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# Evaporation Rates of Water from Concentrated Oil-in-Water Emulsions

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We have investigated the rate of water evaporation from concentrated oil-in-water (o/w) emulsions containing an involatile oil. Evaporation of the water continuous phase causes compression of the emulsion with progressive distortion of the oil drops and thinning of the water films separating them. Theoretically, the vapor pressure of water is sensitive to the interdroplet interactions, which are a function of the film thickness. Three main possible situations are considered. First, under conditions when the evaporation rate is controlled by mass transfer across the stagnant vapor phase, model calculations show that evaporation can, in principle, be slowed by repulsive interdroplet interactions. However, significant retardation requires very strong repulsive forces acting over large separations for typical emulsion drop sizes. Second, water evaporation may be limited by diffusion in the network of water films within the emulsion. In this situation, water loss by evaporation from the emulsion surface leads to a gradient in the water concentration (and in the water film thickness). Third, compression of the drops may lead to coalescence of the emulsion drops and the formation of a macroscopic oil film at the emulsion surface, which serves to prevent further water evaporation. Water mass-loss curves have been measured for silicone o/w emulsions stabilized by the anionic surfactant SDS as a function of the water content, the thickness of the stagnant vapor-phase layer, and the concentration of electrolyte in the aqueous phase, and the results are discussed in terms of the three possible scenarios just described. In systems with added salt, water evaporation virtually ceases before all the water present is lost, probably as a result of oil-drop coalescence resulting in the formation of a water-impermeable oil film at the emulsion surface.

## Introduction

Evaporation rates are of interest from many viewpoints including assessment of hazards arising from the spillage of volatile chemicals, drying processes, and the release of volatile active species such as perfumes and flavors from commercial products. In many systems of practical interest, evaporation occurs from liquid mixtures that may be multiphase and possess microstructure. As part of a program to study evaporation rates in different types of nonstructured and structured liquid systems, we have previously investigated rates for pure liquids,<sup>1</sup> water contained within porous solids,<sup>2</sup> water-in-oil microemulsions,<sup>3</sup> different liquid mixtures including water/surfactant systems showing a variety of microstructured liquid crystalline phases,<sup>4</sup> and creamed emulsions.<sup>5</sup> Evaporation from a range of related surfactant colloidal mixtures has also been studied by the group of Friberg.<sup>6–8</sup>

Oil-in-water (o/w) emulsions are thermodynamically unstable dispersions of micrometer-sized oil drops in water. In a previous study, we used a mass-loss method under controlled gas flow conditions to investigate the

evaporation rates of o/w emulsions containing relatively low oil-drop volume fractions.<sup>5</sup> During evaporation, the dispersed oil drops cream under gravity to the emulsion surface but remain separated from the vapor phase by a thin water film. Oil mass transfer from the drops to the vapor phase occurs via dissolution and diffusion across the water film, *not* by entry of the oil drops into the air–water surface. As a result of this mechanism, the rates of evaporation of oils from o/w emulsions are retarded relative to those for pure oils by factors of up to 20-fold, with greater retardation for those oils that have a low solubility in water. In a gravity-creamed o/w emulsion containing a low volume fraction of mutually repulsive oil drops, the drops remain virtually spherical (ignoring minor distortions due to gravity) and are widely separated by thick water films. The evaporation rates of the continuous-phase water contained within the relatively thick films in such creamed emulsions are found to be identical to that for pure water.<sup>5</sup>

In the present study, we have investigated the evaporation of water from o/w emulsions containing high volume fractions of involatile oil droplets. In emulsions with an oil-drop volume fraction above the close-packing limit for spheres, evaporation of the water continuous phase leads to increased oil-droplet distortion and progressive thinning of the nanometer water films separating them. As discussed theoretically in the following, such thinning by evaporation is resisted by repulsive colloidal forces between the oil-drop surfaces, which increase in magnitude as the films thin. Under these circumstances, the water evaporation rate is slowed relative to pure water and is sensitive to the variation of the colloidal forces with the water film thickness. Therefore, the rate of water evaporation from *concentrated* o/w emulsions is expected to differ from that for dilute o/w emulsions containing widely separated, undistorted oil drops for which, as noted

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(1) Beverley, K. J.; Clint, J. H.; Fletcher, P. D. I. *Phys. Chem. Chem. Phys.* **1999**, *1*, 149.

(2) Beverley, K. J.; Clint, J. H.; Fletcher, P. D. I.; Thubron, S. *Phys. Chem. Chem. Phys.* **1999**, *1*, 909.

(3) Clint, J. H.; Fletcher, P. D. I.; Todorov, I. T. *Phys. Chem. Chem. Phys.* **1999**, *1*, 5005.

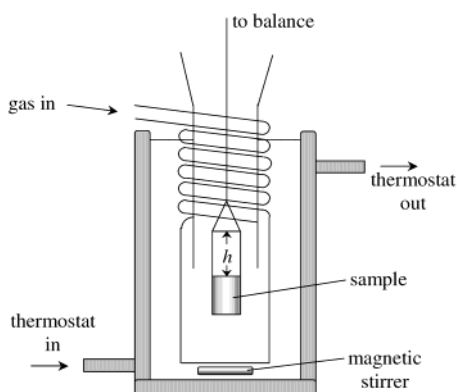
(4) Beverley, K. J.; Clint, J. H.; Fletcher, P. D. I. *Phys. Chem. Chem. Phys.* **2000**, *2*, 4173.

(5) Aranberri, I.; Beverley, K. J.; Binks, B. P.; Clint, J. H.; Fletcher, P. D. I. *Langmuir* **2002**, *18*, 3471.

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(7) Friberg, S. E.; Langlois, B. J. *Dispersion Sci. Technol.* **1992**, *13*, 223.

(8) Langlois, B. R. C.; Friberg, S. E. *J. Soc. Cosmet. Chem.* **1993**, *44*, 23.



**Figure 1.** Schematic diagram of the gravimetric apparatus used to determine evaporation rates. Under the controlled gas flow conditions used here, the stagnant vapor-phase thickness  $h$  is equal to the separation between the liquid surface and the sample tube mouth.

previously, the rate of water evaporation is equal to that for pure water. One motivation for this study is to gain a better understanding of the relationship between the water evaporation rate from concentrated emulsions and the colloidal forces between emulsion drops.

### Experimental Section

Water was purified by reverse osmosis followed by passage through a Milli-Q reagent water system. Poly(dimethylsiloxane) oil (PDMS, Dow Corning) had a kinematic viscosity of 300 cS and was found to be completely involatile over the experimental time scales used here. Sodium dodecyl sulfate (SDS, BDH, specially pure grade) and NaBr (BDH, >99%) were used as received.

PDMS-in-water emulsions were prepared using an Ultra Turrax rotor-stator homogenizer fitted with a T25 shaft. Samples (10 mL) were homogenized at 11 000 rpm for 1 min. Emulsion drop size distributions were measured using a Malvern Mastersizer MS20 instrument. Optical micrographs of emulsion samples were obtained using a Nikon Labophot transmission microscope equipped with a digital camera.

Evaporation rates were determined gravimetrically using the apparatus fully described in ref 1 and shown schematically in Figure 1. Briefly, a weighed sample of emulsion was placed in a cylindrical, open-topped glass tube suspended from a balance. The sample was mounted within a thermostatted chamber, and nitrogen gas was flowed vertically around the sample tube. For this experimental geometry and gas flow configuration, the thickness of the stagnant vapor layer above the liquid surface ( $h$ ) has been demonstrated to be equal to the distance between the liquid surface and the mouth of the sample tube.<sup>1</sup> The knowledge of  $h$  from the experimental configuration is important because it enables a full quantitative analysis of the measured evaporation rates. All measurements were made at 25.0 °C.

### Theoretical Considerations

Two possible limiting situations can arise in considering the rate of evaporation of a volatile species from a multicomponent liquid mixture across a stagnant vapor layer of thickness  $h$ . The first case arises when the rate of vapor diffusion from the liquid surface across the stagnant vapor space is slow relative to diffusion of the volatile species within the liquid mixture to the surface. In this case, denoted here as “vapor-diffusion controlled”, the liquid composition remains uniform throughout the liquid as evaporation proceeds because the volatile species is depleted only slowly relative to diffusion within the liquid. The second case (“liquid-diffusion controlled”) arises when the diffusion rate in the liquid is slow relative to that in the vapor space. Under these circumstances, depletion of one component by evaporation leads to the development of a concentration gradient through the liquid

depth, that is, the concentration of the volatile species at the liquid surface is reduced relative to the depth-averaged composition. Clearly, whether one of these limiting cases is achieved experimentally depends not only on the physical properties of the system (e.g., vapor pressures, vapor- and liquid-phase diffusion coefficients, viscosities, etc.) but also on the geometrical dimensions of the vessel, in particular the depth of liquid in the sample and the thickness  $h$  of the stagnant vapor space. For the sample tube used here (with an internal depth of approximately 40 mm),  $h$  can be adjusted (by control of the depth of the emulsion sample) over the range 3–37 mm.

We first consider the rate of water evaporation from a concentrated o/w emulsion containing an involatile oil under conditions of vapor diffusion control; that is, we assume that the water volume fraction at the liquid surface is identical to the overall average water volume fraction. Under conditions of high gas flow rate, the steady-state water evaporation rate  $E$ , expressed as the rate of mass loss, is independent of the gas flow rate and is given by<sup>1</sup>

$$E = -\frac{dm}{dt} = \frac{MAD_v Pz}{hRT} \quad (1)$$

where  $m$  is the sample mass at time  $t$ ,  $M$  is the molar mass of water,  $A$  is the liquid surface area of the sample,  $D_v$  is the diffusion coefficient of water vapor in the stagnant vapor space of thickness  $h$ ,  $P$  is the equilibrium water vapor pressure,  $R$  is the gas constant, and  $T$  is the absolute temperature. The parameter  $z$  is a correction factor that allows for additional convection resulting from the concentration gradient of the second gas component (nitrogen) within the stagnant layer and is given by

$$z = \left[ \frac{P_{\text{atm}}}{P} \ln \left( \frac{1}{1 - (P/P_{\text{atm}})} \right) \right] \quad (2)$$

where  $P_{\text{atm}}$  is atmospheric pressure. For this study, the flow rate of nitrogen was kept constant at 1710 mL min<sup>-1</sup>, sufficiently high that eq 1 is valid within 2% or so. The same sized sample tube was used for all measurements, and, thus, the area  $A$  was constant (258.4 mm<sup>2</sup>). The initial value of  $h$  was either 26.7 mm (when 3.0 g of the emulsion sample was used) or 36.5 mm (when 0.5 g of the emulsion was used).

The vapor pressure  $P$  of water confined in the thin water films separating the oil drops is affected by the disjoining pressure (repulsive force per unit area of film)  $\Pi$  operating between the drop surfaces according to<sup>9</sup>

$$P = P_0 \exp \left( -\frac{\Pi v}{kT} \right) \quad (3)$$

where  $P_0$  is the vapor pressure of bulk water,  $v$  is the molecular volume of water, and  $k$  is Boltzmann's constant. From eq 3, it can be seen that a positive disjoining pressure (i.e., a repulsive force between oil drops) causes a decrease in the water vapor pressure and, from eq 1, a corresponding decrease in the evaporation rate. For the purposes of estimating the magnitude and range of the disjoining pressure necessary to produce measurable changes in the mass-loss rates for emulsions under conditions similar to those used here, we assume that the total disjoining pressure decays exponentially with film thickness  $d$  according to

(9) Derjaguin, B. V.; Churaev, N. V.; Muller, V. M. *Surface Forces*; Plenum Press (Consultants Bureau): New York, 1987.

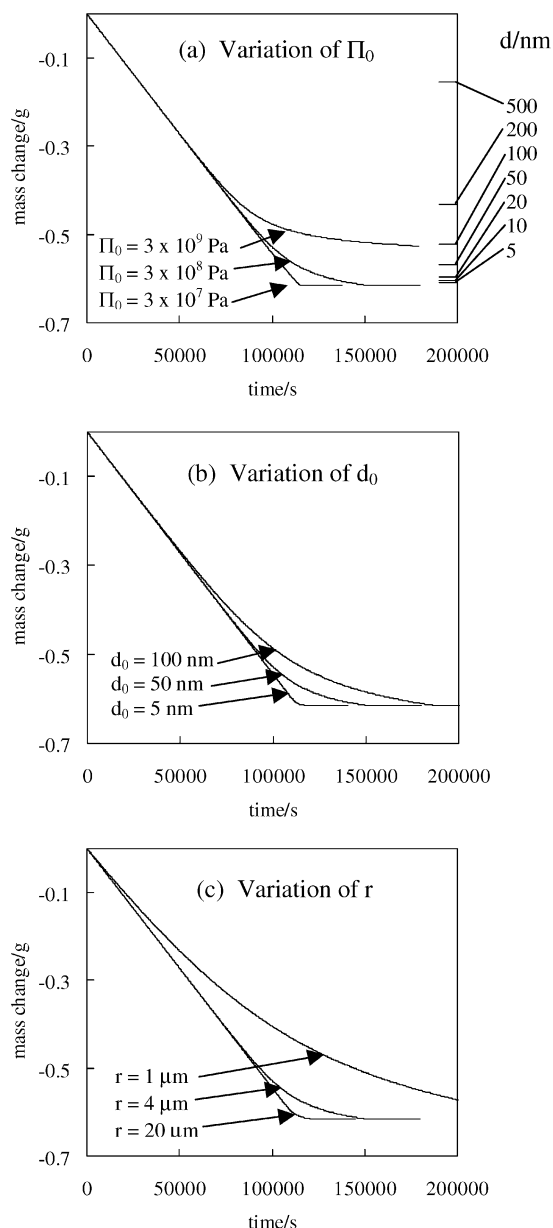
$$\Pi = \Pi_0 \exp(-d/d_0) \quad (4)$$

where  $\Pi_0$  is the disjoining pressure corresponding to virtually zero thickness of the water film between opposing emulsion drop surfaces (i.e.,  $d = 0$ ) and  $d_0$  is the decay length. This exponential force law corresponds to solely electrostatic repulsive forces for which the decay distance  $d_0$  is equal to the Debye length.<sup>10</sup> This very crude approach neglects contributions to the overall disjoining pressure between compressed drops arising from van der Waals, steric, hydration, and oscillatory forces associated with micelle stratification but has the advantage of involving only two unknown parameters ( $\Pi_0$  and  $d_0$ ). It is adopted here solely to estimate the approximate magnitude and range of the disjoining pressure required to significantly affect the shapes of the mass-loss curves.

For an emulsion containing monodisperse drops with a mean undistorted spherical radius  $r$  and volume fraction of water  $\phi_w$ , the drop surface area per unit volume of emulsion (neglecting the distortion of the drops from sphericity) is  $3(1 - \phi_w)/r$ . Noting that the network of films separating the drops has an area equal to  $1/2$  that of the drops and a volume fraction equal to  $\phi_w$ , it follows that the average water film thickness  $d$  is approximately

$$d \approx \frac{2\phi_w r}{3(1 - \phi_w)} \quad (5)$$

Equations 1–5 can be used to make an approximate estimation of the sensitivity of the evaporative mass-loss versus time curves for concentrated emulsions to the strength and range of repulsive interdroplet forces (i.e., through variation of  $\Pi_0$  and  $d_0$ ) and emulsion drop radius  $r$ . Figure 2 shows a series of simulated mass-loss curves corresponding to water evaporation at 25 °C from 3.0 g of o/w emulsion samples initially containing 20 vol % water. Figure 2a shows the effect of changing the magnitude of repulsive disjoining pressure through variation of  $\Pi_0$ . When repulsive forces are weak (i.e., when  $\Pi_0$  is low), the mass-loss curves show a sharp kink corresponding to the point at which all the water initially present is lost. Stronger repulsion acts to reduce the water vapor pressure and slow the evaporation before all the water is lost, that is, the kink is “smoothed”. A repulsive disjoining pressure on the order of  $10^7$  Pa is required to produce a measurable reduction in the vapor pressure (and, hence, evaporation rate) of about 10%. For this magnitude of repulsive interaction to give an observable “smoothing” of the sharply kinked mass-loss curve, the disjoining pressure must operate over a film thickness of at least 20 nm (see right-hand scale of Figure 2a). Both the magnitude and the range of the repulsion required to significantly affect the evaporative mass-loss curves are much higher than the experimentally measured values. For o/w emulsions stabilized by SDS at a concentration equal to the critical micelle concentration, the disjoining pressure decays exponentially from approximately  $4 \times 10^6$  Pa at  $d = 2.5$  nm to  $2 \times 10^5$  Pa at  $d = 5$  nm.<sup>11</sup> Figure 2b shows the influence of the range  $d_0$  of the electrostatic repulsive forces. Short-range forces (e.g.,  $d_0 = 5$  nm) give a strongly kinked mass-loss curve because virtually all the available water must be lost before the films are thin enough to be affected by the colloidal forces. Longer-range



**Figure 2.** Simulated water loss curves for o/w emulsions containing 80 vol % dispersed drops of an involatile oil. Unless stated otherwise,  $r = 4 \mu\text{m}$ ,  $\Pi_0 = 3 \times 10^8$  Pa, and  $d_0 = 50$  nm. In Figure 2a, the right-hand scale shows the film thickness corresponding to the mass loss indicated on the left-hand scale.

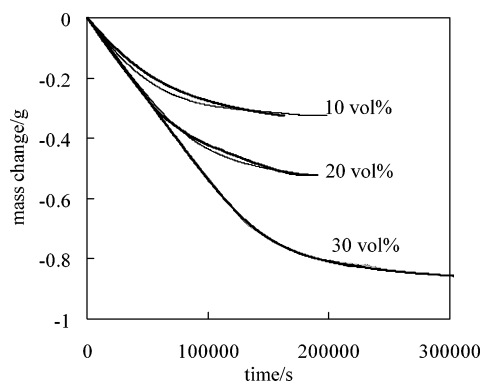
forces give smoother curves. Figure 2c shows the influence of the emulsion oil-drop radius. When all other parameters are kept constant, the largest drop size produces the lowest film surface area and, hence, the thickest film, weakest interdroplet repulsion, and most kinked mass-loss curve. Overall, comparison of the calculated curves and the disjoining pressure isotherms of ref 11 shows that emulsions stabilized by SDS possess interactions of too low a magnitude and range to produce a significant smoothing of the mass-loss curves from the limiting kinked shape corresponding to negligible interactions.

The simulated mass-loss curves of Figure 2 correspond to a hypothetical situation in which mass transport across the stagnant vapor phase is rate limiting and the water volume fraction is virtually uniform throughout the emulsion. It is also assumed that the oil drops remain intact as they are compressed together by progressive evaporation of the water continuous phase. In fact, two additional scenarios are possible. First, when water mass

(10) See, for example, Hunter, R. J. *Foundations of Colloid Science*; Clarendon Press: Oxford, 1991; Vol. 1, p 406.

(11) Sonnevile-Aubrun, O.; Bergeron, V.; Gulik-Krzywicki, T.; Jonsson, B.; Wennerstrom, H.; Lindner, P.; Cabane, B. *Langmuir* **2000**, *16*, 1566.



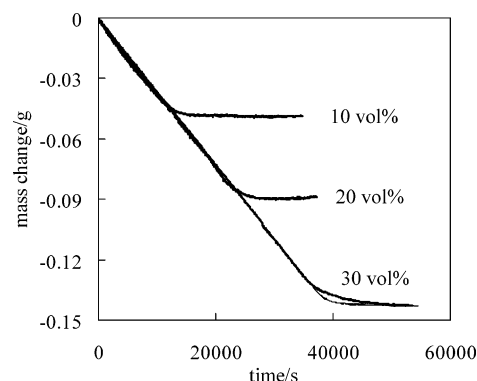


**Figure 3.** Water mass-loss curves for PDMS-in-water emulsions containing 20 mM SDS and the vol % water indicated. The initial mass of the emulsion was 3.0 g, corresponding to an initial  $h = 26.7$  mm. For each plot, the narrow line is a best-fit to the model described in the text.

transport within the network of emulsion films within the liquid emulsion is fully or partially rate limiting, water evaporation causes a concentration gradient in water throughout the depth of the emulsion. This gives thinner emulsion films at the emulsion–vapor surface and produces slower water evaporation. Second, as shown by Bibette,<sup>12</sup> osmotic compression of monodisperse emulsion drops can commonly cause drop coalescence above a critical disjoining pressure that is around  $10^5$  Pa for o/w emulsions stabilized by SDS, much less than the values of  $\Pi_0$  required to significantly affect the evaporation rate. Extensive oil-droplet coalescence to produce a water-impermeable oil film of macroscopic thickness at the emulsion surface would act to strongly retard the further evaporation of water. This type of behavior has been observed in drying studies of concentrated o/w emulsion films by Bouchama et al.,<sup>13</sup> albeit without the controlled gas flow and knowledge of the thickness of the stagnant vapor space as used in this study. Further information on aspects of evaporation from concentrated emulsions can be found in the study of film formation from reactive silicone emulsions by Guigner et al.<sup>14</sup> and references therein.

### Results and Discussion

Figure 3 shows experimental water mass-loss curves measured for a series of 3.0 g of emulsion samples with initial water volume fractions of 0.1, 0.2, and 0.3. The average oil-droplet radius (defined as the radius value at which the cumulative, volume-weighted distribution curve reaches 50%) was  $4.0 \mu\text{m}$  for all samples. The experimental curves were globally fitted to the “vapor-diffusion-control” model (eqs 1–5) to obtain an approximate estimate of the strength and range of repulsive interactions that would be consistent with the data if the rate was limited solely by vapor diffusion. Because the crude model neglects nonelectrostatic forces, droplet polydispersity, and the fact that the ionic strength of the aqueous phase increases as the water evaporates and changes the range of the electrostatic interactions, the apparent best-fit values of  $\Pi_0 = 3.0 \times 10^8$  Pa and  $d_0 = 110$  nm are order-of-magnitude estimates only. Despite this, the comparison still serves to show that the assumptions inherent in the “vapor-diffusion-control” model do not apply to our experimental situation. First, the best-fit value of  $\Pi_0$  of  $3.0 \times 10^8$  Pa corresponds to disjoining pressures much larger than those



**Figure 4.** Water mass-loss curves for PDMS-in-water emulsions containing 20 mM SDS and the vol % water indicated. The initial mass of the emulsion was 0.5 g, corresponding to an initial  $h = 36.5$  mm. For each plot, the narrow line is a best-fit to the model described in the text.

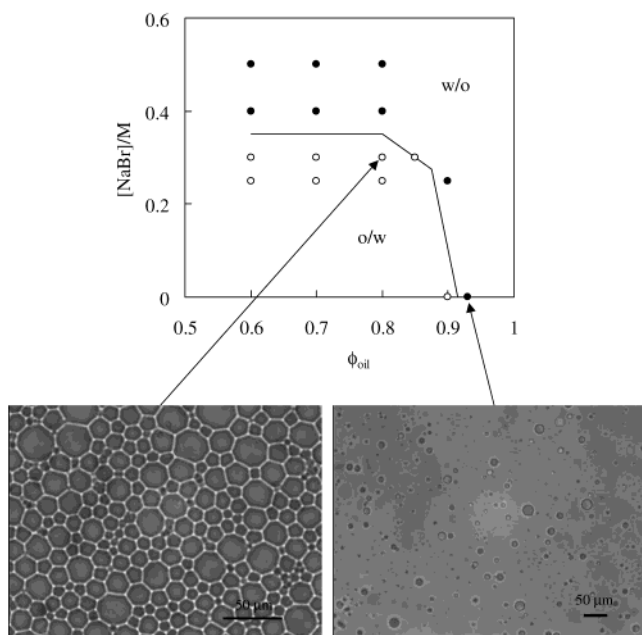
measured in comparable systems<sup>11</sup> and than the value of critical disjoining pressure required to induce droplet coalescence in similar emulsion systems.<sup>12</sup> Second, the best-fit value of  $d_0$  (110 nm) is much larger than the Debye length estimated for the electrolyte concentration in the emulsion samples. SDS (20 mM) in the aqueous phase corresponds to an initial Debye length of less than 1 nm, which will become even shorter as the water evaporates and the ionic strength in the remaining water is increased. Although crude, these comparisons strongly suggest that the smooth slowing down of evaporation rates observed in Figure 3 before all the water is lost is *not* due to vapor pressure reduction within thinned water films in emulsions of uniform composition. It is likely that water diffusion within the film network of the emulsion is (at least partly) rate-limiting and that this produces a gradient in the water concentration and film thickness.

Further evidence that the limiting “vapor-diffusion-control” mechanism is not achieved in the systems of Figure 3 is provided by comparison with mass-loss curves measured at a smaller depth of emulsion sample corresponding to a higher stagnant layer thickness  $h$ . Under these conditions, water diffusion times in the liquid will be shorter and those in the vapor will be longer, making it more likely for vapor diffusion to be rate limiting. If vapor diffusion were rate limiting under the conditions of Figure 3, then the mass-loss curve shapes and best-fit values of  $\Pi_0$  and  $d_0$  should be identical for different  $h$  values. Figure 4 shows plots of water loss versus time measured for a series of 0.5 g of emulsion samples with initial water volume fractions of 0.1, 0.2, and 0.3. For this series, the initial value of  $h$  was 36.5 mm, compared with 26.7 mm when 3.0 g of emulsion sample was used. The emulsion sample depth was approximately 2 mm for 0.5 g of emulsion compared with 12 mm for 3.0 g. In comparing corresponding plots in Figures 3 and 4, it can be seen that increasing  $h$  causes the mass-loss curves to become significantly more kinked, and this shape change is reflected in the best-fit value of  $d_0$  of 12 nm, compared with 110 nm for the data of Figure 3. The best-fit value of  $\Pi_0$  is virtually unchanged at  $2.7 \times 10^8$  Pa. The observed change in the shape of the mass-loss curves at different  $h$ 's clearly confirms that liquid-phase transport is rate limiting (at least partially) and, hence, that a water concentration gradient is generated during evaporation. The fact that virtually all the available water is lost by evaporation suggests that oil-droplet coalescence to produce a macroscopic oil film at the emulsion surface

(12) Bibette, J.; *Langmuir* **1992**, *8*, 3178.

(13) Bouchama, F.; Estramil, G.; Autin, A. J. E.; Koper, G. J. M. *Colloids Surf., A* **2002**, *210*, 120.

(14) Guigner, D.; Fischer, C.; Holl, Y. *Langmuir* **2001**, *17*, 3598.



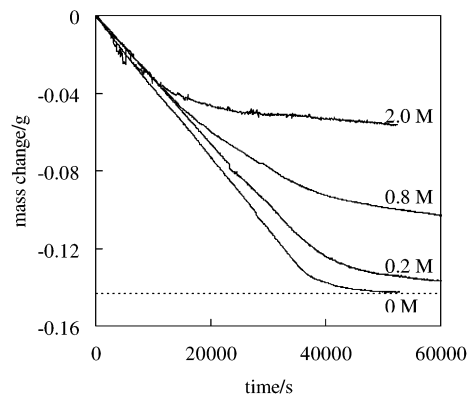
**Figure 5.** Phase-inversion map for batch emulsions containing PDMS and aqueous NaBr solutions and stabilized by 20 mM SDS. Open circles correspond to o/w emulsions, whereas filled circles correspond to w/o emulsions. The line is a guide to the eye for the locus of phase inversion. The micrographs show the emulsion appearance at the compositions indicated by the arrows.

apparently does not occur, except possibly in the final stages of water loss.

In a further series of experiments, we have investigated the effect of electrolyte (NaBr) addition on the water evaporation rates. Increased aqueous-phase electrolyte concentration is expected to reduce the range of the interdroplet electrostatic repulsion. As seen in the simulated plots of Figure 2b, reducing  $d_0$  is expected to enhance the sharpness of the kinks in the mass-loss curves. A second effect of the addition of NaBr is that it promotes phase inversion of the emulsions from o/w to w/o, for which the first stage is coalescence of the oil drops. Figure 5 shows the locus of the phase-inversion transitions for batch emulsions homogenized separately at each composition. o/w emulsions are produced at low [NaBr] and  $\phi_{oil}$  (open points), whereas w/o emulsions are favored at high [NaBr] and  $\phi_{oil}$  (filled points). Illustrative micrograph images of the emulsions are also shown.

For emulsions that are initially o/w, water loss by evaporation increases both [NaBr] and  $\phi_{oil}$  (and [SDS]) and is, therefore, expected to trigger phase inversion and production of an oil film, which serves to prevent further water evaporation. In the absence of added NaBr, the batch-homogenized emulsions of Figure 5 invert from o/w to w/o at  $\phi_{oil}$  of 0.92, that is, at  $\phi_{water}$  of 0.08. From Figures 3 and 4, water evaporation ceases when  $\phi_{water}$  reduces to less than approximately 0.01. Clearly, water evaporation retardation does not occur at the same composition as phase inversion in the batch-homogenized emulsions. This may be related to the difference in SDS concentration induced by water evaporation or the lack of re-homogenization as the emulsion composition is altered by evaporation.

Figure 6 shows mass-loss curves for a series of o/w emulsions (0.5 g) initially containing 30 vol % water and the NaBr concentrations indicated in the legend. The emulsion samples were prepared by addition of the required volume of a concentrated aqueous NaBr solution



**Figure 6.** Water mass-loss curves for PDMS-in-water emulsions with 20 mM SDS and 10 vol % water containing different initial NaBr concentrations (shown on the curves). The initial mass of each emulsion was 0.5 g, corresponding to an initial  $h = 36.5$  mm. The horizontal dashed line corresponds to the plateau value expected for complete water loss.

to an aliquot of an o/w emulsion prepared without NaBr. For the emulsion containing zero added NaBr, the evaporative mass-loss stops when virtually all of the water in the original emulsion is lost (approximately 0.15 g). As the NaBr concentration is increased, the evaporation slows and stops well before all the water is lost. This behavior is *not* expected if the only effect of NaBr addition is to reduce the range of the electrostatic repulsion between droplets. As noted previously, this should enhance the kinks in the curves but is not predicted to alter the final plateau values of mass loss. The most likely explanation, qualitatively consistent with the observation (Figure 5) that NaBr promotes phase inversion, is that NaBr addition induces oil-droplet coalescence and the formation of a water-impermeable film of oil that strongly retards further water loss.

## Conclusions

We have investigated the rate of water evaporation from concentrated o/w emulsions containing an involatile oil. Evaporation of the water continuous phase causes compression of the emulsion with progressive distortion of the oil drops and thinning of the water films separating them. Theoretically, the vapor pressure of water is sensitive to the interdroplet interactions, which are a function of the film thickness. Three possible situations are considered. First, under conditions when the evaporation rate is controlled by mass transfer across the stagnant vapor-phase, model calculations show that evaporation can, in principle, be slowed by repulsive interdroplet interactions. However, significant retardation requires very strong repulsive forces acting over large separations for typical emulsion drop sizes. Second, water evaporation may be limited by diffusion in the network of water films within the emulsion. In this situation, water loss by evaporation from the emulsion surface leads to a gradient in the water concentration (and in the water film thickness). Third, compression of the drops together may lead to coalescence and the formation of a macroscopic oil film at the emulsion surface, which can serve to prevent or strongly retard further water evaporation.

Water mass-loss curves have been measured for PDMS-in-water emulsions stabilized by the anionic surfactant SDS with different water contents, stagnant vapor-phase layer thicknesses, and aqueous-phase electrolyte concentrations. Under conditions of slow vapor-phase transport (i.e., large stagnant layer thickness) and zero added electrolyte, virtually all the water is lost by evaporation

at a rate similar to that for pure water. This is consistent with theoretical calculations that indicate that interdroplet repulsive forces are unlikely to be sufficiently strong to significantly retard the evaporation rate. Under conditions of faster vapor-phase transport (i.e., reduced stagnant layer thickness) and zero added electrolyte, there is a significant reduction in the evaporation rate prior to complete water loss. A likely explanation for this observation is that depletion of water by evaporation in the emulsion surface region has caused water films in the surface region to be thinner than the values estimated using an average water concentration. Addition of electrolyte is shown to promote oil-drop coalescence and phase

inversion in batch emulsions. Water evaporation from emulsions containing added electrolyte is strongly retarded well before all the water is lost, probably as a result of oil-drop coalescence and the formation of a macroscopic oil film at the emulsion surface, which strongly retards further water evaporation.

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