

Evaporation rates of water from water-in-oil microemulsions

John H. Clint, Paul D. I. Fletcher* and Ilian T. Todorov

Surfactant Science Group, Department of Chemistry, University of Hull, Hull, UK HU6 7RX.
E-mail: P.D.Fletcher@chem.hull.ac.uk

Received 20th August 1999, Accepted 20th September 1999

We have used a gravimetric technique to measure the rate of evaporation of water from water-in-dodecane microemulsions stabilised by AOT. Evaporation rates were measured under controlled gas flow conditions for a series of different microemulsion drop sizes and concentrations. Even for microemulsion samples where the equilibrium vapour pressure of water is similar to that of pure water, the evaporation rates are slower by more than an order of magnitude. The measured rates for the different microemulsion compositions are found to be approximately consistent with a model in which it is assumed that diffusion of the water microemulsion drops through the microemulsion to the surface is rate limiting. The subsequent processes of transfer of water across the liquid/vapour surface and the stagnant vapour space are not rate limiting.

Evaporation rates are of interest from a number of viewpoints including assessment of hazards arising from the spillage of volatile liquids, drying processes, release of volatile active components from commercial products and the retardation and control of evaporation by adsorbed monolayers or entrapment of the liquid within colloidal microstructures such as porous solid materials and liquid dispersions including emulsions and microemulsions. In this study we have used a simple gravimetric technique, described previously,^{1,2} to investigate evaporation rates of water from water-in-oil microemulsions stabilised by the anionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT) under conditions of controlled gas flow. Both the dispersed water and the continuous oil phase evaporate and contribute to the measured sample mass loss. In order to investigate the evaporation of the dispersed water drops, we selected dodecane (with relatively very low volatility) as the oil component and obtained the water evaporation rate by subtraction of the separately determined dodecane loss rate. Although investigations of evaporation from surfactant solutions have been described previously (see, for example, refs. 3–6), the experimental arrangement used here enables us to quantitatively compare measured evaporation rates with theoretical predictions.

Water-in-oil (w/o) microemulsions consist of thermodynamically stable dispersions of nm sized water drops stabilised by monolayers of surfactant. For water-in-alkane microemulsions stabilised by AOT the drops are spherical and reasonably monodisperse. For heptane as oil, it has been shown that the hydrodynamic drop radius r is linearly related to the molar ratio of water to AOT (w_o) according to:

$$r = \frac{3V_w w_o}{A_s} + \delta \quad (1)$$

where V_w is the molecular volume of water, A_s is the area per AOT molecule at the interface between the water core of the droplet and the surfactant monolayer (0.5 nm²) and δ is the thickness of the monolayer (1.4 nm).⁷ Using a fluorescence anisotropy method, Keh and Valeur⁸ showed that the drop hydrodynamic volumes (at constant w_o) are independent of n-alkane solvent chain length from hexane to dodecane implying that A_s and δ do not vary with oil type. Hence, for dodecane as oil, the drop radius is easily controlled by variation of w_o according to $r/\text{nm} \approx 0.179w_o + 1.4$. At constant w_o ,

the concentration of drops is proportional to the concentration of AOT and can be varied independently.

For non-interacting, spherical particles the diffusion coefficient D is given by the Stokes–Einstein relation

$$D = \frac{kT}{6\pi\eta r} \quad (2)$$

where k is the Boltzmann constant, T is the absolute temperature and η is the viscosity of the continuous phase.⁹ Drop diffusion coefficients estimated using eqn. (2) together with the radius– w_o relationship given above are listed in Table 1. The viscosity of dodecane was taken from ref. 10. For w/o microemulsions, eqn. (2) is valid at low drop concentrations at temperatures close to the solubilisation phase boundary (which forms the low temperature phase boundary of the single phase microemulsion domain) where the drops behave approximately as hard spheres. At temperatures further from the solubilisation phase boundary (and closer to the haze boundary which forms the upper temperature phase boundary) the drop interactions become increasingly attractive. This leads to clustering of the drops and a reduced diffusion rate. At fixed temperature (as in this study) the drop interactions depend on both w_o and the drop concentration. An additional complication in considering water diffusion in microemulsions arises from the phenomenon of percolation. When the drop volume fraction and attractive interactions are sufficient, the water drops can form a continuous network through the oil phase giving rise to a sharp increase in electrical conductivity, the “percolation transition”. A systematic study of percolation in AOT stabilised w/o microemulsions is described in ref. 11. Within the percolation regime, water diffusion is expected to be faster than that predicted by eqn. (2). These complications

Table 1 Drop radii and diffusion coefficients estimated using eqn. (1) and (2) assuming that the drops are spherical and non-interacting

w_o	r/nm	$D/10^{-11} \text{ m}^2 \text{ s}^{-1}$
5.2	2.3	6.8
10.2	3.2	4.9
15.2	4.1	3.9
20.2	5.0	3.2

are all relevant when considering the rate of water transport to the microemulsion surface prior to evaporation.

We next consider the vapour pressures of the different components of the microemulsion. The AOT surfactant is virtually involatile. The dodecane continuous phase contains only a very low mole fraction of water drops and is thus expected to have an equilibrium vapour pressure virtually identical to that of pure dodecane. Equilibrium vapour pressures in microemulsions have been investigated previously.^{12–15} Although microemulsions are formally single phase systems, the continuous solvent and dispersed particles behave approximately as separate “pseudo-phases”.¹³ According to this approximation for w/o microemulsions, the relative water vapour pressure P/P_0 , where P is the water vapour pressure above the microemulsion and P_0 is the vapour pressure above a flat surface of pure water at the same temperature, is a function of w_o but is independent of the drop concentration. For AOT stabilised microemulsions in a variety of oil solvents it is found experimentally^{12,14,15} that P/P_0 increases with w_o from zero at $w_o = 0$ and asymptotically approaches unity for w_o values higher than approximately 15. To a zeroth order approximation, P/P_0 is equal to the mole fraction X of water within the microemulsion drops (as opposed to the mole fraction within the total microemulsion sample). Assuming that a fraction α of the sodium counterions of the AOT are dissociated within the drops and contribute to the water vapour pressure lowering, P/P_0 is approximately related to w_o according to

$$P/P_0 \approx X = \frac{1}{1 + (1 + \alpha)/w_o} \quad (3)$$

The variation of P/P_0 with w_o estimated using eqn. (3) is compared with experimental results for w/o drops in dodecane taken from ref. 15 in Fig. 1 where it can be seen that the experimental data lie between the limiting theoretical curves corresponding to $\alpha = 0$ and 1. It is an unusual feature of w/o microemulsions that the equilibrium water vapour pressure depends on w_o but *not* on the overall water concentration which is determined by both the drop size (proportional to w_o) and concentration. For example, the equilibrium water vapour pressures for microemulsions containing $w_o = 20$ drops are virtually equal to that of pure water and independent of the water volume fraction.

Since evaporation is a kinetic process, it is relevant to note some aspects of microemulsion dynamics. As discussed, for example, in ref. 16, w/o microemulsion drops undergo continuous fusion/fission to form transient coalesced drop dimers which then re-separate. This process, occurring on a ms time scale, forms the mechanism whereby drops exchange solubilised species and the (time-averaged) drop size distribution is maintained in dynamic equilibrium. One consequence of this is that mixing small drops (with low w_o) and large drops (with

high w_o) rapidly produces a uniform drop population of intermediate size and w_o . Water evaporation from a w/o microemulsion may, in principle, produce gradients in both drop concentration and in w_o . Whereas gradients in drop concentration will produce a diffusional flux, gradients in w_o are expected to be dissipated by the mechanism of drop fusion/fission but may still result in a gradient in drop concentration.

For pure liquids evaporating from partially filled vessels into a flowing gas stream (*i.e.* in the experimental configuration used in this study), the rate limiting step controlling the evaporation rate is vapour diffusion across the stagnant vapour space between the liquid surface and the vessel mouth.¹ In this situation, the evaporation rate is proportional to the equilibrium vapour pressure of the liquid. For w/o microemulsions with high w_o , the equilibrium vapour pressure is only very slightly lower than that for pure water even though the water content may be very low. If vapour diffusion across the stagnant vapour space were to be rate limiting, an evaporation rate similar to that of pure water is expected. However, for water evaporation to occur the water drops must first diffuse to the surface through the bulk microemulsion and then “break through” the liquid surface to enter the vapour space. Either of these processes may form the rate limiting step and would result in water evaporation rates slower than that for pure water. The key question addressed in this study is which of these three possible processes (*i.e.* drop diffusion in bulk, surface “break through” or vapour space diffusion) acts to limit the evaporation rate of dispersed drops in microemulsions. To attempt an answer, we have determined the water loss rates from microemulsions with different w_o values and drop concentrations and compared the rates with that for pure water under identical conditions.

Experimental

Water was purified by reverse osmosis and passed through a Milli-Q reagent water system. n-Dodecane (Avocado, 99%) was columned over alumina prior to use to remove polar impurities. AOT (Sigma, 99%) was vacuum desiccated for 15 days to minimise the water content. Using Karl Fisher titration, the AOT treated in this way was found to contain 0.22 water molecules per molecule of AOT. The w_o values of the microemulsion samples quoted here are corrected for this additional water content. Microemulsion samples were prepared by addition of the correct mass of water to AOT solutions in dodecane. Gentle shaking of the samples produced optically transparent microemulsions within a minute or so.

The apparatus for measurement of the evaporation rates is described fully in ref. 1. Briefly, the liquid samples were contained within vessels of the shape shown in Fig. 2 and suspended from a Precisa 125A balance. Nitrogen gas was passed through a column of activated charcoal (Puritube supplied by Phase Sep.) to remove adsorbing impurities, a column containing type 4A molecular sieve to remove water and a flow meter to record the gas volume flow rate (kept constant here at 1920 ml min⁻¹). The purified nitrogen stream was flowed through a thermostating coil and entered the measurement vessel through an annular opening of approximately 1 mm gap. The gas then flowed vertically upwards around the sample and emerged from the top of the vessel. The vessel containing the suspended sample was contained within a stirred, thermostatted outer vessel. The sample mass loss as a function of time was recorded on the Precisa balance and logged into an EXCEL spreadsheet using a PC equipped with TAL Technologies WinWedge software which allows data transfer from the RS232 interface of the balance. We have demonstrated previously¹ that, for low evaporation rates as found in this study, there is no significant cooling of the sample during the evaporation, *i.e.* the sample remains at the thermostatted temperature. It has also been shown

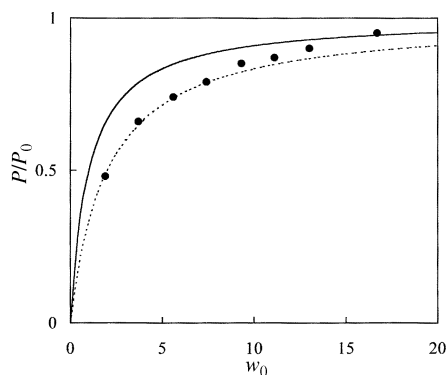


Fig. 1 Variation of P/P_0 with w_o for 0.05 M AOT in dodecane at 40 °C (data from ref. 15). The line shows the behaviour predicted using eqn. (3) with $\alpha = 0$ (solid line) and $\alpha = 1$ (dashed line).

previously¹ that the evaporation rate is independent of gas flow rate at the flow rate used here (1920 ml min⁻¹).

All measurements were made at 25.0 °C.

Results and discussion

The total mass loss from microemulsion samples is small and occurs slowly relative to the pure liquid samples measured previously.¹ In an attempt to improve the measurement precision the mass loss from two sample tubes suspended one above the other was recorded (Fig. 2). Experimentally, the mass loss from two sample tubes was found to be approximately double that for one.

The gravimetric method used here records the microemulsion sample mass loss due to evaporation of both the dispersed water and the continuous dodecane phase. Mass loss curves were recorded separately for both pure dodecane and 0.2 M AOT in dodecane and are shown in Fig. 3. These mass loss curves are the same within the experimental uncertainty confirming the expectation that the addition of AOT (present in the form of reversed micelles with very low mole fraction) has negligible effect on the dodecane evaporation rate. For the microemulsion samples, the mass loss due to water evaporation alone was obtained by subtraction of the 0.2 M AOT–dodecane mass loss curve. Fig. 3 shows an example of the separate curves and final water mass loss curve. The experimental uncertainty, estimated from repeated measurements, was found to be approximately ± 5 mg in the final water mass loss after approximately 1 day and arose primarily from “drift” in the balance. This is shown as the representative error bar in Fig. 3.

For water-in-dodecane microemulsions stabilised by AOT at 25 °C, the maximum w_o achievable is approximately 22. Water mass loss curves were recorded for microemulsion samples with w_o values of 5.2, 10.2, 15.2 and 20.2 and AOT

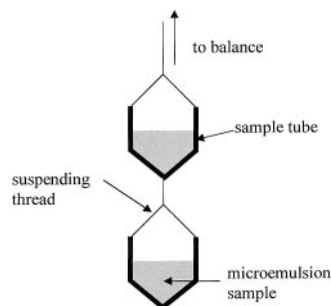


Fig. 2 Configuration of sample tubes used to contain the microemulsion samples within the evaporation rate apparatus. The radius of the tube mouth was 10.25 mm and the volume of microemulsion within each tube was 1.7 ml.

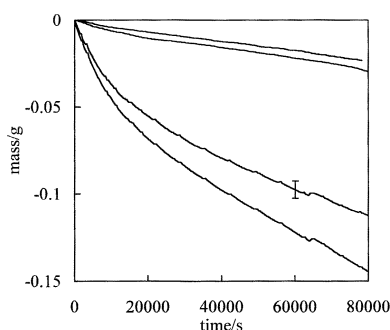


Fig. 3 Mass loss curves for (in descending order) 0.2 M AOT in dodecane, pure dodecane, water loss from 0.2 M AOT with $w_o = 20.2$ (obtained by subtraction) and total mass loss from the same microemulsion. A representative error bar of ± 5 mg is shown on the water loss curve for the microemulsion.

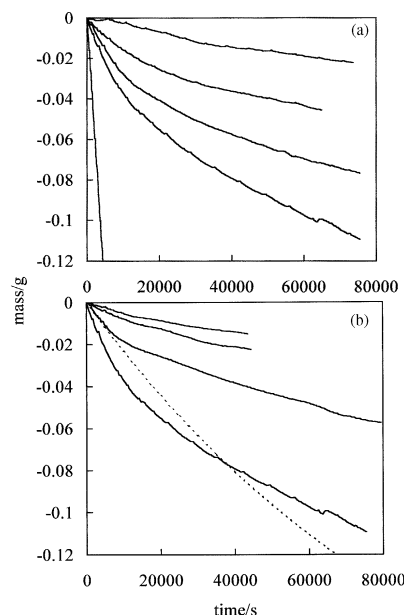


Fig. 4 (a) Water mass loss curves (in descending order) for w_o of 5.2, 10.2, 15.2 and 20.2 with $[AOT] = 0.2$ M and pure water. (b) Water mass loss curves (in descending order) for $[AOT] = 0.05, 0.1, 0.15$ and 0.2 M with $w_o = 20.2$. The dashed curve shows a calculated first order decay (eqn. (4)) for the 0.2 M AOT sample.

concentrations of 0.05, 0.1, 0.15 and 0.2 M. Plots are shown for w_o variation with $[AOT] = 0.2$ M (Fig. 4a) and $[AOT]$ variation for $w_o = 20$ (Fig. 4b). The mass loss curves for samples with lower water contents, although following the same trends as those shown in Fig. 4, had relatively large experimental uncertainties owing to the small mass losses. Fig. 4a also shows the mass loss curve for pure water recorded under identical experimental conditions.

Two main conclusions can be drawn from visual inspection of the mass loss curves. Firstly, the rate of water evaporation from the microemulsion samples is 20–100 times slower than for pure water. Secondly, the microemulsion rates increase with increasing water content. This is true for the series in which w_o increases (for which the equilibrium water vapour pressure P increases and approaches the value for pure water at high w_o) and for samples with increased AOT concentration at constant w_o (for which P is constant). This non-proportionality of rate and vapour pressure together with the slowness of the rates as compared with pure water clearly indicate that the rate-limiting step is not vapour diffusion across the stagnant vapour space between the liquid surface and the mouth of the sample tube. We therefore consider two possible alternative rate-limiting processes.

Firstly, transfer of water across the microemulsion/vapour interface may be rate limiting. Although nothing is known concerning the mechanism of drop transfer across the surface separating an oil-continuous microemulsion and vapour phase, the transfer of species solubilised within w/o microemulsion drops across oil/water interfaces has been studied previously.^{17,18} This latter process is found to be slower than the maximum theoretical rate corresponding to diffusion limited supply of drops to the surface. The energy barrier to interfacial transfer is thought to arise from the barrier to fusion of the drops with the planar surfactant monolayer adsorbed at the oil/water interface formed by contacting a w/o microemulsion with an aqueous phase. However, surfactants do not generally adsorb at the oil/vapour surface and thus the liquid/vapour surface of the w/o microemulsion is expected to be monolayer free. It is thus highly questionable whether transfer of water across the oil/vapour surface is subject to the type of energy barrier observed at oil/water interfaces. If transfer across the surface were rate limiting and much slower

than water diffusion in the bulk microemulsion then the water would remain uniformly distributed throughout the microemulsion during evaporation. If it is assumed that the flux across the surface is proportional to the sub-surface water concentration then the mass loss curves would be expected to show first order kinetics, *i.e.* to decay exponentially according to

$$m = m_0 \exp(-k_i t) \quad (4)$$

where m is the mass of water remaining after time t , m_0 is the total initial mass of water in the sample and k_i is a rate coefficient. The dashed line in Fig. 4b compares the mass loss curve for $w_0 = 20/0.2$ M AOT calculated using eqn. (4) with k_i adjusted to give agreement with the experimental plot at approximately 40 000 s. The calculated curve is very different to the experimental data suggesting that either water transport across the surface is not rate limiting or that the rate coefficient k_i may change with water content.

The second process that may limit the evaporation rate is diffusion of water drops within the bulk microemulsion phase to the surface. We test this hypothesis by comparing the measured mass loss curves with plots calculated on the basis that water diffusion in the microemulsion is rate limiting and that the subsequent processes of water transfer across the interface and the stagnant vapour space are not rate limiting, *i.e.* they can occur as fast as drops can diffuse to the surface. As discussed above, exact calculation of the water diffusion in the bulk microemulsion is complicated by effects due to drop interactions and percolation together with possible coupling of the evaporation process with the dynamics of drop fusion/fission. In order to proceed, these complications are neglected and we assume that water diffuses as drops with the diffusion coefficients listed in Table 1.

The model corresponds to diffusion out of one side of a sample slab of thickness $h/2$. Initially, the water is uniformly distributed throughout the sample. As evaporation proceeds the surface concentration is depleted and a concentration gradient results. Because diffusion in bulk is assumed to be rate limiting with subsequent fast transfer through the surface and stagnant vapour space, the surface concentration of water is taken to be zero for all times greater than zero. Using the theory given by Jost for this model,¹⁹ the mass of water m remaining after time t is

$$m = \frac{8m_0}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-\left(\frac{(2n+1)\pi}{h}\right)^2 D t\right] \quad (5)$$

where m_0 is the initial mass of water in the sample and the sum is calculated up to a maximum value of the integer n necessary to obtain the required precision. For the sample tube configuration used here (Fig. 2) the sample depth is not constant across the tube. We have taken the mean sample depth $h/2$ to be equal to $V_{\text{sample}}/\pi r_t^2$ where V_{sample} is the sample volume and r_t is the radius of the cylindrical region of the sample tube. Because the total water content of the sample is low and the dodecane evaporation rate is slow, the variation in mean sample thickness with time due to evaporation is very small and can be safely neglected.

Fig. 5a and b show the calculated plots for different w_0 values at 0.2 M AOT (corresponding to the data of Fig. 4a) and different AOT concentrations at $w_0 = 20$ (corresponding to the data of Fig. 4b). The curve shapes and the variation with w_0 and AOT concentration show reasonable qualitative agreement with the experimental curves clearly indicating that drop diffusion in bulk is the main process limiting the evaporation rate. The presence of a significant energy barrier to water transport across the surface would produce rates slower than observed and hence may possibly be a contributing factor for the low water content systems where the calculated rates are faster than observed. The measured water loss rate

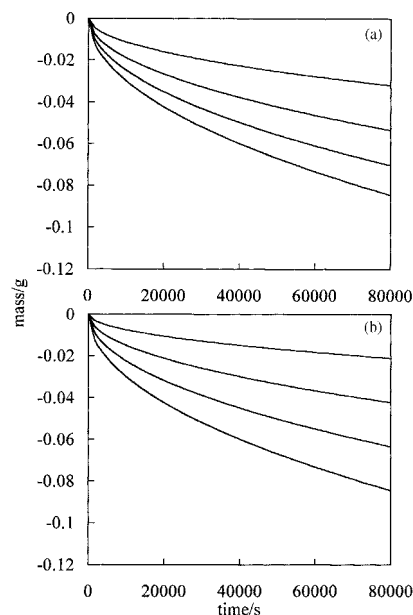


Fig. 5 (a) Water mass loss curves calculated according to eqn. (5) for (in descending order) w_0 of 5.2, 10.2, 15.2 and 20.2 with $[AOT] = 0.2$ M. Drop diffusion coefficients were assumed to equal those in Table 1. (b) Water mass loss curves calculated according to eqn. (5) for (in descending order) $[AOT] = 0.05, 0.1, 0.15$ and 0.2 M with $w_0 = 20.2$. The drop diffusion coefficient was assumed independent of AOT concentration and taken to be $3.2 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ (Table 1).

for the highest water content system ($w_0 = 20$ with $[AOT] = 0.2$ M) is faster than calculated here suggesting that water diffusion is faster than predicted using the value of D from Table 1. Attractive inter-drop interactions would reduce the diffusion coefficient (and the mass loss rate) from that estimated here. One possible explanation for the faster rate is that this particular system may be in a percolating regime where water diffusion rate is enhanced. The explanation is supported by the data of Fig. 2 of ref. 11 which shows that this high water content system is in the percolating regime at 25 °C.

Conclusion

The evaporation rates of microemulsion water drops are very much slower than the rate from pure water even when the equilibrium vapour pressure of the microemulsion is comparable to that of pure water. The microemulsion evaporation rate increases with increasing water content, whether by changing w_0 or the overall drop concentration. The measured rates are approximately consistent with a model in which water drop diffusion within the bulk microemulsion is rate limiting and the subsequent processes of water transfer across the liquid/vapour surface and stagnant vapour space are not rate limiting.

References

- 1 K. J. Beverley, J. H. Clint and P. D. I. Fletcher, *Phys. Chem. Chem. Phys.*, 1999, **1**, 149.
- 2 K. J. Beverley, J. H. Clint, P. D. I. Fletcher and S. Thubron, *Phys. Chem. Chem. Phys.*, 1999, **1**, 909.
- 3 S. E. Friberg, B. Yu, J. W.-P. Lin, E. Barni and T. Young, *Colloid Polym. Sci.*, 1993, **271**, 152.
- 4 S. E. Friberg, T. Young, R. A. Mackay, J. Oliver and M. Breton, *Colloids Surf. A*, 1995, **100**, 83.
- 5 S. Hamdan, Y. Y. Dai and F. B. H. Ahmad, *Oriental J. Chem.*, 1997, **13**, 111.
- 6 S. Hamdan, F. B. H. Ahmad, Y. Y. Dai, K. Dzulkefly and K. H. Ku Bulat, *J. Dispersion Sci. Technol.*, 1999, **20**, 415.
- 7 R. Aveyard, B. P. Binks, S. Clark and J. Mead, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 125.
- 8 E. Keh and B. Valeur, *J. Colloid Interface Sci.*, 1981, **79**, 465.

- 9 See, for example, P.W. Atkins, *Physical Chemistry*, Oxford University Press, Oxford, 5th edn., 1994, p. 795.
- 10 *Selected values of properties of hydrocarbons and related compounds*, ed. C. W. Haas, Thermodynamic Research Center AP144 Hydrocarbon Project, Thermodynamics Research Center, Texas A&M University, Texas, 1978.
- 11 P. Alexandridis, J. F. Holzwarth and T. A. Hatton, *J. Phys. Chem.*, 1995, **99**, 8222.
- 12 K. Kon-No and A. Kitahara, *J. Colloid Interface Sci.*, 1971, **35**, 409.
- 13 J. Biais, L. Oldberg and P. Stenius, *J. Colloid Interface Sci.*, 1982, **86**, 350.
- 14 M. Ueda and Z. A. Schelly, *Langmuir*, 1988, **4**, 653.
- 15 C. H. Chew and M. K. Wong, *J. Dispersion Sci. Technol.*, 1991, **12**, 495.
- 16 P. D. I. Fletcher, A. M. Howe and B. H. Robinson, *J. Chem. Soc., Faraday Trans. 1*, 1987, **83**, 985.
- 17 W. J. Albery, R. A. Choudhery, N. Z. Atay and B. H. Robinson, *J. Chem. Soc., Faraday Trans. 1*, 1987, **83**, 2407.
- 18 W. Nitsch, P. Plucinski and J. Ehrlenspiel, *J. Phys. Chem.*, 1997, **101**, 4024.
- 19 W. Jost, *Diffusion in Solids, Liquids, Gases*, Academic Press Inc., New York, 1952, p. 37.

Paper 9/06769H