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**SOME CURRENT TOPICS IN DISPERSION
STABILITY**

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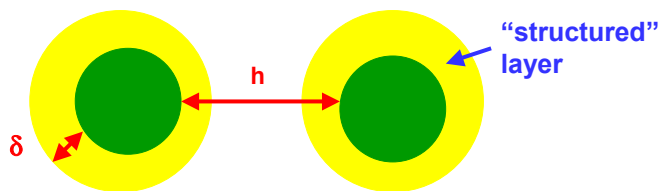
- a review of some of the “classical” concepts concerning dispersion stability.
- a list of some of the more recent, current and future challenges in this field.
- a couple of examples from this list, taken mostly from my own group’s work.

different types of breakdown process

“stability” is a ubiquitous word in colloid science; it may refer to one of several breakdown processes, associated with different types of forces, e.g.

- concentration of particles due to their induced motion in an external field (e.g. gravity, centrifugal, electrostatic, magnetic)
⇒ separation, e.g. settling, creaming.
- inter-particle (attractive) forces ⇒ aggregation [THIS LECTURE]
- interfacial tension (intermolecular forces near an interface) ⇒
 - (a) coalescence of droplets or bubbles; sintering of particles
 - (b) Ostwald ripening – growth of larger droplets or bubbles at the expense of smaller ones (Laplace pressure effect)

summary of main types of inter-particle interaction



(1) van der Waals attraction between particle cores ($h > 0$)

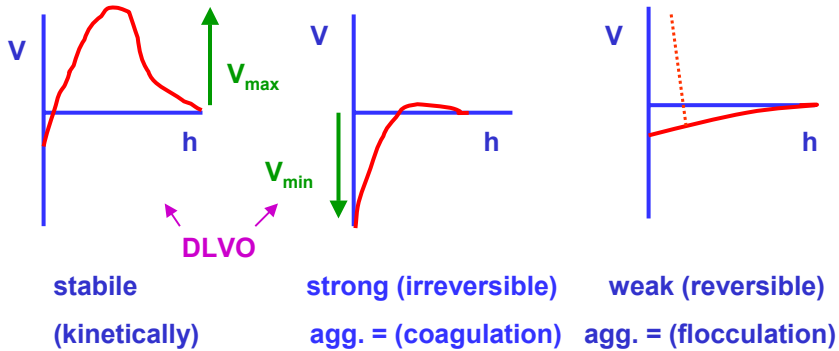
(2) “structural” interactions ($h < 2\delta$), e.g. :

- solvent : hydrophilic (solvation) or hydrophobic interactions
- counter-ions : electrical double layer interaction
- polymer : steric, bridging, depletion interactions.

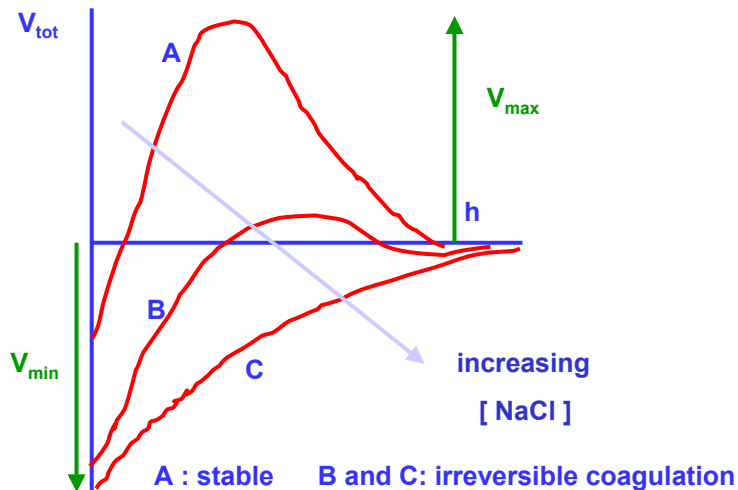
pair potential curves

Classically, one discusses the stability of (dilute) colloidal dispersions in terms of the potential energy of interaction (V), between any two particles, as function of their separation (h):

some common types of behaviour:



DLVO : total interaction : $V_{tot} = V_A + V_E$

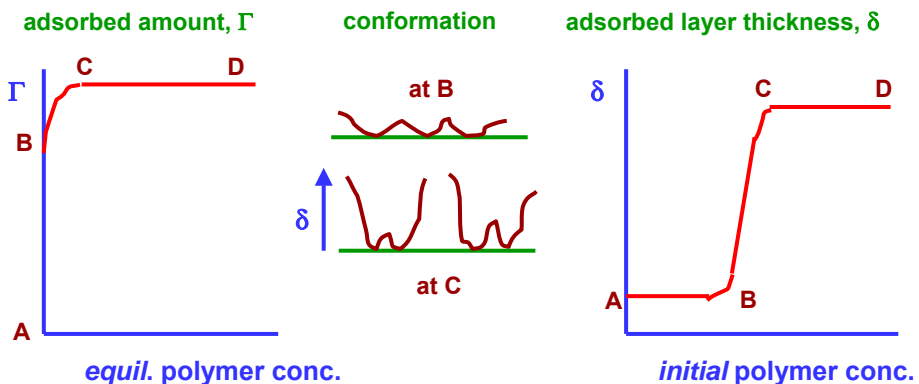


some weaknesses of charge-stabilisation (alone) :

- poor for *non-polar* media (e.g. engine or lube oils).
- in aqueous media, cannot tolerate high electrolyte concentrations (e.g. river estuaries – silting).
- *surface coagulation* can be a problem (particularly if air bubbles are present).
- cannot prepare stable, high volume fraction dispersions.
- can only control the rate of coagulation, not the strength or extent of aggregation, or aggregate structure, very easily.

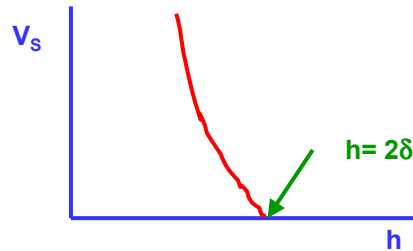
polymers at interfaces

- can overcome all these problems by adding polymers which adsorb at the particle surface.
- it is very important to establish the polymer *adsorption isotherm*, for the system being studied.



steric interaction

this is most effective closest to point C in the adsorption isotherm



requirements for efficient steric stabilization

- (1) high Γ (around point C)
- (2) high δ
- (3) strong adsorption of polymer to the surface
- (4) good solvent environment for the polymeric stabilizer
- (5) not too high a *free* polymer concentration

Note: (3) & (4) are somewhat incompatible for a *homopolymer*

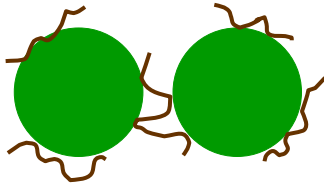
Therefore graft or block copolymers are better

(a non-ionic surfactant is effectively an oligomeric block copolymer)

relaxation of the conditions for steric stabilization

If any of the above conditions is relaxed then aggregation may result, i.e.

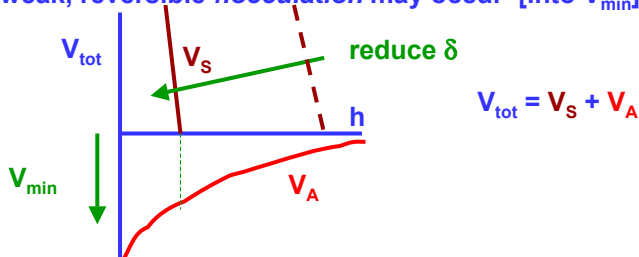
- (1) Γ too low (i.e. between **A** and **B** on the adsorption isotherm)
bridging flocculation can occur:



made use of in, e.g. , water and wine/beer purification,
mineral recovery, bacterial harvesting

relaxation of the conditions (cont.)

- (2) δ not large enough :
weak, reversible *flocculation* may occur [into V_{min}]

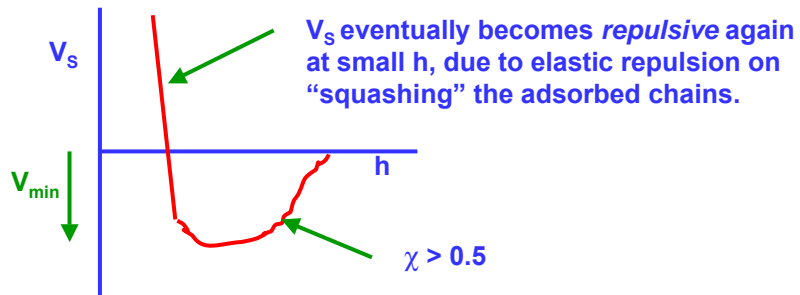


- (3) if the polymer is only weakly adsorbed, then it may be displaced from the surface during a particle collision. This would result in (irreversible) *coagulation*, as the two particles come into primary contact ($h=0$).

relaxation of the conditions (cont.)

(4) *poor solvent* environment for stabilising chains ($\chi > 0.5$)

also leads to weak reversible flocculation [into V_{\min}]:

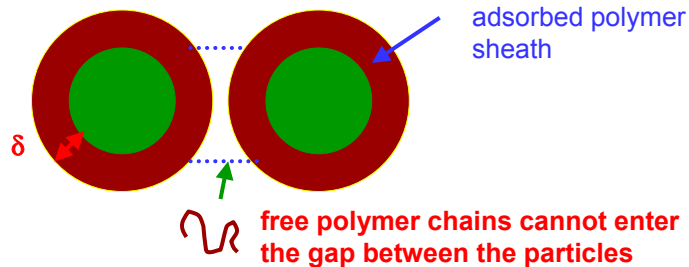


Note : V_A omitted for clarity

relaxation of the conditions (cont.)

(5) too high a *free polymer* concentration, after adsorption equilibrium attained (region **D** of the adsorption isotherm)
Leads again to weak, reversible flocculation [into V_{\min}], i.e.

depletion flocculation can occur.

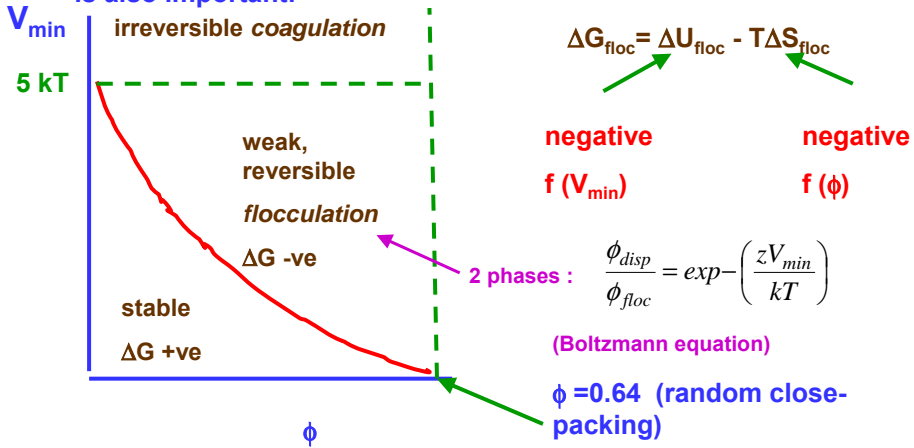


solvent tries to leave the gap (osmotic pressure), pulling the two particles together = “depletion” attraction \Rightarrow another form of V_{\min}

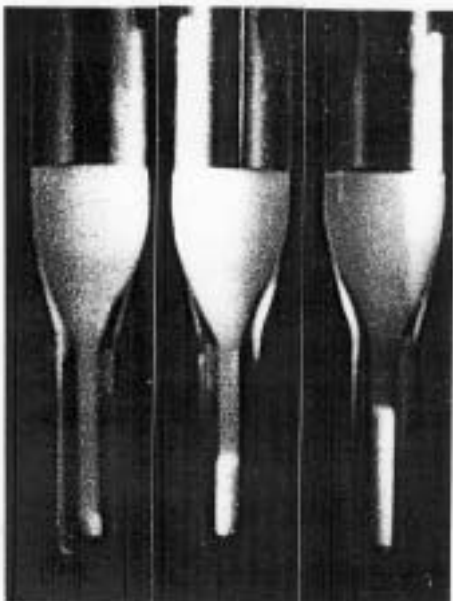
weak, reversible flocculation

occurs when $V_{\min} < \sim 5 kT$ (in the absence of any energy barrier, i.e. V_{\max})

for such systems the particle concentration (volume fraction, ϕ) is also important:



COLLOIDAL PHASE EQUILIBRIA



[Emmett and Vincent, 1985]

- SiO_2 particles with fully grafted $n\text{-C}_{18}$ chains, in cyclohexane.

$$V_A = -\frac{A_{eff} \cdot a}{12h} = -\frac{(A_p^{1/2} - A_m^{1/2})^2 a}{12h}$$

- A_p and A_m are near-matched at ambient temperature, but A_m depends more strongly on T .
recall $A = \pi^2 \rho^2 \lambda$
- the 3 tubes show the effect of decreasing T ($L \rightarrow R$)

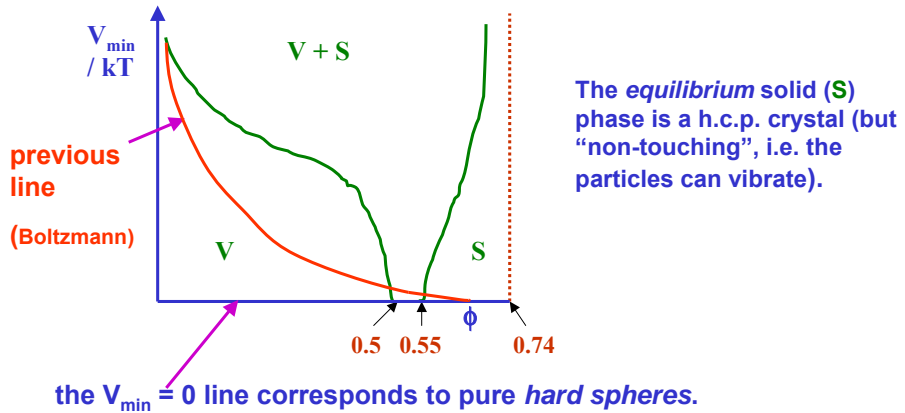
SOME OF THE CHALLENGES !

- understanding colloidal phase separation and gelation.
- dispersions of *soft* particles (e.g. microgels, droplets).
- heteroaggregation in *mixed* dispersions (incl. particles + droplets)
- dispersions of non-spherical particles and polydisperse systems.
- stability in “structured” solvents (e.g. high concentrations of polymers and /or surfactants, polymer melts, liquid crystals, super-critical fluids, ionic liquids).
- stability during particle formation, especially from complex mixtures (e.g. latices, polymers + associating surfactants)
- understanding particle interactions (e.g. in concentrated dispersions, non-additivity, short-range interactions, the long-range “hydrophobic” interaction).
- aggregation on solid surfaces and at fluid interfaces.
- assessing and quantifying aggregation.

COLLOIDAL PHASE SEPARATION, GELATION AND GLASS FORMATION

hard-sphere systems, and systems with *short-range* attraction ($D < \sim a/3$)

the *equilibrium* phase diagram is shown schematically below



Hard-Sphere Particles

[Pusey and van Meegen, Nature, 1986]

increasing ϕ : 0.45 to 0.65



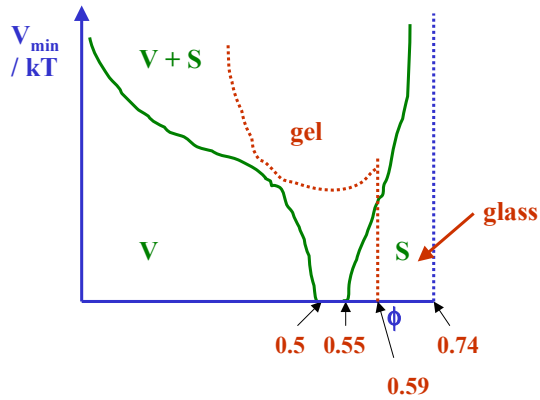
$$V_A = -\frac{A_{eff} \cdot a}{12h} = -\frac{(A_p^{1/2} - A_m^{1/2})^2}{12h} a$$

$$A_p = A_m$$

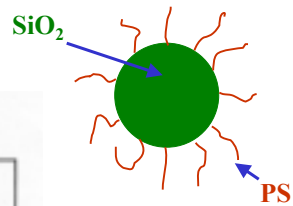
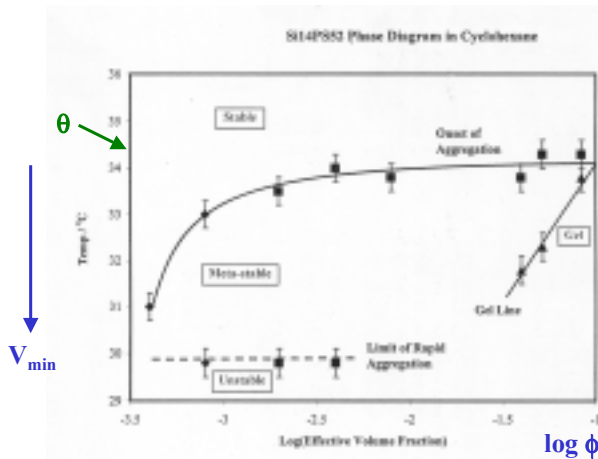


non-equilibrium effects

recent *non-equilibrium* theories have predicted the existence of **gel** and **glass** states



experimental system showing gelation



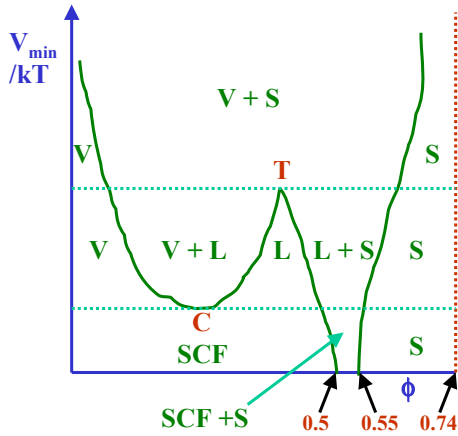
in cyclohexane

NB y-axis inverted

[Van Duijneveldt, Vincent and Weeks, 2001]

systems with *longer-range* attraction ($D > a$)

the *equilibrium* phase diagram is shown below:



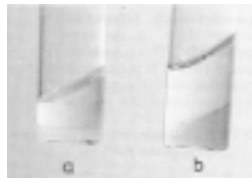
T = triple point

C = critical point

a liquid-like phase can now be sustained

this is the direct analogue of the phase diagram for *spherical* molecules

Example of “vapour-liquid” equilibrium



$\text{SiO}_2\text{-g-C}_{18}$ particles ($d = 15$ nm) in cyclohexane + PDMS

i.e. a long-range depletion attraction

(a) vapour - solid : high [PDMS]

(b) vapour - liquid : low [PDMS]

note: the tubes have been tilted !

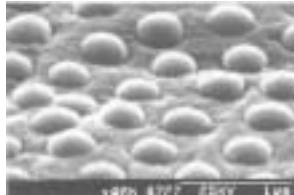
[Vincent and Edwards, 1990]

DISPERSIONS OF (SOFT) MICROGEL PARTICLES

- cross-linked poly(N-isopropylacrylamide) [PNIPAM] particles in water, as function of temperature and NaCl concentration.

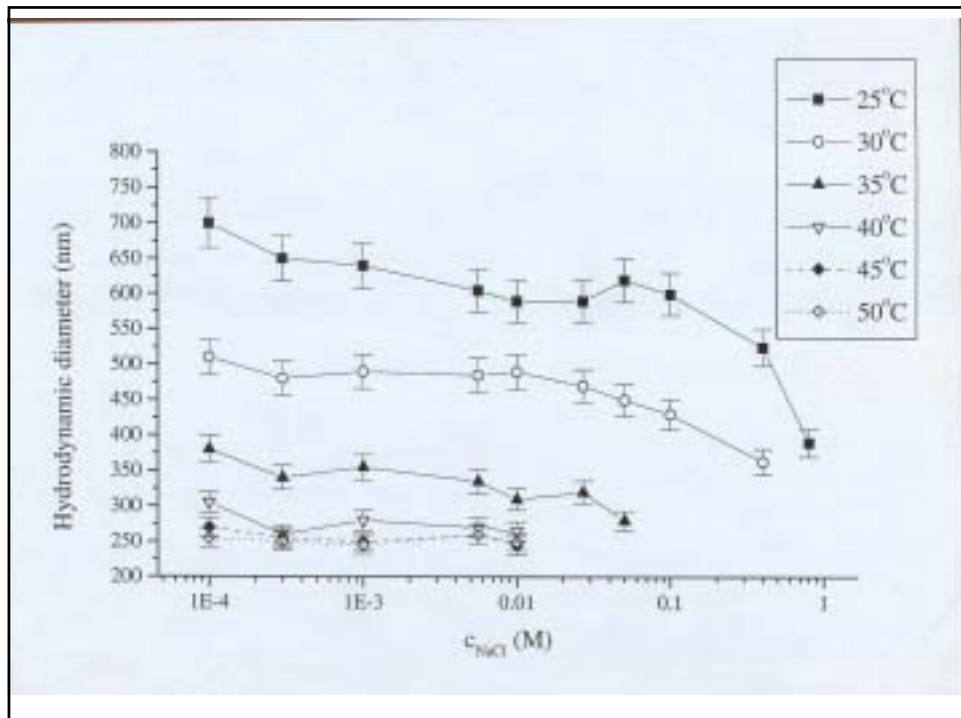
(Rasmusson, Routh and Vincent, 2003, submitted)

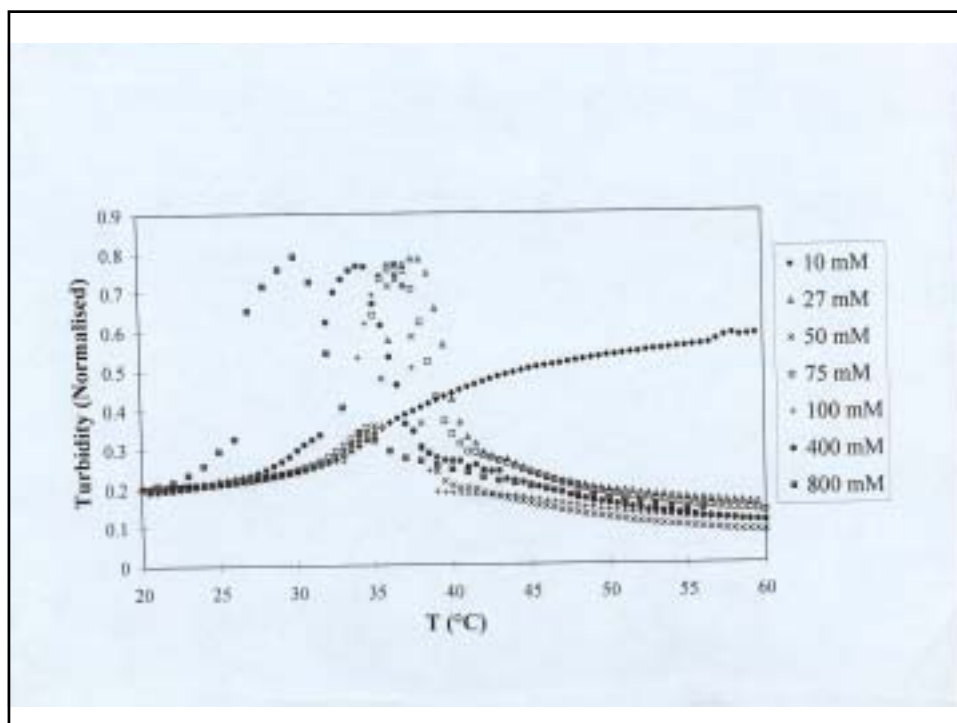
- PNIPAM as a lower solution critical temp. in water at $\sim 35^{\circ}\text{C}$.



- SEM of PNIPAM at 20°C .

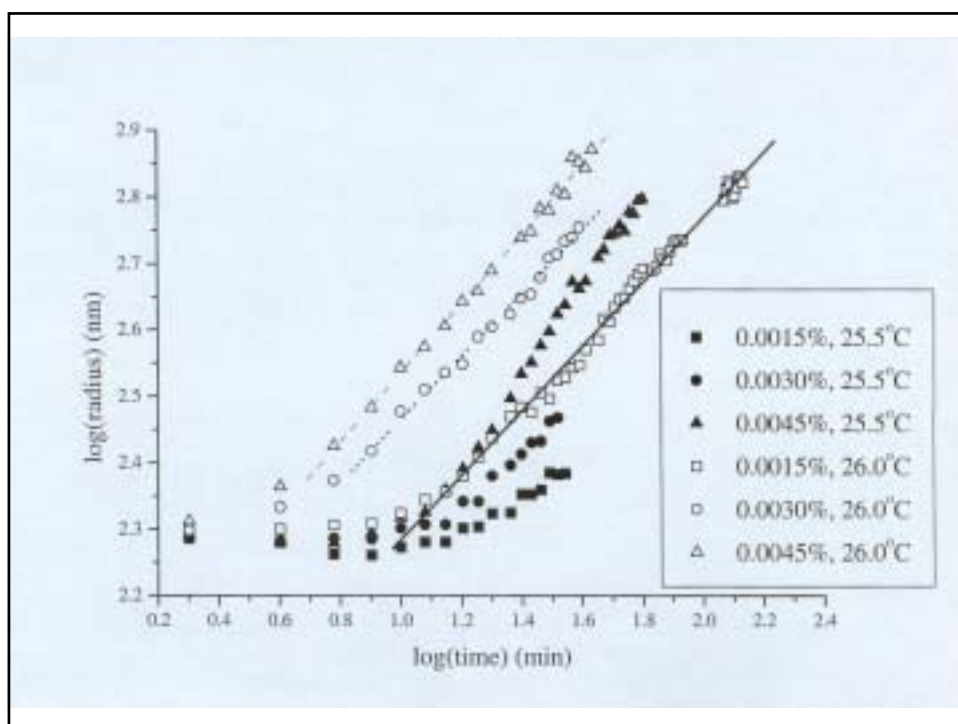
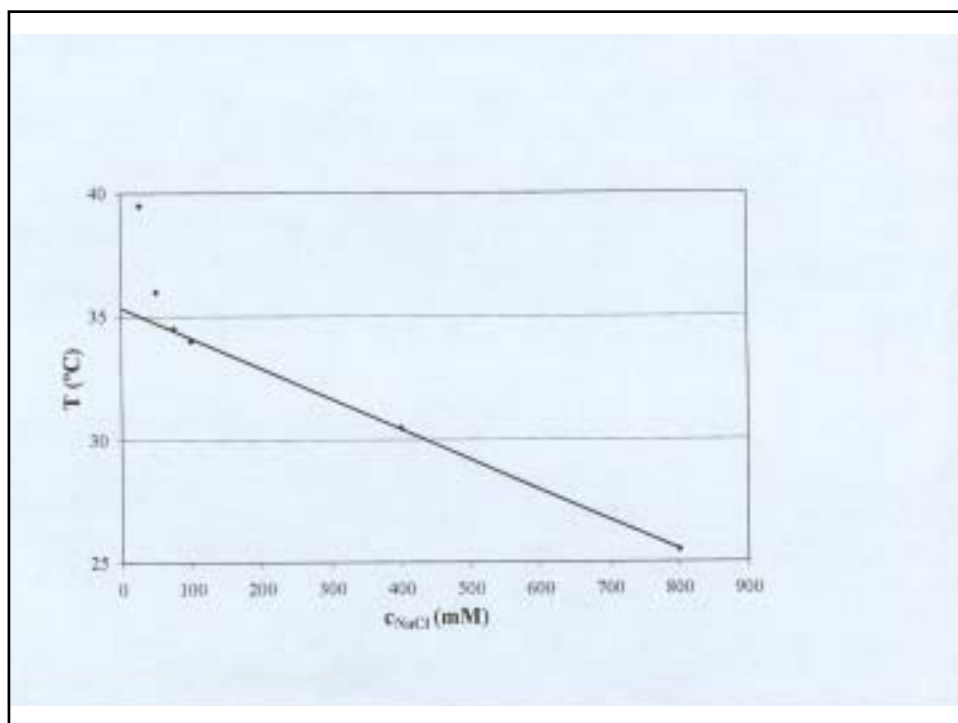
(Saunders and Vincent, 1996)





The critical flocculation temperature (CFT) of the PNIPAM dispersions as a function of NaCl concentration

[NaCl] (mM)	CFT (°C)
27	39.5
50	36.0
75	34.5
100	34.0
400	30.5
800	25.5



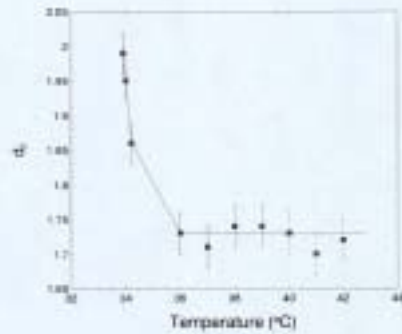


Figure 4: Fractal dimension of PNIPAM flocs in 1M NaCl, at various temperatures.

CONCLUSIONS

- Tried to illustrate that our understanding of colloid stability and aggregation processes has moved on considerably in the last 50 - 60 years, since the publication of the DLVO laid the foundations.
- During that time that have been extensive developments in both theory and experimental techniques.
- However, there are still many unsolved problems !