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NEW RESULTS AND INTERPRETATIONS

BY

D. FENNELL EVANS
SURAJIT MUKHERJEE
D.J. MITCHELL
AND
B.W. NINHAM

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INSTITUTE FOR MATHEMATICS AND ITS APPLICATIONS
UNIVERSITY OF MINNESOTA

514 Vincent Hall
206 Church Street SE.
Minneapolis, Minnesota 55455

Surfactant Diffusion; New Results and Interpretations

D. Fennell Evans,¹ Surajit Mukherjee,¹ D. J. Mitchell,³
and B. W. Ninham^{1,2,3}

¹Department of Chemical Engineering
and Materials Science
University of Minnesota
Minneapolis, MN 55455

²Institute for Mathematics and Its Applications
University of Minnesota
Minneapolis, MN 55455

³Department of Applied Mathematics
Research School of Physical Sciences
Australian National University
Canberra ACT 2600, Australia

Abstract

Data for surfactant diffusion are reported for sodium dodecylsulfate at 25°C and tetradecyltrimethylammonium bromide at 25°, 90° and 135°C, as measured by Taylor tube dispersion. These data are analyzed in terms of two limiting forms of theory, one appropriate to "slow" reaction rates, the other to "fast" rates. It is shown that the usual extrapolation to the critical micelle concentration to infer intrinsic diffusion constants is not permissible. The data is explicable if transport occurs by a process wherein ionic micelles disassociate, diffuse as monomers and reassemble into micelles. This is directly contrary to current ideas on diffusion of surfactants.

1. Introduction

Diffusion measurements have become a widely used technique for characterizing micellar solutions. There are several: Quasi-elastic light scattering,^(1,2) sedimentation equilibrium,⁽³⁾ tracer measurements^(4,5,6) and Taylor tube dispersion.⁽⁷⁾ Judicious interpretation of kinetic studies,⁽⁸⁾ neutron scattering⁽⁹⁾ and NMR⁽¹⁰⁾ give additional complementary information. For ionic surfactants most work has been focussed on sodium dodecylsulfate (SDS) in water. This system provides a convenient benchmark; both to check the consistency of different methods, and to form a foundation on which the beginnings of an intuition concerning mechanisms of transport can be built.

At various times the interpretation of data has involved widely different models from which very different conclusions have been drawn. For example, the pioneering QELS studies of Benedeck et al.⁽²⁾ appeared to give strong evidence for sphere to (highly polydisperse) cylinder transitions with increasing salt in agreement with then extant theoretical expectations. In the later QELS studies of Corti and deGiorgio⁽¹⁾ on precisely the same system, no such conclusion is inferred. Rather, their data is modelled in terms of essentially monodisperse micelles with hydrodynamic interactions accounted for through a DLVO potential description. The tracer measurements appeared a source of additional confusion. The matter was confounded further by the measurements at zero salt concentration of Rhode and Sackmann⁽¹¹⁾ by QELS, and of Weinheimer et al.⁽⁷⁾ by Taylor tube dispersion. Both sets of data are in substantial agreement, and with the careful experiments of Kratochvil and Aminabhavi⁽³⁾ via sedimentation equilibrium. Rhode and Sackmann interpreted their results in terms of a mean field theory of Stephen,⁽¹²⁾ developed for polyelectrolyte solutions. This is tantamount to the assumption that micelles retain their integrity during the time course of a measurement, an

assumption which has hardly been questioned. Their analysis led to an aggregation number N of the order of 20-30, in gross disagreement with expectations ($N \approx 60$) from a whole series of thermodynamic determinations^(13,14) over the years. In direct contrast, Weinheimer *et al.*⁽⁷⁾ interpreted their data via a different model, wherein micelles can disperse into monomers under the influence of an electrostatic diffusion gradient provided by counterions, diffuse as monomers, and reassemble into micelles. Their theory is consistent with the thermodynamic data.

Most of this controversy appeared to have been decently put to rest by the recent review of Corti and deGiorgio,⁽¹⁾ and by two succinct papers by Phillies.^(15,16) Thus, in terms of the accepted interpretation of kinetic experiments,⁽⁸⁾ Phillies reconciled tracer and QELS data, and resolved the problem of polydispersity. The broad conclusions are eminently sensible. Since the Taylor tube measurements involved time scales orders of magnitude larger than those for QELS, the problem of zero salt data was resolved essentially by sweeping it into a regime labelled peculiar.

But some questions do remain. The assignment of "bound" charge to the SDS micellar surface in these models^(1,15) differs from the magnitude of such charge adduced by some other experimental techniques.⁽⁷⁾ The value of the Debye length to be assigned is not known and is a vexed problem. Further, the value of the Hamaker constant to describe van der Waals interactions is too large by a factor of 10.⁽¹⁷⁾ In addition recent experimental and theoretical developments have shown that in the important regime of interactions, below 50 Å, the DLVO theory must be suspect for organic systems in salt water. --- Below 30 Å, both lecithin and CTAB bilayers exhibit strong repulsive hydration forces which completely dominate double layer forces^(18,19,20) and

are highly sensitive to the nature of bound counterions. And between hydrophobic monolayers, the attractive van der Waals forces computed from continuum theories must be replaced by very strong long range hydrophobic forces⁽²¹⁾ for which again there exists no quantitative, or even qualitative theory. These circumstances raise some doubts concerning the quantitative interpretation of high salt experiments, even granted assumptions on micellar integrity, monodispersity and shape. Indeed the paucity of theoretical knowledge of interactions throws the burden of allowable quantitative modelling squarely back into the low salt (limiting law) regime where electrostatic forces clearly dominate, and can be modelled by mean field theories.

In summary, confusion still remains about what information can be gleaned about micellar transport via diffusion measurements. The measurements we report in this paper raise further substantive questions. We have determined diffusion coefficients for $C_{14}TAB$ and SDS using Taylor tube dispersion and find that the diffusion coefficient decreases rapidly just beyond the critical micelle concentration (CMC), goes through a minimum and then increases with concentration at 25°C. Similar behavior is observed for $C_{14}TAB$ at 95° and 130°C. Thus the measured diffusion coefficients do not extrapolate to a value which can readily be identified with a diffusion coefficient of a micelle at the CMC. Such behavior is readily explicable in terms of a modification of a "rapid" reaction rate model developed earlier, and cannot be explained in terms of the slow reaction rate picture which underlies current intuition. This in itself is no source for alarm, as the time scales for Taylor tube measurements and QELS are very different (cf. Appendix B). But the facts that (1) low salt data in SDS by both techniques and by sedimentation equilibrium are in agreement and (2) similar behavior has apparently

been observed by neutron scattering and QELS⁽²³⁾ for other ionic surfactants leads one to again question the universality of the conventional picture as accepted for SDS.

Section 2 begins with a report on diffusion by Taylor tube dispersion in $C_{14}TAB$. Together with data on SDS already alluded to, these results require for their interpretation the subsequent theoretical discussion. Section 3 then lays out for comparison and connects two alternative models valid in the limits of either fast or slow monomer-micelle exchange rates. Related appendices establish the equivalence of the Taylor tube technique and QELS, and deal with the effects of polydispersity. These theories are applied in section 4 to an analysis of the measurements, which cannot be reconciled with the standard picture of micellar transport. Our final section 5 summarizes our view of the present state of the art of extracting information for diffusion measurements.

2. Experimental Methods and Results

The diffusion coefficients were determined using the Taylor dispersion technique. In this method a small sample (20 μl) is injected into the carrier stream as it flows through a capillary tube. Provided the flow is laminar, the combination of flow and diffusion results in a Gaussian distribution of the solute with respect to the axial position along the tube. Experimentally it is more convenient to measure the variation in concentration with time at fixed location. The resulting concentration profile is given by (Appendix B)

$$\frac{c - \bar{c}}{c_{\max} - \bar{c}} = \left(\frac{t_R}{t}\right)^{1/2} \exp\left[-12 D \frac{(t-t_R)^2}{a^2 t}\right]$$

where D is the effective diffusion coefficient, a is the radius of the tube, $\bar{c}$ is the average surfactant concentration without the pulse, c is the surfactant concentration averaged across the tube radius at time t , $c_{\max}$ is the maximum value of c and t_R is the residence time, i.e. tube length divided by the average solution velocity. The diffusion coefficient and t_R were obtained by a non-linear least squares fit of the observed concentration profile.

In an experiment, the carrier stream was a surfactant solution above the CMC and the concentration of the injected sample was slightly (< 0.02 M) higher or lower than that of the carrier stream. Provided that the concentration of the injected sample was above the CMC, the same diffusion coefficient was obtained. For surfactant concentration in the carrier stream just above the CMC the injected sample was always slightly larger (≈ 0.01 M) than that of the carrier stream.

The details of the apparatus have been given elsewhere.⁽⁶⁾ For the measurements above 25°C, the system was pressurized to around 50 psig and the

carrier stream temperature was lowered to 25°C just prior to entering the differential refractometer. The perturbations due to the slight increase in pressure or a change in temperature in the last 1% of the capillary tubing are negligible.⁽²²⁾

The C₁₄TAB surfactants used in the dilute solutions ($\leq 1.5\%$) were recrystallized twice from acetone and dried in a vacuum oven. In order to check for thermal stability, a 4 wt% aqueous C₁₄TAB solution was kept at 135°C for six hours, the typical residence time for the diffusion measurement. Surface tension vs. concentration curves obtained for the thermally treated material gave no indication of a minimum near the CMC. For the C₁₄TAB surfactant concentrations above 1.5 wt%, the surfactant was used as received (+ 99% purity). We found that at these relatively high surfactant concentrations small amounts of impurities did not affect the diffusion coefficient. The SDS used in this study was recrystallized twice from absolute ethanol. The purity of both recrystallized surfactants was checked by surface tension measurements and no minimum was recorded near the CMC.

The measured diffusion coefficients are shown in figures 1 and 2. The diffusion coefficients rather strikingly decrease just above the CMC, go through a minimum and subsequently increase. The most commonly reported micellar diffusion coefficient data has been for surfactant SDS at or around 25°C. But unfortunately this system has not been studied very carefully in the vicinity of its CMC. Thus the upturn in D reported in the present study went unobserved.

From our study it appears that the increase in D near the CMC is a general feature of all ionic surfactant systems in pure water. As the temperature increases, the concentration range over which the diffusion

coefficient decreases becomes larger thus substantiating the results obtained at 25°C. This broadening appears to be related to the larger CMC values at those temperatures. Similar results have been reported for sodium octanoate at 28°C from QELS measurements.⁽²³⁾

3. Basic Theory

These data are inexplicable in terms of the conventional analysis which determines the intrinsic micelle diffusion constant by extrapolation to the CMC. One possibility is that because of widely different time scales Taylor tube and/or sedimentation experiments measure very different quantities to QELS and that available data on SDS at zero salt is incorrect. We shall explore the alternative. Four very different models have been used to interpret the SDS experiments: (i) Micelles are essentially monodisperse, retain their identity during the time scale of a QELS measurement, and the data is explained by involving a DLVO description of interactions.⁽¹⁾ This picture appears to accord with current interpretations of kinetic experiments. (ii) Micelles increase in size with increasing surfactant or salt concentration.⁽⁹⁾ (iii) A mixture of micellar sizes is observed which can become highly polydisperse at very high salt.⁽²⁾ (iv) Monodisperse micelles diffuse directly, and through an indirect process in which they disassemble, diffuse as monomers and reassemble into micelles.⁽⁷⁾ The connection between these models is not clear, nor has the equivalence of Taylor tube dispersion in multicomponent diffusion with QELS been established. But all such models must emerge from a single theoretical framework to which we now proceed. To develop this framework, it is necessary to rehearse the background to QELS and extend the theory to the case of ionic micelles. We can then derive the corresponding theory for the Taylor tube experiment and demonstrate equivalence.

The formulary of the QELS bestiary is by now so much a part of the language that it needs little recapitulation.^(24,25) We shall require only a standard result

$$\frac{I(t)}{I(0)} = \frac{\sum_{i,j} \left(\frac{\partial X}{\partial n_i} \right) \left(\frac{\partial X}{\partial n_j} \right) S_{ij}(q,t)}{\sum_{i,j} \left(\frac{\partial X}{\partial n_i} \right) \left(\frac{\partial X}{\partial n_j} \right) S_{ij}(q,0)} \quad (1)$$

Here $I(t) \equiv \langle \tilde{E}(\underline{r},t) \cdot \tilde{E}(\underline{r},0) \rangle$ where $\tilde{E}(t)$ is the electric field of light scattered from a sample at angle θ received by a detector at distance r . It is assumed that the sample contains a variety of species j ($j=1,2,\dots,s$) solvent (1), surfactant, salt ... and that the susceptibility is additive, i.e.

$$\Delta X(\underline{r},t) = \sum_j \left(\frac{\partial X}{\partial n_j} \right)_{\{n_i\},T} \Delta n_j$$

The partial derivatives are taken at constant temperature and density n_k of all other species. The wave vector q is defined by

$$q = |k_0 - k(\omega)| = \frac{2\pi\sqrt{\epsilon}}{\lambda} (2 \sin \frac{\theta}{2}) \quad , \quad k_0 = \frac{\omega_0 \sqrt{\epsilon}}{c} \hat{k}_0 \quad (2)$$

where k_0 , ω_0 characterize the incident field E_0 and $\epsilon = 1 + 4\pi\chi$ is the relative permittivity at frequency ω_0 of the sample (and implicitly that of the bathing medium in which both source and detector are immersed). $\tilde{S}_{ij}(\tilde{q},t)$ is the spatial Fourier transform of the time-dependent density correlation function

$$S_{ij}(\underline{r}_1 - \underline{r}_2, t_1, t_2) = \langle \Delta n_i(\underline{r}_1, t) \Delta n_j(\underline{r}_2, t) \rangle \quad (3)$$

which for an equilibrium and homogeneous sample has the special form

$S_{ij} = S_{ij}(\underline{r}_1 - \underline{r}_2, t_1 - t_2)$. The derivation of Eq. (1) assumes that the time dependent correlation function is that of an equilibrium system. To reduce it

further it is necessary to assume that the sample is incompressible, i.e.

$$\frac{\partial n_i}{\partial p} = 0 = \sum_j \frac{\partial n_i}{\partial \mu_j} \frac{\partial \mu_j}{\partial p} = \sum_j v_j \frac{\partial n_i}{\partial \mu_j} = \sum_j \left(\frac{v_j}{kT} \right) \tilde{S}_{ij}(q,0) \quad (4)$$

where the v_j are partial molar volumes, and the last step follows since equilibrium statistical mechanics requires that $\tilde{S}_{ij}(q,0) = kT \frac{\partial n_i}{\partial \mu_j}$. The observation Eq. (4) allows the solvent to be eliminated in the denominator of Eq. (1).

For denoting solvent by the subscript 1, we have from Eq. (4)

$$\tilde{S}_{1i} = - \sum_{j=2}^S \frac{v_j}{v_1} S_{ij}(q,0) \quad (5)$$

Rearrangement gives

$$\sum_{i,j} \left(\frac{\partial \chi}{\partial n_i} \right) \left(\frac{\partial \chi}{\partial n_j} \right) \tilde{S}_{ij}(q,0) = \sum_{i,j=2}^S \alpha_i \alpha_j \tilde{S}_{ij}(q,0) \quad (6)$$

where we have used $S_{ij} = S_{ji}$ which is a matter of definition, and the effective polarisability of species i is defined as

$$\alpha_i = \left(\frac{\partial \chi}{\partial n_i} - \frac{v_i}{v_1} \frac{\partial \chi}{\partial n_1} \right) \quad (7)$$

This standard argument can be made more general. For by definition, for an incompressible system $\sum_i v_i \Delta n_i = 0$, whence

$$\langle n_j(t) \sum_i v_i n_i(0) \rangle \equiv \sum_i v_i S_{ji}(\tilde{r},t) = 0 \quad (8)$$

Rearrangement, as for Eq. (6) then gives

$$\frac{I(t)}{I(0)} = \frac{\sum_{i,j=2}^S \alpha_i \alpha_j \tilde{S}_{ij}(q,t)}{\sum_{i,j=2}^S \alpha_i \alpha_j \tilde{S}_{ij}(q,0)} \quad (9)$$

The two approximations involved in arriving at this expression are that (1) fluctuations in refractive index are due only to fluctuations in the number densities of the specified species (solutes) and (2) incompressibility.

The measured correlation functions $\tilde{S}(q,t)$ can be related to diffusion processes by an ansatz termed the Onsager Regression Hypothesis; viz. that $\tilde{S}(q,t)$ satisfies the same relaxation equations that describe the macroscopic relaxation process.

We have been unable to find a proof of the ansatz in the bestiary, so that we may as well digress briefly to outline such a proof, which can proceed via the following artifice: Consider a perturbation applied to an equilibrium system of the form

$$H' = \sum_i \int d\mathbf{r} \phi_i(\mathbf{r}, t) n_i(\mathbf{r}) \quad (10)$$

For definiteness take an external potential $\phi_i(\mathbf{r}, t) = \phi_i(\mathbf{r})\theta(-t)$ where $\theta(t)$ is the step function. Linear response theory gives

$$\delta n_i(\mathbf{r}, t) = \sum_j \iint d\mathbf{r}' d\mathbf{r} G_{ij}(\mathbf{r}-\mathbf{r}', t-t') \phi_j(\mathbf{r}', t') \quad (11)$$

where G_{ij} is the Green function. ( ) For times $t > 0$ the response of the system to the potential ϕ_i is

$$\begin{aligned}
\delta n_i(\underline{r}, t) &= -\sum_j \int d\underline{r}' \int_t^\infty G_{ij}(\underline{r}-\underline{r}', t') \phi_j(\underline{r}') dt' \\
&= -\sum_j \int d\underline{r}' \mathcal{G}_{ij}(\underline{r}-\underline{r}', t) \phi_j(\underline{r}')
\end{aligned} \tag{12}$$

In the limit of classical statistical mechanics we have the relation⁽²⁶⁾

$$S_{ij}(\underline{r}-\underline{r}', t) = kT \mathcal{G}_{ij}(\underline{r}-\underline{r}', t)$$

whence

$$\delta n_i(\underline{r}, t) = -\frac{1}{kT} \sum_j \int d\underline{r}' S_{ij}(\underline{r}-\underline{r}', t) \phi_j(\underline{r}')$$

or taking Fourier transforms

$$\delta n_i(\underline{q}, t) = -\frac{1}{kT} \sum_j \tilde{S}_{ij}(\underline{q}, t) \phi_j(\underline{q}) \tag{13}$$

On the other hand for $t \leq 0$, $\delta n_i(\underline{r}, t)$ is a constant, viz.

$$\begin{aligned}
\delta n_i(\underline{r}, t) &= -\sum_j \int d\underline{r}' \int_0^\infty G_{ij}(\underline{r}-\underline{r}', t') \phi_j(\underline{r}') dt' \\
&= \delta n_i(\underline{r}, 0)
\end{aligned} \tag{14}$$

For a one component system then $\delta \tilde{n}(\underline{q}, t) = \tilde{S}(\underline{q}, t) \phi(\underline{q})$; $\delta \tilde{n}(\underline{q}, 0) = \tilde{S}(\underline{q}, 0) \phi(\underline{q})$

which relations together imply

$$\delta \tilde{n}(\underline{q}, t) = \frac{\tilde{S}(\underline{q}, t) \delta \tilde{n}(\underline{q}, 0)}{\tilde{S}(\underline{q}, 0)} \tag{15}$$

Hence if we choose an initial density profile $\delta n(\underline{q}, 0) = \tilde{S}(\underline{q}, 0)$, the correlation function $\tilde{S}(\underline{q}, t)$ will evolve as $\delta \tilde{n}(\underline{q}, t)$. For a many component system the corresponding generalization of Eq. (15) is

$$\delta \tilde{n}(\underline{q}, t) = \tilde{S}(\underline{q}, t) \tilde{S}^{-1}(\underline{q}, 0) \delta \tilde{n}(\underline{q}, 0) \quad (16)$$

where $\delta \tilde{n}$ is now a column vector with components δn_i (i labels each species) and $\tilde{S}$ is the matrix of correlation functions with components $\tilde{S}_{ij}$. Again if we choose an initial condition $\delta \tilde{n}_i(\underline{q}, 0) = \tilde{S}_{ij}(\underline{q}, 0)$ (j arbitrary), $\tilde{S}_{ij}(\underline{q}, t)$ will satisfy the same equations as those of the $\delta \tilde{n}_i$.

We remark that Eq. (9) is only valid if we treat monomers and different sized micelles as different solute species (except in the unlikely event that $\alpha_i = i\alpha$ where α is the effective polarisability of a monomer). The interpretation of QELS is in fact intractable unless one assumes $\alpha_i \propto i$ as is normally done. Since the scattering is dominated by micellar contributions, this assumption is reasonable.

3.1 Rate Constants and Polydispersity

Having established that QELS measures $S_{mm}(\underline{q}, t)$ and that the $S_{ij}(\underline{r}, t)$ satisfy the (linear) macroscopic relaxation equations satisfied by perturbations in concentration δn_i , we proceed to explicit examples. Consider first non-ionic micelles, and suppose that micellization is characterized by the reaction

(This is consistent with inferences from kinetic experiments which assign to the two observed relaxation times one relatively slow process, corresponding

to this picture, and one very fast associated with individual monomer exchanges with micelles. The second process can be ignored and all such events lumped to form an "effective" micelle).

Assume that the two solute species satisfy Fick's law

$$\tilde{J}_i = -D_i \nabla n_i \quad (17)$$

where n_i is the number density, J_i is the current density and D_i the diffusion constant of the i -th species, and that the continuity equation for each species has the form

$$\frac{\partial n_l}{\partial t} + \nabla \cdot \tilde{J}_l = N(R_b n_m - R_f n_l^N) \approx N(R_b \delta n_m - N R_f (n_l^0)^{N-1} \delta n_l) \quad (18a)$$

and

$$\frac{\partial n_m}{\partial t} + \nabla \cdot \tilde{J}_m = R_f n_l^N - R_b n_m \approx R_f (n_l^0)^{N-1} \delta n_l - R_b \delta n_m \quad (18b)$$

In Eqs. (18) the subscript l refers to monomers and the subscript m refers to micelles (assumed monodispersed) and N is the aggregation number. The term $R_f n_l^N$ represents the rate of formation of micelles and $R_b n_m$ represents the rate of breakup of micelles. Strictly speaking one should show that "effective" rate constants R_b , R_f emerge naturally from an infinite set of such coupled equations (cf. Appendix A). Such a protocol is impossible in general and in any event will be seen to be unnecessary. The quantities δn_l and δn_m are the (small) deviations from the equilibrium concentrations n_l^0 , n_m^0 .

At equilibrium $R_b n_m^0 = R_f (n_l^0)^N$ so our equations can be recast as

$$\frac{\partial n_l}{\partial t} - D_l \nabla^2 n_l = N R_b \left(\delta n_m - \frac{N n_m^0}{n_l^0} \delta n_l \right) \quad (19a)$$

and

$$\frac{\partial n_m}{\partial t} - D_m \nabla^2 n_m = -R_b \left(\delta n_m - \frac{N n_m^0}{n_1^0} \delta n_1 \right) \quad (19b)$$

The Fourier transforms of $\delta n_i(r, t)$ we shall call $\tilde{n}_i(q, t)$. They satisfy

$$\frac{\partial \tilde{n}_1}{\partial t} + D_1 q^2 \tilde{n}_1 = NR_b \left(\tilde{n}_m - \frac{N n_m^0}{n_1^0} \tilde{n}_1 \right) \quad (20a)$$

and

$$\frac{\partial \tilde{n}_m}{\partial t} + D_m q^2 \tilde{n}_m = -R_b \left(\tilde{n}_m - \frac{N n_m^0}{n_1^0} \tilde{n}_1 \right) \quad . \quad (20b)$$

These then are the equations satisfied by the $\tilde{S}_{ij}(q, t)$ with $n_i = \tilde{S}_{ij}(q, t)$.

In this case the initial condition for the $\tilde{n}_i$ will be

$$\tilde{n}_i(q, 0) = \tilde{S}_{ij}(q, 0) = n_i^0 \delta_{ij} \quad (21)$$

where δ_{ij} is the Kronecker delta. In Eq. (21) as in Eqs. (18) we have assumed that the micelles and monomers are non-interacting.

The relaxation equations can be solved using Laplace transforms and yield the general solutions

$$n_1 = NR_b \sum_{i=1}^2 \frac{x_i}{D_1 - \lambda_i} e^{-\lambda_i q^2 t} \quad (22)$$

and

$$n_m = R_b \sum_{i=1}^2 \frac{\chi_i}{\lambda_i - \bar{D}_m} e^{-\lambda_i q^2 t} \quad (23)$$

where the λ_i are the roots of the equation

$$(\lambda - D_1)(\lambda - D_m) - \frac{R_b}{q^2} [(\lambda - D_1) + (N^2 n_m^0 / n_1^0)(\lambda - D_m)] = 0 \quad (24)$$

and the χ_i are given by

$$\chi_i = \frac{\tilde{n}_m(0)(D_1 - \lambda_i) - (N n_m^0 / n_1^0) \tilde{n}_1(0)(D_m - \lambda_i)}{(D_1 - \lambda_i) + (D_m - \lambda_i) + (R_b / q^2)(1 + N^2 n_m^0 / n_1^0)} \quad , \quad (25)$$

Two limits of interest are $R_b \rightarrow 0$ and $R_b \rightarrow \infty$. The first is trivial and yields

$$\tilde{n}_1(q, t) = \tilde{n}_1(q, 0) e^{-D_1 q^2 t} \quad , \quad \tilde{n}_m(q, t) = \tilde{n}_m(q, 0) e^{-D_m q^2 t} \quad (26)$$

The second limit is more involved. One root tends to $\bar{D}$ where

$$\bar{D} = \frac{n_1^0 D_1 + N^2 n_m^0 D_m}{n_1^0 + N^2 n_m^0} \quad (27)$$

and the other root $\lambda \sim (R_b / q^2)(1 + N^2 n_m^0 / n_1^0) \rightarrow \infty$. We find that for $R_b \rightarrow \infty$

$$\tilde{n}_1(q, t) = \frac{\tilde{n}_1(q, 0)}{(1 + N^2 n_m^0 / n_1^0)} e^{-\bar{D} q^2 t} \quad (28)$$

$$\tilde{n}_m(q, t) = \frac{(N n_m^0 / n_1^0) \tilde{n}_1(q, 0)}{(1 + N^2 n_m^0 / n_1^0)} e^{-\bar{D} q^2 t} \quad , \quad (29)$$

where $\tilde{n}(q,0) \equiv \tilde{n}_1(q,0) + N\tilde{n}_m(q,0)$ is the Fourier transform of the total surfactant concentration. The significance of Eqs. (29) is that micelles and monomers will instantaneously equilibrate at $t = 0$ and remain in local equilibrium as both micelles and monomers diffuse. The apparent diffusion constant $\bar{D}$ arises because the micelles can diffuse by two processes: direct diffusion with diffusion constant D_m and indirect diffusion in which the micelles disassemble into monomers, diffuse as monomers and then reassemble.

It is worth noting that for finite R_p/q^2 the two exponents depend on q . Since, in a light scattering experiment $q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$, the exponents will depend in principle on the angle of scattering θ and the wavelength λ .

In the limit of large R_p/q^2 there is only one (finite) exponent and thus $\ln S(q,t)$ will be a linear function of t .

In the opposite limit, small R_p/q^2 , there are two exponents: the light scattering experiment measures

$$\begin{aligned} S(q,t) &= \alpha_1^2 S_{11}(q,t) + \alpha_m^2 S_{mm}(q,t) \\ &= \alpha_1^2 n_1^0 e^{-D_1 q^2 t} + \alpha_m^2 n_m^0 e^{-D_m q^2 t} \end{aligned} \quad (30)$$

where α_1 , α_m are the effective polarisabilities of the monomer and micelle.

In practice the first term of Eq. (30) will be negligible and experimentally undetectable so that $\ln S(q,t)$ will normally appear linear in t with a slope of $D_m q^2$. The (theoretical) coefficient of $q^2 t$ in $\ln S(q,t)$ is $(\alpha_1^2 n_1^0 D_1 + \alpha_m^2 n_m^0 D_m) / (\alpha_1^2 n_1^0 + \alpha_m^2 n_m^0) = \bar{D}$ if we assume $\alpha_m = N\alpha_1$, whereas the apparent experimental coefficient of $q^2 t$ is D_m .

We emphasize and remark in passing that even for this extremely simple case of non-ionic micelles modelled by monomer-micelle exchange only, no

polydispersity, no interactions, and assumptions concerning shape, the measured $S(q,t)$ involves a sum of two exponentials with a fair number of unknown parameters: $\alpha_l, \alpha_m; n_l^0, n_m^0$ (both model dependent), n, R_b, D_l and D_m . In a best possible scenario several of these may be determined to sufficient accuracy (e.g. N, D_l) by independent experiment. Even then the number of parameters (implicit and explicit) remains large. The limiting formulae (27)-(30) are truly limiting. If R_b/q^2 for a particular situation lies in an accessible range between 0 and ∞ , a measurement which sweeps over a range of values of q^2 (which might vary by a factor of say at maximum 10^2) will then span both limiting forms. Given experimental, instrument and sample preparation error, it is improbable that any information could be gleaned concerning an assumed R_b (cf. Appendix A). In this Appendix we show that polydispersity is undetectable in general in the fast reaction rate limit. The theory so far for $R_b/q^2 \rightarrow 0$ is equivalent to that most used for analysis provided it is decorated to include interactions. More hope lies in a situation where R_b/q^2 lies outside the accessible range. At least then one further parameter is eliminated.

3.2 Ionic Micelles

For the more complicated ionic micellar system, we therefore consider only the limits of zero R_b and infinite R_b . With the exception of the work of ref. (7), the former seems to be the only case considered in analysis of light scattering or diffusion generally. As shown by Krahtovil⁽²⁴⁾ this assumption leads to apparently absurd results for SDS at low salt concentrations. The approximate analysis of ref. (11) is based on a theory equivalent to setting $R_b = 0$.

Apart from the solvent, we assume that the system consists of micelles, monomers, counterions and co-ions only. The micelles will be assumed to be monodispersed, i.e. the aggregation number N of surfactant molecules and the number Q of bound counterions are the same for all micelles and are independent of surfactant concentration (but not co-ion concentration). [The number Q is an ill-defined phenomenological concept which is nonetheless inescapable if a range of experiments on ionic micelles are to be interpreted. Precisely what this number means, e.g. actually "bound" ions, the number of ions in the "Stern layer"; and what detailed electrophoretic phenomena due to surface conductance are subsumed by its existence; are unknown; see however ref. (28).] The various solute species shall be considered to be non-interacting except via the diffusion potential and the very strong, very short-range interactions which cause micelles to form. For thermodynamic equilibrium the monomer, counterion and micelle concentrations in moles/liter (C_1 , C_2 and C_m , respectively) are coupled by the relation

$$C_1^N C_2^Q = K C_m \quad (31)$$

and the restrictions (assuming to avoid proliferating algebra that monomers, counterions and co-ions are univalent)

$$C = C_1 + N C_m = C_2 + Q C_m - C_3 \quad (32)$$

Here C and C_3 are the concentrations in moles/liter of the surfactant and co-ions, respectively. [The symbol C denotes moles/liter and n concentration in molecules/cm³.] Eqs. (31) and (32) determine C_1 , C_2 and C_m as functions of C and C_3 . If we define C_0 by the relation

$$K = N C_0^N (C_3 + C_0)^Q \quad (33)$$

it can be shown that for large N the system exhibits a $\text{CMC} \approx C_0$. Thus Eq. (33) can be taken to determine K in terms of the experimentally known CMC.

It should be pointed out that if one plots $\ln C_1$ as a function of $\ln C$ one observes an apparent "second CMC." Any experimental plot could not distinguish a sharp break from the continuous curve given by Eq. (33).

For the dynamic properties assume that the various solute species satisfy the generalized Fick's law

$$\underline{J}_i = -D_i \nabla n_i - \frac{D_i n_i^0 z_i e}{k_B T} \nabla \psi, \quad (34)$$

where ψ is the electrostatic (diffusion) potential,

(1) Slow reaction rate limit $R_b \rightarrow 0$. For this limit we assume each species separately obeys the continuity equation

$$\frac{\partial n_i}{\partial t} + \nabla \cdot \underline{J}_i = 0 \quad (35)$$

so that the relaxation equations are

$$\frac{\partial n_i}{\partial t} = D_i \nabla^2 n_i + \frac{D_i n_i^0 e z_i}{k_B T} \nabla^2 \psi. \quad (36)$$

The term $\nabla^2 \psi = -4\pi \sum n_i^0 z_i e / \epsilon$ where $z_i e$ is the charge on the i -th species and ϵ the dielectric constant of the solvent couples the Eqs. (36). These equations will describe any system comprising any number (I) of independent ionic species. Fourier transformation of Eqs. (36) yields

$$\frac{\partial \tilde{n}_i(q,t)}{\partial t} = -D_i q^2 \tilde{n}_i - \frac{4\pi e^2}{\epsilon k_B T} D_i n_i^0 z_i \left(\sum_j \tilde{n}_j z_j \right) . \quad (37)$$

This then is the equation satisfied by $\tilde{n}_i = \tilde{S}_{ij}(q,t)$. The initial condition on $\tilde{S}_{ij}(q,t)$ is

$$\tilde{S}_{ij}(q,0) = n_i^0 \delta_{ij} - \frac{n_i^0 n_j^0 z_i z_j}{\sum_l n_l^0 z_l^2} . \quad (38)$$

The right hand side of Eq. (38) is the Fourier transform of the correlation function $S_{ij}(\underline{r},0) = \langle [n_i(\underline{s}) - n_i^0(\underline{s})][n_j(\underline{r}+\underline{s}) - n_j^0(\underline{r}+\underline{s})] \rangle$ with respect to $\underline{r}$ for an ionic system in the limit of infinite dilution. The $\tilde{S}_{ij}(q,0)$ satisfy the charge neutrality condition

$$\sum_i z_i \tilde{S}_{ij}(q,0) = 0 .$$

The general solution of Eq. (37) is

$$\tilde{n}_i(q,t) = \frac{D_i n_i^0 z_i e}{k_B T} \sum_{j=1}^I \frac{\chi_j}{D_i - \lambda_j} e^{-\lambda_j q^2 t} , \quad (39)$$

where the λ_j are the roots of the equation

$$\frac{4\pi e^2}{\epsilon k_B T} \sum_j \frac{D_j n_j^0 z_j^2}{\lambda - D_j} = q^2 \quad (40)$$

and the χ_i are given by

$$X_i = \frac{k_B T}{e} \left[\sum_j \frac{\tilde{n}_j(q,0) z_j}{D_j - \lambda_i} \right] / \sum_j \frac{D_j n_j^0 z_j^2}{(D_j - \lambda_i)^2} \quad (41)$$

If the D_i are ordered, i.e. $D_1 < D_2 < D_3 < \dots < D_I$, then the roots satisfy the inequalities $D_1 < \lambda_1 < D_2 < \lambda_2 < \dots < D_I < \lambda_I$. If any two of the D_i coincide, (e.g. suppose $D_{i-1} = D_i$) then $\lambda_i = D_i$ and the two ionic species $i-1$ and i can diffuse together without coupling with the other ionic species. But in general, even if the initial conditions on the n_i satisfy charge neutrality ($\sum n_i z_i = 0$), charge distributions and potential gradients will be set up and the diffusion of all ions will be coupled. Further the roots λ_i will depend on q .

We are normally interested in the limit $q \ll \kappa$ where κ is the inverse Debye length ($\kappa^2 = \frac{4\pi e^2}{\epsilon k_B T} \sum_i n_i^0 z_i^2$). In this limit one of the roots of Eq. (40) is

$$\lambda_I \approx \frac{4\pi e^2}{k_B T} \sum_j \frac{D_j n_j^0 z_j^2}{q^2}$$

while the other roots are approximately those of the equation

$$\sum_j \frac{D_j n_j^0 z_j^2}{\lambda - D_j} = 0 \quad (42)$$

For $i < I$, the X_i will remain finite and Eq. (41) will remain (formally) unchanged whereas $X_I \rightarrow 0$ as $q \rightarrow 0$. Hence in this limit ($q \ll \kappa$)

$$\tilde{n}_i(q,t) \approx \frac{D_i n_i^0 z_i e}{k_B T} \sum_{j=1}^{I-1} \frac{X_j}{D_i - \lambda_j} e^{-\lambda_j q^2 t} \quad (43)$$

where the λ_i are the roots of Eq. (42) and the X_i are given by Eq. (41). We note that the $\tilde{n}_i(q,t)$ given by Eq. (43) satisfy the charge neutrality condition $\sum \tilde{n}_i z_i = 0$.

In the special case $I = 2$, the root of Eq. (42) is

$$\lambda_1 = \frac{D_1 D_2 (n_1^0 z_1^2 + n_2^0 z_2^2)}{n_1^0 D_1 z_1^2 + n_2^0 D_2 z_2^2} = \frac{D_1 D_2 (|z_1| + |z_2|)}{D_1 |z_1| + D_2 |z_2|} \quad (44)$$

and

$$\tilde{S}_{ij}(q,t) = \tilde{S}_{ij}(q,0) e^{-\lambda_1 q^2 t}, \quad (45)$$

where the $\tilde{S}_{ij}(q,0)$ are given by Eq. (38) and λ_1 by Eq. (34).

Another special case of interest is the case $D_I \ll D_1, D_2, \dots, D_{I-1}$. Here $\lambda_1, \lambda_2, \dots, \lambda_{I-2}$ will be approximately the same as in the absence of the I -th species, and

$$\lambda_{I-1} \simeq D_I \left[1 + \frac{n_I^0 z_I^2}{(n_1^0 z_1^2 + \dots + n_{I-1}^0 z_{I-1}^2)} \right]. \quad (46)$$

With the proviso that the n_i^0 are computed via Eqs. (31)-(33), assumed to encapsulate the thermodynamics of micelle formation, the preceeding analysis is equivalent to that of Stephen.⁽¹²⁾

(2) Fast reaction rate limit $R_b \rightarrow \infty$. In this limit the individual species (monomers, micelles and counterions) do not separately satisfy the continuity equations. However we have seen in the section on non-ionic surfactants that in this limit the monomers, micelles and counterions will be in local equilibrium, i.e. C_1 , C_2 and C_m will satisfy Eq. (31) locally. Also in the region

$q^2 \ll \kappa^2$ charge neutrality will be satisfied so that Eq. (32) will hold locally.

Thus C and C_3 may vary spatially and C_1 , C_2 and C_m are determined locally by Eqs. (31) and (32). For small fluctuations about global equilibrium these equations can be recast as

$$\frac{N\delta n_1}{n_1^0} + \frac{Q\delta n_2}{n_2^0} = \frac{\delta n_m}{n_m^0} \quad (47)$$

$$\delta n = \delta n_1 + N\delta n_m = \delta n_2 + Q\delta n_m - \delta n_3 \quad (48)$$

The total surfactant concentration n and the co-ion concentration n_3 will satisfy the continuity equations

$$\frac{\partial n}{\partial t} + \nabla \cdot \underline{J} = 0 \quad (49)$$

$$\frac{\partial n_3}{\partial t} + \nabla \cdot \underline{J}_3 = 0 \quad (50)$$

where the total surfactant current $\underline{J} = \underline{J}_1 + N\underline{J}_m = \underline{J}_2 + Q\underline{J}_m - \underline{J}_3$, and $\underline{J}_1$, $\underline{J}_2$, $\underline{J}_3$ and $\underline{J}_m$ satisfy Eq. (34). The charge neutrality condition $\sum z_i \underline{J}_i = 0$ allows us to eliminate $\nabla \psi$ so that Eq. (34) can be replaced by

$$\underline{J}_i = -D_i \nabla n_i + \frac{D_i n_1^0 z_i}{\sum_j D_j n_j^0 z_j^2} \sum_j D_j z_j \nabla n_j \quad (51)$$

Consider first the case $n_3 = 0$; i.e. surfactant in pure water. Then Eqs. (49) and (51) yield

$$\frac{\partial n}{\partial t} = D_1 \nabla^2 n_1 + N D_m \nabla^2 n_m - (D_1 n_1^0 z_1 + N D_m n_m^0 z_m) \left[\frac{\sum_j n_j z_j \nabla^2 n_j}{\sum_j D_j n_j^0 z_j^2} \right] \quad (52)$$

It remains to express $\nabla^2 n_1$, $\nabla^2 n_2$ and $\nabla^2 n_m$ in terms of $\nabla^2 n$ using Eqs. (47) and (48) whence Eq. (52) will be transformed into a diffusion equation

$$\frac{\partial n}{\partial t} = D \nabla^2 n \quad (53)$$

with

$$D = \frac{(D_1 D_2 + D_1 D_m Q^2 n_m^0 / n_2^0 + D_2 D_m N^2 n_m^0 / n_1^0)(n_1^0 z_1^2 + n_2^0 z_2^2 + n_m^0 z_m^2)}{(1 + Q^2 n_m^0 / n_2^0 + N^2 n_m^0 / n_1^0)(D_1 n_1^0 z_1^2 + D_2 n_2^0 z_2^2 + D_m n_m^0 z_m^2)} \quad (54)$$

In this case the $S_{ij}(q, t)$ have the form $S_{ij}(q, 0) e^{-Dq^2 t}$ and the light scattering experiments therefore measure D as given by Eq. (54).

The extension to the case of non-zero n_3 is straightforward but extraordinarily tedious. We therefore present only the answer which is obtained from Eqs. (39), (40) and (41) and the condition $\sum z_i J_i = 0$, subject to the initial conditions

$$\tilde{S}_{1m}(q, 0+) = \frac{N n_m^0}{\left[1 + \frac{N^2 n_m^0}{n_1^0} + \frac{Q^2 n_m^0}{n_2^0} \right]} - \frac{n_1^0 z_1 n_m^0 z_m}{\sum_j n_j^0 z_j^2} \quad (55a)$$

$$\tilde{S}_{2m}(q, 0+) = \frac{Q n_m^0}{\left[1 + \frac{N^2 n_m^0}{n_1^0} + \frac{Q^2 n_m^0}{n_2^0} \right]} - \frac{n_2^0 z_2 n_m^0 z_m}{\sum_j n_j^0 z_j^2} \quad (55b)$$

$$\tilde{S}_{mm}(q, 0+) = \left[1 - \frac{1}{\left[1 + \frac{N^2 n_m^0}{n_1^0} + \frac{Q^2 n_m^0}{n_2^0} \right]} \right] n_m^0 - \frac{(n_m^0 z_m)^2}{\sum_j n_j^0 z_j^2}$$

$$\tilde{S}_{3m}(q,0+) = - \frac{n_3^0 z_3^0 n_m^0 z_m^0}{\sum_j n_j^0 z_j^2} . \quad (55d)$$

These equations have been derived from Eq. (38) assuming instantaneous equilibration between micelles, monomers and counterions. Since the light scattering is due almost exclusively to $\tilde{S}_{mm}(q,t)$ we present the result for $\tilde{S}_{mm}(q,t)$ only. It is

$$\tilde{S}_{mm}(q,t) = \sum_i \frac{F - E\lambda_i}{B - 2A\lambda_i} e^{-\lambda_i q^2 t} , \quad (56)$$

where the λ_i are the roots of the equation $A\lambda^2 - B\lambda + C = 0$ and

$$A = \left[1 + \frac{N^2 n_m^0}{n_1^0} + \frac{Q^2 n_m^0}{n_2^0} \right] (D_1 n_1^0 z_1^2 + D_2 n_2^0 z_2^2 + D_3 n_3^0 z_3^2 + D_m n_m^0 z_m^2) \quad (57)$$

$$\begin{aligned} B = & (n_1^0 z_1^2 + n_2^0 z_2^2 + n_m^0 z_m^2) \left[D_1 D_2 + \frac{Q^2 n_m^0}{n_2^0} D_1 D_m + \frac{N^2 n_m^0}{n_1^0} D_2 D_m \right] \\ & + D_3 \left[1 + \frac{N^2 n_m^0}{n_1^0} + \frac{Q^2 n_m^0}{n_2^0} \right] (D_1 n_1^0 z_1^2 + D_2 n_2^0 z_2^2 + D_m n_m^0 z_m^2) \\ & + D_3 n_3^0 z_3^2 \left[\left[1 + \frac{Q^2 n_m^0}{n_2^0} \right] D_1 + \left[1 + \frac{N^2 n_m^0}{n_1^0} \right] D_2 + \left[\frac{N^2 n_m^0}{n_1^0} + \frac{Q^2 n_m^0}{n_2^0} \right] D_m \right] \end{aligned} \quad (58)$$

$$C = D_3 (n_1^0 z_1^2 + n_2^0 z_2^2 + n_3^0 z_3^2 + n_m^0 z_m^2) \left[D_1 D_2 + \frac{Q^2 n_m^0}{n_2^0} D_1 D_m + \frac{N^2 n_m^0}{n_1^0} D_2 D_m \right] , \quad (59)$$

and where

$$E = AS_{mm}(\underline{q}, 0+) \quad (60)$$

and

$$\begin{aligned} F = & \left[D_3 \left[1 + \frac{N^2 n_m^0}{n_1^0} + \frac{Q^2 n_m^0}{n_2^0} \right] (D_1 n_1^0 z_1^2 + D_2 n_2^0 z_2^2 + D_m n_m^0 z_m^2) \right. \\ & + \left. \left[\frac{N^2 n_m^0}{n_1^0} D_2 + \frac{Q^2 n_m^0}{n_2^0} D_1 \right] D_3 n_3^0 z_3^2 \right] S_{mm}(\underline{q}, 0+) \\ & + D_3 n_3^0 z_3^2 \left[D_2 \frac{N n_m^0}{n_1^0} S_{1m}(q, 0+) + D_1 \frac{Q n_m^0}{n_2^0} S_{2m}(q, 0+) \right] \\ & - \left[n_m^0 z_m \left[D_1 D_2 + \frac{Q^2 n_m^0}{n_2^0} D_1 D_m + \frac{N^2 n_m^0}{n_1^0} D_2 D_m \right] \right. \\ & \left. - D_3 \left[N n_m^0 D_1 z_1 + Q n_m^0 D_2 z_2 + \left[\frac{N^2 n_m^0}{n_1^0} + \frac{Q^2 n_m^0}{n_2^0} \right] D_m n_m^0 z_m \right] \right] z_3 S_{3m}(q, 0+) \quad . \end{aligned} \quad (61)$$

From numerical calculation of $S_{mm}(q, t)$ we find that one exponent (the smaller) predominates and therefore conclude that the experimentally measured D should in this case be the smaller root of the equation $A\lambda^2 - B\lambda + C = 0$.

3.3 The Taylor Tube Experiment

We are now in a position to establish the equivalence of QELS and the Taylor tube dispersion measurement for multicomponent systems. The analysis is relegated to Appendix B where the equivalence of the two techniques is established in either of the two limits $R_b/q^2 \rightarrow \infty$ or $R_b/q^2 \rightarrow 0$. In either limit both measurements are dominated by a single exponent. However as discussed in Appendix B for micellization characterized by a given R_b , it is possible that QELS measurements could be in the slow reaction rate limit, whereas corresponding Taylor tube measurements are in the fast reaction rate limit.

4. Analysis of Results

We now have expressions for effective diffusion constants for ionic micellar systems valid in two extreme limiting cases, slow and fast reaction rates. We have already remarked that the q dependence of QELS will not necessarily discriminate between these different limits. Most analyses (for SDS) have been based (implicitly) on the slow reaction rate theory extended to include intermicellar interactions, and most experiments have been carried out at high salt concentrations (>0.1 M). In this region the theory of Corti and deGiorgio (1) is consistent with current interpretations of kinetic experiments. Further QELS data for SDS when extrapolated to the CMC gives intrinsic micelle diffusion constants D_m consistent with accepted aggregation numbers. However inferred effective micellar charge $Z = (N-Q)$ required to fit the measured variation of diffusion constants $\bar{D}$ with surfactant concentration are not consistent into some other experiments. In addition the required Hamaker constant is ten times too large, although this last could reflect on expected breakdown of continuum theories of interactions and the onset of large long range hydrophobic interactions.⁽²¹⁾

Apart from the difficulty with $N-Q$ which implies that inferences from a whole series of different equilibrium experiments are wrong, a much more serious problem is the behavior of $\bar{D}$ at low salt concentrations. At least for $C_{14}TAB$ Fig. (1) and SDS Fig. (2) there is no way that the Taylor tube data can be extrapolated to the CMC to give D_m , as would be permitted if a slow reaction rate description holds. Here electrostatic effects certainly dominate and attractive interactions are negligible. QELS data for sodium octanoate show the same behavior.⁽²³⁾

4.1 SDS in Zero Salt

Each of the limiting expressions Eqs. (46) (54) involve the parameters

n_1^0 , D_1 (monomer), n_2^0 , D_2 (counterion), n_m^0 , D_m (micelle). In addition we have N the micelle aggregation number and Q the number of "bound" counterions, both of which connect n_1^0 , n_2^0 , n_m^0 by the (assumed) equilibrium condition

$$n_m^0 = K(n_1^0)^N (n_2^0)^Q \quad (62)$$

and the conservation conditions

$$n_2^0 = n_1^0 + (N - Q) n_m^0 \equiv n_1^0 + \frac{Z}{N} (N n_m^0) \quad (63)$$

$$n^0 = n_1^0 + N n_m^0. \quad (64)$$

For a given surfactant concentration n , and given cmc, n_1 , n_2 , n_m will be determined as follows.

In this determination it is necessary to settle on a convention which defines the cmc. We rewrite eq. (62) as

$$\left(\frac{N n_m}{n_0} \right)^{1/N} = \left(\frac{n_1}{n_0} \right) \left(\frac{n_2}{n_0} \right)^{Q/N}, \quad (65)$$

where we have redefined $K = 1/N n_0^{N+Q-1}$. Then for $N \rightarrow \infty$, Q/N fixed we have

$$1 = \left(\frac{n_1}{n_0} \right) \left(\frac{n_2}{n_0} \right)^{Q/N}, \quad n \geq n_0 \quad (66)$$

$$n_1 = n_2 = n \quad n \leq n_0$$

Thus n_0 can be taken to be the measured cmc. The monomer concentration n_1 is that determined by rewriting eq. (65) as

$$\left(\frac{n_1}{n_0} \right) = \left(\frac{n_2}{n_0} \right)^{Q/N} \left(\frac{N n_m}{n_0} \right)^{1/N} = \left[\frac{Q}{N} \left(\frac{n_1}{n_0} \right) + \left(\frac{Z}{N} \right) \left(\frac{n}{n_0} \right) \right]^{Q/N} \left[\frac{n}{n_0} - \frac{n_1}{n_0} \right]^{1/N} \quad (67)$$

or

$$\left(\frac{n_1}{n_0}\right) = \frac{n}{n_0} - \left(\frac{n_1}{n_0}\right)^N \left[\left(\frac{Q}{N}\right) \left(\frac{n_1}{n_0}\right) + \left(\frac{Z}{N}\right) \left(\frac{n}{n_0}\right) \right]^Q$$

which can be solved by iteration. The pseudophase approximation used in ref. (7) corresponds to dropping the term in $(n/n_0 - n_1/n_0)^{1/N}$ and leads to serious error. (We remark in passing that independent determinations of n_1 from the surfactant-ion electrode (29) are not in agreement with the predictions of eq. (67), although n_2 is. This indicates that the inferences from these experimental measurements are wrong, or that the model eq. (62) is itself wrong. However, since all expressions we shall use are derived assuming the correctness of eq. (62) it would be inadmissible to use "experimental" values of n_1 which disagree with eq. (62) as was done in ref. (7).

There remain five independent parameters of which D_1 , D_2 can be taken as given from independent experiment, leaving N , Q and D_m . N and Q are assumed constant with increasing surfactant concentration. The work of Gunnarsson et al.⁽²⁸⁾ indicates that Q varies, but slowly. At this point one can take one of several points of view:

(A). With three free parameters, virtually any data can be reproduced. For example, taking $\text{cmc} = .008$ moles/litre⁽³⁰⁾, $D_1^{(5,6)} = 5.7 \times 10^{-6}$ the sets of data listed below all fit equally well to the measured diffusion constant (over the entire SDS concentration range) in the fast reaction rate limit.

(B) A second procedure is to fix Q by independent experiment, or in the slow reaction rate limit only, to extrapolate the measured D to the cmc. For this case only, $D \rightarrow D_m$ from which the aggregation number N can be inferred.
 $n \rightarrow n_0$

This procedure has difficulties: Assume the Stokes-Einstein relation

$D_m = kT/6\pi\eta a_H$ where a_H is the hydrodynamic radius of an (assumed) spherical micelle. e.g. for $D_m = 10^{-6}$, $\eta = .01$ poise, $T = 25^\circ\text{C}$, we have $a_H = 21.2\text{\AA}$.

Table 1

Typical three parameter fits to measured $\bar{D}$ for SDS (no salt). All are equally acceptable. The last values * are obtained using n_1 values with an assumed cmc = 0.006 required to reproduce the surfactant ion electrode data ⁽²⁹⁾. Similar absurdities hold for the slow reaction rate formulae.

N	30	58	58	58	50	58
Q	0.7	0.7	0.8	0.84	0.8	0.84
$D_m \times 10^6$ (cgs units)	0.8	0.45	0.8	1.1	0.9	0.9*

To connect this radius with that of the hydrocarbon core of a micelle, we must assume the existence of, and a value for, the thickness of the Stern layer⁽³²⁾. Take it to be $4.6\text{\AA}$. The core volume is then $V = \frac{4}{3} (a_H - 4.6)^3 \approx 15,000\text{\AA}^3$. The SDS carbon chain⁽³³⁾ has volume $v \approx 350\text{\AA}^3$ whence $N = \frac{V}{v} \approx 58$. Corresponding D_m and N values computed by this procedure are compared in Table 2. Small uncertainties in D_m produce large variations in N ($N \propto D_m^3$), and strong deviations from sphericity must occur whenever N deviates from its optimal packing value⁽³³⁾. Only rough consistency can be achieved. Apart from this, extrapolation is simply not possible in general, as we have seen for $C_{14}\text{TAB}$, and SDS, and Na Octanoate.

(C) A further procedure is to take N and Q as given. These are after presuming their existence all thermodynamic data, and must be more easily determinable than from kinetic experiments. A number of experiments⁽¹³⁾ give $N = 58$, $\frac{Q}{N} = .84$, with some uncertainty in the last. Fixing these parameters we can then compare experimental and theoretical diffusion constants over the SDS concentration range, for both fast and slow reaction rate models.

A cursory inspection of Table 3 indicates that we could fit the measured diffusion constant to either slow or fast reaction rate theories. But to fit the former we require $D_m > 1.3 \times 10^{-6}$ (which cf. Table 2) corresponds to an aggregation number $N < 20$. The computation is unambiguous and the conclusion inescapable that the fast reaction rate theory $D_m \sim 1 - 1.1 \times 10^{-6}$ is correct corresponding to an aggregation number $N \sim 58$. In Table 4 we indicate an important point. The fast reaction rate theory does not extrapolate at the cmc to D_m . Indeed it decreases until a value of C above the cmc and then increases dramatically to $2D_1D_2/(D_1 + D_2)$ i.e. the apparent diffusion constant of the monomer. Table 4b lists the corresponding computations for $C_{14}\text{TAB}$ which fit the TT data.

Table 2. Comparison of D_m vs. N for spherical SDS micelles

$D_m \times 10^6$	.8	.9	1.0	1.1	1.2	1.3
N	105	74	54	40	31	24

Table 3

SDS in H_2O , $N=58$, $\frac{Q}{N}=0.84$, $cmc = .008$ moles/l $D_1 = 5.7 \times 10^{-6}$,
 $D_2 = 1.35 \times 10^{-6}$

Fast and slow reaction rate theories compared with experimental diffusion constant for various D_m . Experimental data from Taylor tube measurements (7). Data for light scattering (4) and sedimentation equilibrium not significantly different. (See Fig. 2)

	$D_m = 8 \times 10^{-7}$		$D_m = 1.0 \times 10^{-6}$		$D_m = 1.1 \times 10^{-6}$		$D_m = 1.3 \times 10^{-6}$		Expt (1)
C moles/litre	$\bar{D}$ (slow)	$\bar{D}$ (fast)	S	F	S	F	S	F	
.01	.95	1.31	1.18	1.55	1.29	1.66	1.52	1.96	1.76
.02	1.55	1.77	1.89	2.14	2.05	2.32	2.35	2.68	2.40
.03	2.04	2.30	2.44	2.76	2.67	2.98	2.97	3.40	3.03
.04	2.44	2.74	2.88	3.27	3.08	3.51	3.44	3.98	3.65
.05	2.77	3.10	3.23	3.68	3.43	3.95	3.79	4.44	4.03
.06	3.04	3.41	3.51	4.02	3.72	4.30	4.07	4.82	4.05
.07	3.26	3.66	3.75	4.30	3.95	4.59	4.30	5.13	4.39

Table 4

(A) SDS in H_2O . Extrapolation to CMC. $D_m = 10^{-6}$, $N = 58$, $Q = 0.84$, $CMC = .008$

C	.007	.008	.009	.01
$\bar{D}$ (slow)	1.00	1.02	1.10	1.18
$\bar{D}$ (fast)	8.02	2.69	1.64	1.55

(B) $C_{14}TAB$ in H_2O . Extrapolation to CMC. $D_m = 0.77 \times 10^{-6}$, $N = 67$, $Q = 0.85$,
 $CMC = 3.79 \times 10^{-3} m$.

$C \times 10^3$ (m)	3.9	4.1	4.7	6.1	11.9	17.9	29.4	65.3
$\bar{D} \times 10^6$ (slow)	0.8	0.83	0.91	1.1	1.75	2.25	2.92	3.88
$\bar{D} \times 10^6$ (fast)	2.0	1.41	1.25	1.33	2.07	2.75	3.70	5.12

4.2 SDS in 0.1 M salt

The appropriate computations and comparisons have been made from Eq. 56 for 0.1 M salt and listed in Table 5. Here the situation is much less clear since Q is unknown. However with increasing salt Q certainly increases, and the results are not sensitive to the value of Q which gives a best fit. What emerges is that both theoretical formulae are indistinguishable numerically across the entire SDS concentration range. A similar conclusion holds for 0.3 M NaCl. The light scattering data and sedimentation equilibrium data are consistent. The TT results as published (0.1 M) fit with $D_m = 1.1 \times 10^6$ ($N \approx 40$) which is inconsistent. Repetition and reanalysis of these experiments reveals that the data of Corti and deGiorgio and those of Kratochvil and Adaminabhavi are the more reliable. In the Taylor tube experiments the concentration gradient in surfactant can here give rise to multi-component diffusion effects.⁽³⁴⁾ Note that the inferred value of Q is consistent with accepted values but very different from that of Corti and deGiorgio who used a different value consistent with electrophoresis work. Attractive interactions obviously become increasingly important with increasing salt, but cannot be reliably estimated. The important point is that one cannot here discriminate between fast and slow reaction rate theories. And if the diffusion proceeds by the fast reaction mechanism, as for low salt, there exists no theory which builds in attractive interactions even if these were known.

Table 5. SDS in 0.1 M Salt

parameters: CMC = 0.0015, N = 93, Q = .89, $D_m = .95 \times 10^{-6}$

C(moles/l)	.01	.02	.03	.04	.05	.06	.07	.08	.09	.10
slow	.99	1.04	1.09	1.13	1.18	1.23	1.27	1.31	1.36	1.40
fast	1.00	1.05	1.09	1.14	1.18	1.23	1.27	1.32	1.36	1.40
QELS	1.00	1.05	1.09	1.14	1.18	1.23	1.27	1.32	1.36	1.40
TT	1.18	1.2	1.28	1.29	1.34	1.35		1.45		1.47

5. Conclusion

We have reported diffusion measurements on C_{14} TAB and SDS and analyzed these measurements and those for SDS in terms of two simple models for micellization. Provided the model for micellization is correct (Eq. 31) i.e. that the concept of an "effective" bound charge is valid, extrapolation to the CMC is not generally permissible. The conclusion is inescapable that at low salt concentrations ionic surfactant diffusion proceeds via the fast reaction rate process. (The interpretation that micelles disassemble, diffuse as monomers and then reassemble need not be taken literally. The connection between very rapid monomer-micelle molecular exchange processes and "effective" rate constants which must emerge from a detailed theory is obscure.) There is no ambiguity on this point whatever. In this limit polydispersity cannot be detected. Above 0.03 M salt concentration it is impossible to discriminate between fast and slow reaction rate theories. It is possible that with increasing salt concentration the reaction rates for micellization decrease, although this seems improbable. There is agreement between the values of D_m , aggregation numbers, and number of bound charges inferred from our theory of micellar diffusion and those from a variety of thermodynamic measurements. These conclusions are somewhat startling, since they are directly contrary to the current interpretation of kinetic experiments, whose major time scale implies that QELS should be in the slow reaction rate regime. This problem is unresolved. We believe that evidence which might be adduced in favor of "fast" (whose polydispersity is undetectable) and slow (whose polydispersity is in principle detectable) reaction rate theories from kinetic experiments must be tempered by the knowledge that if a nucleation or initiation rate process is involved, even the simplest exactly soluble models can exhibit quite extraordinary relaxation phenomena. Thus the model for relaxation

kinetics of Ninham, Nossal and Zwanzig⁽³⁵⁾ (which can be mapped directly into a kinetic scheme appropriate however only to long cylindrical micelles), exhibits two very different eigenvalues. These two relaxation times have a very different interpretation than that extant for spherical micelles, and arrived at, not through an exactly soluble model, but by plausible analogy.

Finally we wish to emphasize again that we are well aware of the deficiencies of the P. Mukherjee Q model (Eq. 31) for micellization, and of the kinetic scheme, on which our analysis, and for that matter all concerned advocates, has been based. The former represents a simple rough phenomenological thermodynamic description of the process so far acceptable to chemists, unacceptable to physicists, but has the extreme virtue that it has been tested and found not wanting for a variety of apparently unconnected experiments. It may well be completely inadequate for transport phenomena. It is more likely that the more complicated first principle theories of micellar solutions which build in our developing intuition regarding kinetics and interactions will reduce to forms which mimic this tractable characterization.

In any event the problem of micellar transport appears to be not such a simple matter as it seemed.

Figure 1.

Figure 2.

Figure Legend

- Figure 1. Diffusion coefficients of tetradecyltrimethylammonium bromide in water as a function of surfactant concentration at 25, 95 and 135°C. The solid curve is the calculated values of D using Eq. (54) with $n = 67$ and $z/n = 0.15$.
- Figure 2. Diffusion coefficients of sodium dodecyl sulfate in water near the critical micelle concentration. D_m is the intrinsic diffusion coefficient of the micelle.

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34* A careful reanalysis of the dispersion peaks in the three component system, SDS, NaCl and water shows a slight departure from a Gaussian distribution of solute. Although no concentration gradient initially exists for NaCl, a concentration gradient in surfactant can generate a concentration gradient in NaCl. This situation can give rise to two superimposed Gaussians which accounts for this discrepancy.

Appendix A

Polydispersity in the Fast Reaction Rate Limit

We here expand upon and make explicit our assertion in the main text that polydispersity is undetectable in the limit of rapid monomer-micelle exchange. For simplicity consider only non-ionic surfactants and ignore interactions. Assume that the only significant reactions proceed via exchange of individual monomers, so that the set of reactions which characterize the aggregation process are

Here S_m denotes an aggregate of m monomers. The evolution of the system is described by the equations

$$\begin{aligned} \frac{\partial}{\partial t} n_m - D_m \nabla^2 n_m = & (R_f^{(m)} n_{m-1} n_1 - R_b^{(m)} n_m) \\ & - (R_f^{(m+1)} n_m n_1 - R_b^{(m+1)} n_{m+1}) , \quad m > 1 \end{aligned} \quad (A.2)$$

$$\frac{\partial n_1}{\partial t} - D_1 \nabla^2 n_1 = 2(R_b^{(2)} n_2 - R_f^{(2)} n_1^2) + \sum_{m=3}^{\infty} (R_b^{(m)} n_m - R_f^{(m)} n_{m-1} n_1), \quad (A.3)$$

The equilibrium conditions are

$$R_f^{(m)} n_{m-1} n_1 - R_b^{(m)} n_m = 0 \quad ; \quad m > 1 \quad (A.4)$$

or

$$n_m = \frac{R_f^{(m)}}{R_b^{(m)}} n_{m-1} n_1 = K^{(m)} n_1^m \quad ; \quad K^{(m)} = \prod_{j=2}^m R_f^{(j)} / R_b^{(j)} \quad (A.5)$$

In the fast reaction rate limit ($R_b^{(m)} \rightarrow \infty$, $\frac{R_f^{(m)}}{R_b^{(m)}}$ finite) the system

always maintains local equilibrium. (This can be seen by writing the right hand side of eqn. (A.2) as

$$R_b^{(m)} \left(\frac{R_f^{(m)}}{R_b^{(m)}} n_{m-1} n_1 - n_m \right) - R_b^{(m+1)} \left(\frac{R_f^{(m+1)}}{R_b^{(m+1)}} n_m n_1 - n_{m+1} \right).$$

The terms in brackets must tend to zero as $R_b^{(m)}, R_b^{(m+1)} \rightarrow \infty$ in order that whole expression remains finite (for all m): This condition gives the equilibrium conditions eqs. A.4).] Denote equilibrium concentrations by n_m^0, n_1^0 so that from eq. (A.5)

$$K^{(m)} = \frac{n_m^0}{(n_1^0)^m} ; \quad K^{(1)} \equiv 1 \quad (A.6)$$

We seek solutions to eqs. (A.2), (A.3) for small deviations $\delta n_m, \delta n_1$ about these equilibrium concentrations. From (A.5) we have

$$\delta n_m = m K^{(m)} (n_1^0)^{m-1} \delta n_1 = m \left(\frac{n_m^0}{n_1^0} \right) \delta n_1 \quad (A.7)$$

$$\delta n = \delta \left(\sum_{m=1}^{\infty} m n_m \right) = \sum_{m=1}^{\infty} m^2 \left(\frac{n_m^0}{n_1^0} \right) \delta n_1 \quad (A.8)$$

and corresponding expressions for $\nabla^2 n_m, \nabla^2 n$. In terms of the total surfactant concentrations $n = \sum_{m=1}^{\infty} m n_m$ we have

$$\delta n_m = \frac{m n_m^0}{\sum_{j=1}^{\infty} j^2 n_j^0} \delta n \quad (A.9)$$

so that the time dependence of n_m is the same as that of the total

surfactant concentration n . Now summing eqs. (A.2), (A.3) we have the condition for conservation of total surfactant

$$\sum_{m=1}^{\infty} \frac{\partial}{\partial t} (mn_m) - mD_m \nabla^2 n_m = 0 \quad ; \quad \frac{\partial n}{\partial t} = \sum_{m=1}^{\infty} mD_m \nabla^2 n_m \quad (\text{A.10})$$

where substituting from (A.7), (A.8 for $\nabla^2 n_m$ the diffusion equation becomes

$$\frac{\partial n}{\partial t} = \frac{\sum_{m=1}^{\infty} m^2 D_m n_m^0}{\sum_{j=1}^{\infty} j^2 n_j^0} \nabla^2 n \equiv \bar{D} \nabla^2 n \quad (\text{A.11})$$

We conclude that n has a solution in the form of single exponential, as will the individual concentrations δn_m (A.9). This exponential behaviour does depend on polydispersity, but only indirectly through the single entity $\bar{D}$. No direct measure of polydispersity as reflected in a presupposed variance or skewness will be exhibited. It is only in the slow reaction rate limit which will yield a sum of exponentials that polydispersity can, in principle be detected.

Appendix B

Relation between Light Scattering and Taylor Tube Measurements

All of our analysis has been based on the assumption that measurements via these two different techniques are equivalent. For multicomponent diffusion this is by no means obvious, and probably not generally true. We exhibit the connection explicitly and show how this equivalence arises for our problem.

First consider light scattering:-

The relaxation equations we have used to determine the $\tilde{S}(\underline{q}, t)$ in general have the form

$$\frac{\partial n_i(\underline{r}, t)}{\partial t} = \sum_j M_{ij} \nabla^2 n_j(\underline{r}, t) \quad (B.1)$$

or in Fourier space

$$\frac{\partial \tilde{n}_i(\underline{q}, t)}{\partial t} = -q^2 \sum_j M_{ij} \tilde{n}_j(\underline{q}, t) \quad (B.2)$$

Note that the M_{ij} are independent of q provided we assume $q \ll \kappa$ and either $R_p/q^2 \gg 1$ or $R_p/q^2 \ll 1$, i.e. fast or slow reaction rates. Eqn. (B.2) was solved by Laplace transform techniques. Taking Laplace transforms we have ($\hat{n}_i$ is the L.T. of $\tilde{n}_i$)

$$p \hat{n}_i(\underline{q}, p) = -q^2 \sum_j M_{ij} \hat{n}_j(\underline{q}, 0) + \tilde{n}_j(\underline{q}, c) \quad (B.3)$$

whence follows the formal solution

$$\hat{n}_i(q, p) = \sum_j (pI + q^2 M)_{ij}^{-1} \tilde{n}(q, 0) \quad (B.4)$$

It can be written in a more convenient form for our purpose as follows. Let T denote the matrix whose columns are the eigen- of M and Λ the diagonal matrix whose diagonal elements are the eigenvalues of M so that $M T = T \Lambda$. Then

$$(pI + q^2 M)^{-1} = T(pI + q^2 \Lambda)^{-1} T^{-1} \quad (B.5)$$

and

$$\hat{n}_i(q, p) = \sum_{j, l} \frac{(T)_{ij} (T^{-1})_{jl}}{(p + q^2 \lambda_j)} \tilde{n}_l(q, 0) \quad (B.6)$$

so that inverting the Laplace transform gives

$$\tilde{n}_i(q, t) = \sum_{j, l} T_{ij} (T^{-1})_{jl} \tilde{n}_l(q, 0) e^{-\lambda_j q^2 t} \quad (B.7)$$

The quantities T_{ij} and λ_j which appear in eq. (B.7) are independent of q and in our particular case so is $\tilde{n}_l(q, 0)$.

For the Taylor tube ^(26,27) experiment eq. (B.1) has to be modified to allow for a convection term. The appropriate equation for multicomponent diffusion is

$$\frac{\partial n_i(r, t)}{\partial t} + U(\rho) \frac{\partial n_i(r, t)}{\partial x} = \sum_j M_{ij} \nabla^2 n_j(r, t) \quad (B.8)$$

where the x-axis is taken to coincide with the axis of the cylinder and ρ is the distance from the axis. If we assume steady uniform flow the flow velocity ^(36,37) is $U(\rho) = 2\bar{U}(1 - \rho^2/a^2)$ where $\bar{U}$ is the mean velocity and a the radius of the cylinder. We use a method of solution of eqs. B8 different to that developed previously ^(36,37).

First Fourier transform with respect to x and expand the n_i in terms of the complete set of functions

$J_n(k_{mn}\rho/a)e^{in\phi}$ where the k_{mn} are the roots of

$$J'_n(k_{mn}) = 0$$

and the prime denotes differentiation with respect to the argument.

These functions are the appropriate basis set because the flow must

satisfy the boundary condition $\frac{\partial n_i}{\partial \rho} = 0$ at $\rho = a$.

We thus have

$$n_\alpha(r, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk e^{ikx} \sum_{m=0}^{\infty} \sum_{n=-\infty}^{\infty} A_{mn}^\alpha(k, t) J_n(k_{mn}\rho/a) e^{in\phi} \quad (B.10)$$

Substitution of this equation into eq. (B.8) will yield an equation

for the coefficients $A_{mn}^\alpha(k, t)$, viz

$$\frac{\partial}{\partial t} A_{mn}^\alpha(k, t) = -(k^2 + k_{mn}^2/a^2) \sum_{\beta} M_{\alpha\beta} A_{mn}^\beta(k, t) - ik \sum_j U_{mnj} A_{jn}^\alpha(k, t) \quad (B.11)$$

where the U_{mnj} are defined by the relation

$$U(\rho) J_n(k_{mn}\rho/a) = \sum_j U_{jnm} J_n(k_{jn}\rho/a) \quad (B.12)$$

i.e.

$$U_{jnm} = \frac{\int_0^a U(\rho) J_n(k_{mn}\rho/a) J_n(k_{jn}\rho/a) \rho d\rho}{\int_0^a J_n^2(k_{jn}\rho/a) \rho d\rho}$$

Now for the Taylor tube experiment we are interested only in the averaged quantity

$$\begin{aligned}
\bar{n}_\alpha(x,t) &\equiv \frac{1}{\pi a^2} \int_0^{2\pi} d\phi \int_0^a \rho d\rho n_\alpha(r,t) \\
&= \frac{1}{2\pi} \int_{-\infty}^{\infty} dk e^{ikx} A_{\hat{c}\hat{c}}^\alpha(k,t)
\end{aligned} \tag{B.14}$$

Hence we need solve eq. (B.11) only for $A_{\hat{c}\hat{c}}^\alpha(k,t)$. For notational convenience define

$$B_m^\alpha \equiv A_{m0}^\alpha, \quad \eta_m \equiv k_{m0} \quad \text{and} \quad V_{jm} \equiv U_{jom} \tag{B.15}$$

so that the equation whose solution is required is

$$\frac{\partial}{\partial t} B_m^\alpha = -(k^2 + \eta_m^2/a^2) \sum_\beta M_{\alpha\beta} B_m^\beta - ik \sum_j V_{mj} B_m^\alpha \tag{B.16}$$

or, Laplace transforming

$$p \hat{B}_m^\alpha = -q_m^2 \sum_\beta M_{\alpha\beta} \hat{B}_m^\beta - ik \sum_j V_{mj} \hat{B}_j^\alpha + B_m^\alpha(k,0) \tag{B.17}$$

where $q_m^2 = k^2 + \eta_m^2/a^2$. To solve this equation we first define

$\hat{X}_m^\alpha$ by the relation

$$B_m^\alpha = \sum_\beta \left(T \right)_{\alpha\beta} X_m^\beta \tag{B.18}$$

i.e.

$$X_m^\alpha = \sum_\beta \left(T^{-1} \right)_{\alpha\beta} B_m^\beta \tag{B.19}$$

and rewrite eq. (B.17) as

$$p \hat{X}_m^\alpha = -\lambda_a q_m^2 \hat{X}_m^\alpha - ik \sum_j V_{mj} \hat{X}_j^\alpha + \hat{X}_m^\alpha(k,0) \tag{B.20}$$

The problem has now been reduced to the solution of an one component system. The solution of eq. (B.20) has the form

$$X_m^\alpha(k, t) = \sum_n Y_{mn}(k) e^{-\mu_{\alpha n} t}$$

where the $\mu_{\alpha n}$ are the eigenvalues of the infinite order matrix

with elements $\lambda_\alpha q_m^2 \delta_{mn} - ikV_{mn}$. Now as $k \rightarrow 0$ (cf. eq. B. 20)

$\mu_{\alpha n} \rightarrow \lambda_\alpha q_n^2 / a^2$ and $Y_{mn}(k) \rightarrow \delta_{mn} X_m^\alpha(k, 0)$. Therefore for large t

and small k (large x) we have approximately

$$X_0^\alpha(k, t) = X_0^\alpha(0, 0) e^{-\mu_{\alpha 0} t} \quad (B.21)$$

where $\mu_{\alpha 0}$ is the smallest eigenvalue (which tends to zero as $k \rightarrow 0$).

We determine the $\mu_{\alpha 0}$ to order k^2 using second order perturbation theory, whence

$$\mu_{\alpha 0} \approx \lambda_\alpha k^2 + ikV_{00} + k^2 \sum_{m \neq 0} \frac{V_{0m} V_{m0}}{\lambda_\alpha q_m^2} \quad (B.22)$$

$$= ik\bar{U} + k^2 \left[\lambda_\alpha + \frac{\bar{U}^2 a^2}{48 \lambda_\alpha} \right] \quad (B.23)$$

where the last line follows using standard results of the theory of Bessel functions. Then, from (B.18)

$$\begin{aligned} B_0^\alpha(k, t) &= \sum_\beta T_{\alpha\beta} X_0^\beta(0, 0) e^{-\mu_{\beta 0} t} \\ &= \sum_{\beta \gamma} T_{\alpha\beta} \left(\frac{T}{\lambda} \right)^{-1}_{\beta\gamma} B_0^\gamma(0, 0) e^{-\mu_{\beta 0} t} \end{aligned} \quad (B.24)$$

and

$$\bar{n}_\alpha(x,t) = \frac{1}{2\pi} \sum_{\beta\gamma} T_{\alpha\beta} (T^{-1})_{\beta\gamma} \int_{-\infty}^{\infty} e^{-\mu_{\beta 0} t} B_0^\gamma(0,0) e^{ikx} dk \quad (B.25)$$

with

$$B_0^\gamma(0,0) = \int_{-\infty}^{\infty} \bar{n}_\gamma(0,0) dx = \frac{1}{\pi a^2} \int_{\text{cylinder}} n_\gamma(r,0) \rho d\rho d\phi dx \quad (B.26)$$

The final integral of (B.25) is straightforward yielding

$$\bar{n}_\alpha(x,t) = \sum_{\beta\gamma} T_{\alpha\beta} (T^{-1})_{\beta\gamma} B_0^\gamma(0,0) \sqrt{\frac{\pi}{D_T^\alpha t}} e^{-(x-\bar{U}t)^2/4D_T^\alpha t} \quad (B.27)$$

where

$$D_T^\alpha \equiv \lambda_\alpha + \frac{\bar{U}^2 a^2}{48\lambda_\alpha} \approx \bar{U}^2 a^2 / 48\lambda_\alpha \quad (B.28)$$

By comparison of (B.27) and (B.7) it is clear that given a solution of the multicomponent diffusion equation (B.1) the solution of the Taylor tube problem eq. (B.8) can immediately be written down. In the problem considered in the main text of this paper both experiments (light scattering and Taylor tube) are dominated by a single exponent so that both measure the same quantity - provided, however, that in both cases one is in the same limit $R_b/q^2 \gg 1$ or $R_b/q^2 \ll 1$. For the light scattering experiment the meaning of q is unambiguous and is typically $O(10^4 \text{ cm}^{-1})$. For the Taylor tube experiment (in real space) what constitutes small q or k is not so clear. But for our analysis where it is clear that $k \ll \frac{1}{x}$ with x the

tube length i.e. $O(10^4 \text{ cm})$, $k \sim O(10^{-4} \text{ cm})$. This means that for a given experiment almost certainly Taylor tube measurements will be in the fast reaction rate limit, while the corresponding light scattering experiment could be in the slow reaction rate limit. For our problem as we have shown, both are in the fast reaction rate limit. Further analysis requires sensible models for the kinetics of micelle formation, none of which presently exist.