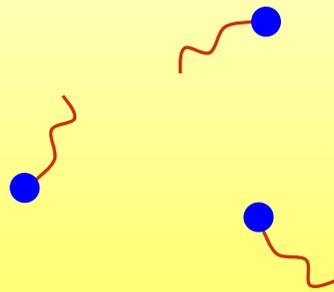
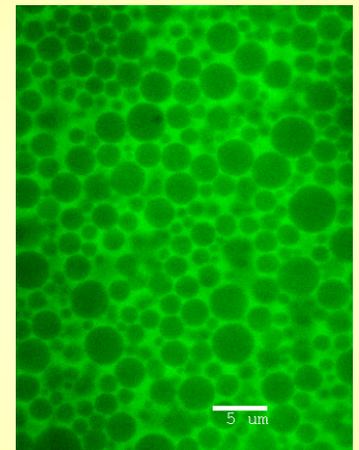
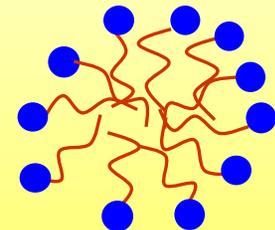




# Micelle Kinetics at Surfaces and in Solution

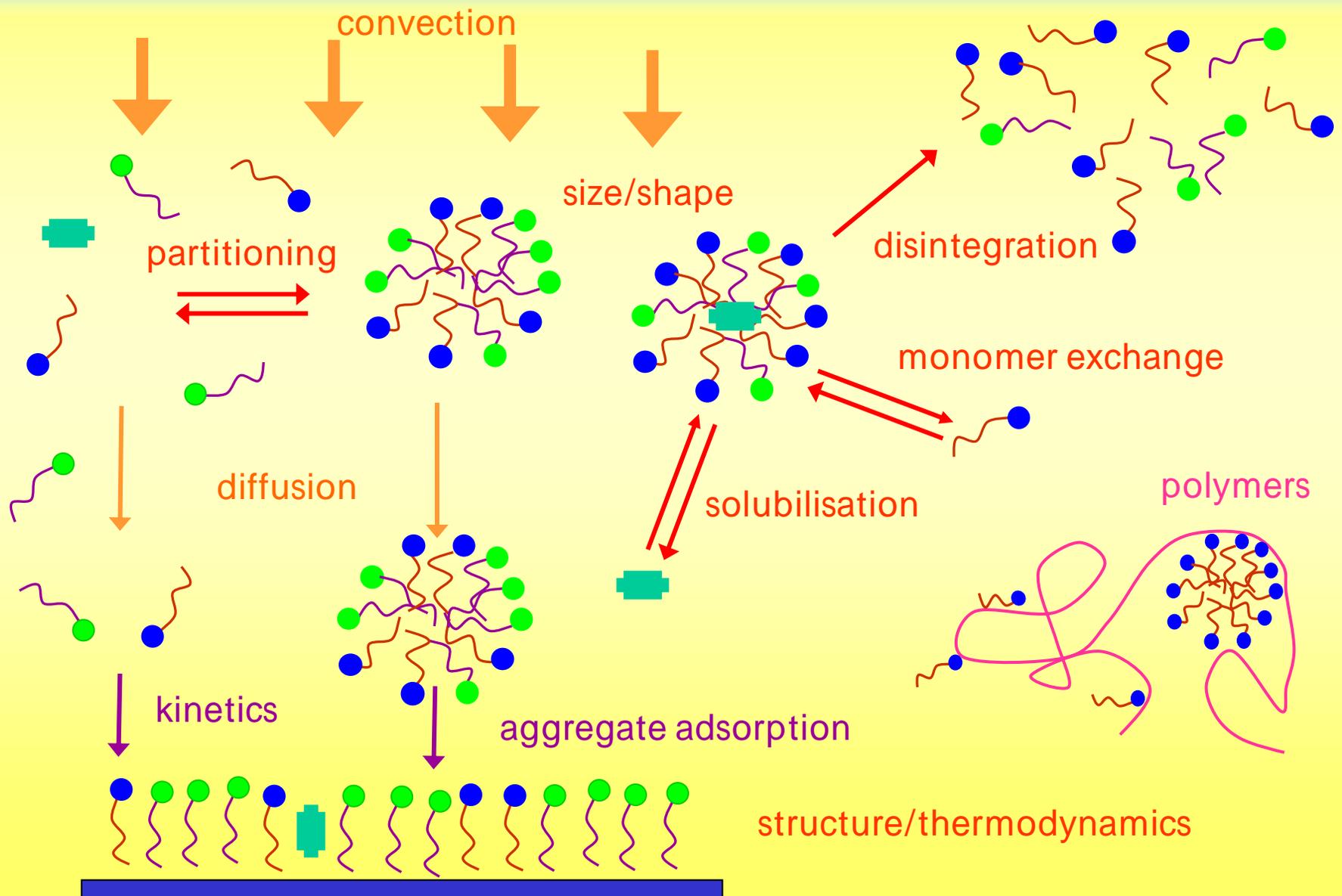


Prof. Colin D. Bain  
Department of Chemistry,  
Durham University, U.K.

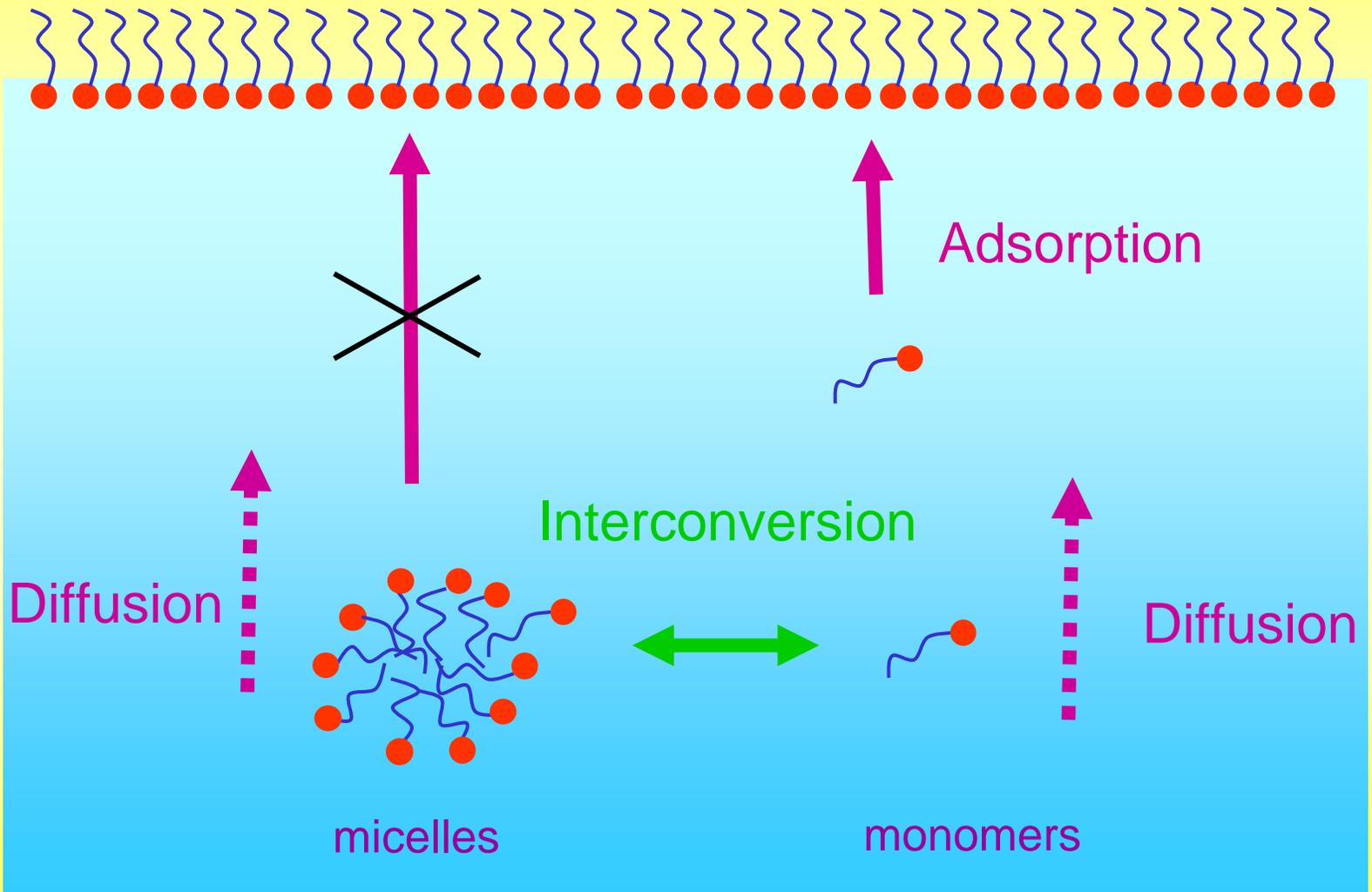


McBain Symposium  
11 December 2009

# Some issues in adsorption kinetics



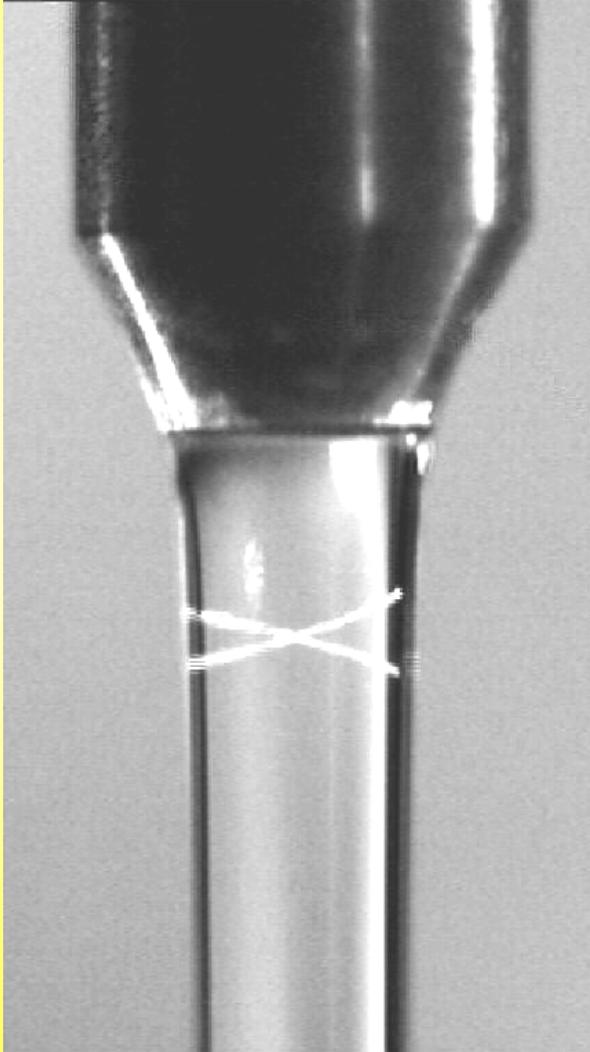
# Adsorption kinetics in micellar solutions



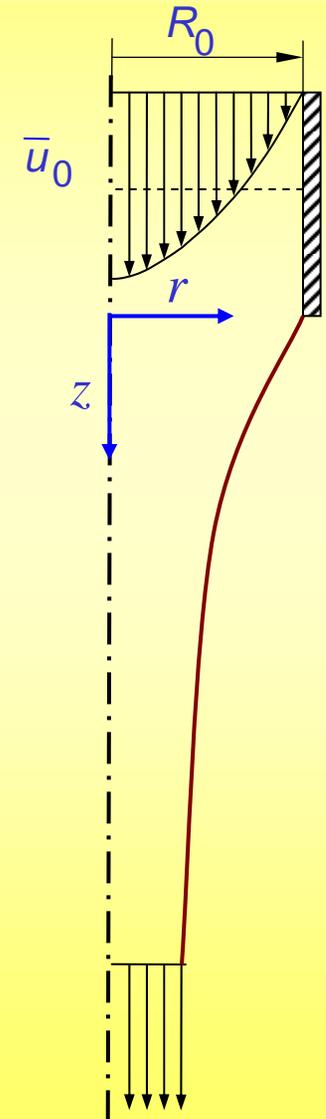
Colegate and Bain *Phys. Rev. Lett.* 2005, *95*, 198302



# Liquid jet



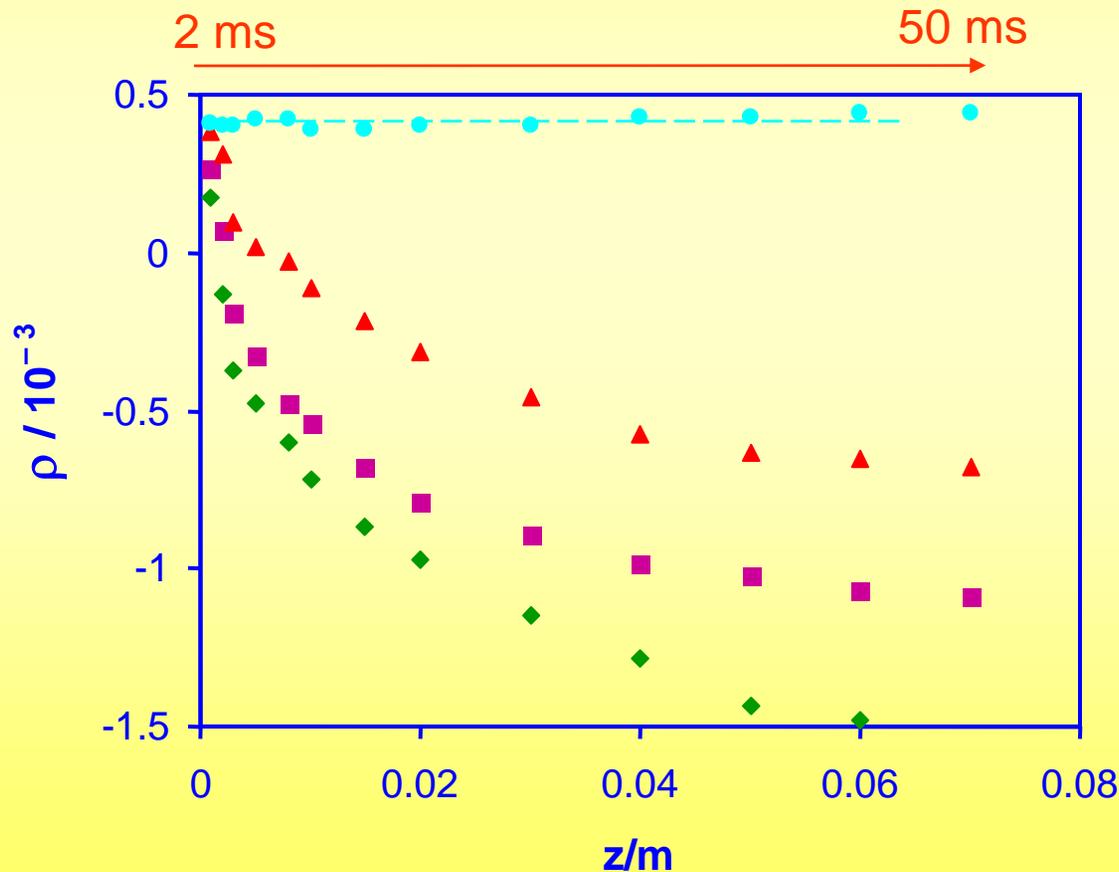
- $R_0 = 250 - 750 \mu\text{m}$
- $\bar{u}_0 = 1 - 3 \text{ ms}^{-1}$
- $\text{Re} = 1200 - 2000$
- Length = 5 - 10 cm
- 1 - 10 mM
- Surface age = 1-100 ms



# Nonionic Surfactants in the Liquid Jet



Use ellipsometry to measure surfactant adsorption to surface of jet



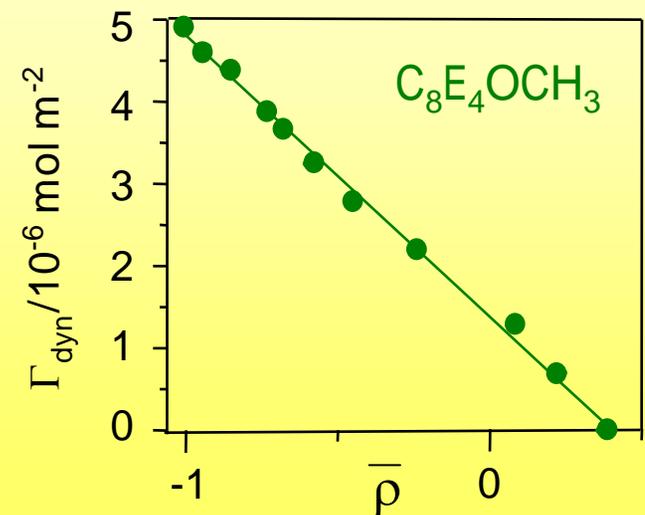
water

cmc  
( $\mu\text{M}$ )

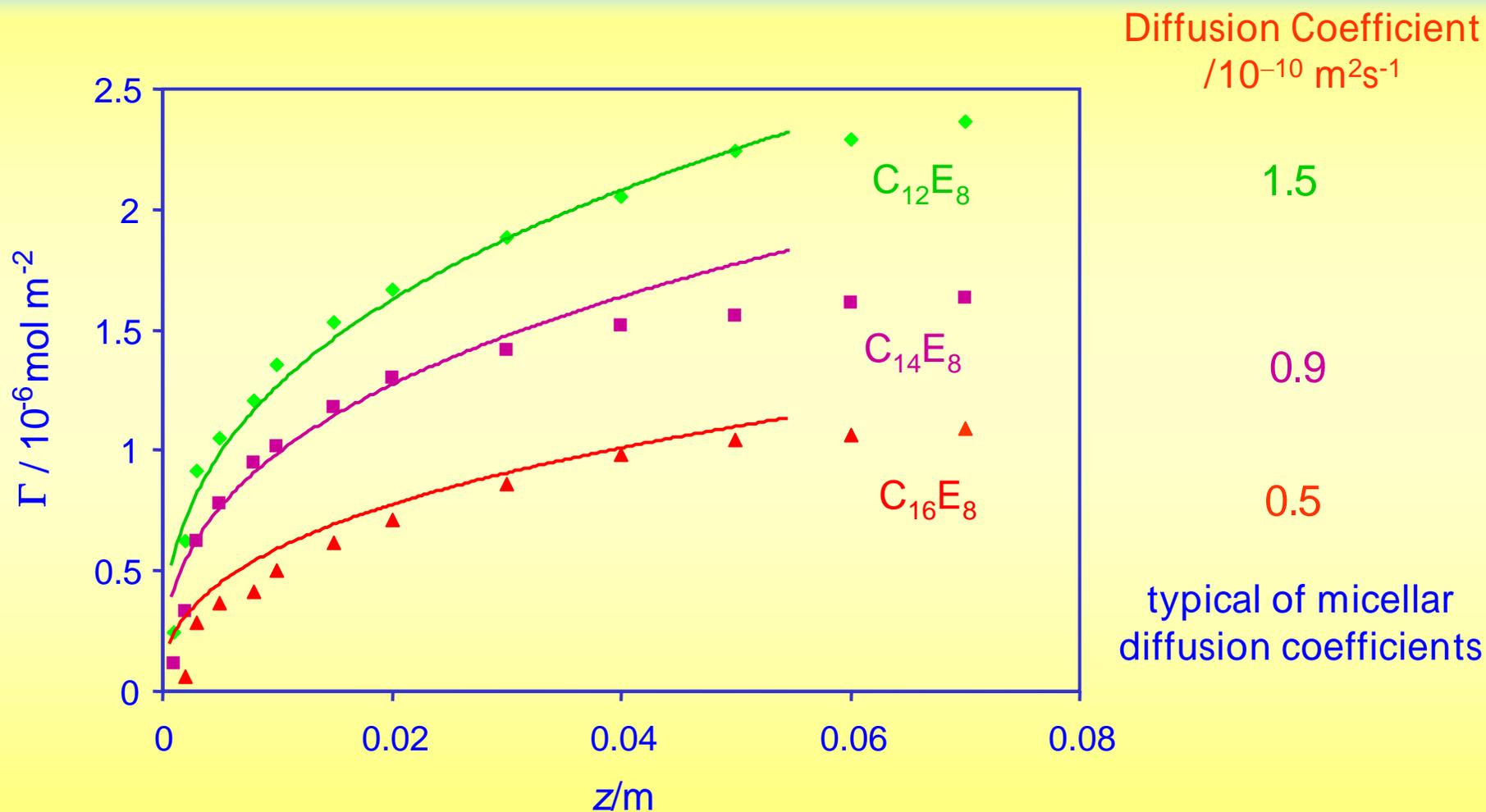
- $\blacktriangle$   $C_{16}E_8$
- $\blacksquare$   $C_{14}E_8$
- $\blacklozenge$   $C_{12}E_8$

1  
10  
100

Micelles  
important

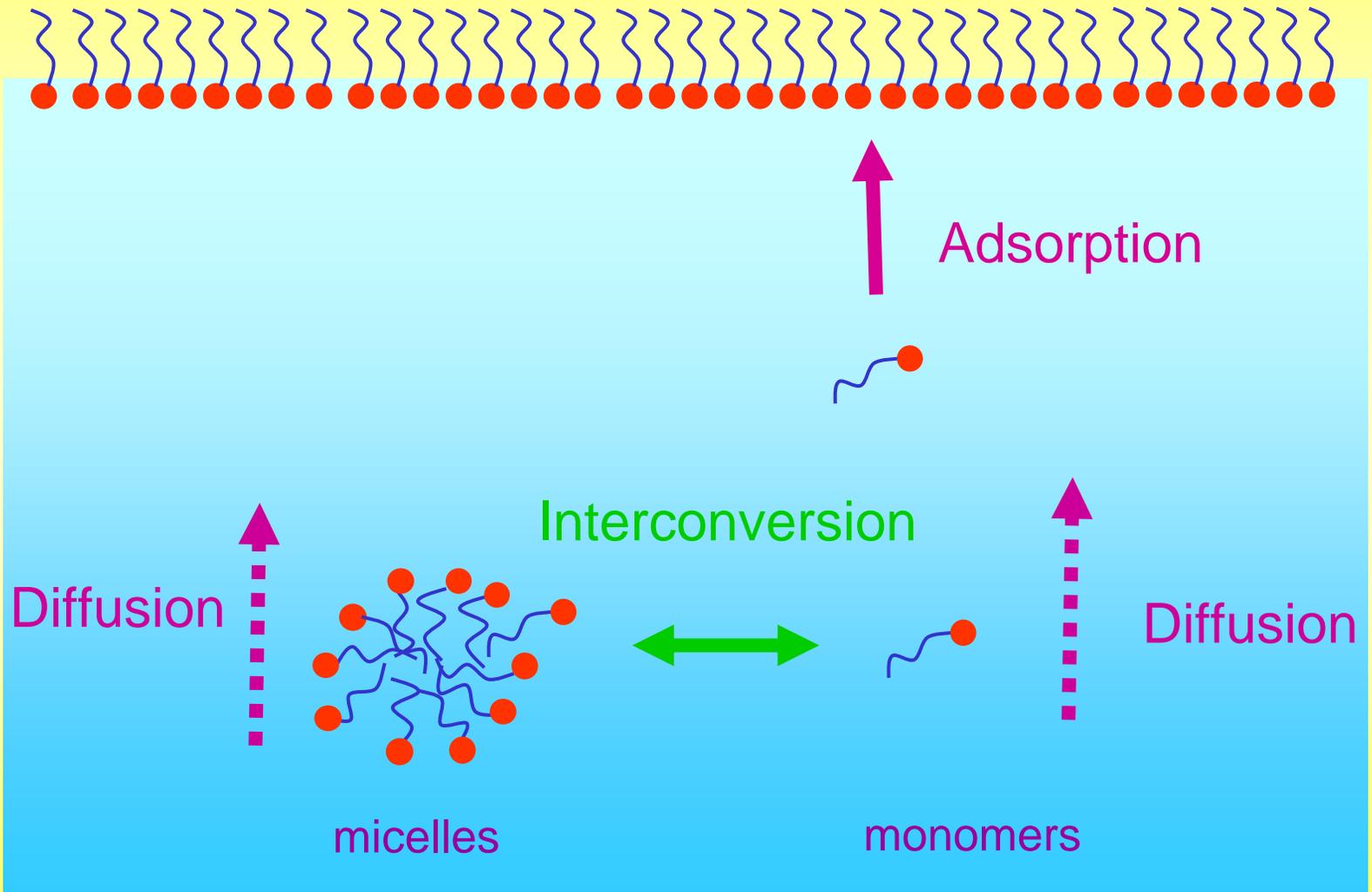


# Surface Excess of Nonionics in Jet

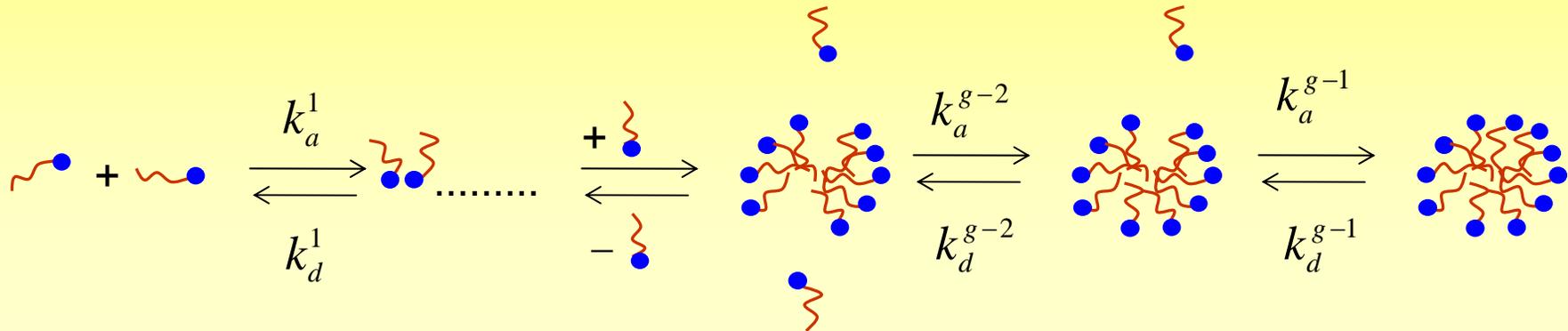


Weiss, Darton, Battal and Bain *Ind. Eng. Chem. Res.* 2004, 43, 5203

# Can micelles break down fast enough?



# Conventional mechanism for micelle breakdown

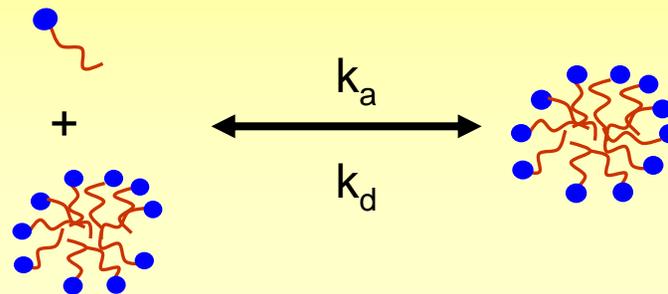


- Redistribution of surfactant between aggregates occurs by step-wise addition and loss of monomers
- Set of parallel differential equations governing the aggregate distribution known as the Becker-Döring equations (1935)

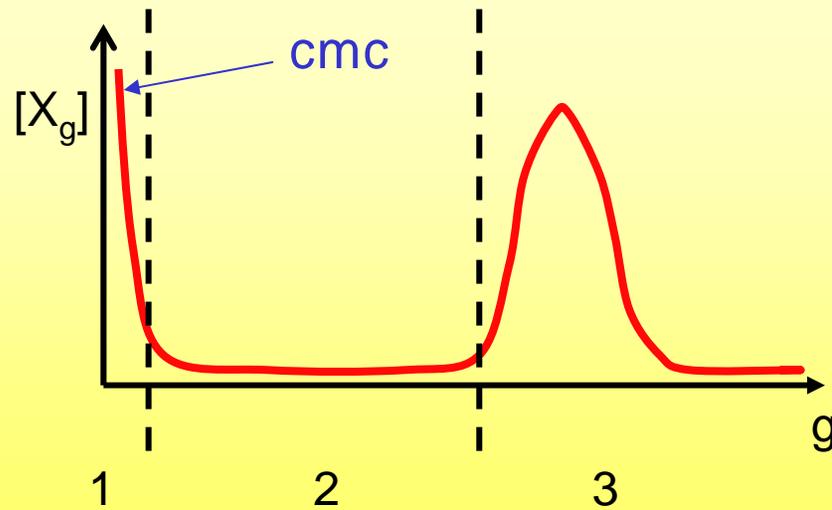
# Aniansson and Wall solution



## 1) Becker-Döring mechanism

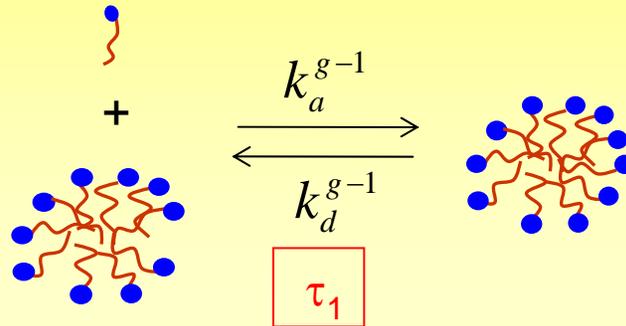


## 2) three distinct regions in size distribution

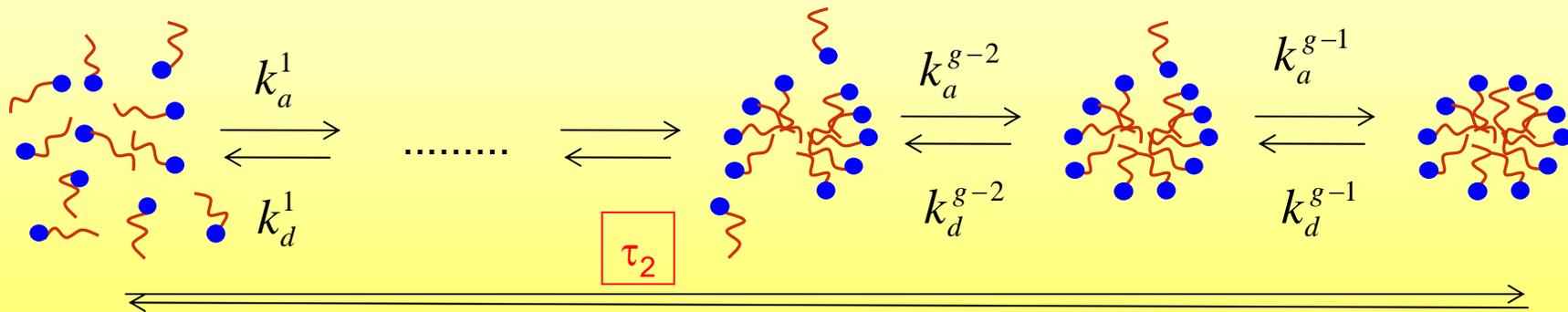


3) Perturbation is SMALL

# Aniansson and Wall solution



**FAST:** Diffusion-controlled monomer exchange. Rate  $\propto$  [monomers]



**SLOW:** Complete micelle breakdown. Rate determined by quantity of material in region 2.

# Breakdown kinetics of $C_{14}E_8$

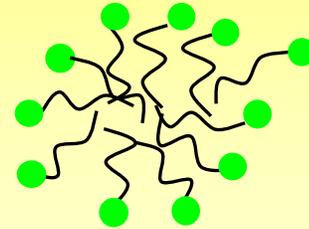
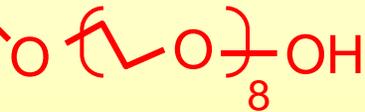


$C_{14}E_8$ : cmc = 0.01 mM

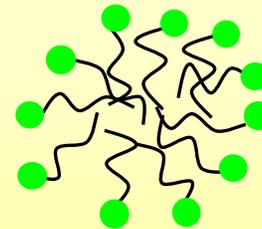
$$\bar{N} = 120$$

$$\tau_1 \sim 20 \mu\text{s}$$

$$\tau_2 = 4 \text{ s}$$



$\tau_1$



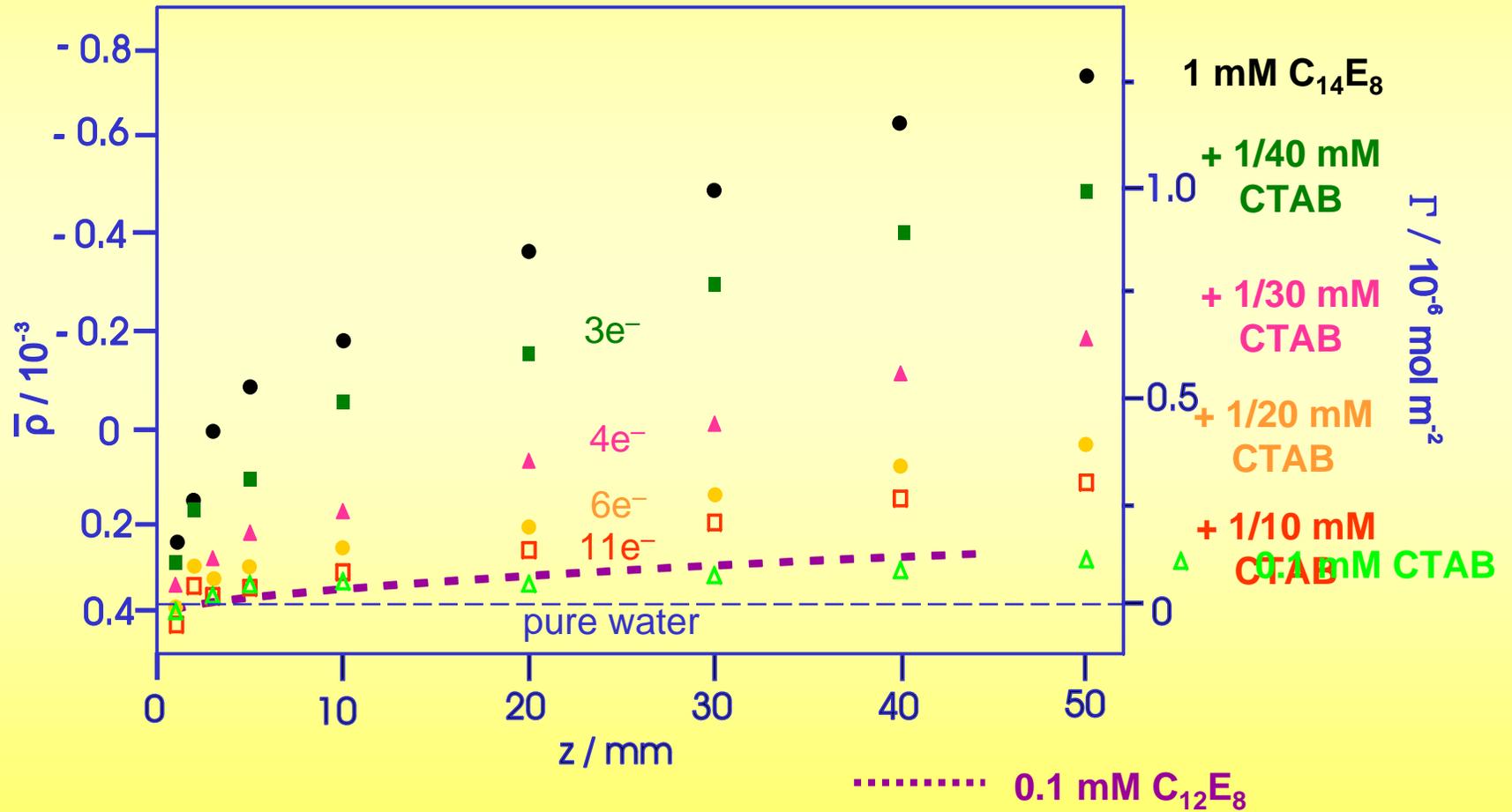
$\tau_2$

If  $\tau_2$  is so long, how can the surfactant adsorb?

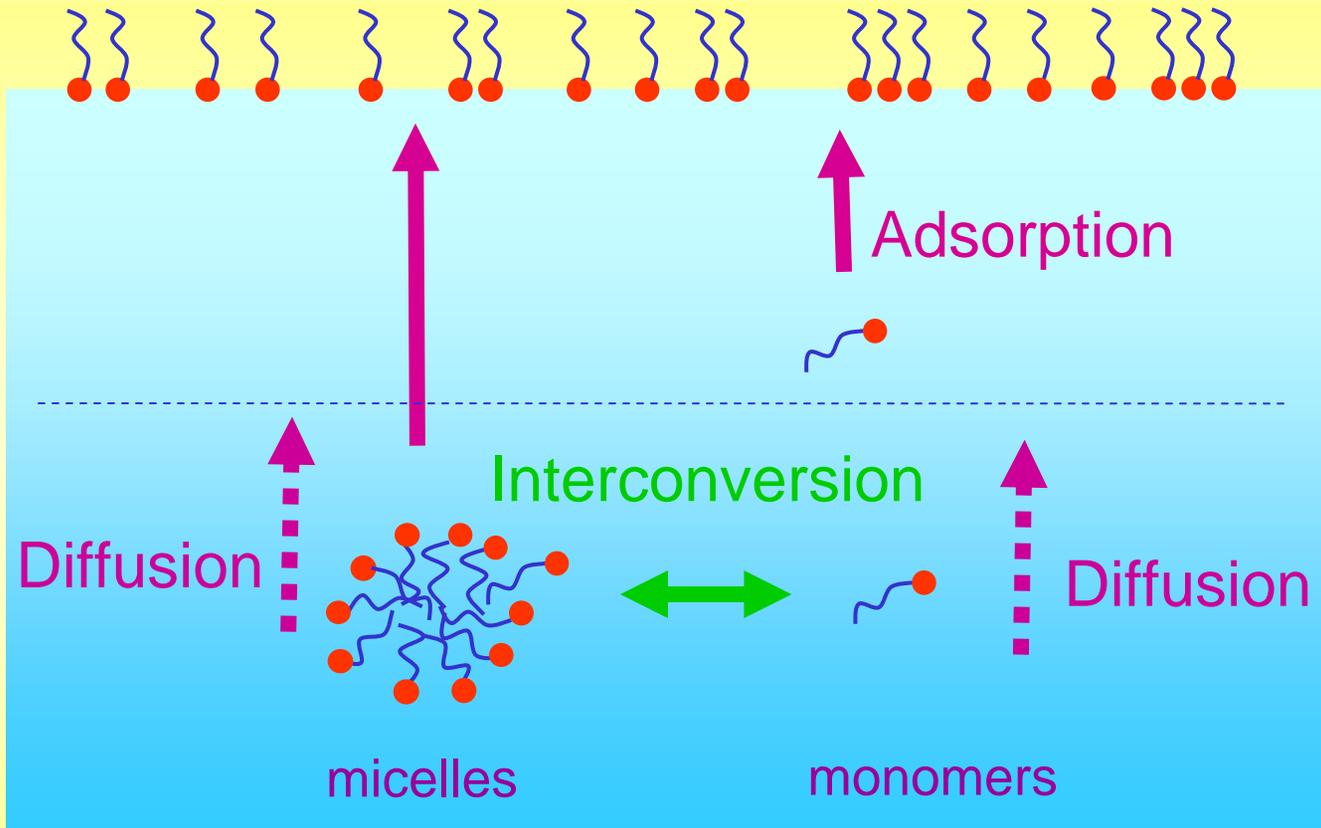
# Can micelles adsorb without breaking down?



CTAB: cmc = 0.9 mM

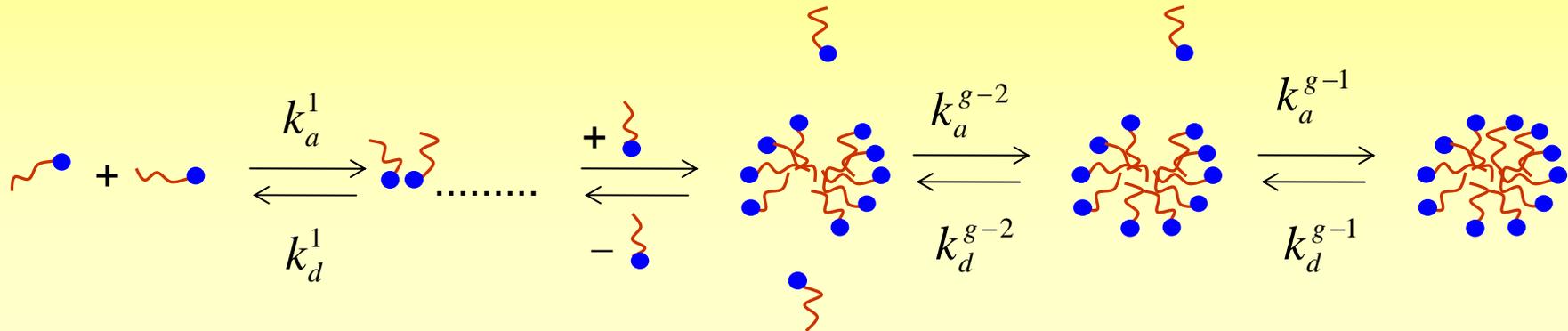


# Micelle kinetics far from equilibrium



Near a fresh surface, the monomer concentration may be much less than the cmc. Are micelle kinetics the same near a surface as in the bulk solution?

# Back to Becker-Döring ...



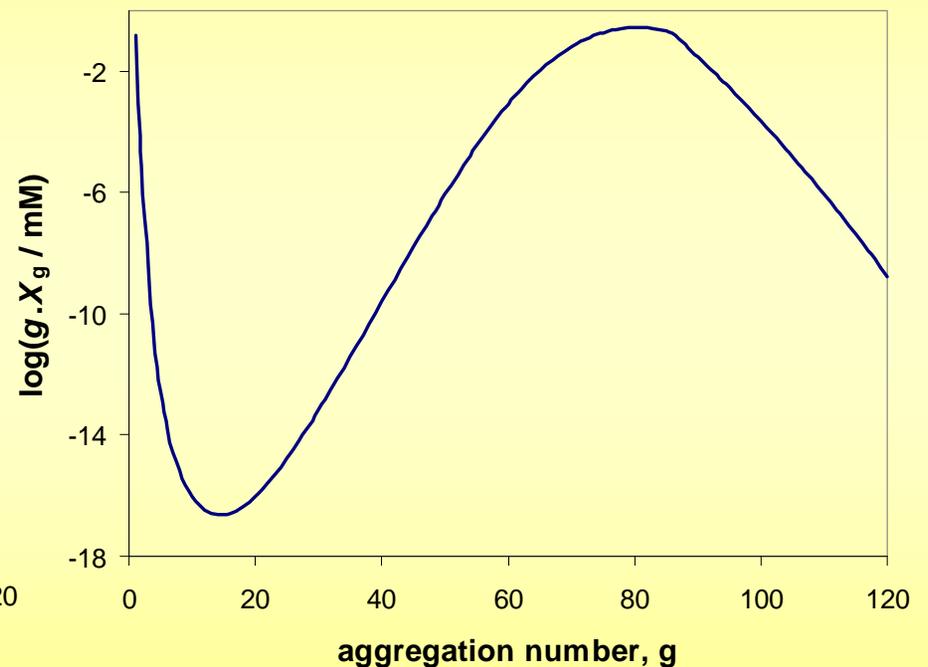
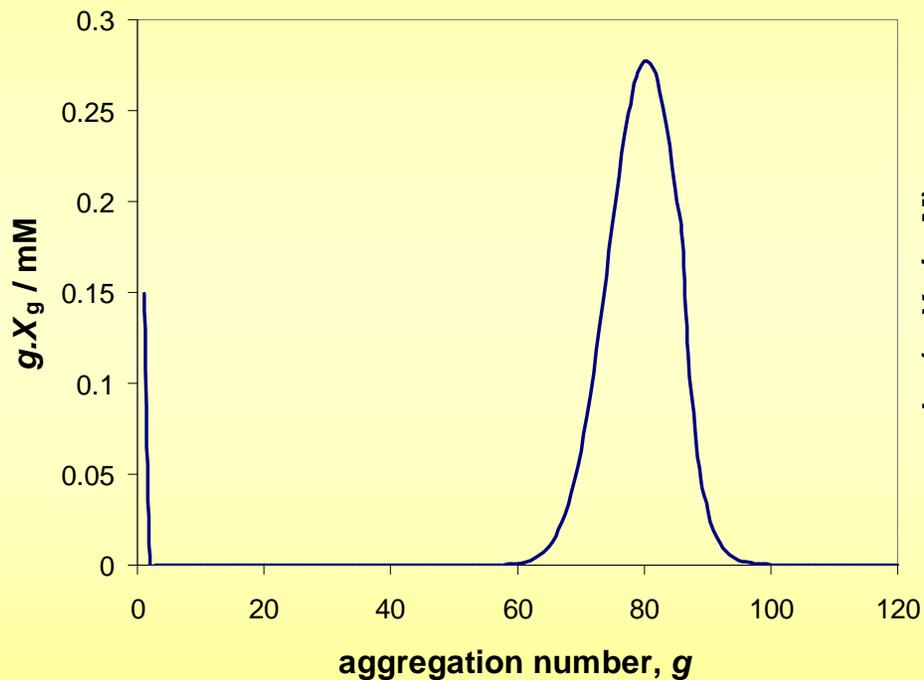
- Adsorption step occurs at a rate that is close to diffusion-controlled
- Desorption rates determined by the thermodynamic stability of aggregates of different sizes
- Need to evaluate the chemical potential of a monomer in a micelle as a function of the aggregation number,  $g$
- Use a semi-empirical method known as 'molecular thermodynamics' to determine the free energies of micelles

# Size distributions for $C_{12}E_8$



For 4mM  $C_{12}E_8$

Calculated cmc and aggregation number are excellent



Size distribution gives Aniansson and Wall relaxation times

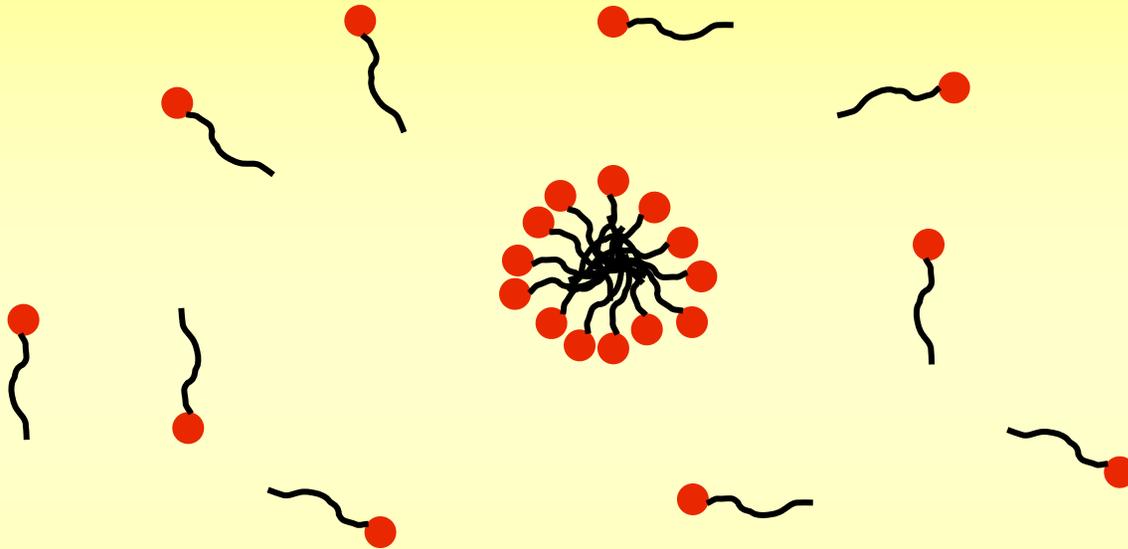
$$\tau_1 = 2 \times 10^{-6} \text{ s}$$

$$\tau_2 = 100 \text{ years}$$

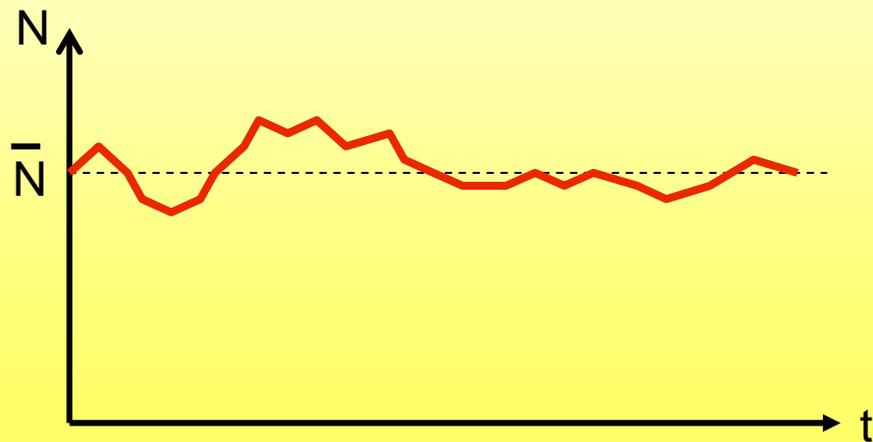
# Stochastic breakdown simulations



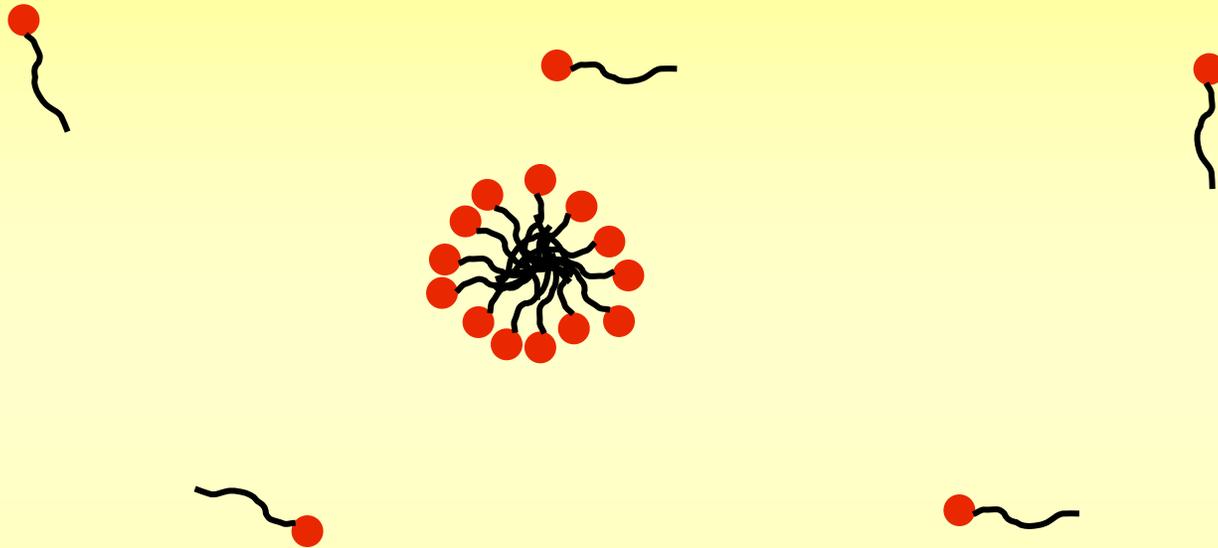
Consider a single micelle surrounded by monomers



When  $c_{\text{mon}} = \text{cmc}$  the probability of complete breakdown is very small



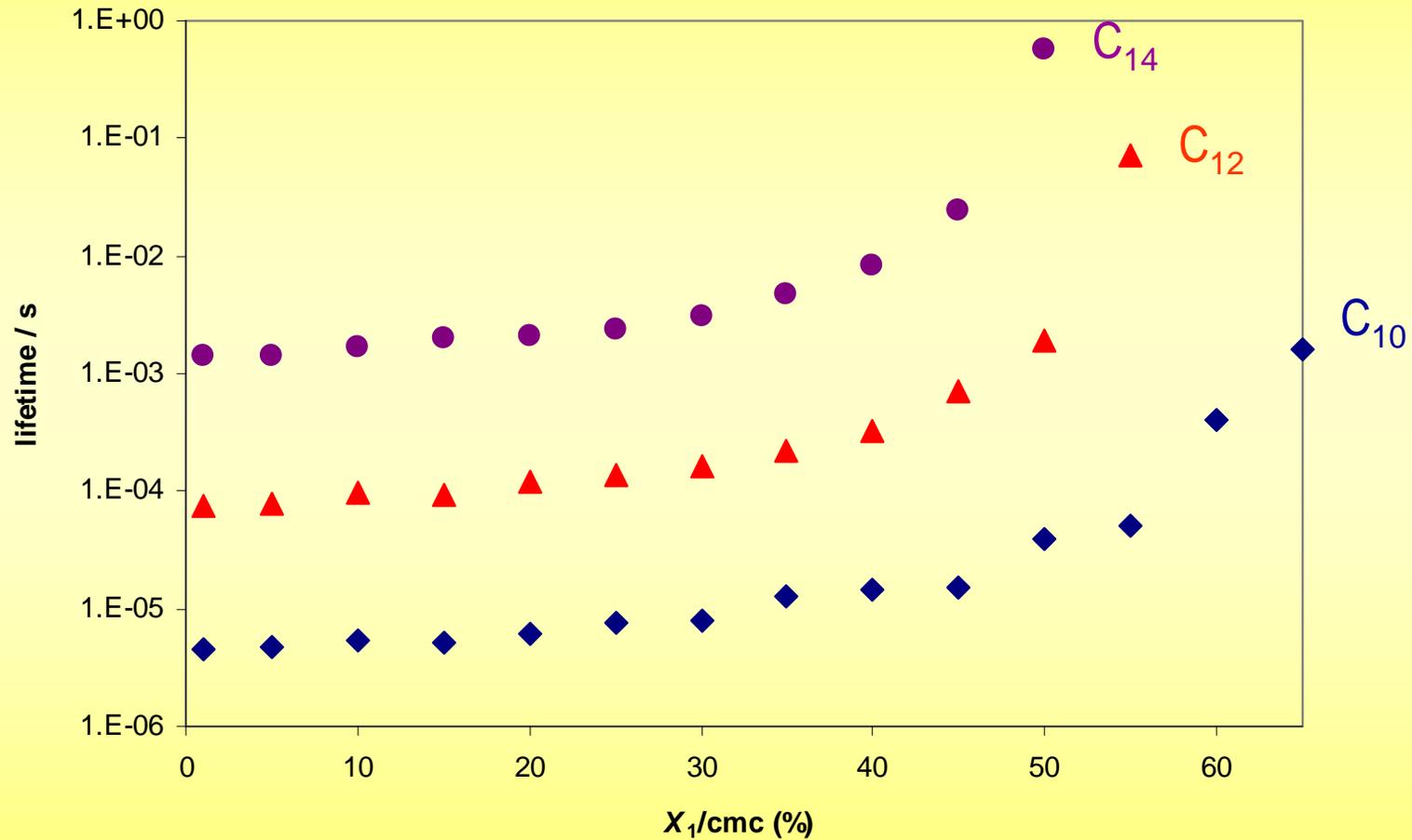
# Stochastic breakdown simulations



When  $c_{\text{mon}} < \text{cmc}$  the probability of complete breakdown increases



# Lifetime of $C_n E_m$ micelles



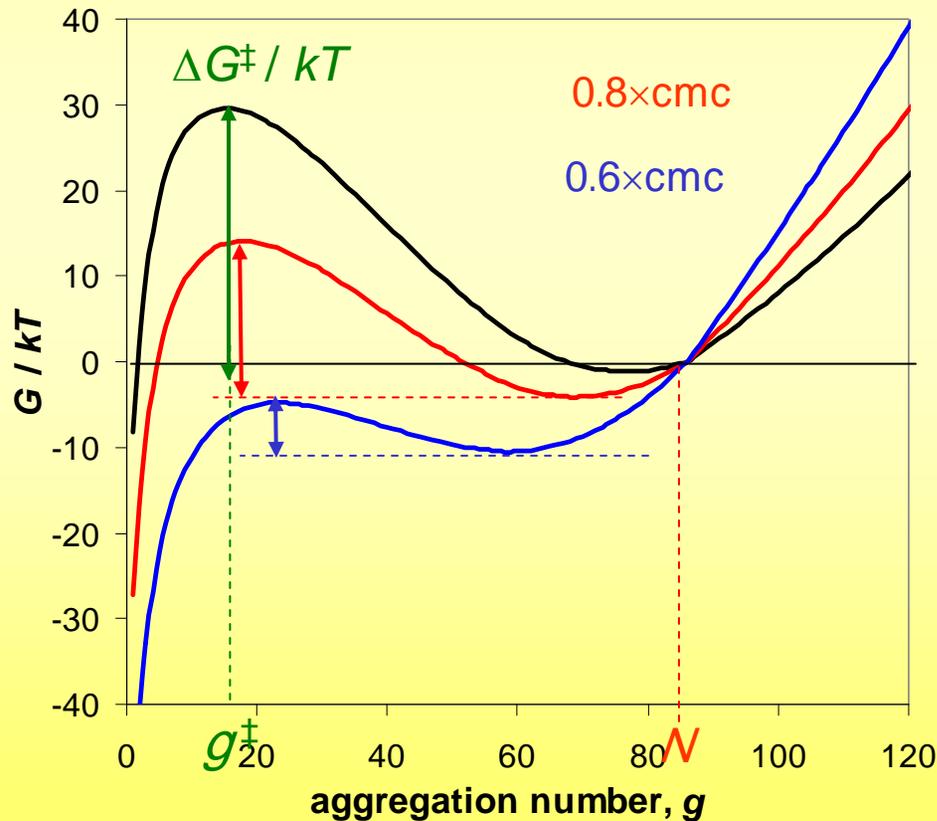
For large perturbations ( $X_1 \ll \text{cmc}$ ), breakdown is very fast  
Lifetime increases when  $X_1 > 0.5 \text{ cmc}$

# Transition state theory



Treat the aggregation number as a reaction coordinate .

Consider an  $N$ -mer with free energy  $G^o(N)$  breaking down into a  $g$ -mer with energy  $G(g) = G^o(g) + (N - g)\mu_1$



This free energy curve gives the (quasi) equilibrium distribution function:

$$X_g \propto e^{-G(g)/kT}$$

Provided that breakdown rate is slow compared to  $\tau_1$ , there will be a quasi-equilibrium of aggregates with sizes greater than  $g^\ddagger$ . We can therefore use transition state theory to write

$$k_{dis} = \nu e^{-\Delta G^\ddagger/kT}$$

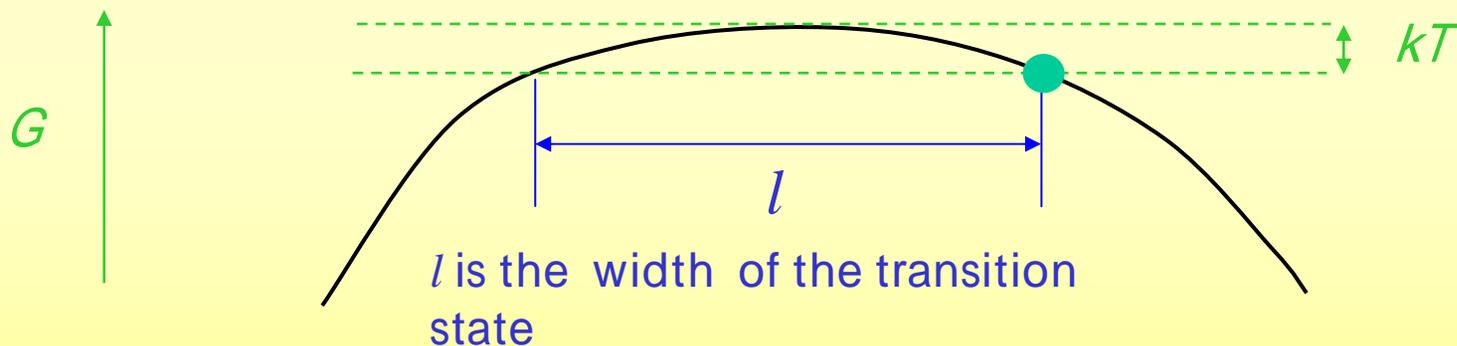
What happens when the monomer concentration is less than the cmc?

# Frequency factor in TST



First guess:  $\nu = k_d(g^\ddagger)$

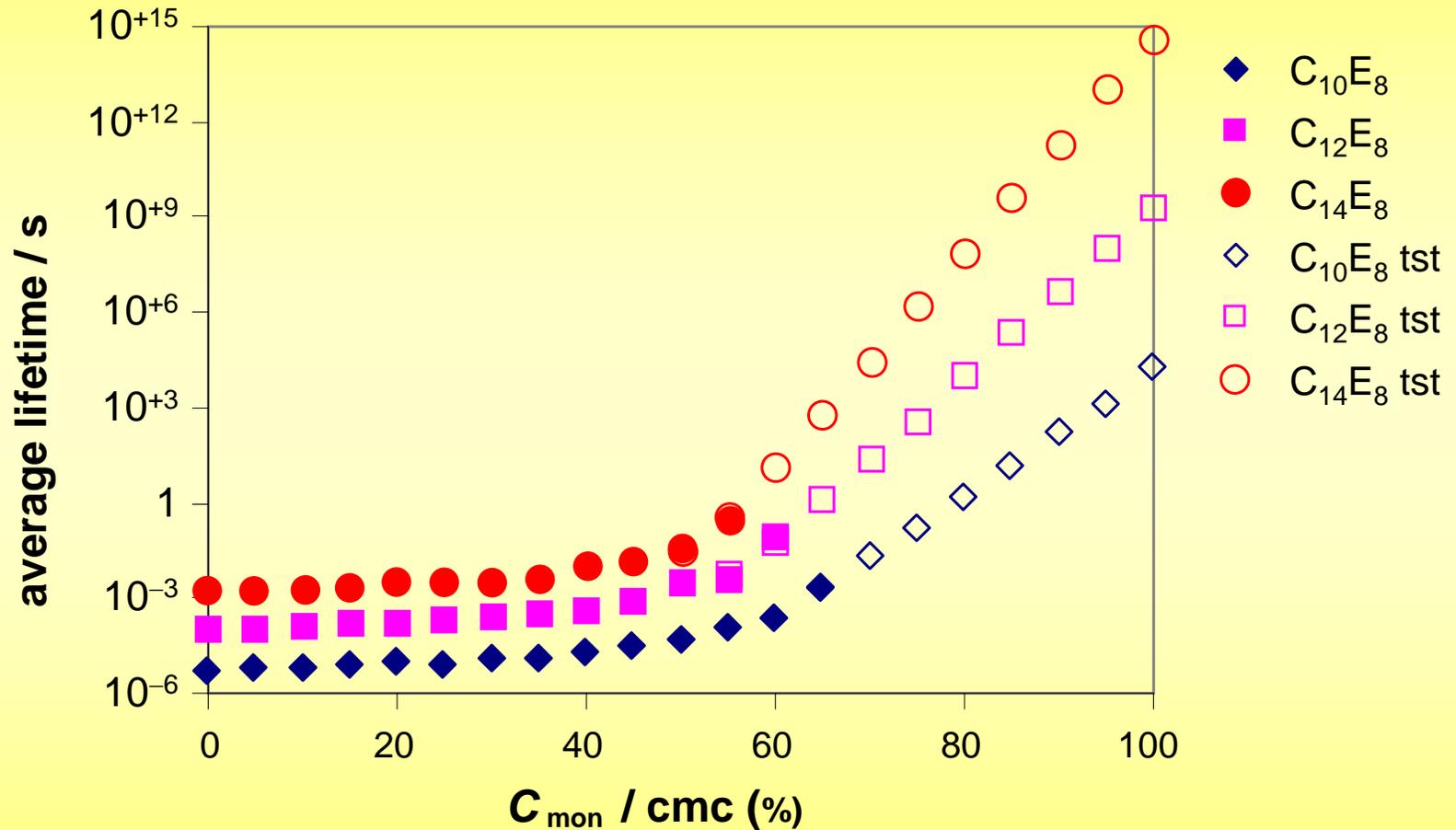
This guess overestimates the rate, since the transition state is flat



Treat motion over transition state as diffusive, with a step time of  $k_d(g^\ddagger)$

Then  $\nu \approx k_d(g^\ddagger) / l^2$

# Micelle lifetimes

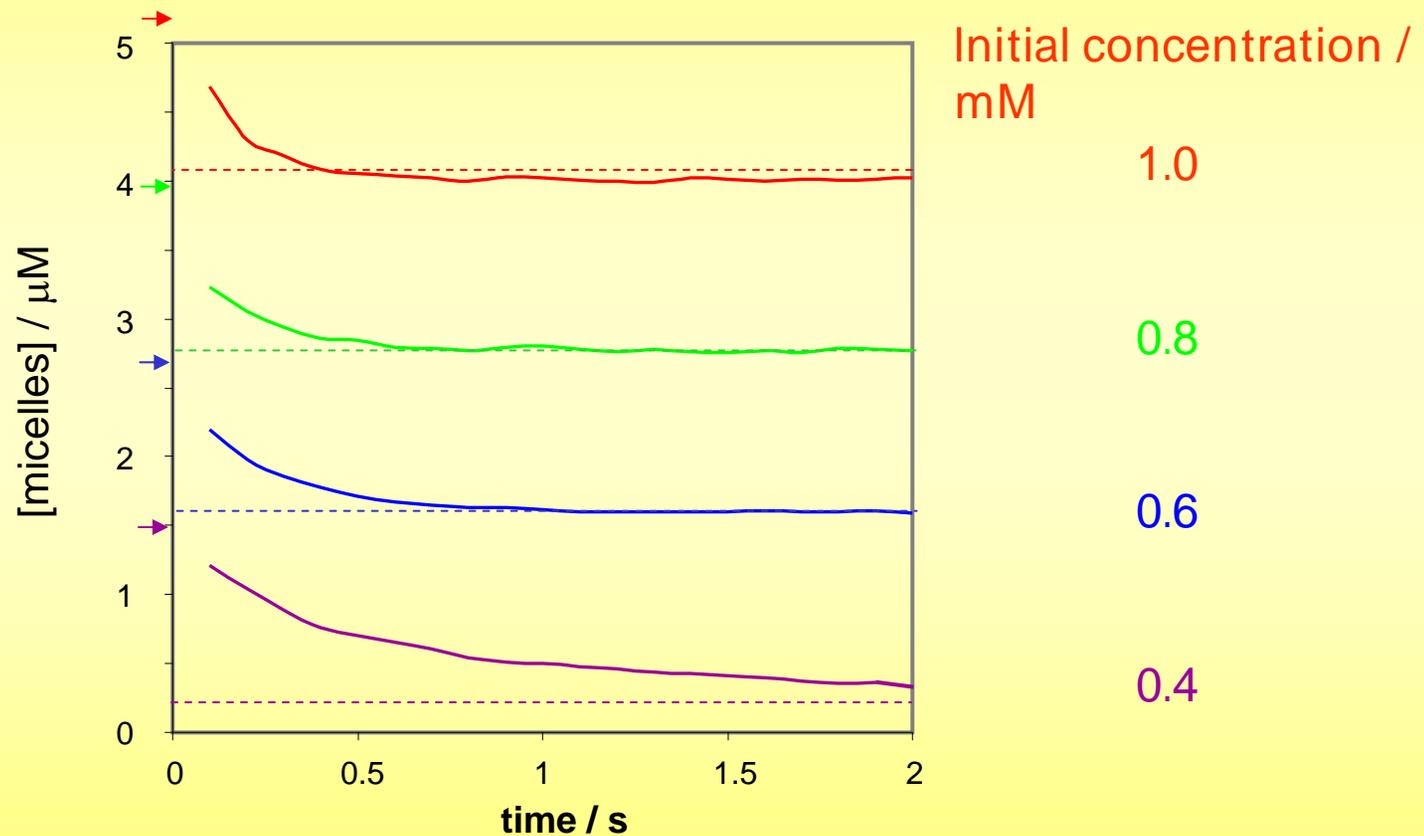


- Micelle lifetimes are very strongly dependent on the size of the perturbation to the monomer concentration: for  $C_{14}E_8$ , the dissociation rate varies by 18 orders of magnitude!



# Stopped flow measurements of micelle breakdown

The breakdown of  $C_{12}E_8$  micelles at 293 K following 2-fold dilutions

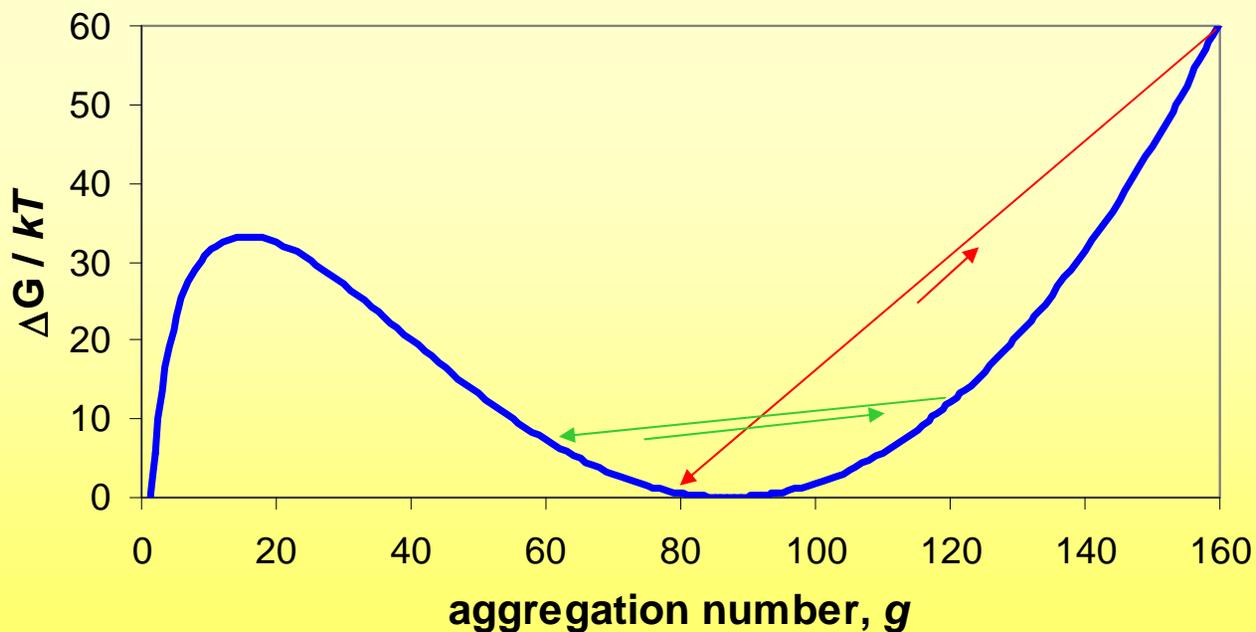
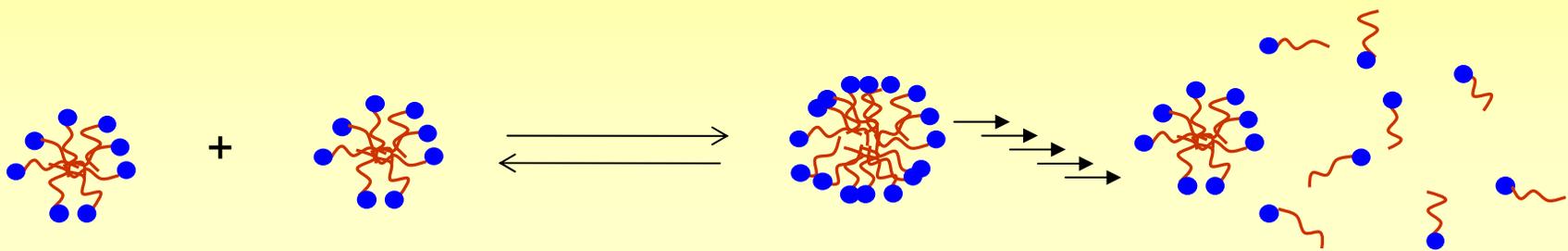


- Breakdown occurs on the sub-second timescale
- Rate increases with increasing bulk concentration

# Merge-release mechanism



Fusion of micelles to form a super-micelle that loses monomers by the Becker-Döring mechanism has the net effect of destroying one micelle

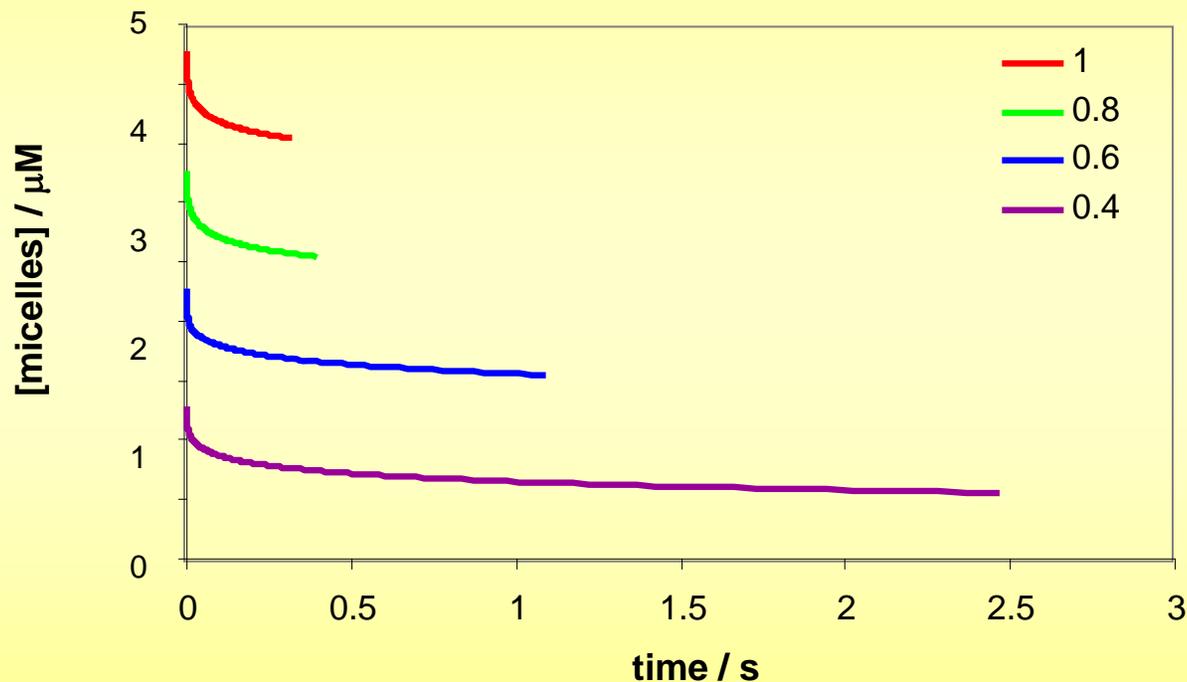


The smaller the value of  $g$ , the more likely it is that the super-micelle will decay by the Becker-Döring route  
→ complex dependence of lifetime on concentration and size of perturbation



# Predictions of merge-release model

Relaxation to equilibrium in  $C_{12}E_8$  solutions following 2-fold dilutions



Approximate solution  
working with  
mathematicians at  
Oxford on exact solution

- Micelles break down on the sub-second timescale
- Relaxation rate increases with increasing bulk concentration, as observed in the stopped flow experiment

# Conclusions



- Micelles can adsorb to an interface at a diffusion-controlled rate without first breaking down into monomers.
- The break-down rate for micelles of **nonionic** surfactants is an extremely strong function of the size of the perturbation
- A combination of stochastic simulations and a transition-state approach allows the calculation of breakdown rates by the Becker-Döring mechanism over 20 orders of magnitude in rate.
- The Becker-Döring mechanism does not provide a viable route for micelle break down at monomer concentrations near the cmc
- Micelle fusion followed by Becker-Döring decay is a possible alternative mechanism for micelle break down
- These results have significant implications for kinetic processes in micellar systems

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Ian Griffiths (Oxford)  
Peter Howell (Oxford)  
Chris Breward (Oxford)

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