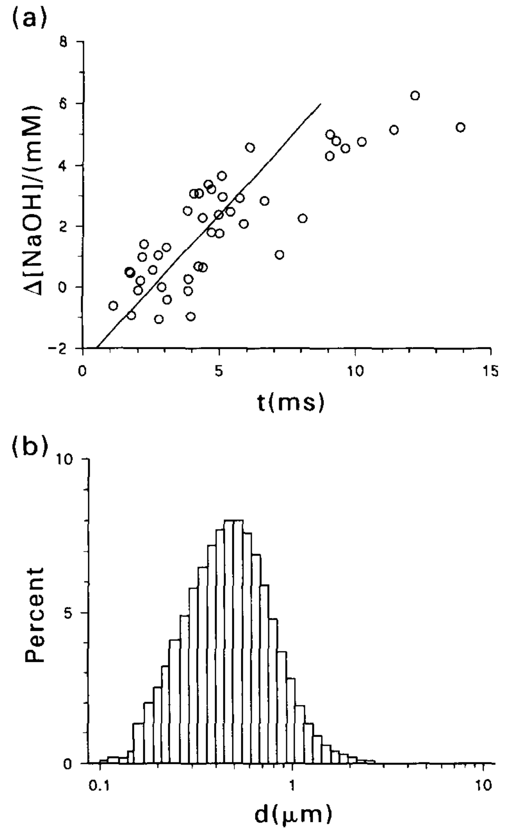

Fig. 3 Time taken for the neutralisation of a concentration of NaOH in the aqueous phase by benzoic acid diffusing from oil droplets in a sunflower oil-in-water emulsion prepared with SDS. The droplet volume distribution is shown below.

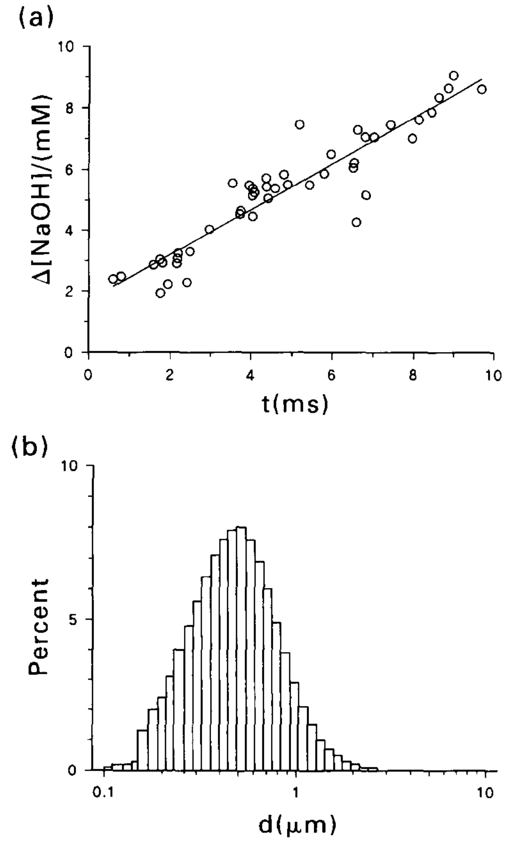

Fig. 4 Time taken for the neutralisation of a concentration of NaOH in the aqueous phase by benzoic acid diffusing from oil droplets in a sunflower oil-in-water emulsion prepared with Tween-80. The droplet volume distribution is shown below.

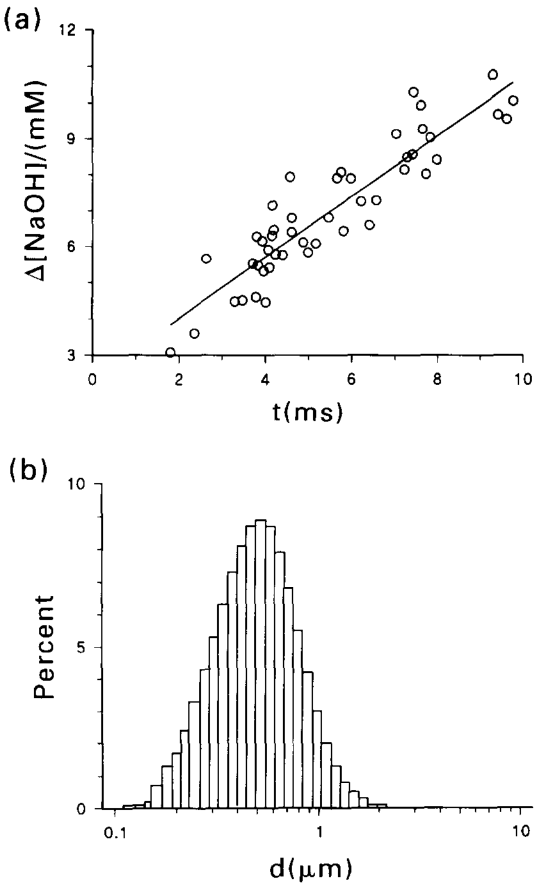

Fig. 5 Time taken for the neutralisation of a concentration of NaOH in the aqueous phase by benzoic acid acid diffusing from oil droplets in a sunflower oil-in-water emulsion prepared with whey protein. The droplet volume distribution is shown inset.

This equation is adapted from that for diffusion of a solute from a single sphere (Crank, 1957). Numerically, the value of M_t/M_∞ is equal to c_t/c_∞, where c represents the concentration when the corresponding mass of solute is divided by the volume of aqueous phase surrounding the droplets. c_t is the concentration of NaOH neutralised by the diffusing benzoic acid at time t. c_∞ is the initial concentration of benzoic acid in the oil expressed in terms of the volume of the aqueous phase after the emulsion and the NaOH solution are mixed. The values of c_∞ for the experiments reported here were 11.1 ± 0.3 ($n = 45$), 9.6 ± 0.4 ($n = 46$) and 11.9 ± 0.4 mM ($n = 47$) for emulsions containing SDS, Tween-80 and whey protein, respectively. This allows us to express the (initial) rates as $\mathrm{d}(c_t/c_\infty)/\mathrm{d}t$ to give 88, 78 and 71 s^{-1} or experiments with the three emulsifiers, respectively.

Integration of equation (10) over the droplet size distributions shown in Figs 3(b), 4(b) and 5(b), after conversion to number probability, suggests that the value of D which corresponds to the measured rates (for the range of c_t/c_∞ values encountered) is of the order 10^{-13} m^2 s^{-1} and, clearly, too small to be realistic. It is inferred that, in the system investigated here, the effective diameter of the droplets is somewhat greater than given by the droplet size distributions. The value of r which is required to give a rate of the magnitude observed in this investigation at a nominal value of $D = 5 \times 10^{-10}$ m^2 s^{-1} is of the order 10 μm.

Such a situation arises if the water surrounding the oil droplets is stagnant and the boundary layer extends significantly into the aqueous phase. In the limit where this boundary layer occupies the entire aqueous phase, the NaOH will not be completely neutralised until sufficient benzoic acid has travelled to every location in that phase. This means that a concentration gradient of benzoic acid would exist also in the aqueous phase and equation (10) ceases to apply. The modelling of this type of diffusion behaviour is in progress.

Despite the limitation of our interpretation of the data, it can be seen that, in practice, the transport of benzoic acid in the three emulsions is fast. Even on the millisecond timescale, any kinetic effect of the adsorbed surfactant layer is small, if at all significant, and it is likely that, in the present system, the rate of transport is controlled by diffusion through the aqueous phase.

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We are grateful to Dr M. J. Hey for his comments on the manuscript. In particular he made the following estimate of the boundary layer thickness to compare with our estimate of 10 μm. The number of droplets with typical radius 0.25 μm in an emulsion consisting of 10% (v/v) oil is 1.5×10^{15} dm^{-3}. In order to account for an observed rate of NaOH neutralisation of 0.85 mol dm^{-3} s^{-1}, each droplet releases 5.7×10^{-16} (mol benzoic acid)/s giving a flux of 7.3×10^{-4} mol m^{-2} s^{-1}. A diffusion coefficient of 5×10^{-10} m^2 s^{-1} implies a concentration gradient of 1.5×10^6 mol m^{-4} which, for a decrease in benzoic acid concentration from 0.01 mol m^{-3} to zero across the boundary layer gives a thickness of 70 μm. This estimate is of the same order of magnitude as calculated in this paper and adds credence to the diffusion model which is proposed.

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