SWELLING OF POLYMER-OLIGOMER PARTICLES

HABIBA RAJABU MFUTAKAMBA

A Thesis Submitted for the Degree of Master of Science in the University of Dar-es-Salaam.

January, 1980.

ACKNOWLEDGEMENT

First and foremost, I would like to thank my supervisor, Professor, Dr.Philos. John Ugelstad, for helping me to choose this topic of study. I am also very grateful for his constant advice, suggestions and discussions during the entire time of study. I would also like to acknowledge Professor G. Ndaalio and Professor A. Hassanali for initiating me into this field of study.

I gratefully acknowledge my indebtness to Ass.Prof. P.C. Mørk for his very helpful advice, discussion and guidance which has been especially valuable. Much thanks must also go to Kari H. Kaggerud, Lise Holm and all my colleagues at the institute of Industrial Chemistry, the Norwegian Technical University, Norway who made this study possible.

I express my indebtness to Norwegian Agency for Internal Development (NORAD) for the fellowship and financial support for my studies. I am equally indebted to both the Tanzania Govt. and University of Dar-es-Salaam for allowing me to carry this study in Norway.

I am very grateful to Karin Haaheim for typing this manuscript.

It is a great pleasure to acknowledge my gratitude to all the other persons, some named and unnamed who helped so much.

Lastly, I am deeply indebted to my daughter, Kakuua, who missed her motherly care while I was doing this work, and my husband, for whom this undertaking has resulted in many months when I was unavailable for tasks more important and pleasant to them, and to my parents without whose hard work and encouragement I would never have reached the point of being able to undertake this work.

CONTENT

SUMMARY

A quantitative study of the swelling capacity of polymer-oligomer particles, and the rate of transport of slightly water soluble compound 1, e.g. chlorobenzene, from bulk phase to the particles has been carried out. A much higher swelling capacity was attained when compound 1 was subdivided (before it was added to the swelling experiments) than when it was added as a bulk at the same experimental conditions. It is shown that the increased swelling capacity when compound 1 is subdivided may lead to a much higher value of the equilibrium swelling with compound 1.

In previous studies and at the beginning of this work, one was not sufficiently aware of the importance of the kinetics of swelling where the rate is much faster when compound 1 is subdivided, such that it depends on the number and radius of the particles $N_p r_p$ while when compound 1 is added as a bulk phase, the rate dependend on the number and radius of droplets, $N_d r_d$.

It was possible to swell polymer-oligomer particles of $\sim$ 2.5μm with v/v rates of polymer to oligomer of 2:1 up to 40 μm in a relatively short time when compound 1 was subdivided. When compound 1 was added as a bulk, the size reached with the same polymer-oligomer particles was $\sim$ 16μm.

The dependence of the rate and swelling capacity on such factors as the type and amount of oligomer used and the nature of emulsifier, was found to agree well with theoretical considerations. The speed of stirrer was also found to be an important factor affecting the rate of transport of compound 1 to the particles.

Bidisperse emulsions were made by competitive swelling, and the radii of two kinds of particles agree experimentally well with theoretical calculations. Diffusion of compound 1 from polymer-oligomer particles swollen with compound 1 to polymer-oligomer particles was very fast. The compound 1 is distributed on a large number of particles with a very high total surface.

1. INTRODUCTION

Monodisperse particles in the range 0·1 - 2·0μm have been produced in quantity and are readily available for scientific use. The first monodisperse particles were accidentally produced in 1947. These < 2μm particles can be produced by ordinary emulsion polymerization. The basic theory of emulsion polymerization is due to Harkins[50] while the experimental verification of this theory was performed by Smith and Ewart.[51] The kinetics and mechanism of emulsion polymerization has been further developed by Ugelstad and coworkers.[52-54]

Where as Smith and Ewart found out that the rate of polymerization depends principally on the number of particles present, and this, in turn is largely dependend on emulsifier concentration, recently Ugelstad and coworkers established that the number of particles was independent of the initiator cencentration; the differential rate of polymerisation, taken at a given conversion was proportional to the square root of the initiator concentration; the rate increased with increasing conversion and the rate was determined by the number of particles formed by the emulsifier.

Much work has so far been done on preparation of < 2μm latex particles under a variety of different conditions, e.g without addition of emulsifying agents,[55-57] and seeded growth procedure.[58,59] For preparation of large particles one applies today a suspension polymerization technique which gives very low yield and does not give monodisperse particles.

Recently, a Lehigh Research Project [60] has proposed orbital flight tests and spacelab experiments leading to production of large size monodisperse latexes in microgravity.

A new method of preparation of stable monomer emulsions by diffusion has been recently described by Ugelstad et al.[27-29].

The method is a two step swelling method where in the first step an insoluble compound, 2, is introduced into ordinary made polymer particles and then conditions are changed such that the compound 2 cannot be transported out of the particles. Then in the second step is added a slightly water soluble compound 1, which diffuses through water and become absorbed into the particles consisting of polymer and compound 2. And since the particles contain a considerable amount of compound 2, they are able to take up in them a volume of compound 1 up to a v/v ratio of > 1000. It has been possible to prepare monodisperse particles with large size. If the compound 2 is an oil soluble initiator, and is absorbed by a monomer like styrene, polymerization can later be carried out and in this case initiation is in the monomer droplets. The two step swelling of polymer particles provides a new method of formation of stable o/w emulsions of relatively low molecular weight compounds. The method is especially favourable since it is possible to make monodisperse particles of predetermined size and size distribution.

There are many uses of monodisperse particles. Some of the main uses are in photography, for calibration of various instruments e.g electron microscopy, in several areas of medical research like cancer, syphillis, as model system for study of such colloidal properties as rheology, stability and light scattering, and also as standards to determine pore size. The application of these new principles seems still to be in their beginning, and a lot more research is needed.

2. THEORY:

2.1 EMULSIONS:

(a) Definition: An emulsion is a heterogeneous system, consisting of at least one immiscible liquid intimately dispersed in another in the form of droplets, whose diameters, in general, exceed 0.1μ. Such systems possess a limited stability, which may be increased by such additives as surface active agents, finely divided solids, etc.[1]

An emulsion is a result of two competing processes, namely the disruption of the bulk liquids to produce fine droplets and the recombination of droplets to give back the bulk liquids, hence it is thermodynamically unstable since the latter process is spontaneous. Emulsification is therefore treated as two independent problems: (a) the formation of new droplets and (b) the stabilisation of droplets once they are produced.

To disperse one liquid in another in the form of emulsion requires amount of work upon the system, W such,[2]

$$W = \gamma \Delta S \qquad 2.1.1$$

W: Work done in ergs/

γ: Interfacial tension of oil-water in ergs/cm^2

ΔS: Increase in surface of dispersed phase due to formation of emulsion droplets. S is in cm^2.

The original surface of dispersed phase is negligble compared to the dispersed phase extended in form of droplets, therefore the increase in surface ΔS is related to the total volume of emulsion droplets

$$\Delta S = 6V/d \qquad 2.1.2$$

V: total volume of emulsified internal phase in cm^3
d: diameter of droplets in cm.

Hence,

$$W = 6 \gamma V/d \qquad 2.1.3$$

Hence, for emulsification, a definite amount of work has to be done.

(b) Emulsification: The thermodynamically stable state of two immisible liquids is their bulk form with a minimum of interface, the heavier liquid lying below the lighter one. To get a metastable emulsion, considerable ingenuity must be employed.

In general, droplets of required size may be obtained in two different ways.[3]

1. Condensation Method: In this method one starts from very tiny nuclei and then allow them to grow to required size. As an example, the vapour of one liquid (the dispersed phase) is injected below the surface of another liquid, which forms the external phase of the emulsion, the vapour becomes supersaturated and condenses as micron-sized particles.

2. Dispersion Methods: The method requires the break up of large drops of the bulk liquid into small droplets. This is common method, and there are many variants, which generally are classified into three categories, mixing, colloid milling and homogenizing.

(i) A special simple way of forming an emulsion is by intermittent shaking, and it was found out by Briggs (1920) that intermittent shaking , with rest periods between two shakes was more effective than uninterrupted shaking.

In handshaking, the globules are polydisperse and are in the size range 50 ~ 100μ. To get smaller droplets, the agitation must be on a microscale, which requires large velocity gradients.

(ii) Mixers: A paddle is rotated in a large cylindrical vessel. The liquid is rotated, the free surface attains a rough parabolic shape. Mixing is best accomplished where there are lateral and vertical flows which distribute the materials rapidly to all parts of the tank, for example by using vertical baffles near the walls, using propellershaped stirrers which impels the liquids axially up or down and contributes to the mixing. Usually, in this case the particle diameters in the emulsions are usually of the order of 5μ.

(iii) Colloid Mills: Here, emulsification of the liquids is carried out under strong shearing flow in a narrow gap between a high speed rotor and a stator surface. In this case, particle diameters of the order of 2μ are obtained.

(iv) Homogenizers: It is a device in which dispersion of the liquids is achieved by forcing the mixture through a small orifice under very high pressures. This results in particle sizes of about 1μ or less.

(c) Emulsifying Agents: In early days, the interfacial tension γ, was regarded as a very important factor in determining stability and particle size of emulsion. From eqn. 2.1.1 above, low γ favoured emulsification. Thus the primary advantage of emulsifiers was considered to be the reduction of γ brought about by them.

But, it is now recognized that not only do they facilitate emulsification, but they also promote emulsion stability. The following characters of an emulsifier are desirable[4], in summary.

(i) It must reduce the interfacial tension to about 0.5 ~ 5 dyne/cm.

(ii) It must adsorb quickly around the dispersed drop as a condensed, non-adherent film which will not thin out when two drops collide and thus will not permit coagulation or coalescence.

(iii) It must have specific molecular structure with the polar end attracted to water and non-polar end attracted to oil.

(iv) It must be more soluble in the continous phase so as to be readily available for adsorption around the emulsion droplets.

(v) It must impart adequate electrokinetic potential.

(vi) It must influence the viscosity of the emulsion.

(vii) It should be able to emulsify required system with small concentrations of emulsifier.

(viii) It should be relatively inexpensive.

(ix) It should be nontoxic and safe to handle.

(d) Type of Emulsion: The emulsion consists of three phases; the internal, external and the interface. The internal, or discontinous, phase is present in the form of finely divided droplets. This is also known as the dispersed phase. The external, or continous, phase forms the matrix in which the droplets are suspended. In order to make the system stable for any length of time, a third constituent, the interface, must be present. It consists primarely of an emulsifier that bind the internal and external phases.

In nearly all emulsions, one of the phases is aqueous and the other an oil[5]. If the oil is the dispersed phase, the emulsion is termed oil in water (O/W) emulsion; if the water is the dispersed phase, the emulsion is termed water in oil (W/O) emulsion.

2.2 EMULSION STABILITY:

(a) Emulsions can show instability in three ways; by creaming, by inversion and by breaking (demulsification).

(i) Creaming. Creaming results from a density difference between the two phases, and is not necessarily accompanied by droplet flocullation, although this facilitates the process. Separation of the two liquid phases is incomplete.

Generally, stability of an emulsion can be analogous to a suspension of solids in a liquid and is related to the rate of sedimentation[6]. The linear rate of sedimentation (stability function) is given by Stokes' law,

$$U = \frac{2\ gr^2(d_1-d_2)}{9\eta_2} \qquad 2.2.1$$

where,

U: rate of sedimentation in cm|sec
g: acceleration of gravity in cm|sec^2
r: droplet radius in cm
d_1: density of sphere (internal phase) in g/cm^3
d_2: density of liquid (external phase) in g/cm^3
η_2: viscosity of continous phase in poises.

Hence, emulsion stability is favoured by small droplet radius, small density difference, and high viscosity of external phase.

Eqn 2.2.1 describes rate of creaming of a single drop, when cosidering the mass rate of creaming, Stokes'law involves a distribution of droplet radii[7], and mass rate of creaming is

$$\bar{U} = \sum_i \frac{8\pi}{27\eta V}\ gn_i r_i^5 (d_1-d_2) \qquad 2.2.2$$

n_i: droplets of radius r_i
V : Total volume of the dispense phase

Eqn 2.2.2 reduces to eqn. 2.2.1 when an emulsion is of uniform droplet size.

(ii) Inversion. The emulsion may change from o/w to w/o, and vice versa. It was calculated by Ostwald[8] on stereometric ground that spheres occupy 72·02 per cent of total volume assembly, and this was the densest packing. Hence at phase volume $\Phi > 0.74$ the emulsion is inverted or breaks. It has also been found that inversion depends on emulsifier type and concentration, change of pH or bacterial action and temperature.[9]

(iii) Demulsification: This is the most important and most complete example of emulsion instability. It is the spontaneous joining of small droplets in the emulsion to form larger ones leading ultimately to two separate liquid layers.

Flocculation of emulsion droplets i.e the droplets of the disperse phase form aggregates in which the drops have not entirely lost their identity (this is often reversible) is the first stage of demulsification.

The second stage is coalescence, where each aggregate combines to form a single drop. This is an irreversible process ultimately leading to complete demulsification.

The overall rate of reaction is determined by the slower of the two stages. In very dilute oil-in-water emulsion, the rate of flocculation is rate determining and in highly concentrated emulsions, rate of coalescence is rate determining.

It was shown[10] using Smoluchowski's theory of emulsion, that the total number of particles, whether frocculated or not, in a coagulating emulsion is found by adding the number of

unreacted primary particles n_1 to the number of particles in the aggregates i.e

$$n = n_1 + n_v \cdot m = \frac{n_o}{1+an_o t} + \frac{an_o^2 t}{(1+an_o t)^2} \left\{ \frac{an_o}{K} + \left(1 - \frac{an_o}{K}\right) e^{-Kt} \right\} \qquad 2.2.3$$

Where,

n_v : number of aggregates
m : average number of separate particles in aggregate at time, t
n_o : number of particles at time t = 0
a : Rate determing constant, $\simeq 10^{-11} cm^3/s$ for rapid coagulation of a monodisperse sol.
K : Measure of rate of coalescence
t : time

The first term in eqn 2.2.3, $\frac{n_o}{1+an_o t}$, is the number of particles which would be found if each aggregate had been counted as a single particle.

Where K = ∞ (i.e immediate coalescence)

eqn 2.2.3 reduces to $n = n_o/1+an_o t$ 2.2.4

n: number of particiles in unit volume.

K = 0 (no coalescence), eqn 2.2.3 gives

$n = n_o$ for all values of t.

for intermidiate values ($0 < K < \infty$), the effect of change in particle concentration on rate of coagulation is given by eqn 2.2.3.

Van den Tempel has made several approximations of the eqn 2.2.3, such

1. In a flocculating concentrated emulsion,

$an_o/K \gg 1$, since $K \ll 1$

Hence $an_o t \rightarrow > 1$ very quickly, hence contribution of primary particles is neglected.

eqn 2.2.3 reduces to

$$n = an_o^2 t(1+an_o t)^{-2} \{an_o/K(1-e^{-Kt})\} \qquad 2.2.5$$

$$an_o t >> 1$$

$$n = \frac{n_o}{Kt}(1 - e^{-Kt}) \qquad 2.2.6$$

Hence, in concentrated emulsions, rate of coalescence no longer depends on rate of flocculation.

2. In extremely dilute emulsions:

$an_o/K << 1$, provided coalescence occurs at a sufficiently high rate. After coagulation has taken place for quite a long time, $Kt >> 1$, hence second term on R.H.S. of eqn 2.2.3 may be neglected, eqn 2.2.3 reduces to eqn 2.2.4, which doesn't contain K, hence flocculation is rate-determining.

3. If coalescence is very slow, expanding the exponential form of eqn 2.2.3, neglecting after the second term when $Kt << 1$:

$$n = n_o\{1 - Kt(1 + an_o t)^{-1} + Kt(1 + an_o t)^{-2} \qquad 2.2.7$$

hence, very slow decrease in particle number.

4. After a long time of coagulation, Kt may be much greater than unity, hence exponential term is neglected, an_o/t (in the denominator) is greater than unity, eqn 2.2.3 simplifies to

$$n = n_o/Kt + 1/at \qquad 2.2.8$$

(b) Stability against droplet flocculation:

Encounters between particles dispersed in liquid media is a result of Brownian motion. The principal cause of aggregation is the Van-der-Waals attractive forces between the particles, while stability against aggregation is a result of repulsive interaction between similary charged electric double layers and particle solvent affinity.

Derjaguin and Landau (1941) and Verwey and Overbeek (1948) (D.L.V.O) independently developed a quantitative theory in which the stability of lyophobic sols is treated in terms of energy changes which take place when the particles approach one another.

Dispersed particles are subject to two kinds of long range forces, [11)]

I: London - Van der Waals forces of attraction
II: Electrostatic repulsion between electric double layers of like sign.

(i) London - Van der Waals energy of two dispersed particles

Energy of attraction, V_A is given by Hamaker's eqn:

$$V_A = -\frac{Ar}{12H} \qquad 2.2.9$$

r: radius of sphere
A: Hamakers Constant
H: Shortest distance between spheres.

Hamakers treatment was modified to allow for

1. The influence of dielectric permeability of the medium on the propagation of the London force.
2. The influence of "retardation" of the London force between atoms that are at relatively great distarces comparable with or greater than the wavelength of London electrons ($\sim 10^{-5}$cm i.e 0.1μ) for transparent dielectrics.

3. The influence of sheath of emulsifying agent. The adsorbed layer will have a different Hamaker constant, A, from that of the interior of the droplet it protects. If the emulsifier is a relatively small molecule like soap, this fact may be neglected.

(ii) Electrostatic repulsion.

V_R, Repulsive energy results from the overlapping of the diffuse parts of the double layers around two identical spherical particles.

A simple expression of Gouy-Shapman theory is given by Reerink and Overbeck[12].

$$V_R = \frac{B\varepsilon k^2 T^2 r_\gamma^2}{z^2} \exp\,[-\kappa H] \qquad 2.2.10$$

k: Boltzmann constant
B: Constant, $= 3.93 \times 10^{39} A^{-2} s^{-2}$
z: Counter-ion charge number
ε: Permitivity of medium
κ: Debye parameter, determined by ionic strength of solution
T: Absolute temperature

Two other factors must be considered.

1. The possibility of distortion of droplets as they interact.
2. The existence of diffuse layers within the droplets themselves.
3. Exact form of potential distribution depends on what ions, surface active or otherwise are to be found in the system.

(iii) Total Interaction Curves

As V_A and V_R operate independently, the total interaction energy is obtained by summing the two terms.

See fig.1, where the addition of a Short-range Born repulsion energy is shown[13] (i.e repulsion due to overlapping of electron clouds predominates at very small particles when the particles come into contact.

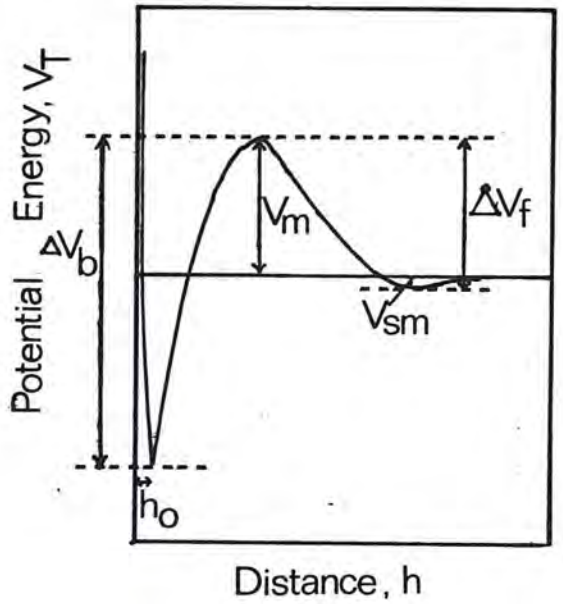


Fig.1: Schematic form of the curve of total potential energy V_T, against the distance separation, h for interaction between two particles. V_m = height of primary maximum, V_{sm} = depth of secondary minimum ΔV_f = energy barrier to a forward transition, ΔV_b = energy barrier to backward transition.[13]

At short distances, a deep potential energy minimum occurs at the distance of closest approch, h_o. At intermediate distances, the electrostatic repulsion makes the largest contribution, hence a maximum occurs in the potential energy curve, V_m. At larger distances, the exponential decay of the electric double layer term causes it to fall off more rapidly than the power law of attractive term, and a second minimum, V_{sm} appears.

When the primary maximum had a large positive value, say greater than 10 kT, the system was kinetically stable because of large activation energy opposing a transition into the primary minimum.

But as $V_T \rightarrow 0$, or became negative, the transition was helped and the system became unstable.

Hence theoretically, for instability,

$$V_T = 0, \text{ and } \partial V_T/\partial h = 0$$

Emulsions that coagulate under the conditions of secondary minimum are very loosely bonded and can be redispersed by agitation. Coagulation in the primary deep minimum results in particle to particle bonding that defies separation by normal mixing.

(c) Stability against droplet coalescence
It mainly depends on mechanical properties of the interfacial film.

STERIC STABILISATION: It is a generic term that encompasses all aspects of the stabilisation of colloidal particles by nonionic macromolecules.[14]

When a macromolecular material is adsorbed on to the particle surface, the polymeric chains extend into the dispersion medium, interaction between these chains as the particles approach one another is accompanied by decrease in entropy. Since the enthalpy change is negligble, this interaction involves a positive free energy change (i.e $\Delta G = \Delta H - T\Delta S$), and so opposes particle aggregation.

One characteristic feature of sterically stabilized latexes is they flocculate rapidly over a narrow temperature range[15], which is usually quite reversible.

Flocculation occurs when ΔG_R, Gibbs free energy of close approach of the particles, is negative.

$$\Delta G_R = \Delta H_R - T\Delta S_R \qquad 2.2.11$$

Temperature dependence of ΔG_R is

$$\frac{\partial(\Delta G_R)}{\partial T} = - \Delta S_R \qquad 2.2.12$$

hence e.g. dispersions that flocculate on cooling, must have ΔS_R as positive, i.e ΔG_R change from minus to plus on heating. Table 1 summarises the flocculation behaviour of sterically stabilised systems. Latexes that flocculate on heating are enthalpically stabilised, and those flocculating on cooling are entropically stabilised. A combined enthalpic - entropic type cannot flocculate at any temperature as ΔH_R and $- T\Delta S$ are both positive.

ΔH_R	ΔS_R	ΔG_R	$\lvert\Delta H_R\rvert / T\lvert\Delta S_R\rvert$	Flocculate	Type
-	-	+	< 1	cool	entropic
+	+	+	> 1	heat	enthalpic
+	-	+	$\gtrless 1$	inaccessible	combined

Table 1: Ways of obtaining positive ΔG_R

(d) Instability via molecular diffusion route.
It has recently been pointed out by Higuchi and Misra[16] that even when coalescence effect is absent the concentration of large droplets may increase, hence total droplet concentration decrease, by means of molecular diffusion through the continous phase when there is modest solubility of disperse phase in continuous phase. The droplets diffuse from small to large droplets due to difference in interfacial potential caused by the difference in droplet size.

Higuchi and Misra considers a simple case where an emulsion contains two sizes only with radii r_A and r_B, and their number concentrations are n_A and n_B respectively. At t = 0 $r_A = r_{AO}$, $r_B = r_{BO}$

$$r_{AO} \leq r_{BO}$$

The rate of dissolution G of a sphere of radius r, may be expressed[17] by the following equation when the process is diffusion controlled in the external phase

$$G = 4\pi r D(C_s - C_o) \qquad 2.2.13$$

where C_s is the miscibility of the dissolving or growing phase, C_o is the concentration of the material at some distance from the sphere, large compared to r.
G is the rate and D is the diffusion coefficient of the internal phase material to external phase.

The chemical potential of the pure oil droplet μ_r, of radius 'r' is related to the chemical potential of the same oil at a plane surface, μ_r^P by [18]

$$\mu_r - \mu_r^P = \frac{2V_m\gamma}{r} = \frac{2M\gamma}{\rho_o r} \qquad 2.2.14$$

where, V_m, M, ρ_o are molar volume, molecular weight and density of oil respectively. γ is the surface free energy, or interfacial tension.

$$\text{Since, } \Delta\mu = RT\ln a/a^o, \quad a \text{ is the activity} \qquad 2.2.15$$

$$\Delta\mu = \mu_r - \mu_r^P = RT\ln C_r/C_\infty$$

C_r is solubility of oil in droplets of radius 'r' in water, C_∞ is the solubility of infinitely large droplet.
Hence from eqn 2.2.14 and 2.2.15

$$RT\ln C_r/C_\infty = \frac{2\gamma M}{r\rho} \qquad 2.2.16.$$

Hence, solubility in water of oil in drop of radius r is

$$C_r = C_\infty \exp \frac{2\gamma M}{RTr\rho} \quad , \text{ where } K = \frac{2\gamma M}{RT\rho}$$

$$C_r = C_\infty \exp \frac{K}{r} \qquad 2.2.17$$

Hence, the miscibility of internal phase material with external phase is expressed by eqn 2.2.17, in the Henrys law region. The solubilities increase as the radius decrease, hence the small droplets are thermodynamically unstable with respect to the large ones, hence the latter will grow at the expense of the former. Higuchi and Misra[16] arrived at the expression for rate of change of radii of two sizes in emulsion.

From eqn 2.2.13 and 2.2.17

$$G = 4\pi Dr(C_\infty \exp \frac{K}{r} - C_o) \qquad 2.2.18$$

for radius r_A and r_B,

$$G_A = 4\pi Dr_A(C_\infty \exp \frac{K}{r_A} - C_o) \qquad 2.2.19$$

$$G_B = 4\pi Dr_B(C_\infty \exp \frac{K}{r_B} - C_o) \qquad 2.2.20$$

from mass balance equations, the total oil lost into by the oil phase equals amount gained by aqueous phase.

$$n_A G_A + n_B G_B + \frac{d\bar{c}}{dt} = 0 \qquad 2.2.21$$

where $\bar{c}$ is the average amount of dissolved internal phase material in the external phase per unit volume of emulsion. Combining eqn 2.2.19, 2.2.20 and 2.2.21, and neglecting $\frac{d\bar{c}}{dt}$, one can find C_o, and neglect the higher exponential terms.

$$C_o = C_\infty \left[1 - \frac{K(n_A+n_B)}{n_A r_A + n_B r_B}\right] \qquad 2.2.22$$

Substituting eqn 2.2.22 in eqns 2.2.19 and 2.2.20,

$$G_A = - \frac{4\pi D C_\infty K n_B (r_B - r_A)}{n_A r_A + n_B r_B} \qquad 2.2.23$$

$$G_B = \frac{4\pi D C_\infty K n_A (r_B - r_A)}{n_A r_A + n_B r_B} \qquad 2.2.24$$

The rate of dissolution of particle must equal to its rate of change of mass,

$$G_A = 4\pi\rho r_A^2 \frac{dr_A}{dt} \qquad 2.2.25$$

$$G_B = 4\pi\rho r_B^2 \frac{dr_B}{dt} \qquad 2.2.26$$

Combining 2.2.25 and 2.2.26 with eqns 2.2.23 and 2.2.24.

$$\frac{dr_A}{dt} = - \frac{DC_\infty K}{\rho r_A^2} \left[\frac{n_B (r_B - r_A)}{n_A r_A + n_B r_B}\right] \qquad 2.2.27$$

$$\frac{dr_B}{dt} = \frac{DC_\infty K}{\rho r_B^2} \left[\frac{n_B (r_B - r_A)}{n_A r_A + n_B r_B}\right] \qquad 2.2.28$$

Ways of retarding diffusion would be,

1. to narrow the distribution i.e $r_B - r_A$ made small.
2. Increase viscosity of external phase, since D is decreased.

$$D \simeq \frac{kT}{G\pi\eta\alpha} \qquad 2.2.29$$

η, viscosity of external phase, α is molecular radius of diffusing material and k is Boltzmanns' constant.

3. Reducing γ by a suitable surfactant, but one must avoid solubilisation of the oil in water when using surfactants, otherwise increase in C_∞ may cancel the decrease in γ.

From eqns 2.2.27 and 2.2.28, the stability of droplet is proportional to $(r)^{-3}$, hence decreasing radius r_A ten times, the change will be a thousand times faster. Higuchi and Misra [16] have also calculated that, even if the solubility of the oil is as low as 3×10^{-8} g/ml, the diffusion is rather significant. These general quantitative conclusions have been shown to be applicable to more complex systems, such as where the distribution of radii follows the distribution law.

Higuchi and Misra also came to the conclusion that incorporation of a very small amount of a third component, soluble in the disperse phase, but quite insoluble in the continous phase will inhibit the diffusion process. In this case, the rate of degradation by diffusion is determined by the added insoluble compound.

2.3 THERMODYNAMICS OF POLYMER SOLUTIONS:

Solubility relations in polymer systems are more complex than those among low molecular weight compounds because of the size of the polymers, the viscosity of their solutions, and the possible presence of a crystalline phase. A homogeneous solution obtained when the Gibbs free energy of solution, G_{12} is lower than the Gibbs function of the components of the mixture G_1 and G_2.[19] i.e Gibbs free energy of mixing $\Delta G^m \leq 0$.

$$\Delta G^m = G_{12} - (G_1 + G_2) \qquad 2.3.1$$

(a) Thermodynamics of ideal mixtures:

The chemical potential μ of ideal mixture of A and B molecules of almost the same size and shape and similar force fields is

given by,[20]

$$\mu_A = \mu_A^{\circ} + RT\ln X_A \qquad 2.3.2$$

where μ_A and μ_A° are chemical potential of A in mixture and in pure A respectively, X_A is the mole fraction of A

From defination of μ,

$$\Delta\mu_A = \left(\frac{\partial \Delta G}{\partial n_A}\right)_{T,\bar{P},n_B} = \overline{\Delta G}_A \qquad 2.3.3$$

from eqns 2.3.2 and 2.3.3

$$\overline{\Delta G}_A = RT\ln X_A \qquad 2.3.4$$

$$\left(\frac{\partial \overline{\Delta G}_A}{\partial T}\right)_P = \frac{\partial^2 \Delta G}{\partial T \partial n_A} = \frac{\partial^2 \Delta G}{\partial n_A \partial T} = \frac{\partial}{\partial n_A}(-\Delta S) = \overline{\Delta S}_A$$

$$\overline{\Delta S}_A = \left(\frac{\partial \overline{\Delta G}_A}{\partial T}\right)_P = R\ln X_A \qquad 2.3.5$$

Total free energy of mixing, ΔG_{mix};

$$\Delta G_{mix} = \Delta\overline{G}_A n_A + \Delta\overline{G}_B n_B$$

$$= (RT\ln X_A) n_A + (RT\ln X_B) n_B$$

Multiplying and dividing by $n_A + n_B$ where n_A and n_B are number of moles of A and B molecules respectively

$$\Delta G_{mix} = RT(n_A+n_B)\ [X_A\ln X_A + X_B\ln X_B] \qquad 2.3.6$$

$$\Delta S_{mix} = S_{mix} - S \text{ beginning} = \Delta\overline{S}_A n_A + \Delta\overline{S}_B n_B$$

S beginning = 0,

substituting on eqn 2.3.5

$$\Delta S_{mix} = - R(n_A+n_B) \; [X_A \ln X_A + X_B \ln X_B] \qquad 2.3.7$$

for ideal mixing heat of mixing $\Delta H_{mix} = 0$

(b) Entropy and heat of mixing in polymer solutions.
Polymer solutions show large deviations from Raoults law eqn 2.3.7, except at extreme dilute solutions where ideal behaviour is approached as an asymptotic limit. Deviations from ideality of ΔH_{mix} are caused by the need to break solvent (1-1) contacts and polymer (2-2) contacts to form new polymer solution (1-2) contacts. Entropy of mixing due to rearrangement of different molecules is called the geometrical or combinatorial entropy of mixing. There is also a nongeometrical or noncombinatorial contribution to the entropy of mixing due to energy interaction between the components in the solution, resulting in contraction of the solvent and formation of oriented solvate layers. This involves a decrease in entropy of the solvent. $\Delta S^m_{comb} > 0$ favours dissolution while $\Delta S^n_{noncomb} < 0$ does not favour dissolution. The large deviations in ΔS_{mix} for polymer solution compared to ideal solution are also due to great differences in size between polymer and solvent molecules.

Flory[21] and Huggins[22] derived an expression for ΔG_{mix} for athermal mixing i.e $\Delta H = 0$. Both chose a simple lattice representation for the polymer solution and calculated the entropy change on a statistical basis by estimating the total number of ways the polymer and solvent moleculer could be arranged on the lattice. This was made on the assumption that the size of a polymer segment was comparable to that of a solvent molecule. They showed that, in the first approximation, the entropy of mixing was given by replacement of mole fraction by volume fraction Φ_1 and Φ_2 in Raoults law expression eqn. 2.3.7.

$$\Delta S_{mix} = -R(n_1 \ln \Phi_1 + n_2 \ln \Phi_2) \qquad 2.3.8$$

where

$$\Phi_1 = \frac{n_1}{n_1 + jn_2}, \quad \Phi_2 = \frac{jn_2}{n_1 + jn_2}$$

where j is the molar volume fraction, i.e the number of segments of polymer molecule. $V_2 = V_1 j$.

The excess free energy of mixing ΔH^E_{mix} of polymer solutions arising from heat of mixing effects was expressed by Scatchard[23] as

$$\Delta H^E_{mix} = a_{12} V \Phi_1 \Phi_2 \qquad 2.3.9$$

V is molal volume of solution, $X_1 V_1^o + X_2 V_2^o$ where V_1^o and V_2^o are molal volume of 1 and 2 respectively.
a_{12} is the parameter expressing deviation from ideal solution behaviour such,

$$a_{12} = [(\frac{\Delta E_1}{V_1})^{\frac{1}{2}} - (\frac{\Delta E_2}{V_2})^{\frac{1}{2}}]^2 \qquad 2.3.10$$

ΔE's are molal energy of vaporization and V's are molal volume of pure liquid components. When considering 1 mole of solution, with n_1 moles of solvent, eqn 2.3.9 takes the form

$$\Delta H^E_{mix} = w_1 n_1 \Phi_2 \qquad 2.3.11$$

where $w_1 = a_{12} V_1^o = \chi_{12}$, interaction parameter
$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$, substituting 2.3.8 and 2.3.9

$$\Delta G_{mix} = RT[n_1 \ln \Phi_1 + n_2 \ln \Phi_2 + \chi_{12} n_1 \Phi_2] \qquad 2.3.12$$

The change in chemical potential $\Delta\mu$, from 2.3.3
Differentiating 2.3.12 in steps

The partial free energy of compound 1 is accordingly

$$\Delta\mu_1 = (\overline{\Delta G}_1) = \left(\frac{\partial \Delta G_{mix}}{\partial n_1}\right)_{P,T,n_i} = RT(\ln\Phi_1 + (1-\frac{1}{J})\Phi_2 + \Phi_2^2\ \chi_{12} \qquad 2.3.13$$

χ_{12} is characteristic of intermolecular forces between the molecules in solution, and depends both on entropy and enthalpy effects. From eqn. 2.3.13 and eqn 2.2.15,

$$\ln a_1 = \ln\Phi_1 + (1-\frac{1}{J})\Phi_2 + \chi_{12}\Phi_2^2 \qquad 2.3.14$$

If all solution non idealities are put in χ_{12}, eqn 2.3.14 may be written as [24]

$$\ln a_1 = (\ln a_1)_{combinatorial} + (\ln a_1)_{non\text{-}combinatorial}$$

$$= \ln\Phi_1 + (1-\frac{1}{J})\Phi_2 + \chi_{12}\Phi_2^2$$

$$\chi = (\ln a_1)\ non\text{-}comb/\Phi_2^2$$

$$\chi = f(\Phi_2, T) \qquad 2.3.15$$

Hence, the activity of component is expressed as a sum of combinatorial entropy and non-combinatorial free energy of mixing, which is characteristic of 1-2 interactions.

2.4 SWELLING AND SWELLING CAPACITY

(a) Swelling of polymer-oligomer particles.

Combining equation 2.3.13 for swelling polymer in bulk with eqn 2.2.14 gives us the equilbrium condition for swelling of the particles. This is the Morton equation.[25]

$$\ln\Phi_1+(1-\frac{1}{J_2})\Phi_2+\chi_{12}\Phi_2^2+\frac{2V_{IM}\gamma}{rRT}=0 \qquad 2.4.1$$

The equation shows that the swelling caused by the change in the energy by mixing is balanced by the increased interfacial energy.

Where r is the particle radius at equilbrium and V_{IM} molar volume of solvent, γ is the interfacial tension at swelling equilbrium. Hence, the swelling equilbrium of a latex particle is a function of its size, as long as the interfacial tension is constant. It was concluded by Gardon[26] that "even if the monomer is a good solvent for the polymer and is miscible with the polymer at any ratio in bulk, only a limited amount of monomer is adsorbed by the latex particles because the surface energy increase on swelling partially compensates for the free energy of mixing." He calculated the swelling capacity of polymers expressed as the volume of monomer absorbed per volume of polymer particles to be in the order of 0·5-5, using reasonable values of r, χ and γ.

As was discussed earlier, section 2.2(d). Higuchi and Misra have discussed that the addition of small amounts of insoluble compound in the disperse phase, will inhibit the diffusion process. This founded the basis for the preparation of emulsions by diffusion as was recently developed by Ugelstad et al[27,28,29]. They considered an aqueous emulsion of water insoluble compound 2, where water, emulsifier and slightly water soluble compound 1, which exist as large droplets, was added under ordinary stirring. The molar free energy of compound 1, $\bar{\Delta}G_1$ in droplets was expressed by [27],

$$\overline{\Delta G_1} = RT(\ln\Phi_1 + (1-\frac{1}{j_2})\Phi_2 + \Phi_2^2\chi + \frac{2V_{1M}\gamma}{rRT}) \qquad 2.4.2$$

j_2 for polymers is $\simeq \infty$

j_2 is the ratio of molar volumes of species 2 and 1 i.e

if j_1' = segments in 1, j_2' = segments in 2

$V_{1M} = V_s j_1'$, V_s is volume of segment, and

$V_{2M} = V_s j_2'$, $j_2 = j_{2/j_1}' = \frac{V_{2M}}{V_{1M}}$.

Φ_1 Φ_2 are volume fractions of compounds 1 and 2 respectively at equilbrium.

$$\Phi_1 = \frac{V_1}{V_1+V_2} \text{ and } \Phi_2 = \frac{V_2}{V_1+V_2}$$

V_1 is total volume of 1 at equilbrium and V_2 is the volume of 2 used in preparation of emulsion.

r is defined as,

$$r = r_o \left[\frac{V_1+V_2}{V_2}\right]^{1/3} \qquad r_o\text{: radius of droplets of 2}$$

Ugelstad et al, pointed out that from eqn 2.4.2 the swelling capacity V_1/V_2, which can be calculated by setting the equation equal to zero, would be very highly influenced by the value of j_2. In figure 2 are given the swelling ratios V_1/V_2 as a function of γ/r_o at different values of j_2

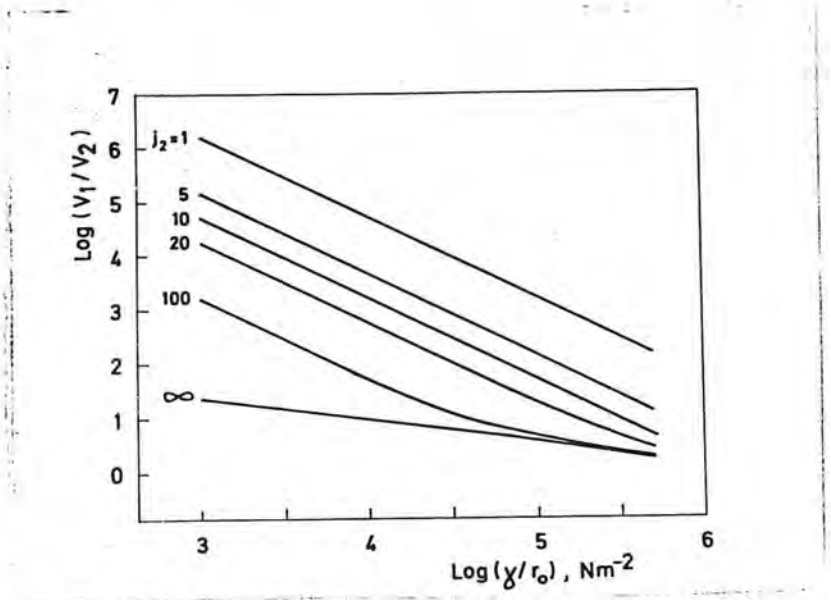


Fig.2: Swelling capacity as a function of γ/r_o for various values of $j_2 = V_{2M}/V_{IM}$ as calculated from eqn 2.4.2. r_o is the initial radius of the droplets of compound 2, γ is the interfacial tension, $\chi = 0.5$, $V_{IM}=10^{-4}m^3$, T=323K[30]

As shown in the figure the swelling capacity increases drastically as the value of j_2 is decreasing. The increase in swelling with decreasing value of j_2 is more pronounced the lower the value of γ/r_o. In the present work I have been studying the swelling capacity of particles which consist of a mixture of polymer molecules and water insoluble oligomers. Applying Flory's expression for three component systems, the equilbrium swelling of the polymer-oligomer particles with compound 1 may be derived to be [27]

$$\ln\Phi_1+(1-\frac{1}{j_2})\Phi_2+(1-\frac{1}{j_3})\Phi_3+\Phi_2^2\chi_{12}+\Phi_3^3\chi_{13}+\Phi_2\Phi_3(\chi_{12}+\chi_{13}-\frac{\chi_{23}}{j_2})+$$

$$\frac{2V_{1M}\gamma}{rRT} = \frac{\overline{\Delta G}_1}{RT} = 0 \qquad 2.4.4$$

where, the volume of a molecule of monomer (compound 1) is equal to that of one segment of compounds 2 and 3 i.e $j_1 = 1$. 1 represents slightly water soluble compound, 2 represents low molecular weight, water insoluble compound and 3 is polymer so that $J_3 = V_{3M}/V_{1M} \simeq \infty$. χ_{12} and χ_{13} are interaction parameters per molecule of 1 with 2 and 3 respectively. χ_{23} is the interaction parameter per molecule of 2 with 3, hence χ_{23}/j_2 is the interaction intensity per segment and is compared to χ_{12} and χ_{13}. It was calculated that eqn 2.4.4 predicted a drastic increase in the swelling capacity of particles containing a substantial amount of compound 2 as compared to pure polymer.[27-29] Figures 3 and 4 shows the swelling capacity V_1/V_2+V_3 as a function of γ/r_o[27-30], according to eqn 2.4.4 for various values of j_2 for figure 3, and various values of V_2 for figure 4.

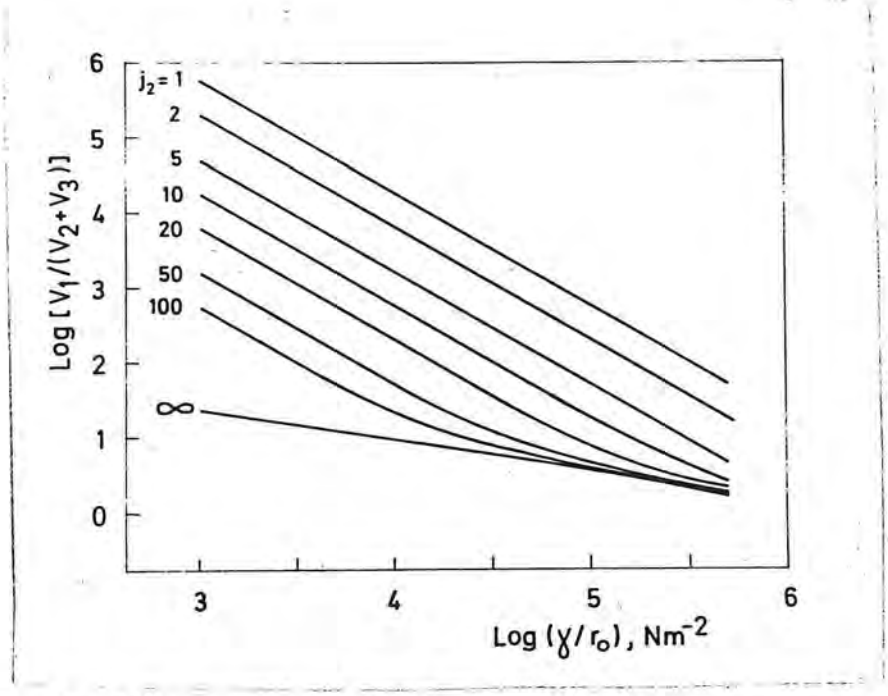


Fig.3: Swelling capacity of polymer-oligomer particles as a function of γ/r_o for various values of j_2 as shown in figure. r_o = radius of polymer-oligomer particles before swelling with compound 1. $V_2 = V_3 = 0.5$, $\chi_{12} = \chi_{13} = 0.5$, $\chi_{23} = 0$, $V_{1M} = 10^{-4} m^3$, T = 323K.

The value for $j_2 = \infty$ is for pure polymer. The swelling capacity increases with decreasing j_2, and is more pronounced the lower the values of γ/r_o.

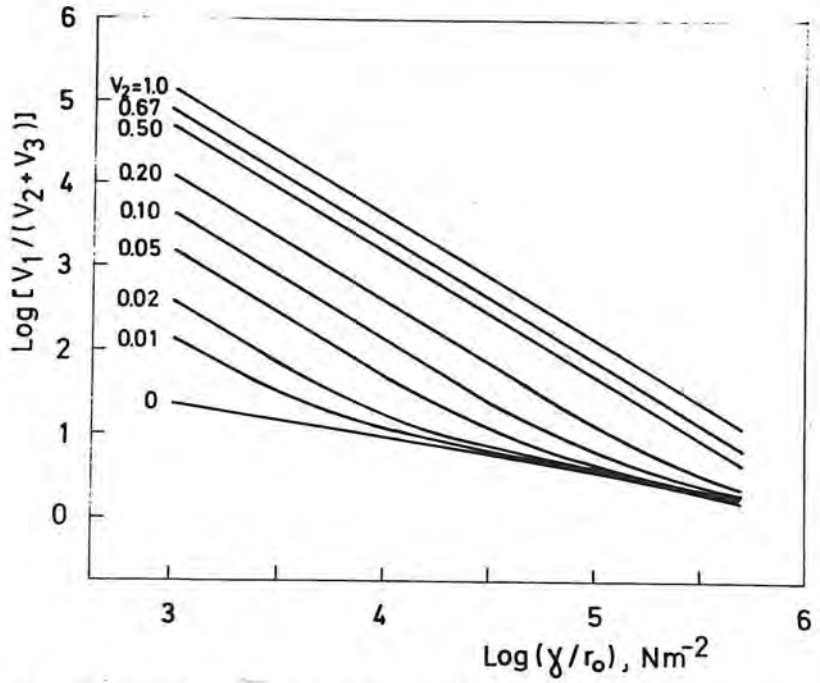


Fig.4: Swelling capacity of polymer-oligomer particles as a function of γ/r_o for various values of V_2. r_o is the radius of polymer-oligomer particles before swelling with compound 1 $V_2+V_3=1$, $j_2=5$, $\chi_{12}=\chi_{13}=0.5$, $\chi_{23}=0$. $V_{1M}=10^{-4}$ m , T = 323K.

Hence the swelling capacity increases even when using low amounts of compound 2, when operating at low valves of γ/r_o, where the swelling is more pronounced.

In figure 5 is given the values of $\overline{\Delta G}_1/RT$ as a function of swelling capacity V_1/V_2+V_3 where $V_2+V_3 = 1$, $V_2 = 0.67$, with $j_2 = 4$ at different values of γ/r_o.

It is seen from the figure that the $\overline{\Delta G}_1/RT$ values are close to zero even at values of V_1 which are far from equilbrium values. The effect is more pronounced the lower the value of γ/r_o.

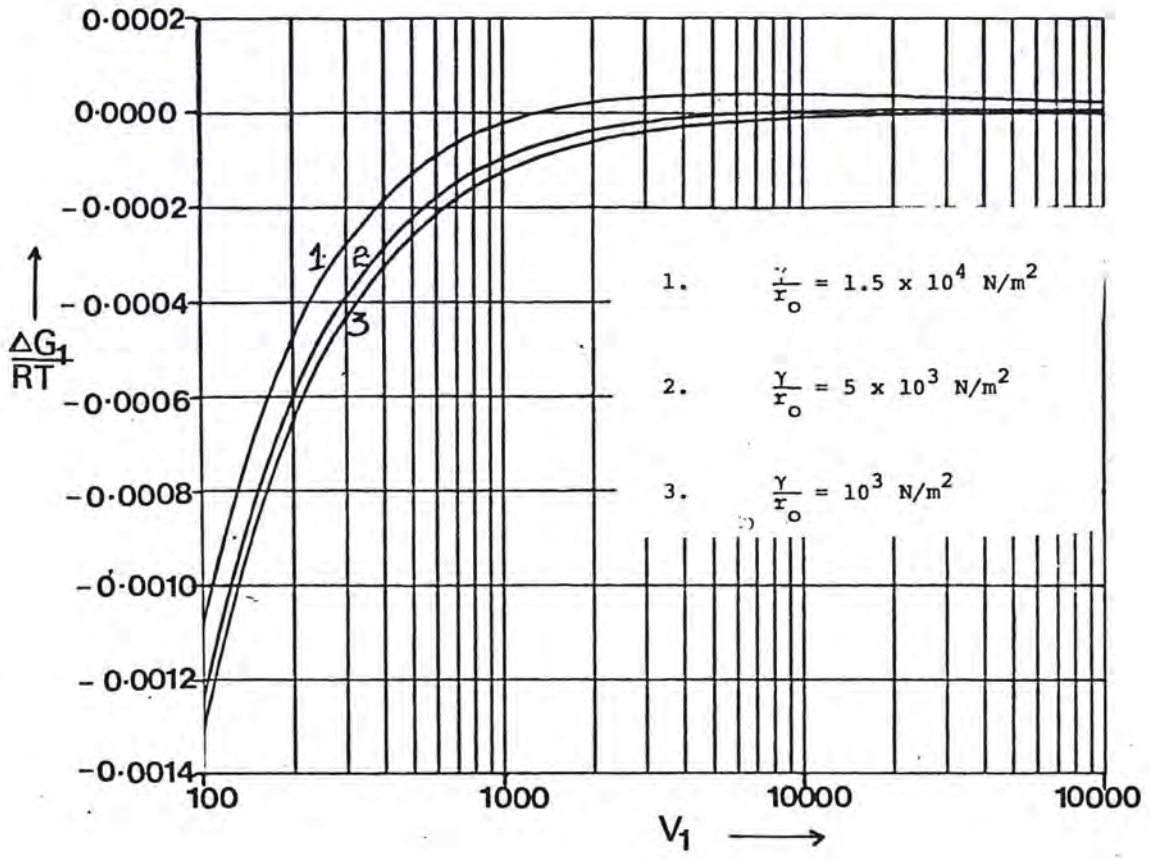


Figure 5: Partial molar free energy of compound 1 versus swelling capacity, V_1/V_2+V_3 for vaious values of γ/r_o, as calculated from eqn 2.4.4. r_o is radius of polymer particles. $\chi_{12} = \chi_{13} = 0.5$, $\chi_{23} = 0$, $T = 323K$, $j_2 = 5$, $V_{IM} = 10^4 m^3$, $V_2=2/3$, $V_3=1/3$

(b) Rate of diffusion:

Consider a swollen seed, 'a' particles containing compounds 1, 2 and 3 (as defined above) and mixed with seed b containing compounds 2 and 3. The diffusion of compound 1 from a to b particles can be described by Ficks law of diffusion,[31] if the distance between the particle R is much greater than the radius of the particles.

$$J_{out} = 4\pi r_a N_a D_w (C_{ia} - C_w) \qquad 2.4.5$$

$$J_{in} = 4\pi r_b N_b D_w (C_w - C_{ib}) \qquad 2.4.6$$

C_{ia}, C_{ib} are concentration at surface of particles a & b respectively. N_a, N_b and r_a, r_b their number and radius of a and b respectively.

Since $J_{out} = J_{in}$, $\frac{dC_w}{dt} = 0$

C_w can be calculated from 2.4.5 and 2.4.6

Also

$$\Delta\bar{G}_{ib} = RT\ln \frac{C_{ib}}{C_w^{\infty}} \quad , \quad \Delta\bar{G}_{ia} = RT\ln \frac{C_{ia}}{C_w^{\infty}} \qquad 2.4.7$$

C_w^{∞}: equilbrium constant of slightly soluble compound 1, in water, i.e it is a concentration of continous phase where radius $r = \infty$

from eqn 2.4.7

$$C_{ib} = C_w^{\infty} \exp(\frac{\Delta\bar{G}_{ib}}{RT}) \qquad 2.4.8a$$

$$C_{ia} = C_w^{\infty} \exp(\frac{\Delta\bar{G}_{ia}}{RT}) \qquad 2.4.8b$$

Substituting the above equations into eqn 2.4.6

$$\frac{dV_b}{dt} = \frac{4\pi r_b N_b D_w C_w^{\infty} r_a N_a}{r_a N_a + r_b N_b} \left[\exp. \frac{\Delta\bar{G}_{ib}}{RT} - \exp. \frac{\Delta\bar{G}_{ia}}{RT}\right] \qquad 2.4.9$$

$\Delta\bar{G}$ is defined by eqn 2.4.4

One can calculate the rate of swelling of polymer particles with compound 2 from eqn 2.4.9 if the conditions are such that there is rapid distribution of 2 within the particles. When one considers the absorption of compound 1 in the second step with a large excess of compound 1, then eqn 2.4.9. reduces to

$$\frac{dV}{dt} = 4\pi N r C_w^{\infty}(1-\exp(^{\Delta\bar{G}_1}/_{RT})) \qquad 2.4.10$$

The negative values of $\overline{\Delta G}/RT$ decreases with increasing swelling, hence from eqn 2.4.10, the rate of swelling decreases at high degrees of swelling.

(c) Competitive swelling.

By using different amounts of compound 2 in two samples from the same monodisperse latex, then later mixing the two with emulsifier and compound 1, a bidisperse emulsion is formed.

When compound 1 is added, a competitive swelling of the two types of particles takes place and its distribution is thermodynamically determined. Consider a and b which are two samples of particles from the same monodisperse seed, but different amounts of compound 2.

The partial molar free energy of the two particles is written according to eqn 2.4.4

$$\Delta\overline{G}_{1a} = \ln\Phi_{1a} + (1-\frac{1}{j_2})\,\Phi_{2a} + (1-\frac{1}{j_3})\,\Phi_{3a} + \Phi_{2a}^2\,\chi_{12} + \Phi_{3a}^2\chi_{13} + \Phi_{2a}\Phi_{3a}(\chi_{12}+\chi_{13}+\chi_{23}/j_2) + \frac{2V_{1M}\gamma}{r_a RT} \qquad 2.4.11$$

$$\Delta\overline{G}_{1b} = \ln\Phi_{1b} + (1-\frac{1}{j_2})\Phi_{2b} + (1-\frac{1}{j_3})\Phi_{3b} + \Phi_{2b}^2\chi_{12} + \Phi_{3b}^2\chi_{13} + \Phi_{2b}\Phi_{3b}(\chi_{12}+\chi_{13}+\chi_{23}/j_2) + \frac{2V_{1M}\gamma}{r_b RT} \qquad 2.4.12$$

At equilbrium swelling, $\Delta\overline{G}_{1a} = \Delta\overline{G}_{1b}$

Hence,

$$\ln(\Phi_{1a}/\Phi_{1b}) + (1-\frac{1}{j_2})(\Phi_{2a}-\Phi_{2b}) + (1-\frac{1}{j_3})(\Phi_{3a}-\Phi_{3b}) + \chi_{12}(\Phi_{2a}^2-\Phi_{2b}^2) + \chi_{13}(\Phi_{3a}^2-\Phi_{3b}^2) + (\chi_{12}+\chi_{13}-\chi_{23}/j_2)(\Phi_{2a}\Phi_{3a}-\Phi_{2b}\Phi_{3b}) + \frac{2V_{1M}\gamma}{RT}(\frac{1}{r_a}-\frac{1}{r_b}) = 0 \qquad 2.4.13$$

The radius of the two types of particles can be calculated with respect to the total amount of compound 1 added. Figures 6 and 7 shows curves calculated[30], from eqn 2.4.13

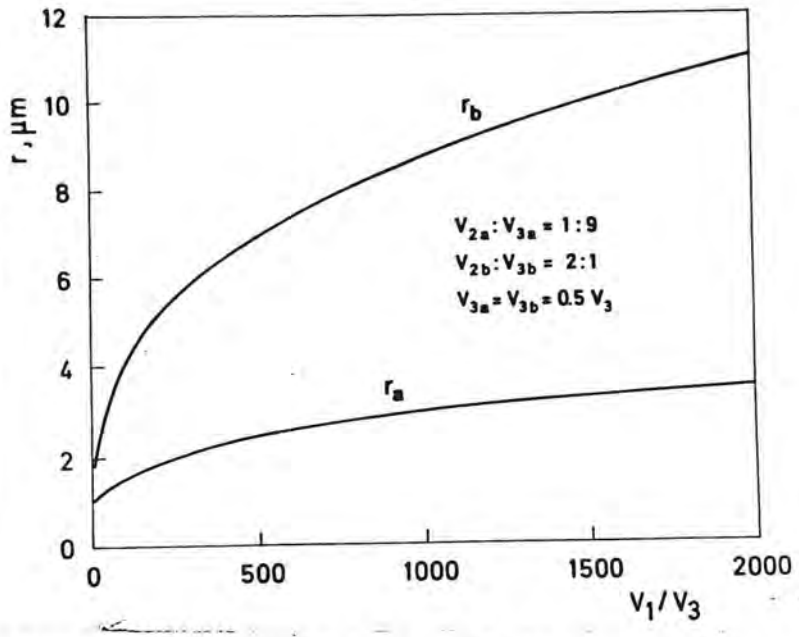


Fig.6 Competitive swelling. Radii of a and b particles as a function of total amount of 1 absorbed per unit volume of polymer. $V_{2a}:V_{3a}$ = 1:9, $V_{2b}:V_{3b}$ = 2:1, $V_{3a}=V_{3b}$= $0.5V_3$. r_3 = 0.7μm, γ=5mNm^{-1}, j_2=5, $\chi_{12}=\chi_{13}$=0.5, χ_{23}=0, T = 308K.

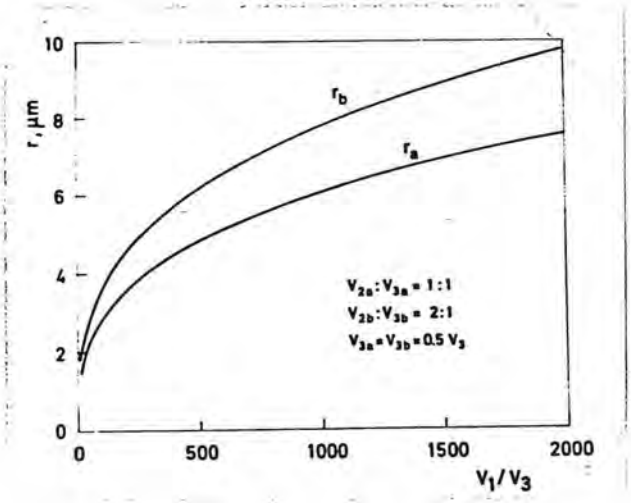


Fig.7. Radii of a and b particles as a function of total amount of 1 absorbed per unit volume of polymer. $V_{2a}:V_{3a}$=1:1, $V_{2b}:V_{3b}$= 2:1, $V_{3a}=V_{3b}$=0.5V_3, r_3 = 0.7μm, γ = 5mNm^{-1}, j_2 = 5, $\chi_{12}=\chi_{13}$ = 0.5, χ_{23} = 0, T = 308K.

3. LITERATURE SURVEY:

Emulsions in various forms, have been known for thousands of years. The Greek physician Galen (131-c 201) was apparently the first person to record the emulsifying power of beeswax.[32] It was seen from early days the use of ionic emulsifiers reduces the interfacial tension γ, which is a very important factor in determining the stability and particle size of emulsions. Apart from the reduction of γ, the real importance of emulsifier lies in the profoun changes, especially in the electric double layers near the interfaces.

(a) Macromolecular Stabiliseres:

The tough skins formed at the interface between oil and aqueous solutions of macromolecular substances such as gums and proteins, a qualitative collection of early results is done by Serrallach and Jones.[33,34] Recently, Graham and Phillips [35] discussed that proteins with highly ordered native structures adsorb slowly and give highly cohesive interfacial films. They calculated the forces required to rupture the interfacial protein films in an emulsion from centrifugation data, and estimated distances of closest approach from drainage studies of free thin films. They concluded that adsorption process has three stages:

1. Diffusion of the native protein molecules to the interface. The rate is a function of concentration of protein C_p and diffusion coefficient of protein molecules.

2. Penetration of the molecule into the interface and unfolding (the protein is denatured).

3. The adsorbed surface denatured proteins molecules rearrange to the lowest possible free energy state.

The overall kinetics of formation of adsorbed films are fast for flexible, disorded proteins and slow for rigid globular proteins. Globular proteins form adsorbed films which give

lower values of suface pressure, π than flexible proteins at a given surface concentration, hence there is greater cohesion in such films. They noted that proteins can form stable films with as low C_p as 1×10^{-1} g%.

They also suggested that one way to minimize electrostatic and steric interactions is to adjust the pH of the aqueous phase to the isoelectric point, ip of protein. At ip, net charge of a native protein is zero and the electric double layer repulsion is minimized. The steric stabilisation term is also minimized since the osmotic repulsion arising from a change in free energy of mixing of protein segments and water or interpenetration of the adsorbed layers is reduced. The reduction occurs because the solubility of proteins is lowest at the ip and there is a decrease in enthalpic stabilisation.

(b) Addition of insoluble compounds:

Some work has been done where addition of insoluble compound increases the perfomance of emulsifiers. Schulman and Cockbain[36] reasoned that what happens at the oil-water interface was same as what happens at the air-water interface. The stability, on addition of long chain fatty alcohols increased due to the formation of mixed complex monolayer. Emulsion stability was measured by measuring the time required for the first visible sign of separation of the two phases. Tallman[37] et al dissolved the long chain fatty alcohol in the oil phase, keeping the ionic emulsifier in aqueous phase and they concluded that for stable emulsions, the surfactant and fatty alcohols molecules must interact to form a ternary liquid crystalline phase. Barry et al [38-41] suggested that the formation of liquid crystals and gel networks when the amphiphile (cetyl alcohol) was heated with ionic surfactant helped in the stability and rheology of emulsion. Davies and Haydon[42] calculated the interfacial tension, between cetyl alcohol in toluene solution and a solution of sodium decyl sulphate as

emulsifier, and on extrapolation of the curves of γ against concentration of alcohol, they found that γ appears to be negative above certain concentration, which means spontaneous emulsification. Hallworth and Carless [43] reviewed the increased stability on additon of small amount of long chain fatty alcohol due to the formation of a complex interfacial film between the alcohol and surfactant and suggested that the film will resist coalescence primarily by virtue of its rheological properties.

So far the above authors have discussed the possibility of formation of stronger interfacial film formed when fatty alcohol is added to the emulsion. Higuchi and Misra[16] concluded that the addition of small amount of third component soluble in disperse phase but insoluble in continous phase will inhibit instability by diffusion. This was verified by studying carbontetrachloride in water emulsions stabilized by Aerosol OT. The emulsions were unstable but addition of 1% hexadecane or nujol in the internal phase increased stability. Davis and Smith[44] measured the stability of benzene and hexane emulsions with addition of hexadecane and hexadecanol at same molar concentration, and they found hexadecane more effective than hexadecanol. They concluded that hydrocarbon emulsions stabilised by sodium dodecyl sulphate depends on chemical nature of the oil. Davis and Smith prefer the explanation of Higuchi and Misra, that of degradation by diffusion depending on the water solubilities of additives.

Since the droplet sized used by Hallworth's emulsions are considerably longer than used by Davis, the two possible routes of degradation of emulsions, coalescence or molecular diffusion might depend on droplet size and size distribution.

In the above literature, the method used to prepare emulsions was by dissolving the oil soluble long chain alcohol in oil phase prior to mixing with water phase containing the ionic surfactant. High shear rates were required or large amounts of additive used.

Recently, Ugelstad et al,[45,46] discussed a different method of preparing emulsions where ionic surfactant solution and fatty alcohol were mixed at high temperature before addition of oil phase. In this method, small amounts of the additive were used with moderat stirring. They also developed a method for obtaining electron microscope pictures of monomer emulsion by staining emulsion droplets with osmium tetroxide, since the finely dispersed emulsion droplets produced are below resolution of optical microscope. In the work of Ugelstad et al[47], the effect of additives on stability of emulsions of slightly water soluble vinyl monomers was followed by measuring the amount of emulsifier on droplets as a function of time, in some cases followed by electron microscopy. The emulsion were prepared by homogenizing the oil mixture with water and emulsifier at 30°C, stability measured at 60°C with stirring of 600 r.p.m. A decrease in amount of emulsifier adsorbed means that the surface of the droplets decreased, hence concentration of the emulsifier is a measure of degradation of emulsion. They found that the stability of emulsion decreases with decreasing chain length of alkane or fatty alcohol added. They also found that hexadecane was more effective than octadecanol, hence arqued against Hallworth's suggestion of the formation of a more effective barrier since hexadecane and emulsifier is less likely to form a more effective barrier than octadecanol and emulsifier. Also further experiments[48] with branched additives were done, and they gave stable emulsions. These branched compounds would be less likely to form complexes with alkyl chains of the emulsifier. Hence, they concluded that stabilising effect of an additive was closely related to the water solubility of the additive, meaning degradation of emulsion is governed by diffusion of the additive from small to large droplets. This mechanism is likely to dominate with small droplets and relatively broad droplet size distribution. As the droplet size increased, degradation by coalescene becomes important. With fatty alcohol as additive, the existence of a condensed layer of emulsifier and fatty alcohol at the interface is more likely.

The stabilizing effect of small amounts of additives founded the basis of newly developed technique by Ugelstad for preparation of emulsions by diffusion.

Ugelstad et al[39], had done a few experiments of above. A small amount of compound 2 was homogenized with water and emulsifier to form droplet size 0.1 - 0.3μm. The emulsion was heated to 60°C and stirred, and compound 1 (chlorobenzene) was added, and samples were analysed at time intervals and amount of emulsifier adsorbed on droplets was measured. It was found that within 15 minutes, chlorobenzene has been absorbed into droplets of compound 2, which was measured by increased amount of emulsifier adsorbed on droplets and an increase in size of droplets as observed in microscope. As the stirring was continued, the emulsifier adsorbed on droplets starts to decrease due to degradation by diffusion, the rate being determined by the diffusion of compound 2 from small to large drolpets.

(c) Two-step swelling of polymer seed particles.

Preparation of monodisperse latexes and the swelling by the two-step method is still quite new and not much has been done in this field. Ugelstad et al[29] discussed the swelling of polymer/oligomor particles with chlorobenzene under ordinary stirring at 35°C.

In this method, the first step involves the absorption of compound 2, a water insoluble compound, by polymer particles. The transport of the insoluble compound through the aqueous phase, which is added in the form of an emulsion, is helped by adding a water miscible organic solvent e.g acetone. Before the second step, the organic solvent has to be removed by evaporation or dilution, so as to prevent compound 2 from going out of the particles. As an example, in the first step, 1.7μ latex particles are swollen with compound 2 e.g dioetyladipate in a v/v ratio of 1:1, then in a second step, was

swollen with chlorobenzene about 400 times the volume of original particles. The two-step method has been utilised in the preparation of stable emulsions of different monomers and monomer mixtures, and subsequent polymerization have led to development of methods of latex preparations where the initiation is in monomer droplets. Monodispers polymer particles in the size range 2 - 20μm have been prepared. In this method, the compound 2 which is water insoluble may include an oil soluble initiator and water, emulsifier and high rates of monomer is added, after swelling with monomer the temperature is raised and polymerization takes place.[30] Porous monodisperse particles may also be prepared by the incorporation of inert solvents together with monomer into swollable monodisperse polymer particles.[48]

4. EXPERIMENTAL WORK:

4.1 PREPARATION OF MONODISPERSE POLYSTYRENE LATEX OF ~ 0.5μm BY ORDINARY EMULSION POLYMERIZATION.

4.1.1 Materials:

Potassium persulphate, $K_2S_2O_8$ (Merck,Germany), Sodium chloride and Borax, $Na_2B_4O_7 \cdot 10H_2O$ (Merck, Germany) were used without further purification. Sodium lauryl sulphate, NaLS (Merck, Germany) was purified by extraction with diethyl ether and recrystallised from 100% ethyl alcohol, and dried under vacuum. Styrene monomer was distilled under reduced pressure in nitrogen atmosphere twice, the second time immediately before polymerisation.

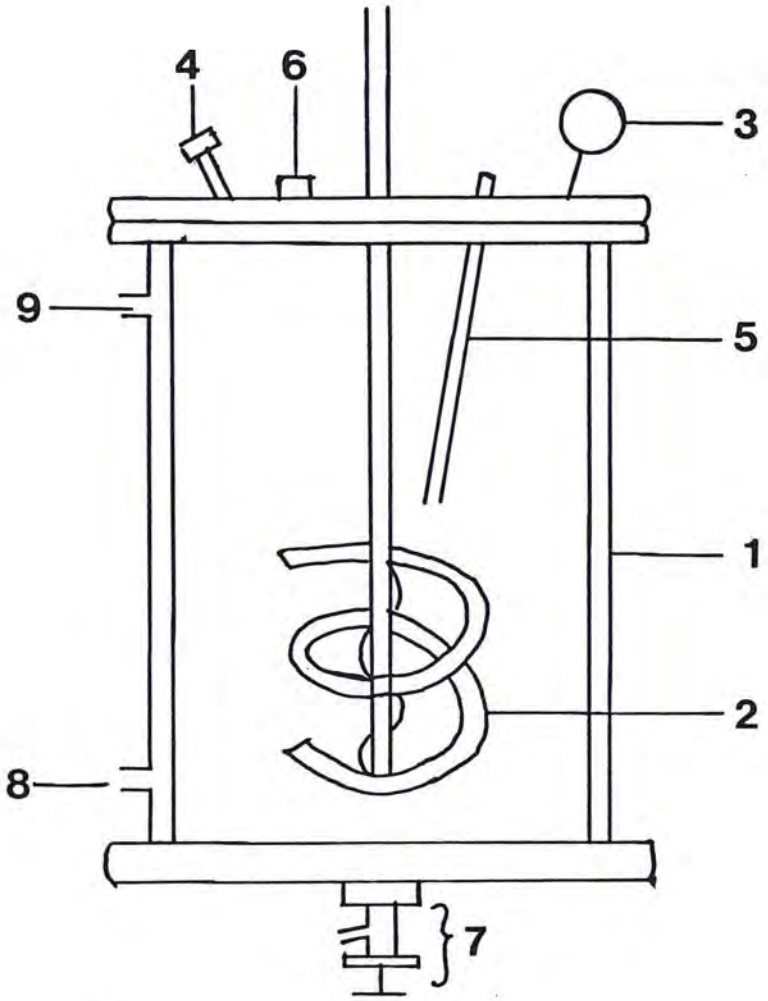
All the water used was doubly distilled, the second distillation was carried out in an all pyrex apparatus. All nitrogen used was Norsk Hydro, highly purified gas.

4.1.2 Apparatus:

The emulsion polymerisation was carried out in a 1.5 dm^3 glass autoclave fitted with a paddle stirrer, manometer, thermometer and valves for charging and sampling. The apparatus is shown in fig.4.1.1.

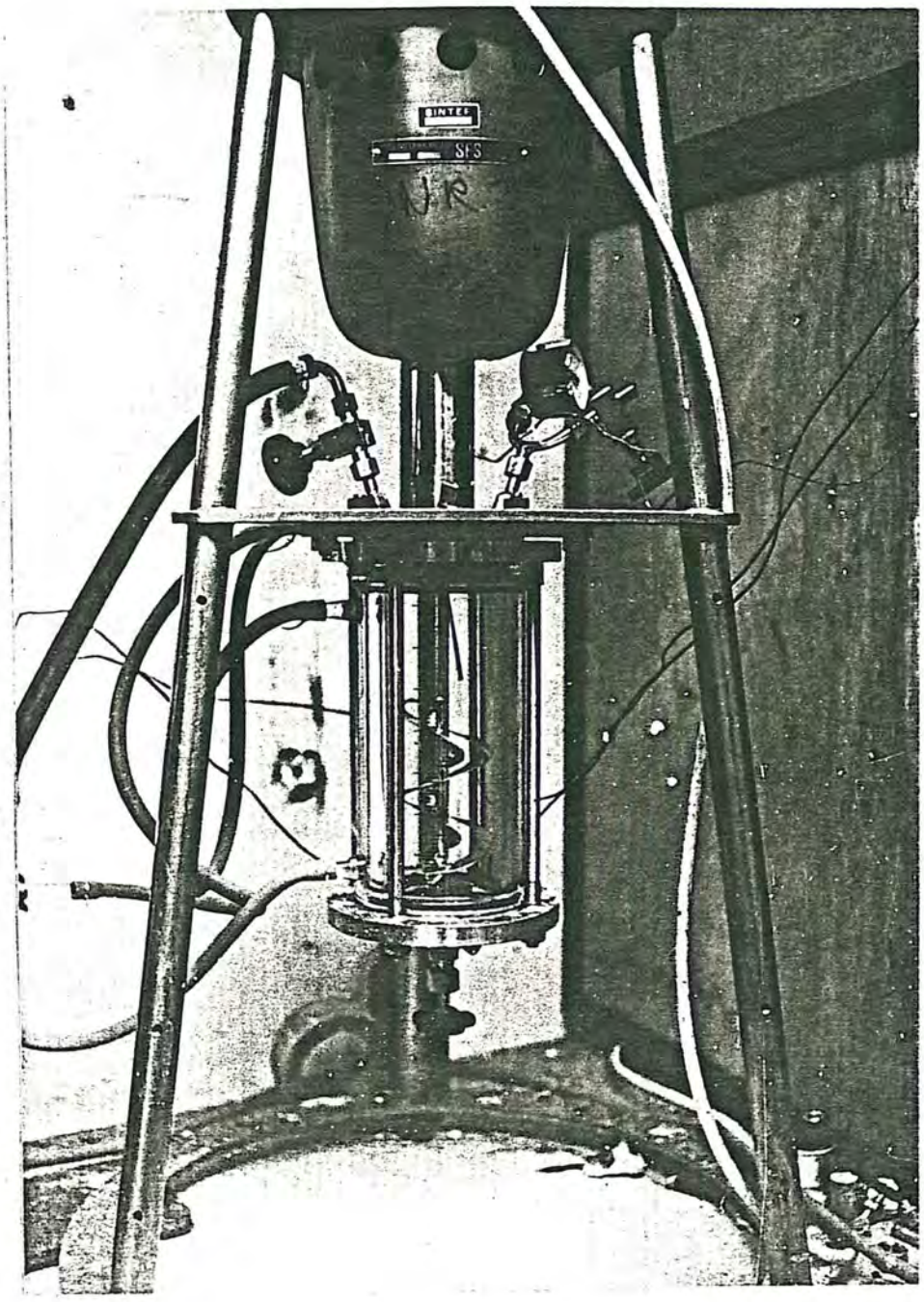
4.1.3 Procedure:

1.14 dm^3 water was added to the autoclave with 0.456g Borax, 1.0g NaCL and 0.1g NaLS. After evacuating (P = 20°C) and passing nitrogen eight times, the solution was heated to 80°C and 0.134 dm^3 double distilled styrene was added to the autoclave under nitrogen at a stirring rate of 350 r.p.m. After 15 minutes stirring, 0.72g $K_2S_2O_8$ plus 0.06 dm^3 water was added under nitrogen. The polymerization was carried out for about 20 hrs. The particle diameter was 0.5μm and latex contained 96.1g polystyrene (PS) per dm^3 water. Picture of the monodisperse particles was taken in an electron microscope (Siemens).



1. Autoclave
2. Stirrer
3. Manometer
4. To nitrogen
5. Thermocouple
6. Input
7. Valve for sampling
8. Water inlet
9. Water outlet

Fig 4.1.1. Diagram of glass autoclave.



A picture of glass autoclave.

4.2 PREPARATION OF MONODISPERSE POLYSTYRENE PARTICLES ~ 1.4μm, BY TWO STEP SWELLING METHOD. INITIATION IS IN THE MONOMER DROPLETS.

4.2.1 Materials:

Nitrogen, styrene and sodium lauryl sulphate as described in section 4.1.1.

Dioctanoylperoxide or perkadox SE-8 (Akzo product), nonylphenol+ 20 ethyleneoxide or Berol 292 (Berol product) and Acetone (Merck Germany) was used without further purification.

Seed latex particles 0.5μm which were prepared in section 4.1. The water used was distilled once.

4.2.2 Apparatus:

(a) Ultraturrax Polytron, type 45/6 Producer Mobil Aaran A.G.

(b) Laboratory homogenisor Model 15M-8TA. Producer Gaulia Corporation, type: double stage homogenisor. Pressure used lst stage 200-300 kg/cm^3, 2nd stage 80-100 kg/cm^3. See fig.4.2.1

(c) 0.5 dm^3 thermostated glass reactor fitted with paddle stirrer and sampling facilities. Prepared by glassblower, N.T.H. Apparatus shown i fig.4.2.2.

(d) Optical microscope, Carl Zeiss standard GFL 654-632 fitted with photomicrographic camera (Carl Zeiss) type CS with C-35 camera attached.

(e) Centrifuge from Beckmann, Model J2-21.

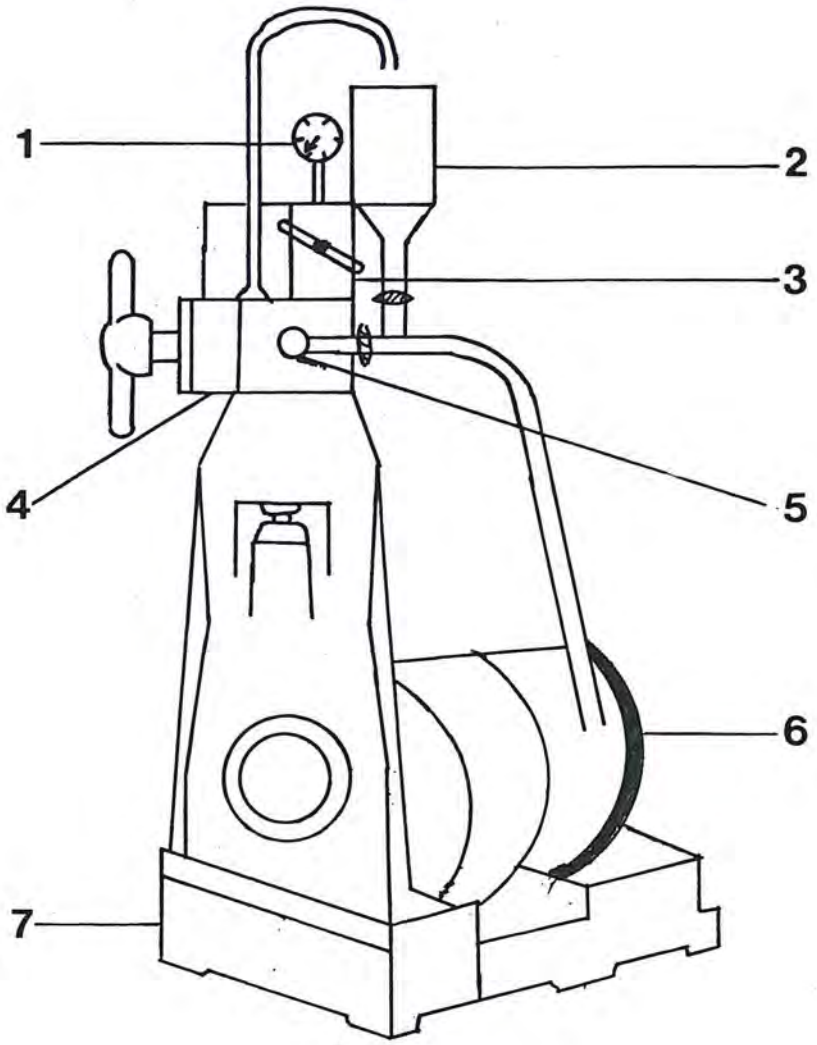
(f) Rotor-vapour , from Heidolph, Type RZR2 (West Germany).

(g) 1.5 dm^3 glass autoclave as described in section 4.1.2.

(h) Siemens electron microscape.

4.2.3 Procedure:

(a) Preparation of Emulsion of perkadox SE-8: Emulsion 'A'.
The emulsion was prepared by using the ultraturrax and homogenisor. 0.1 dm^3 perkadox SE-8 was mixed with 2.5 g NaLS in 1 dm^3



1.Pressure Gauge
2.Supply tank
3.Dampener assembly
4.Homogenising assembly
5.3-Way valve
6.Motor
7.Base

Fig. 4.2.1 Laboratory homogenisor.

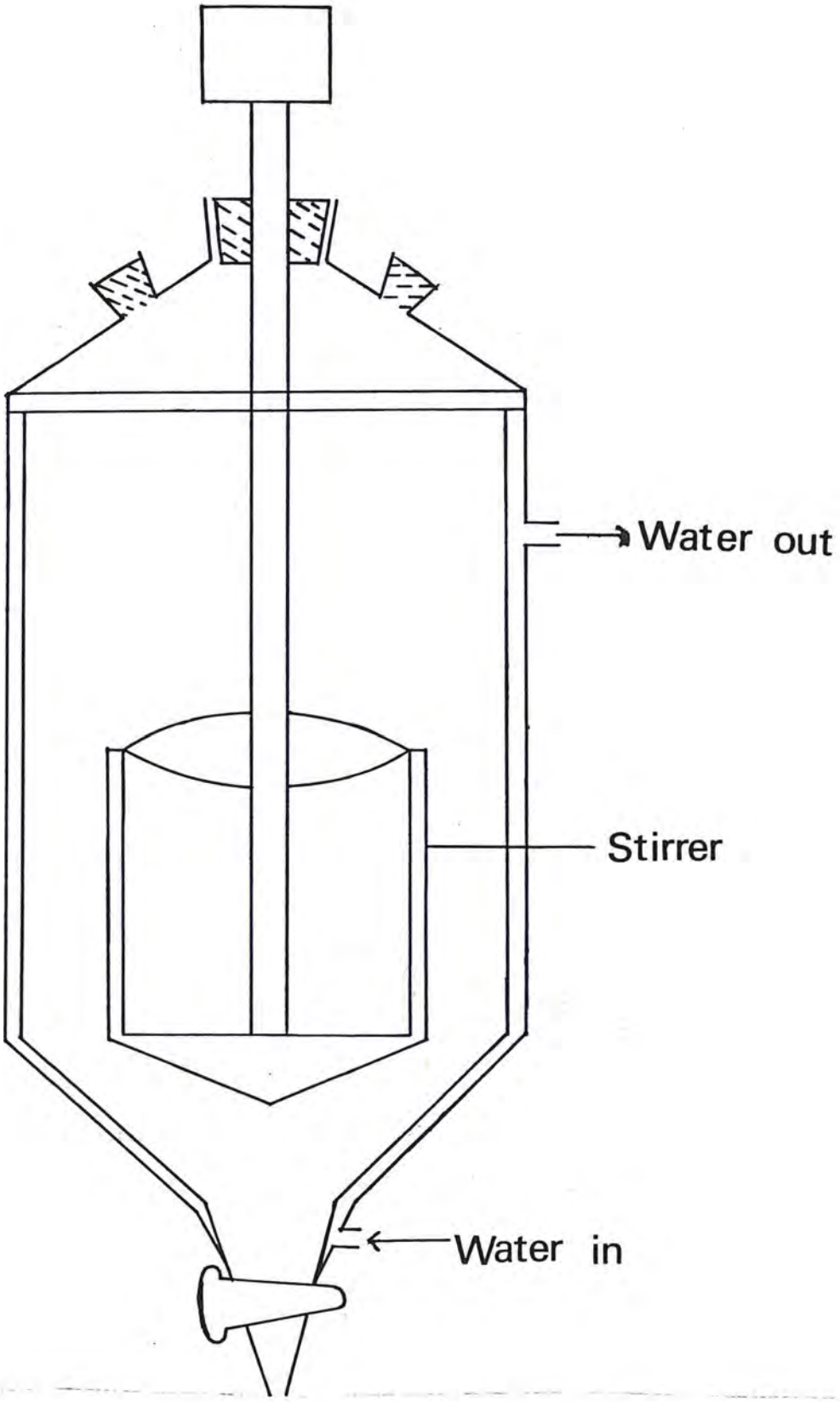


Fig. 4.2.2: Diagram of glass reactor.

A picture of glass reactor.

water and the mixing ultraturraxed for 1 minute at 70, ~ 6000 r.p.m. and then homogenized at a total pressure of 280 kg/cm^2 (~ 2.75 x 10^7 N/m^2). The diameter observed was between 0.5 - 1.0µm.

(b) Swelling seed particles (~ 0.5µm) with water insoluble compound prepared in part (a) above. - Emulsion B. The swelling was performed in a glass reactor at 25°C, a reflux condensor was fitted. 0.473 dm^3 of polystyrene latex of 0.5µm from section 4.1.3 which contained 0.433 dm^3 water, 0.04 dm^3 polystyrene and 0.035g NaLS, was added into the reactor under ordinary stirring. 0.44 dm^3 emulsion 'A' which contained 0.4 dm^3 water, 0.04 dm^3 water was added to make 1 dm^3 total water. Acetone was added in amount corresponding to 10% volume of water present i.e 0.1 dm^3 acetone was added. The stoppers were tightly closed to avoid evaporation of acetone.

After about 24 hours, a sample was taken to be centrifuged at 15 kHz for 15 min., and another sample to look into the optical microscope. Absorption of perkadox SE-8 into the polymer particles is finished if after centrifuging, the aqueous phase is clear, and there is no very small droplets in the background when looked into the microscope. The acetone was then evaporated by opening the stoppers or by using rotor-vapour.

(c) Swelling of polymer-oligoner particles (Emulsion B) and polymerization. The swelling and polymerization were carried in 1.5 dm^3 glass autoclave.

0.162 dm^3 emulsion B prepared above which contains 0.15 dm^3 water, 0.006 dm^3 polystyrene, 0.006 dm^3 perkadox SE-8 and 0.16g NaLS is added into glass autoclave with 1.54g NaLS plus 0.85 dm^3 water. After evacuating and passing nitrogen eight times, 0.209 dm^3 styrene (swelling of ~ 35 times) was added with a stirring of 200 r.p.m. at 25°C. (To prepare different diameters, the amount of styrene added is varied.) The styrene was absorbed for 12-15 hours and a sample was taken and looked in microscope, the absence of small particles ~ 0.5µm indicates all styrene being absorbed. Another sample was centri-

fuged at 15 kHz for 10 - 15 minutes, and if the aquaous phase is clear, and no layer of styrene on top indicates all the styrene is absorbed. The temperature was then increased to 70°C for 6½ hour at 250 r.p.m and to 80°C for 1½ hr. at 150 r.p.m., during which polymerisation is carried out. After 3 hours polymerization time, 1.0g Berol 292 is added to stabilise the big particles. After 8-9 hrs., a sample is taken to look into microscope and to find the dried stuff. Electron micrographs were taken from the electon microscope and final diameter was 1.4μm, with 187 gPS/ dm^3 H_2O.

4.3 SWELLING OF THE POLYSTYRENE PARTICLES PREPARED BY THE TWO-STEP METHOD (SECTION 4.2) WITH CHLOROBENZENE, BY SAME METHOD.

4.3.1 Materials:

Sodium lauryl sulphate, NaLS (Merck), purification as described in section 4.1.1.
Whey protein (Skaraborgs läns Meieriforbund, Sweden), chlorobenzene (Merck, Germany), Dioctyladipate or DOA (Berol), and chlorododecan (Merck, Germany) were used without further purification. Seed latex particles, 1.4μm prepared 4.2.3.

4.3.2 Apparatus:

As described in section 4.2.2, nos (a) to (f).

4.3.3 Procedure:

The procedure involved is the same steps as described in section 4.2.3, but in this case perkadox SE-8, DOA or chlorododecan were used as compound 2, the water insoluble, low molecular weight compound. The swelling was done by using chlorobenzene, hence there were no polymerisation afterwards. The emulsifier used were NaLS and whey protein and their variation together with stirring rate, swelling capacity variation are discussed in the next chapter. The swelling was followed by taking samples in the optical microscope and taking pictures

at different time intervals. The following is an example of swelling experiment.

(a) Emulsion A:

0.1 dm^3 DOA was mixed with 2.5g NaLS in 1.0 dm^3 water and ultraturraxed at 6,000 r.p.m. for 1 minute, and then homogenised five times at a total pressure of 280 kg/cm^2 ($2.75 \cdot 10^7$ N/m^2).

(b) Emulsion B:

0.2625 dm^3 seed particles ~ 1.4μm prepared in section 4.2.3, which contained 0.2225 dm^3 water, 0.04 dm^3 polystyrene, 0.4 g NaLS was added into reactor under ordinary stirring. 0.44 dm^3 emulsion A above which contained 0.40 dm^3 water, 0.04 dm^3 DOA and 1.0 g NaLS was added. 0.3775 dm^3 water was added to make total water 1.0 dm^3 in volume. 0.1 dm^3 acetone was added to help diffusion of doa to the polystyrene particles. The diffusion was carried out for 24 hrs., and a sample was centrifuged at 15 kHz for 10 - 15 minutes, and another sample was looked in the optical microscope, the absence of small DOA particles indicated complete diffusion. The acetone was then evaporated by opening stoppers or using rotor-vapour.

(c) Swelling of the polymer-oligoner particles with chlorobenzene:

The swelling was carried out in glass reactor. 0.0181 dm^3 emulsion B prepared above which contains, 0.67×10^{-3} dm^3 polystyrene, 0.67×10^{-3} dm^3 DOA, 0.0166 dm^3 water and 0.023g NaLS was added into reactor with stirring rate of 140 r.p.m. 3.977g NaLS was dissolved in 0.9834 dm^3 water and added into reactor. Total volume of water is 1.0 dm^3. 0.5 dm^3 chlorobenzene was added and change of diameter was followed by optical microscope and pictures were taken at different time intervals.

4.4 ADDITIONAL EXPERIMENTS:

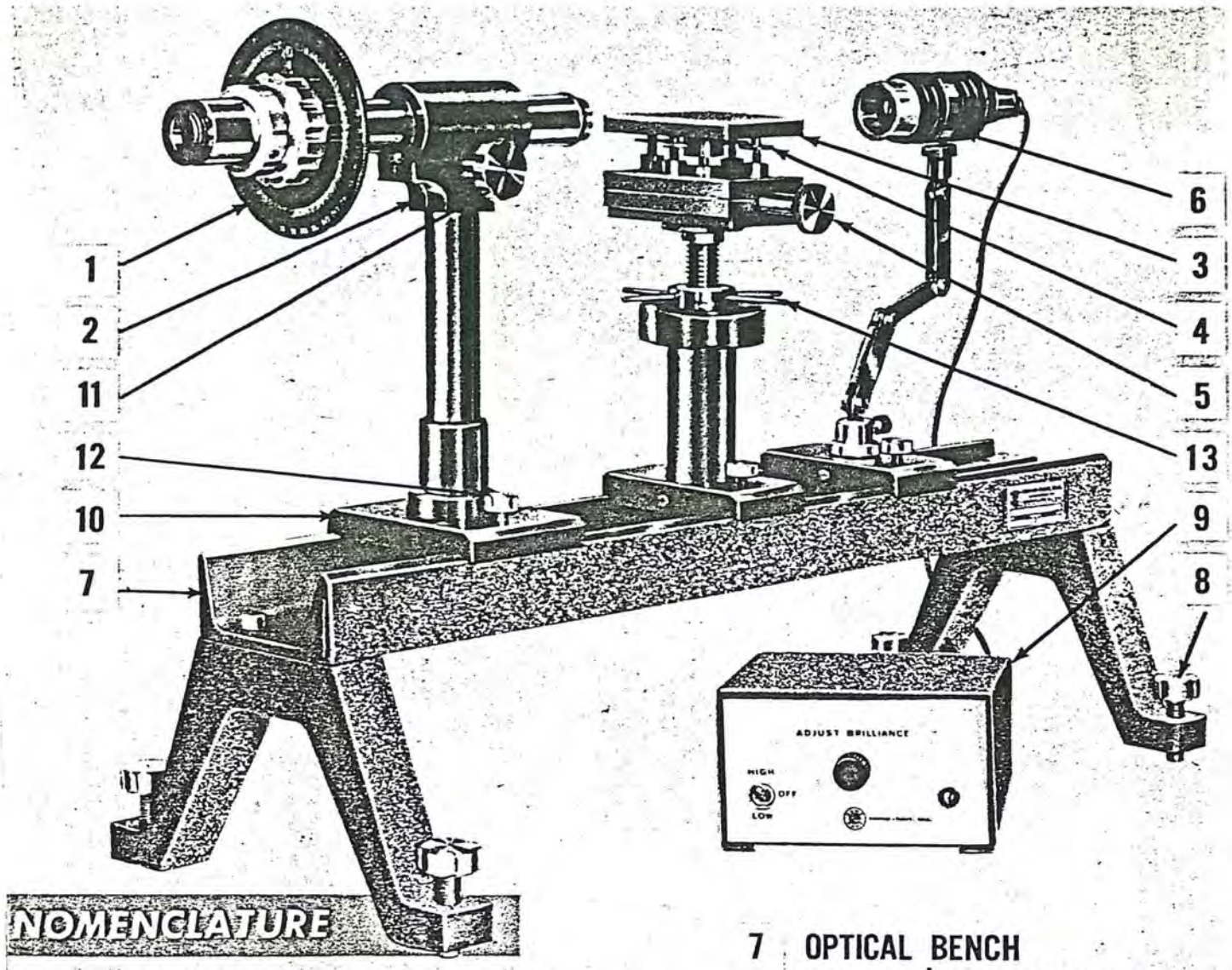
(a) To find interfacial tension of NaLS and whey protein by pendant drop method.

Materials: NaLS and whey protein as described in section 4.3.1.

Apparatus: Contact angel Goniometer Model A-100, shown in fig.4.4.1

Theory: A drop hanging from the tip elongates as it grows larger because the variation in hydrostatic pressure ΔP eventually becomes appreciable in comparison with that given by curvature of apex.

Procedure: A pendant drop of chlorobenzene is suspended in a solution of NaLS or whey protein and a photograph is taken. from the various dimensions of the drop, the inter-facial tension is computed. (See appendix A-1). Inter-facial tension was found for different concentration of emulsifier.



NOMENCLATURE

1 GONIOMETER SCALE
2 MICROSCOPE ASSEMBLY
3 SPECIMEN STAGE
4 STAGE LEVELLING JACKS
5 LATERAL ADJUSTMENT
6 ILLUMINATOR
7 OPTICAL BENCH
8 BENCH LEVELING SCREWS
9 ILLUMINATOR CONTROLLER
10 SLIDE PLATE
11 FOCUSING KNOB
12 SLIDE LOCK
13 ELEVATION ADJUSTMENT

Fig. 4.4.1 Contact angle goniometer

5. RESULTS AND DISCUSSION:

5.1 THE RATE OF SWELLING POLYMER-OLIGOMER PARTICLES:

Table 5.1 shows the result of swelling particles containing polystyrene - DOA, v/v ratio is 1:1 with chlorobenzene in a v/v ratio chlorobenzene: polymer-oligomer of 87:1 at a stirring rate of 250 r.p.m. The emulsion is 7% o/w and the emulsifier used is 4.0 NaLS/ dm^3 water.

time/hr.	Volume/$(\mu m)^3$
0.00	3.6
0.25	15.3
1.08	57.2
2.50	85.7
26.25	154.6
47.00	207.8

Table 5.1: Variation of volume of polystyrene - DOA (V_2+V_3) particles, (v/v ratio 1:1) swollen with V_1, chlorobenzene in the ratio $V_1:V_2+V_3$ of 87:1 with time. The temperature used is 308 K at a stirring rate of 250 r.p.m. d_o = 1.9μm Emulsifier is 4.0gNaLS/dm^3H_2O.

Fig.5.1.1 shows a plot from table 5.1, volume against time. The rate is very high in the beginning and it decreases as the volume, i.e swelling, increases. At point A in the figure, the rate dV/dt is 26 $(\mu m)^3$/hr after 1 hour of the reaction, and it decreased 4 times after about 4 hours to 6:3 $(\mu m)^3$/hr at point B. After around 12 hours at point C, the rate has reduced to 2.3 $(\mu m)^3$/hr and decreases only slowly to 48 hours at point D. This is in agreement with theory. From eqn 2.4.10 and from fig.5, in theory, the partial molar free energy of chlorobenzene $\Delta\bar{G}_1$ increases to zero as the swelling increases. $\hat{\overline{AG}}_1$ is calculated from eqn 2.4.4 and equals zero at equilbrium swelling. In the case where less than the equilbrium chlorobenzene is added, it was usually found that the rate of absorption slowed down drastically at the end before all chlorobenzene was absorbed. This is possibly in part due to a slow transport from chlorobenzene to water.

The rate decreases, as the swelling increases.

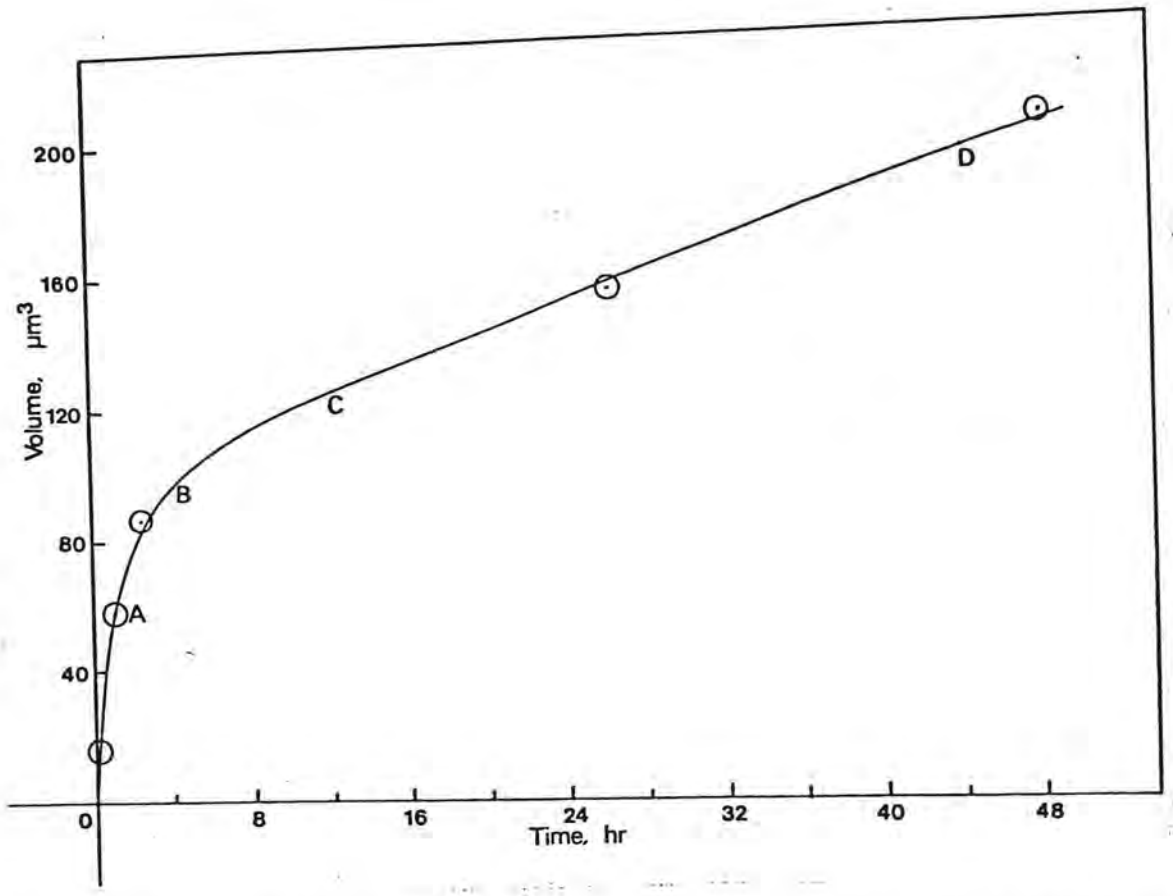


Fig.5.1.1: Variation of volume of polystyrene - DOA particles in a v/v ratio, V_3/V_2 of 1:1, do = 1.9μm, swollen with V_1, chlorobenzene in a v/v ratio, of $V_1:V_2+V_3$ of 87:1, with time. The temp. is 308K, at a stirring rate of 250 r.p.m. using 4.0 g NaLS/dm^3 H_2O. $V_3 = 0.43 \times 10^{-3}$ dm^3 PS/dm^3 H_2O.

5.2. THE RATE AND SWELLING CAPACITY VARIATION WITH THE SPEED OF STIRRER.

Table 5.2A and 5.2B shows the results of swelling particles containing polystyrene - DOA, v/v ratio $V_3:V_2$ of 1:1 with chlorobenzene in a v/v ratio. $V_1:V_2+V_3$ of 87:1. The concentration of the emulsion is 7% o/w and emulsifier used is 4.0 g NaLS/dm^3 H_2O. In table 5.2A, the stirring rate is 500 r.p.m., while in table 5.2B, the stirring rate is 250 r.p.m.

time/hr	diameter/μm
0.00	2.10
0.50	6.11
0.75	6.49
1.00	6.85
1.50	7.12
1.70	7.20
2.92	7.87
4.42	8.13
6.00	8.48
7.00	8.65
22.25	8.65

Table 5.2A: Stirring rate= 500 rpm.

time/hr	diameter/μm
0.00	2.10
0.25	5.02
0.50	5.88
1.00	6.13
2.50	6.40
4.00	6.57
6.50	6.74
22.50	6.74

Table 5.3B: Stirring rate 250 rpm.

Variation of diameter with time of swelling polystryene (3)- DOA(2) particles in the ratio V_2:V_3 of 1:1 with chlorobenzene, V_1, in the ratio V_1: V_2+V_3 of 87:1. The temperature during swelling is 308K, using 4.0g NaLS/ dm^3H_2O. The volume of polystyrene used is $0.43cm^3/dm^3H_2O$, and the diameter of the polymeroligomer particles is 2.10μm

The results of tables 5.2A and 5.2B are plottet in fig.5.2.1 giving the variation of diameter with time. Volume variation with time is shown in appendix A-2.

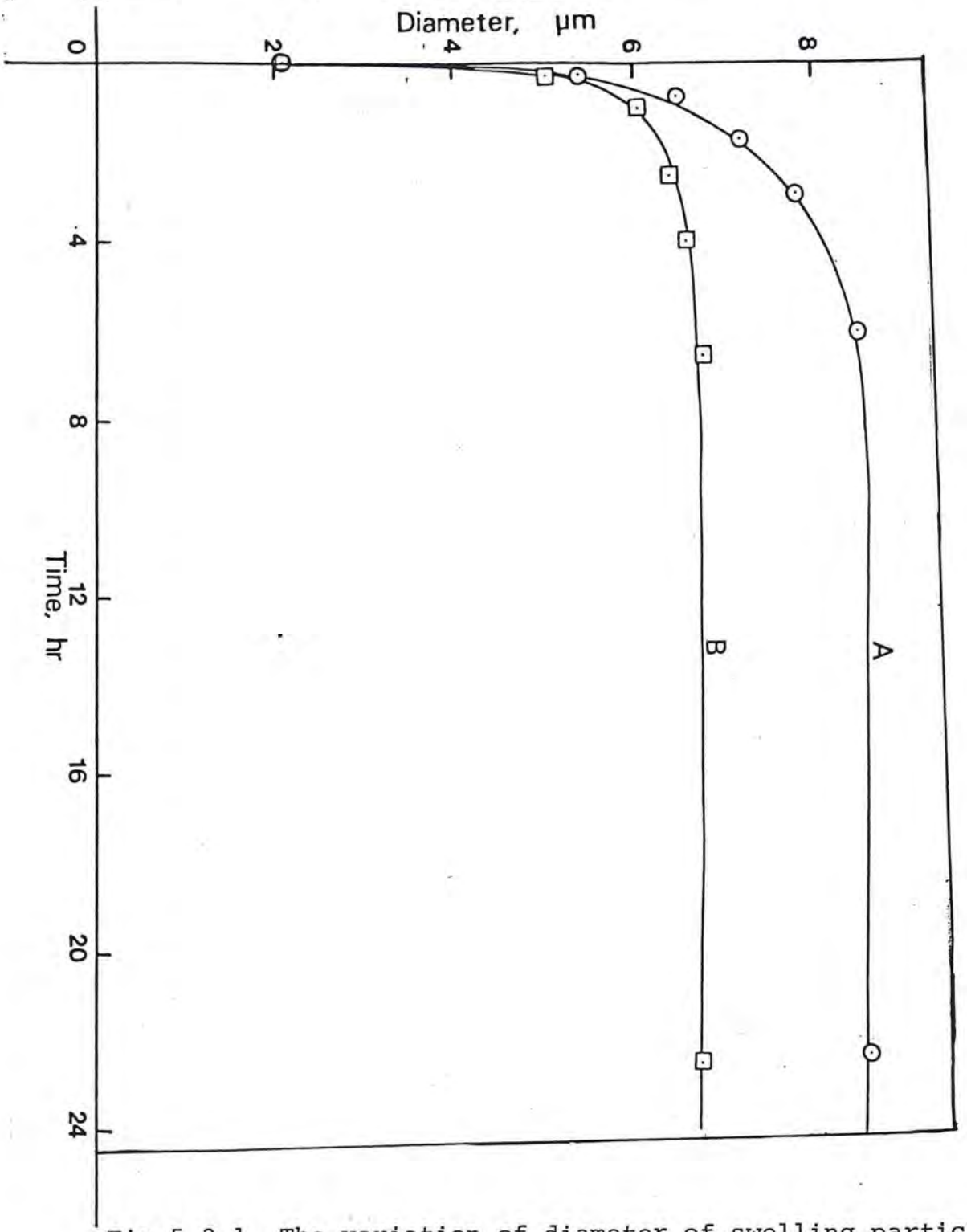


Fig.5.2.1 The variation of diameter of swelling particles with time at different stirring speeds. 500 r.p.m. for curve A and 250 r.p.m. for curve B. Experimental conditions corresponds to those given in tables 5.2A and 5.2B.

Discussion:

When using 250 r.p.m., the rate started to decrease after a swelling of 26 times the original volume of polystyrene - DOA particles, much lower than when using stirring rate of 500 r.p.m. , where the rate started to decrease after a swelling of about 65. At the same time, e.g after 4 hrs., the rate is about 5 $(\mu m)^3$/hr. with stirring rate of 250 r.p.m. while it is much higher with 500 r.p.m., about 26 μm^3/hr. The expected diameter of the particles, with the amount of chlorobenzene used is 9.3μm, but as can be seen from fig.5.2.1 the expected diameter was not reached in any of the cases, the maximum volume of the particle should be 421.2μm^3. Hence using 500 r.p.m., 80% of the chlorobenzene added was absorbed, while with 250 r.p.m. it was ~ 38%.

When using higher speed, the rate is higher and the swelling reached is greater. From eqn 2.4.10, other factors being constant, the number of droplets N, of chlorobenzene is greater for higher than lower rotational speed. The interfacial area increases with increasing rotational speed, and from Ficks law of diffusion

$$dm = - DA \frac{dc}{dx} \cdot dt$$

where, the mass of substance dm diffusing in the x direction in a time dt across an area A is proportional to the concentration gradient. Hence, increasing the interfacial area increases the rate. With intense agitation, turbulent flow of the liquid is produced, and hence turbulent pressures are responsible for the break up of drop. The drop breaks under the dynamical forces which are produced by changes in velocity over a distance at most equal to the diameter of drop. Fig. 5.2.2 show the optical micrograph of the discussed swollen polystyrene - DOA particles with chlorobenzene.

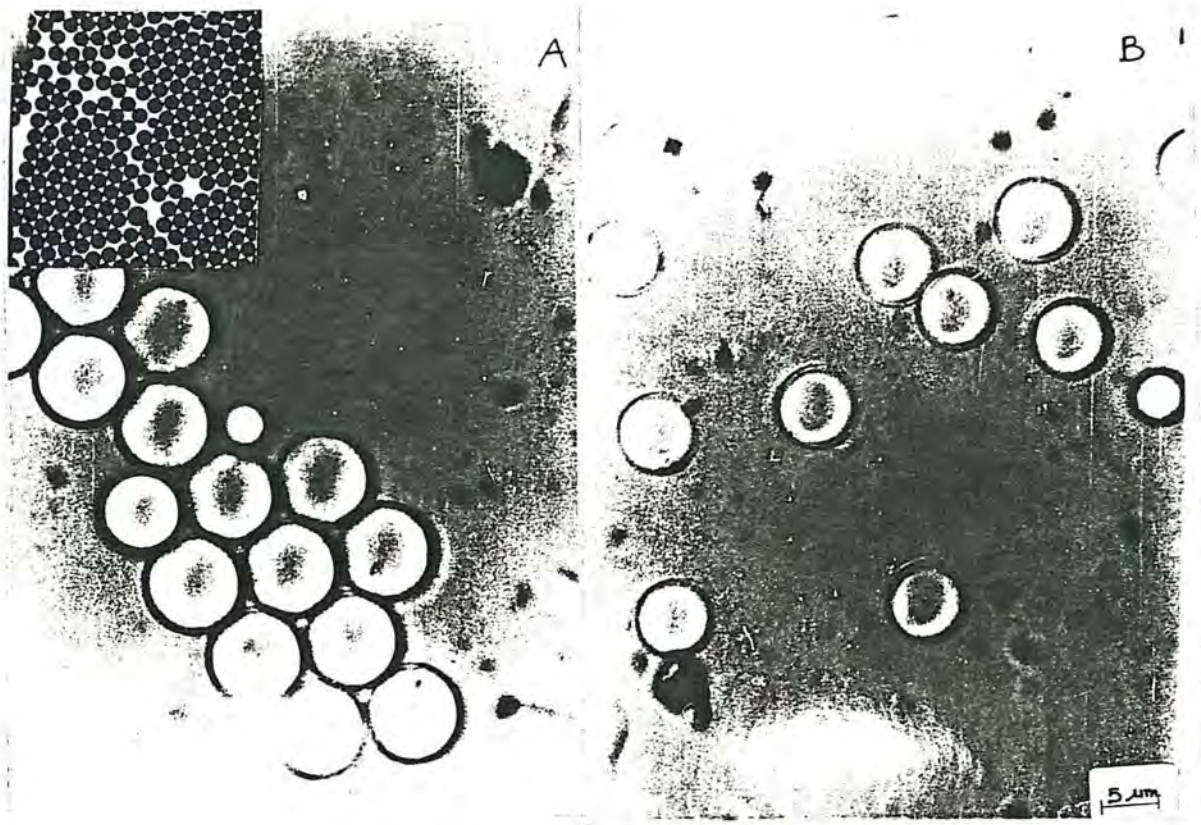


Fig.5.2.2 Optical micrograph of polystyrene - DOA (v/v of 1:1) particles swollen with chlorobenzene, in the ratio of $V_1:V_2+V_3$ of 87:1 after about 6 hours of swelling. 'A' particles are using stirring rate 500 r.p.m. and B particles using 250 r.p.m. Experimental conditions corresponds to those given in tables 5.2A & 5.2B. The monodisperse styrene seed (d_3=1.63µm) is shown in the upper left corner.

It was noted that, when the stirring rate was increased from 250 to 500 r.p.m., the swelling increased to ~ 70%, after it had almost stopped at 38%.

The disadvantage of using high speed is the break up of some of the swollen particles, hence the monodispersity is not very good (~ 70%) using 500 r.p.m. compared to ~ 90% using 250 r.p.m.

5.3 DEPENDENCE OF RATE AND SWELLING CAPACITY ON THE AMOUNT OF COMPOUND 1, CHLOROBENZENE ADDED.

Tables 5.3A, 5.3B and 5.3C shows the result of swelling particles containing polystyrene: chlorododecan v/v ratio of 1:1, with chlorobenzene in a v/v ratio of chlorobenzene: polystyrene - chlorododecan, $V_1 : V_3+V_2$ of 764:1 for A, 373:1 for B and 149:1 for C.

time/hr	diam/μm	volume/μm^3
0.00	1.76	2.8
0.50	4.94	63.7
1.00	5.49	86.7
1.50	6.48	142.4
2.50	7.20	195.6
5.50	8.01	268.9
6.50	8.39	309.1
22.50	9.70	476.2

Tables 5.3A $V_1:V_2+V_3$ of 764:1

time/hr	diam/μm	volume/μm^3
0.00	1.76	2.8
0.50	5.53	88.4
1.00	5.84	104.7
1.50	6.21	125.2
2.50	6.85	167.5
5.50	7.37	209.4
23.50	8.39	309.1

Tables 5.3B $V_1:V_2+V_3$ of 373:1

time/hr	diam/μm	volume/μm^3
0.00	1.76	2.8
1.00	4.84	59.5
2.00	5.09	69.1
3.50	5.90	107.6
5.50	6.46	141.2
22.75	6.78	163.4

Table5.3C $V_1:V_2+V_3$ of 149:1

Tables 5.3A-5.3C, Variation of volume and diameter with time of polystyrene-chlorododecan (v/v ratio, $V_3:V_2$ of 1:1) swollen with chlorobenzene, V_1, in ratios shown above. The starting diameter of polystyrene-chlorododecan particles, d_o is 1.76μm The stirring rate is 140 r.p.m. and temp. 308K. Amount of polystyrene used is 0.67 cm^3/dm^3 H_2O. Emulsifier is 4.0g NaLS/dm^3H_2O.

The results of the above tables are shown is fig.5.3.1,giving the variation of volume of particles with time. Variation of diameter with time is shown in A-2.

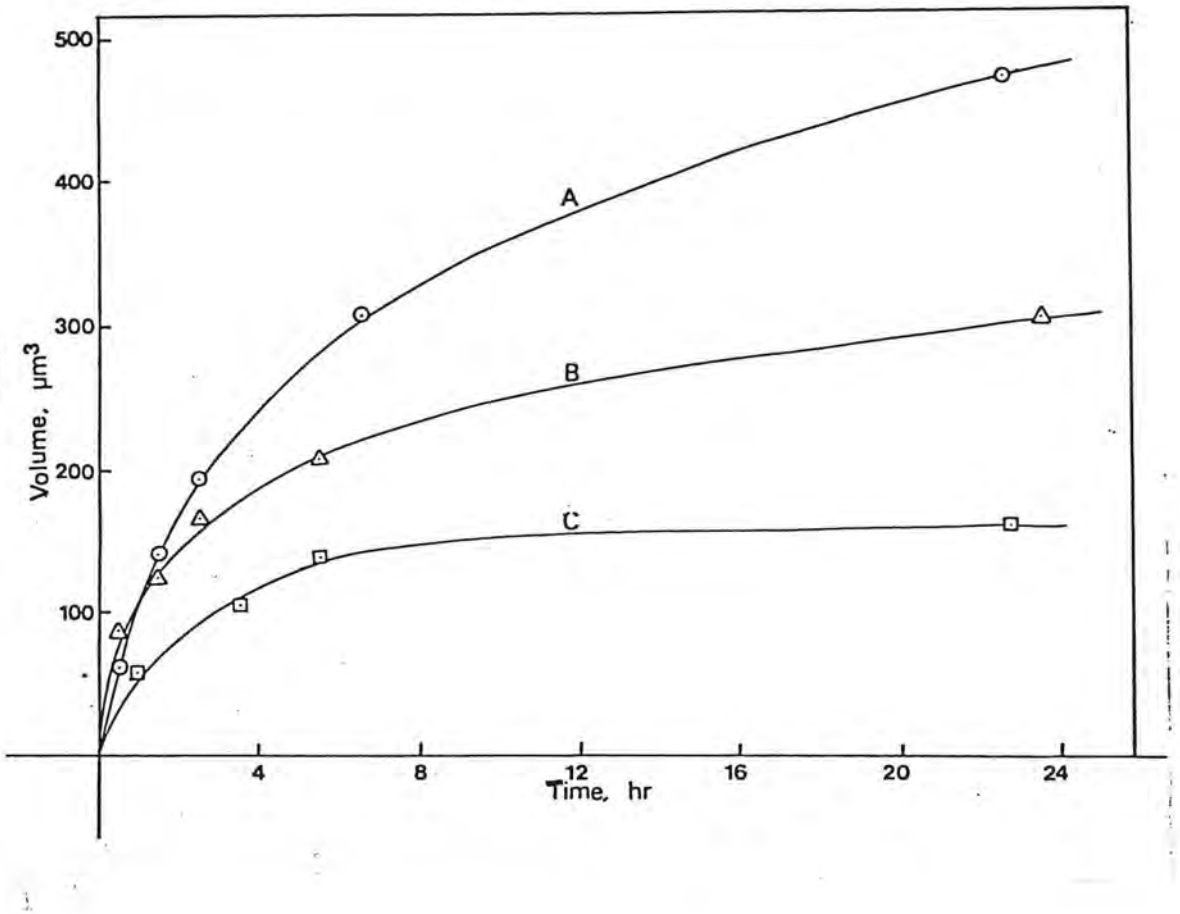


Fig.5.3.1 The variation of volume with time of swelling polystyrene-chlorododecan particles with chlorobenzene in ratios shown above, $V_1:V_2+V_3$ for curve A,B and C is 746:1, 373:1 and 149:1 respectively. Experimental conditions corresponds to those given in tables 5.3A, 5.3B and 5.3C.

Discussion.

It appears from the tables that the rates are very fast at start, the difference are probably within experimental error. As the swelling continues, the counteracting effects come into play. If we compare the rates at the same degree of swelling, the rates of swelling is higher the amount of chlorobenzene applied, (or if we compare the rates after the same time of swelling e.g. 8 hrs from fig.5.3.1, the rates are 15μm^3/hr, 8.8μm^3/hr, and 4.0μm^3/hr for curves A, B and C respectively). This points to that equation 2.4.9 should be applied, where in this case 'a' is for particles and 'b' is for chlorobenzene. At the same degree of swelling the value of $\overline{\Delta G}_{ia}$ for the particles is the same, the difference is therefore probably due to that the value of $N_b r_b$ is higher the larger the amount of chlorobenzene. As we continue to swell the situation may change in the way that with the highest amount of chlorobenzene when the absorption is higher we also reaches a higher value of $\overline{\Delta G}_{ia}/RT$ which means that the driving force for swelling decreases. This is probably the reason why we do not reach complete swelling and this leads to a somewhat less degree with increasing amount of chlorobenzene, such absorption of chlorobenzene was 22%, 29% and 38% for A, B and C respectively.

Fig.5.3.2 shows the optical micrograph of the particles discussed above after 22 hours of swelling.

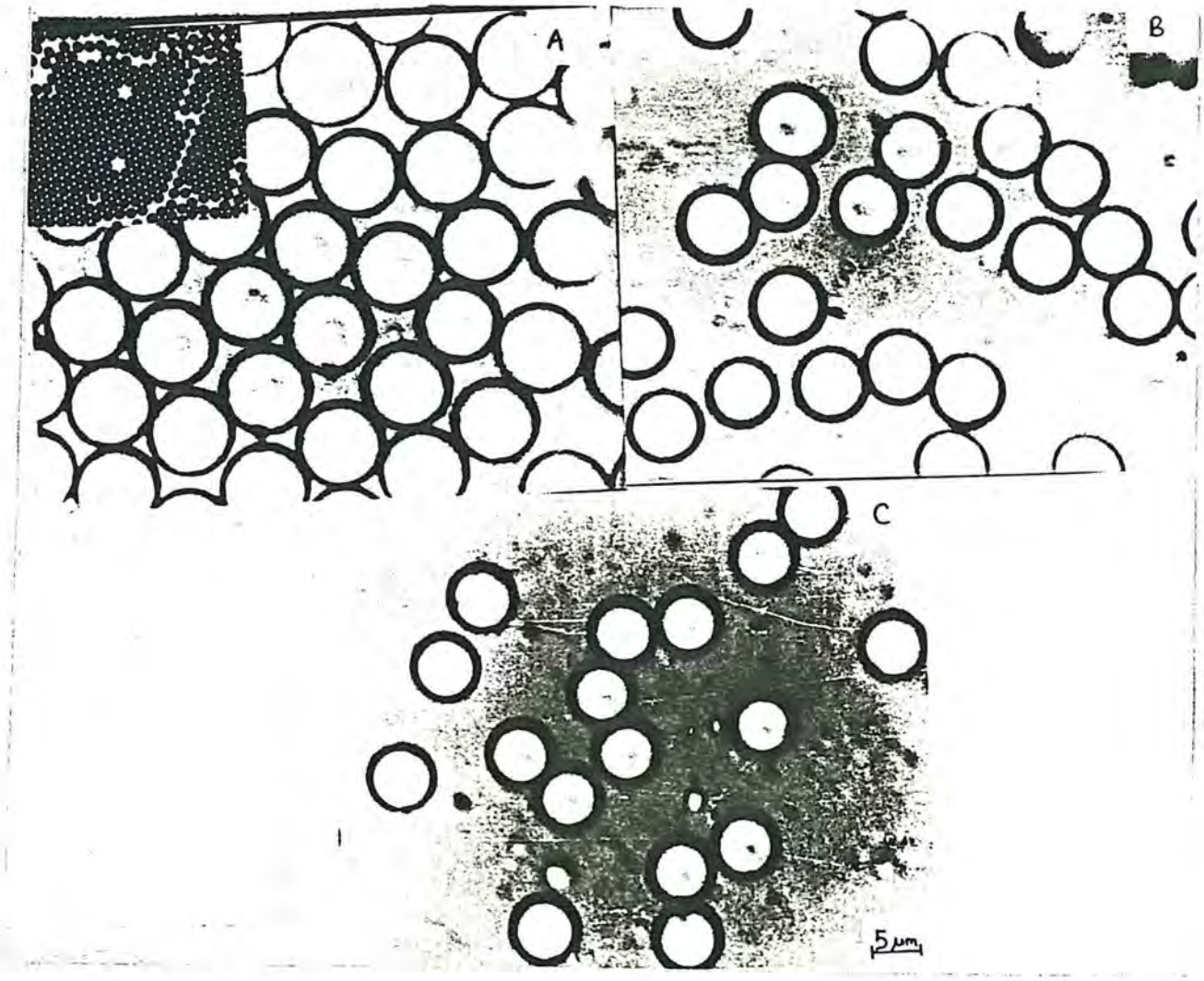


Fig.5.3.2 Optical micrograph of polystyrene-chlorododecan particles V_3:V_2 ratio of 1:1 swollen with chloro-benzene V_1, in the ratio V_1:V_2+V_3 of 746:1, 373:1, and 149:1 for A,B and C respectively after ~ 22 hours of swelling. Experimental conditions corresponds to those given in tables 5.3A, 5.3B and 5.3C. The monodisperse polystyrene seed, d_3=1.4μm is shown in the upper left corner.

From fig.3 in theory of log of swelling capacity against log γ/r_o, the swelling capacity can be tabulated, from variation of interfacial tension γ with NaLS concentration (Appendix A-1), γ is 4 dynes/cm ≡ 4×10^{-3} N/m when NaLS concentration 4.0g/dm^3 H_2O. The diameter of polystyrene-chlorododecan particles, d_o is 1.76μm.

$$\gamma/r_o = 4.55\times10^3 \text{ N/m}^2, \text{ hence } \log \gamma/r_o = 3.66.$$

j_2 for chlorododecan, $C_{12}H_{25}Cl$ is

$$j_2 = \frac{V_{2M}}{V_{1M}} \qquad V_{2M} = \frac{\text{Molecular weight of chlorododecan}}{\text{density of chlorododecan}}$$

$$= \frac{204.79g}{0.8682g/cm^3} = 235.9\ cm^3$$

$$V_{1M} = \frac{\text{Molecular weight of chlorobenzene}}{\text{density of chlorobenzene}}$$

$$= \frac{112.56}{1.1058} = 101.8\ cm^3$$

Hence $j_2 = 2.3$

From fig.3 in theory, using the nearest value of $j_2 = 2$ the swelling capacity at the value of γ/r_o calculated above is $2x10^4$. In all the above cases, we have used much less chlorobenzene hence the equilbrium we get is not a thermodynamic one, but, may be limited by the amount of chlorobenzene added.

The above results were also observed when using the stirring rate of 250 r.p.m. Tables 5.3D and 5.3E shows results of swelling polystyrene-DOA particles in v/v ratio $V_3:V_2$ of 1:1 with chlorobenzene, V_1 in v/v ratio of $V_1:V_2+V_3$ of 87 for D and 500:1 for E.

time/hr	diameter/μm
0.00	1.90
0.25	3.08
1.08	4.79
2.50	5.47
26.25	6.65
47.00	7.35
.....	.....

Table 5.3D: $V_1:V_2+V_3$ ratio is 87:1

time/hr	diameter/μm
0.00	1.90
1.00	4.98
1.50	6.74
2.50	7.83
3.75	8.87
6.75	9.23
24.25	11.00
48.00	11.36

Table 5.3E: $V_1:V_2+V_3$ ratio is 500:1

Variation of diameter with time for polystyrene-DOA particles (V_3+V_2) in v/v ratio of 1:1 swollen with chlorobenzene, V_1 in the ratios shown above, at a stirring rate of 250 r.p.m. and temp. 308K, using 4.0g NaLS/dm^3 H_2O. The diameter of polystyrene-DOA particles, d_o is 1.9μm. Amount of polystyrene used is 0.43cm^3/dm^3 H_2O for D and 1.0 cm^3/dm^3 H_2O for E.

The results of the above tables are shown in appendix, A-2 giving the variation of diameter with time.

5.4 RATE AND SWELLING CAPACITY USING SODIUM LAURYL SULPHATE, NaLS AND WHEY PROTEIN AS EMULSIFIERS.

Tables, 5.4A and 5.4B show the result of swelling polystyrene-DOA particles (v/v ratio $V_3:V_2$ of 1:1) of diameter, d_o = 1.76μm with chlorobenzene, V_1 in v/v ratio V_1: V_2+V_3 of 746:1 at 308K, stirring rate 250 r.p.m. The emulsifier used was 4.0g NaLS/dm^3 H_2O for A, and 3g whey protein/dm^3 H_2O for B. The protein was not heated.

time/hr	diameter/μm
0.00	1.76
1.00	5.22
17.67	8.40
21.17	8.78
25.17	8.73
42.67	9.27

Table 5.4B: Emulsifier is 3.0g whey protein/dm^3H_2O

time/hr	diameter/μm
0.00	1.76
1.00	7.56
2.75	8.79
20.92	12.13
24.58	12.13
45.00	13.35

Table 5.4A: Emulsifier is 4.0g NaLS/dm^3H_2O

Variation of diameter with time for polystyrene-DOA particles (v/v ratio $V_3:V_2$ of 1:1), swollen with chlorobenzene, V_1 in the ratio of $V_1:V_2+V_3$ of 746:1 at a stirring rate of 250 r.p.m. temperature 308K. The emulsifier used are shown in each table. The diameter of the polystyrene-DOA particles d_o, is 1.76μm, and the amount of polystyrene used is 0.67 cm^3/dm^3 H_2O.

The above results are shown in fig.5.4.1 giving the variation of diameter with time.

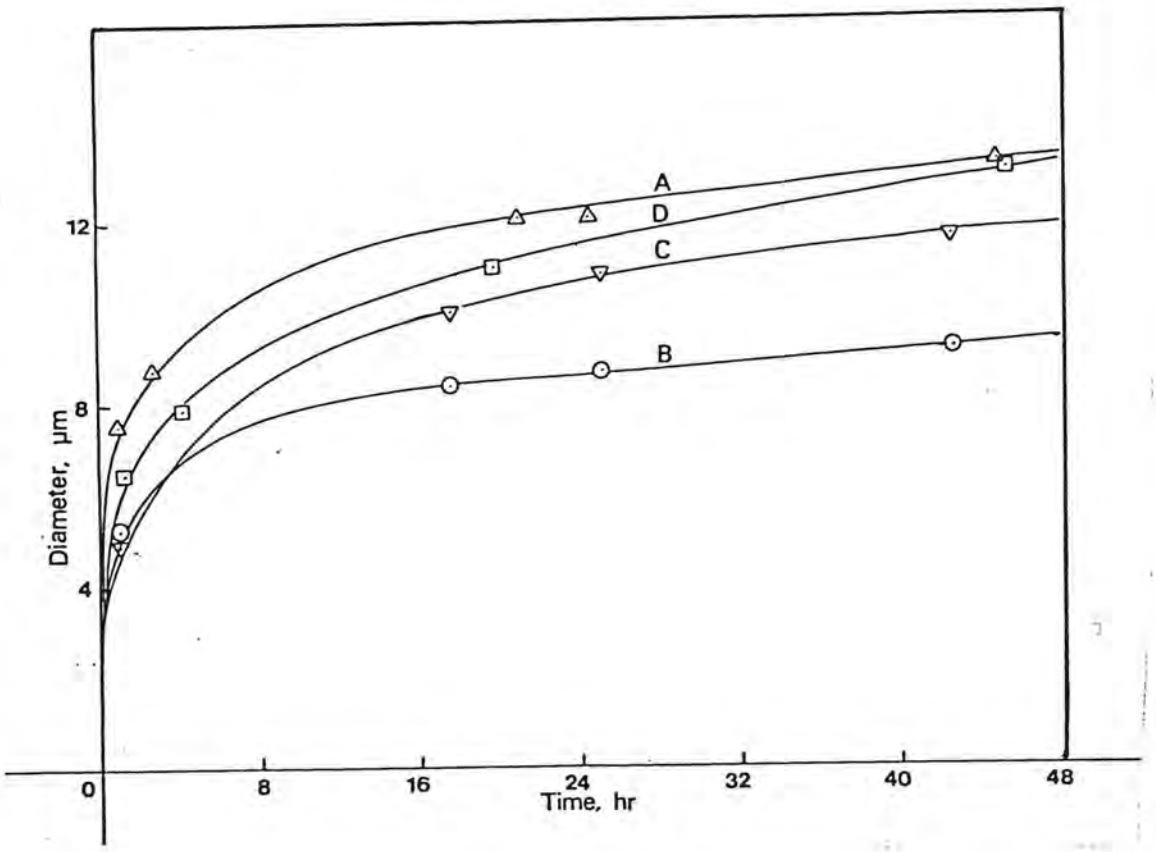


Fig.5.4.1 Variation of diameter with time of swelling polystyrene-DOA particles (v/v ratio $V_3:V_2$ of 1:1) with chlorobenzene, V_1 in ratio $V_1:V_2+V_3$ of 746:1. The emulsifier used are 4.0g NaLS and 3.0g unheated protein/dm^3 H_2O for curves A and B respectively. Experimental conditions corresponds to those given in tables 5.4A and 5.4B.

It is seen that, the rate and swelling is higher from the beginning, for NaLS than for the unheated protein. Fig.5.4.2 shows the optical micrograph of the polystyrene-DOA particles after 1 hr. swelling with chlorobenzene.

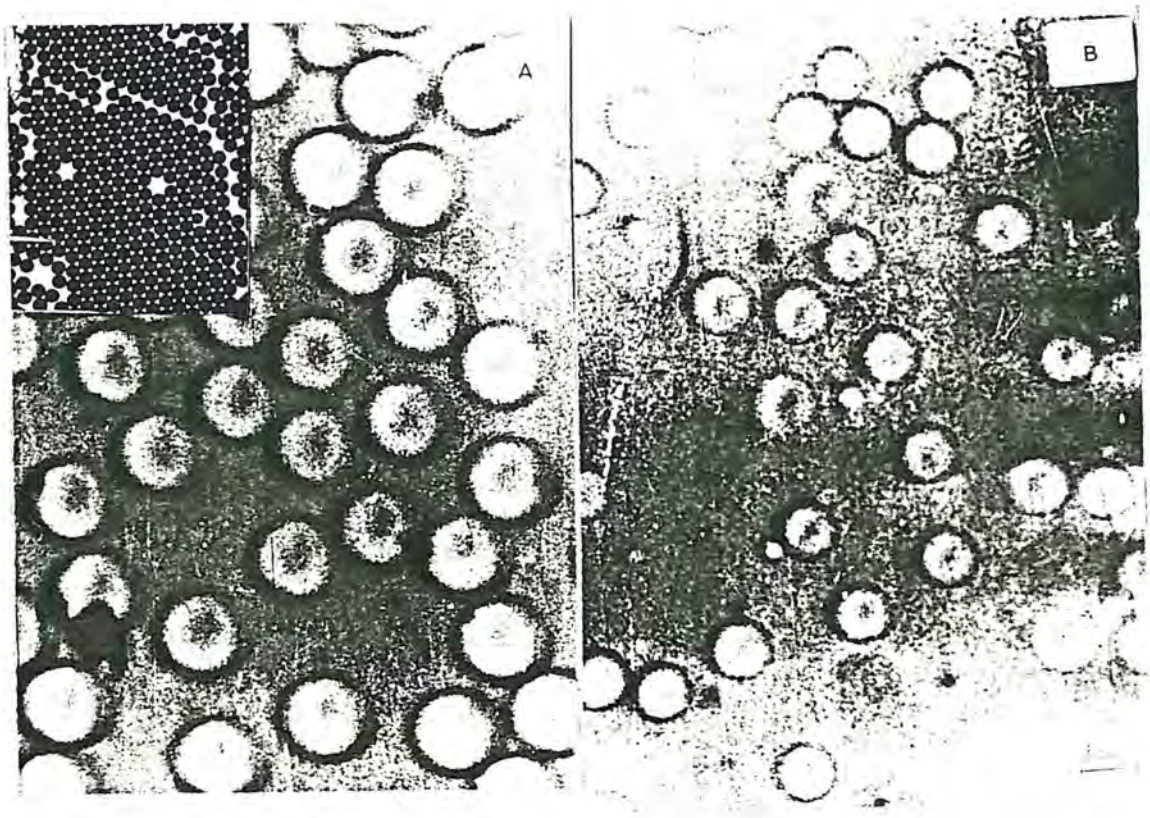


Fig.5.4.2 Optical micrograph of polystyrene-DOA particles in v/v ratio V_3:V_2 of 1:1, swollen with chlorobenzene V_1 in ratio V_1:V_2+V_3 of 746:1 after about 1 hr. of swelling. A particles is using 4.0g NaLS/dm^3 H_2O and B particles is using 3.0 whey protein /dm^3 H_2O. Experimental conditions corresponds to those given in tables 5.4A and 5.4B. The monodisperse polystyrene seed is shown in the upper left corner.

As was noted in the theory, proteins as emulsifier stabilise the particles by forming a layer. Since the formation of the layer process involves 3 stages, i.e diffusion of the protein to the interface, penetration of the molecule into the interface and unfolding, and lastly the adsorbed denatured protein molecules rearranging to the lowest possible free energy state, this process is slower than adsorption of NaLS. It is even slower when the potein is r gid and globular. The composition of whey protein is [49].

α - Lactalbumin	20%
β - Lactoglobulin	55%
γ - Globulins	10%
Blood serum Albumin	5%
Minor whey protein	Traces
Proteose-peptones	10%

The swelling of the particles with chlorobenzene after 40 hours reached a value of 40% of the amount added with unheated protein while with NaLS as emulsifier the corresponding value was 58%. This points to that both the equilbrium swelling as well as the rate of swelling is less with unheated protein than with NaLS. The difference in rate of swelling is clearly apparent from fig.5.4.1 giving variation of diameter with time.

This difference between the protein and NaLS is probably due to a difference in the value of γ, the interfacial tension. At the experimental conditions with concentrations above the critical micelle concentrations, the value of γ for NaLS as determined in appendix A-2 is 4×10^{-3}N/m , while the protein it is 1.3×10^{-2}N/m. The value of j_2 for DOA is

$$j_2 = \frac{V_{2M}}{V_{1M}}, \qquad V_{2M} = \frac{\text{Molecular weight of DOA}}{\text{Density of DOA}}$$

$$= \frac{370\text{g}}{0.9239\text{g/cm}^3} = 401\text{cm}^3$$

Similary, V_{1M} for chlorobenzene $\sim 100\text{cm}^3$

This gives $j_2 = 4$.

The diameter of the polystyrene - DOA particles, d_o = 1.76μm. From the above values, and according to equation 2.4.4. and from fig.3, these values should give a ratio in equilbrium swelling capacity of when using NaLS to unheated whey protein as emulsifiers of about 6.

The larger value of γ for protein also means that the rate of swelling should be lower. It should be pointed out that, as shown in figure 5, the larger the ratio γ/r_o, at the same swelling capacity, the driving force is smaller. Observations shows that while NaLS does not have any interfacial barrier towards absorption of small molecules, it may be that the protein gives such an interfacial barrier which reduces the rate of absorption of chlorobenzene.

Effect of heating protein:

The following tables 5.4C and 5.4D shows the effect of heating protein to 50°C (table 5.4C) and 100° (table 5.4D)

time/hr	diameter/µm
0.00	1.76
1.00	4.95
17.67	10.08
21.17	10.91
25.17	10.91
42.67	11.73

Table 5.4C: Emulsifier is 3.0g whey protein heated to 50°C

time/hr	diameter/µm
0.00	1.76
1.33	6.46
4.17	7.91
19.75	11.04
45.42	13.19
63.42	13.35

Table 5.4D: Emulsifier is 3.0g/dm^3 H_2O whey protein heated to 100°C.

The rest of the variables are same as shown in tables 5.4A and 5.4B. The above results are also plottet in fig.5.4.1. The rate increases as the protein is heated, since the globular part of protein is unfolded during heating, more so at 100°C compared to 50°C.

The swelling reached is 39% and 58% (of the amount of chlorobenzene added) for heated protein to 50°C and 100°C respectively. It is seen that the swelling reached when whey protein is heated to 100°C is the same as when using NaLS, but it took a much longer time for the heated protein.

As was discussed earlier this may be due to a difference in the γ values or it may have been caused by an interfacial barrier in the case of the protein. The interfacial tension of heated protein was almost the same as when protein was not heated, but the values were not very consistent.

It was also noted that when using protein as emulsifier, smaller

particles in the range of 0.5 - 1.0μm are formed, these may be due to chlorobenzene droplets stabilised by the protein layer. These small particles are very few when using NaLS as emulsifier. The emulsified chlorobenzene is more stable when using proteins, hence the small droplets do not dissapear.

Fig.5.4.3 shows the optical micrograph of swollen particles of polystyrene- DOA with chlorobenzene as discussed above, using protein and NaLS as emulsifiers.

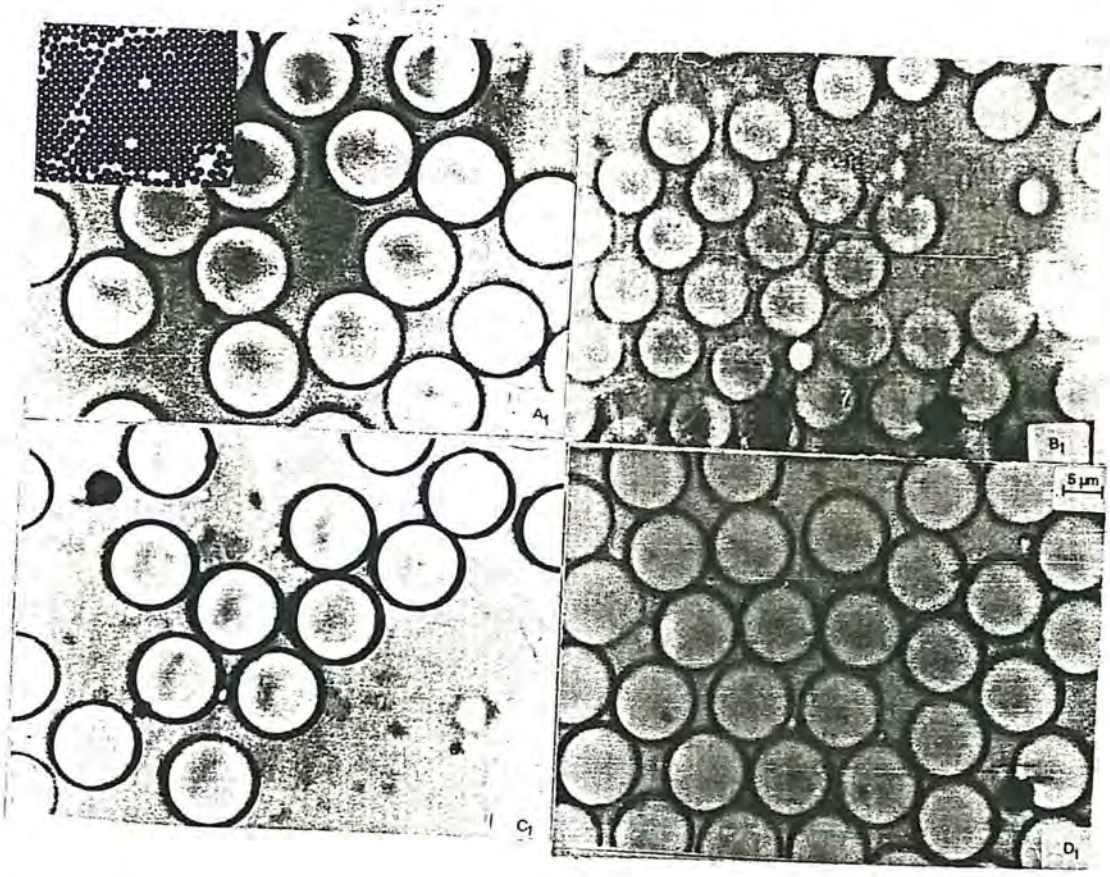


Fig.5.4.3:Optical micrograph of polystryene - DOA particles v/v ratio of olibomer(2) to polymer(3) of 1:1 swollen with chlorobenzene, V_1 in a ratio $V_1:V_2+V_3$ 746:1. The emulsifier used are NaLS, unheated protein, heated protein to 50°C and heated protein to 100°C for A_1, B_1, C_1 and D_1 respectively after 22 hours of swelling. Stirring rate used was 250 r.p.m. at temp. 308K. The starting monodisperse seed is shown on the upper left corner.

When, very small amounts of protein was used, 0.1g whey protein/$dm^3 H_2O$, the particles grew to about 11μm, see fig.5.4.4 and later coalesced. Probably this is due to that the particles are so large so that the small amount of protein is insuffient for a full coverage of particles.

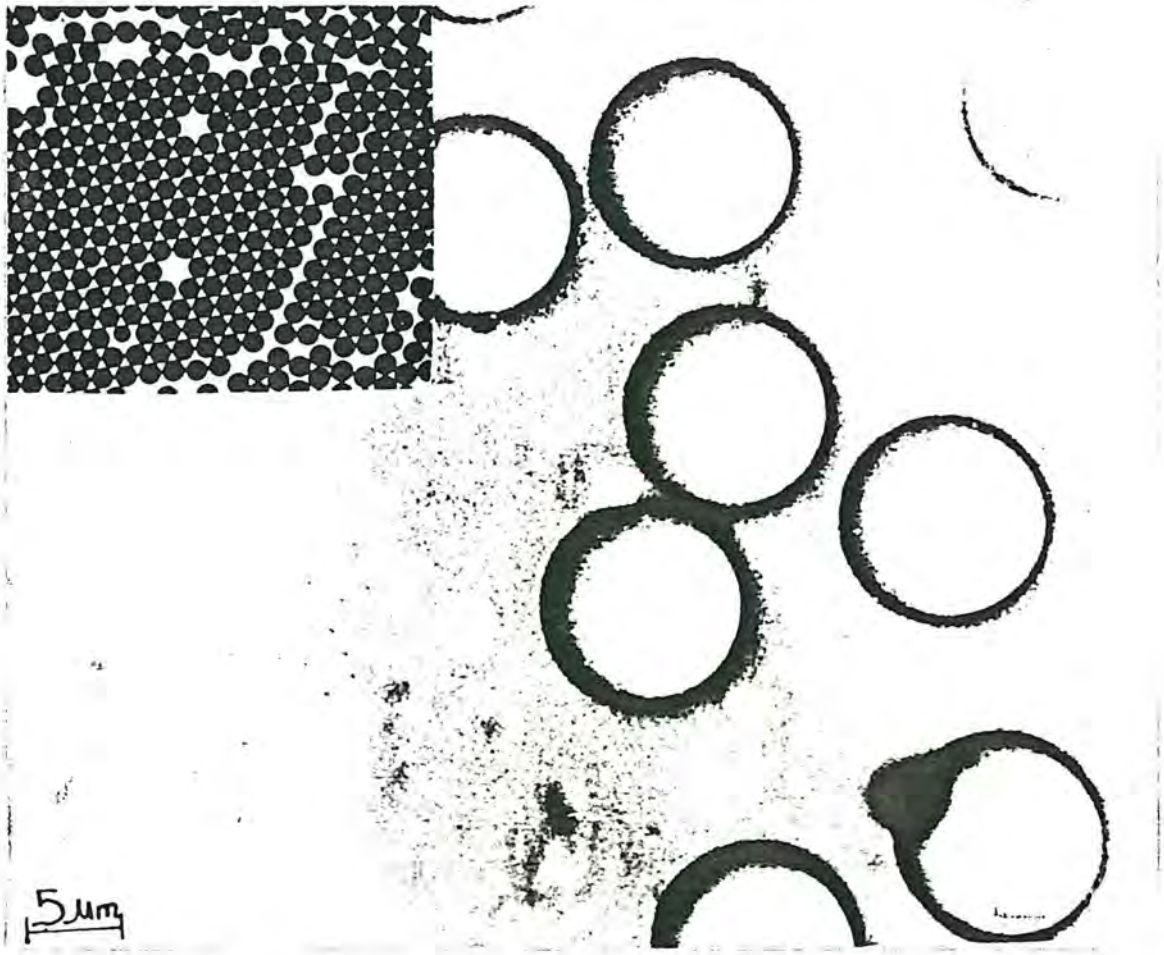


Fig.5.4.4: The other variables are the same as in fig.5.4.3, but here used 0.1g unheated protein/$dm^3 H_2O$.

Using proteins at different pH's.

When using protein as emulsifier, the pH of the emulsions in the experiments was varying from 5-7, and the variation was not consistent. Acetic acid buffer giving a pH of 4.1 led to a higher rate of absorption than was obtained with unbuffered protein. Borax buffer giving a pH of 8.4 led to a lower rate of absorption than obtained with unbuffered protein. The acetic buffered particles were 12.7μm after 25 hours while it took 73 hours for borax buffered particles to reach the same value. These results are in agreement with theory that proteins

are more effective at their isoelectric point, ip. The ip of β-lactoglobulin is 5.1, which is the main constituent of whey protein.

5.5 DEPENDANCE OF THE SWELLING CAPACITY ON AMOUNT OF COMPOUND 2 IN THE PARTICLES

A few investigations were performed to find the influence of the amount of compound 2 on their swelling capacity. Polystyrene latex particles of diameter 1.4μm were swollen with DOA in a ratio

(a) $V_2:V_3 = 1:9$ and

(b) $V_2:V_3 = 1:1$

Setting $V_2+V_3 = 1$, we have in case a) $V_2 = 0.1$ and in case b, $V_2 = 0.5$. The value of r_o for polymer-oligomer particles is in case (a) $7.25\text{x}10^{-7}$m and in case (b) $8.8\text{x}10^{-7}$m. In each case the amount of NaLS = 4.0g/dm^3 H_2O so that even after swelling the concentration of emulsifier is above the critical micelle concentration (A-4). The value of $\gamma = 4\text{x}10^{-3}$N/m (A-2), and accordingly we have,

case (a) $\log \gamma/r_o = 3.74$
case (b) $\log \gamma/r_o = 3.66$

From equation 2.4.4 and figure 4 (in theory), we calculate that the ratio of swelling capacity between case (b) with $\log \gamma/r_o = 3.66$ and $V_2 = 0.5$ and case (a) with $\gamma/r_o = 3.74$ and $V_2 = 0.1$ should be about 10.

Experimentally it was found that the particles in case (a) which after swelling with DOA had a diameter of 1.45μm after 24 hours stirring at 250 r.p.m., had a diameter of 7:3μm that is a swelling ratio of 127. In case (b) the particles after absorption of DOA had a diameter of 1.76μm while they after the same time of swelling with chlorobenzene in the same ratio of V_1: V_2+V_3 of 500:1 as case a, had a diameter of 11.4μm which means a swelling of 270. This gives a ratio of swelling

between case b and case a of about 2. It should be noted, however that in none of the above these cases above have we reached the equilbrium swelling so that the results may be due to a difference in the rate of approach to equilbrium in the two cases. In any case the high degree of swelling after a relatively short time with the low amount of DOA, 10% is surprising. It would be of great interest to do more experiments with relative small amounts of compound 2 to verify the present results.

5.6 RATE AND SWELLING CAPACITY WHEN CHLOROBENZENE IS SUBDIVIDED.

In all the above experiments the chlorobenzene was added as a bulk. At the moderate stirring applied the subdivision of the chlorobenzene is not very effective, only few and relatively large droplets $\sim 30 - 50\mu m$ being formed. As discussed in section 5.2, an increase in the stirring led to a marked increase in the rate and the degree of swelling. However in no case did we reach a swelling which was as high as the calculated one. As discussed above this may be due to the fact that as the swelling increases, the driving force of swelling decreases and moreover the transport of chlorobenzene from the droplets to the aqueous phase may be reduced. Therefore a series of experiments were carried out where the chlorobenzene was much more effective if subdivided before addition to the polymer-oligomer particles. The chlorobenzene was ultraturraxed at $\sim 6{,}000$ r.p.m. with water and enough emulsifier, NaLS, for 2 minutes and droplets in the region of 0.5-20μm were formed, most being in the region 5-7μm.

Table 5.6A shows results where chlorobenzene was subdivided by ultraturraxing before addition to the polymer-oligomer particles, while table 5.6B shows results when the chlorobenzene was added as a bulk. The rest of the variables are the same and are described under the tables. The amount of emulsifier, NaLS, used is enough, as calculated in appendix, A-4.

time/hr	diameter/μm
0.00	2.32
0.50	10.70
1.00	11.80
2.00	13.50
3.00	14.70
4.50	14.90
5.50	14.40
6.50	14.40
8.00	14.80
23.00	15.00
48.00	15.00

Table 5.6A: Ultraturraxed chlorobenzene

time/hr	diamater/μm
0.00	2.32
0.50	7.61
1.50	8.31
2.00	9.34
3.00	9.36
4.50	9.90
5.50	10.10
6.50	10.10
8.00	10.60
23.00	12.90
48.00	13.5
72.00	13.5

Table 5.6B: Non-Ultraturraxed chlorobenzene.

Variation of diameter with time of polystyrene - DOA particles in v/v ratio of $V_3:V_2$ of 1:2 swollen with chlorobenzene, V_1 in the ratio V_1: V_2+V_3 of $\sim$ 290:1 at a stirring rate of 140 r.p.m., using 2.5g NaLS/dm^3H_2O and temp.308K. The diameter of the polystyrene - DOA particles d_o = 2.32μm. The volume of polystryene used is $\sim 0.37 cm^3/dm^3 H_2O$.

The results of tables 5.6A and 5.6B are shown in fig. 5.6.1 giving the variation of diameter with time. Curve A shows the case where the chlorobenzene was added as droplets while curve B shows the case where the chlorobenzene was added as a bulk.

In appear from the figures that the rates is very fast when chlorobenzene is subdivided. The particles were swollen very fast to a swelling ratio of about 218 for case A of ultraturraxed chlorobenzene, while with non-ultraturraxed chlorobenzene the swelling ratio was $\sim$ 40 at the same time. After about 7 hours, all the chlorobenzene was absorbed for case A, where the chlorobenzene was ultraturraxed while when the chlorobenzene was added as a bulk, case B, the chlorobenzene absorbed was $\sim$ 70%, and changed only slowly even after the swelling was continued for $\sim$ 72 hours.

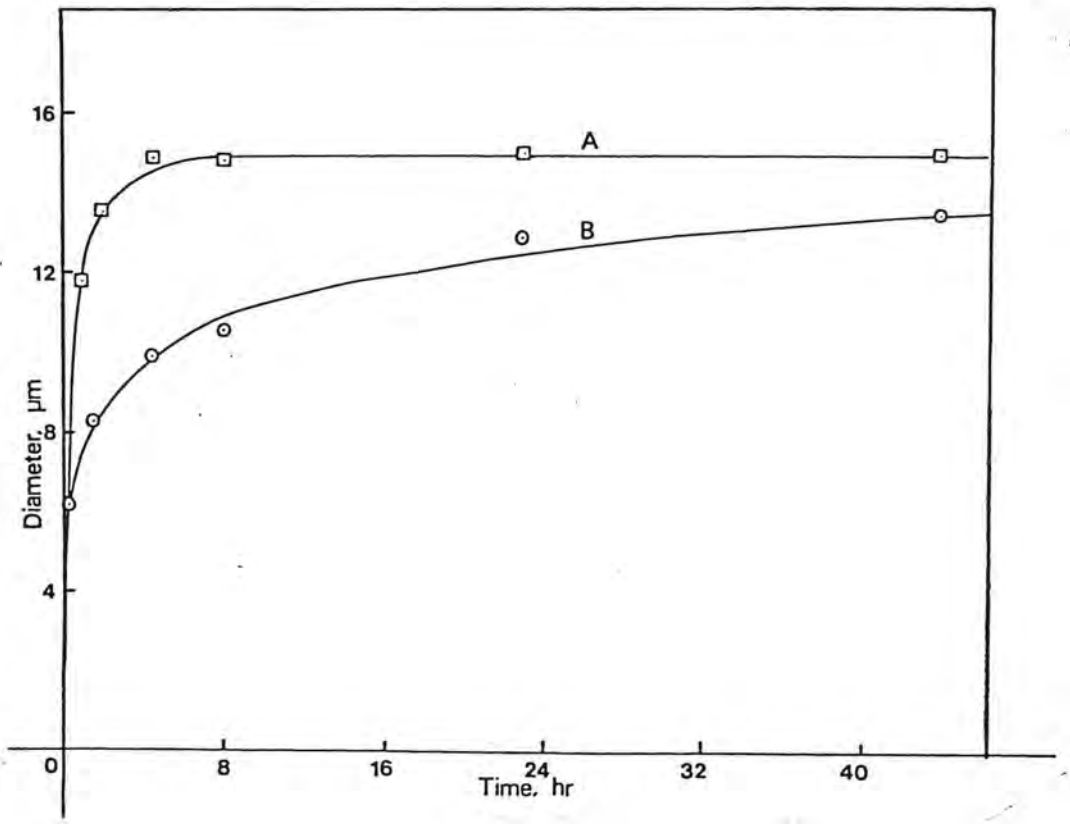


Fig.5.6.1: Variation of diameter with time of swelling polystyrene - DOA particles in a v/v ratio V_3/V_2 of 1:2 using ultraturraxed chlorobenzene for curve A, while in curve B the chlorobenzene was added as a bulk. The ratio of chlorobenzene to polystyrene - DOA particles is 290:1. Experimental conditions correspond to those given in tables 5.6A and 5.6B.

The rate of swelling with chlorobenzene is in accordance with equation 2.4.9 given by

$$\frac{dV_b}{dt} = \frac{4\pi r_b N_b D_w C_w^{\infty} r_a N_a \left[\exp \overline{\Delta G}_{ib}/RT - \exp \overline{\Delta G}_{ia}/RT \right]}{r_a N_a + r_b N_b}$$

where $\overline{\Delta G}_{ib}/RT$ is equal to $\frac{2\gamma V_{lM}}{rRT}$ (eqn 2.2.14) for pure chlorobenzene droplets, and $\overline{\Delta G}_{ia}/RT$ for the particles is given by eqn 2.4.4.

It will be apparent that in the case that we have ordinary stirring which gives large and few droplets, $N_b r_b \ll N_a r_a$ and the rate of swelling will be,

$$\frac{dV_b}{dt} = 4\pi D_w N_b r_b C_w^{\infty} \left(1-\exp \left(\overline{\Delta G}_{ia}/RT\right)\right.$$

$\frac{\overline{\Delta G}_{ib}}{RT}$ is approximately zero because the droplets of choloro-benzene are so large, and so $\exp \overline{\Delta G}_{ib}/RT \approx 1$.

In the case that we applied the ultraturrax and have a large amount of chlorobenzene droplets of much smaller size we will approach a situation where

$$N_b r_b >> N_a r_a$$

In this case we get for the rate of absorption,

$$\frac{dV_b}{dt} = 4\pi D_w C_w^{\infty} N_a r_a \left(\exp \overline{\Delta G}_{ib}/RT - \overline{\Delta G}_{ia}/RT\right)$$

It will be apparent that in the latter case we will have a much higher rate of swelling because $N_a r_a$ is much higher than $N_b r_b$ in the former case. Also the fact that $\exp \overline{\Delta G}_{ib}/RT$ in the latter case is somewhat higher than 1 may contribute to the higher rate, althoughthis effect is probably of minor importance.

Fig.5.6.2 shows the optical micrographs of the particles discussed above.

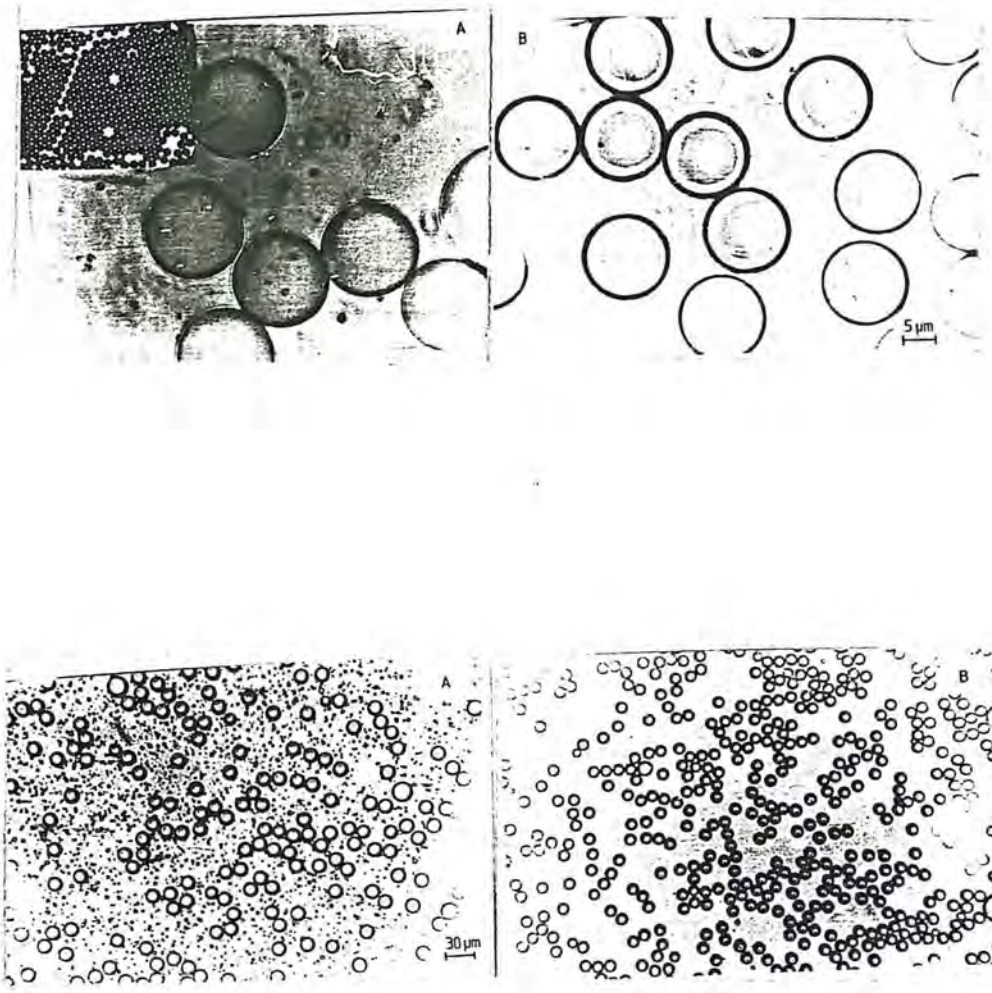


Fig.5.6.2: Optical micrographs of polystyrene - DOA particles v/v ratio V_3:V_2 of 1:2 swollen with chlorobenzene V_1 in the ratio V_1:V_2+V_3 of 290:1. The chlorobenzene is ultraturraxed for A particles, and for B particles the chlorobenzene was added as a bulk. The pictures are taken after 23 hrs of swelling. The same particles are shown at a smaller scale. The original polystyrene seed, d_3 = 1.61µm, is shown on the upper left corner.

Tables 5.6D and 5.6C shows results of ultraturraxing and non-ultraturraxing chlorobenzene respectively at a much lower swelling of, $V_1:V_2+V_3 \sim 46:1$. Experimental conditions are shown on the tables.

time/hr	diameter/μm	volume/μm^3
0.00	2.32	6.54
0.42	4.86	59.9
2.42	6.84	167.5
4.50	7.19	195.2
21.00	7.92	260.1
70.00	7.92	260.1

Table 5.6C: Non-ultraturraxed chlorobenzene.

time/hr	diameter/μm	volume/μm^3
0.00	2.32	6.54
0.25	7.92	260.1
1.67	8.28	297.4
3.50	8.28	297.4
8.00	8.28	297.4
20.00	8.28	297.4

Table 5.6D. Ultraturraxed chlorobenzene.

Variation of volume and diameter with time of polystyrene-DOA particles ($V_3:V_2$ of 1:2) with d_o = 2.32μm swollen with chlorobenzene, V_1 in ratio V_1: V_2+V_3 of 46:1 using 2.5g NaLS /dm^3 H_2O, at a stirring rate of 140 r.p.m., temp 308K. The volume of polystyrene used is 2.4cm^3/dm^3 H_2O.

The above results are plotted in fig.5.63, giving the variation of diameter with time, Variation of volume with time is shown in appendix, A-2.

From figure 5.6.3, and volume variation for the case of ultraturraxed chlorobenzene, the rate increased very fast from ∞ to zero in a very short time. At the same time, eg after 2 hours of swelling, the rate is already zero for ultraturraxed chlorobenzene, while it is ~ 23μm^3/hr where the chlorobenzene is not ultraturraxed. These observation also agree with those seen from tables 5.6A and 5.6B, and hence the same discussion holds.

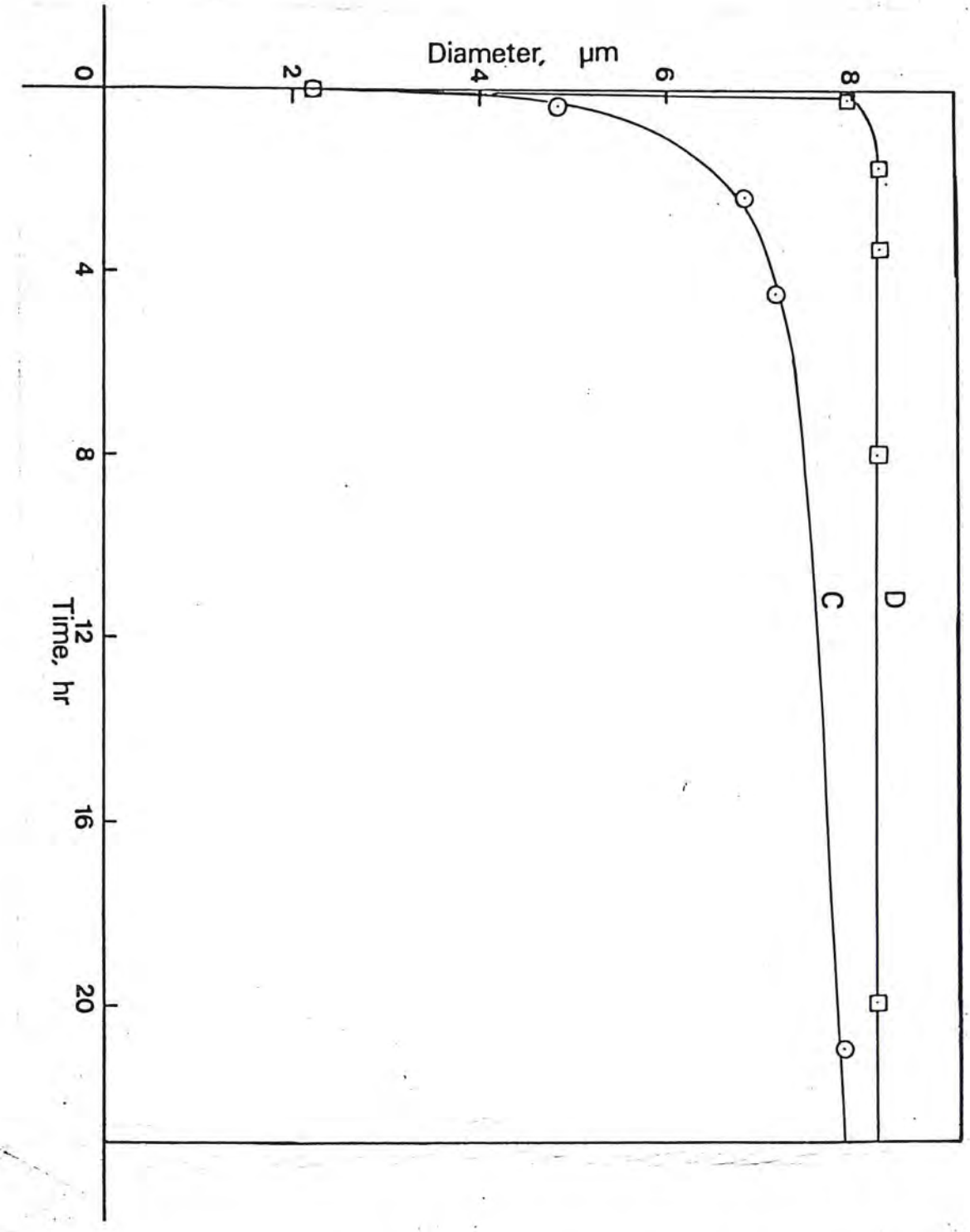


Fig.5.6.3: Variation of diameter with time of swelling polystyrene-DOA particles (V_3:V_2 of 1:2, d_o = 2.32μm) with non-ultraturraxed and ultraturraxed chlorobenzene, V_1 for curve C and D respectively in the ratio V_1: V_2+V_3 of 46:1. Experimental conditions are the same as in tables 5.6C and 5.6D.

Fig.5.6.4 shows the optical micrograph of the particles discussed above.

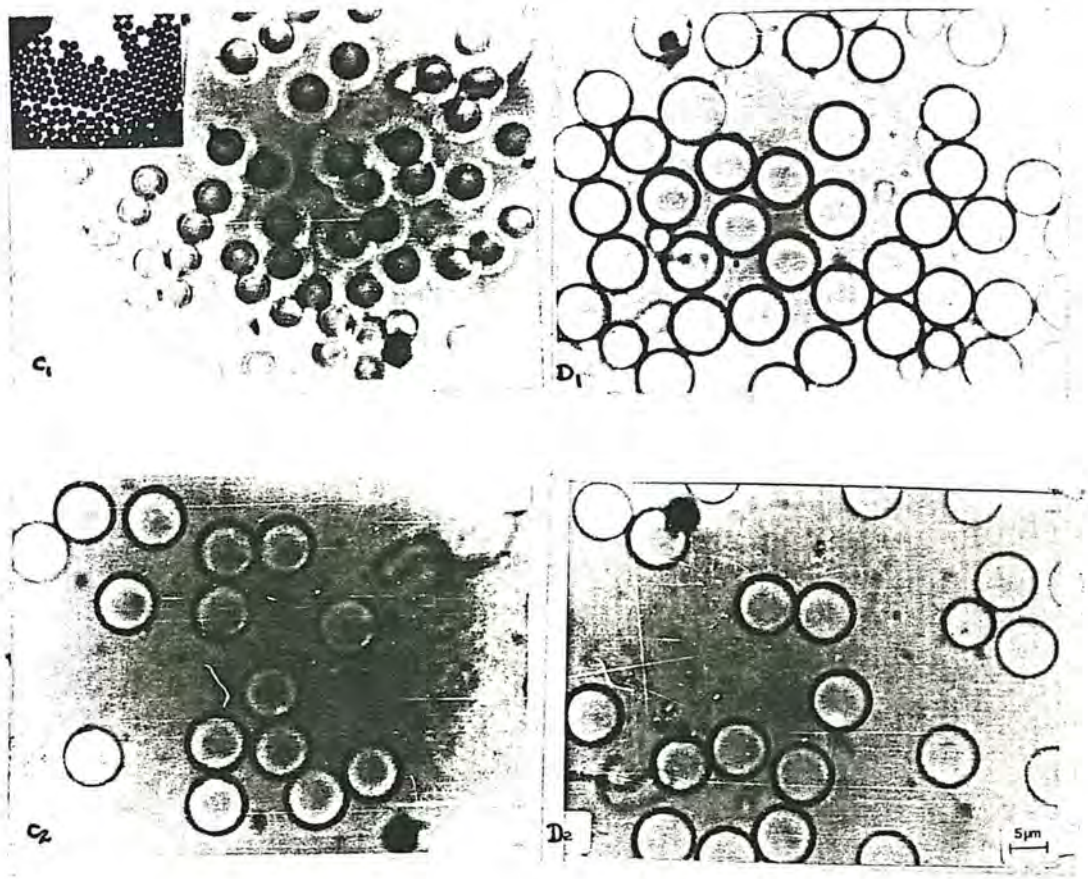


Fig.5.6.4 Optical micrograph of polystyrene-DOA particles in v/v ratio V_3: V_2 of 1:2, swollen with chlorobenzene V_1 in the ratio V_1: V_2+V_3 of ~ 4.6:1. The chlorobenzene is not ultraturraxed for C_1 and C_2 after 25 minutes and 21 hr. swelling time respectively, and it is ultraturraxed for D_1 and D_2 after 15 minutes and 1 1/3 hr. swelling time respectively. The polystyrene seed (d_3 = 1.61μm) is shown on the upper left corner.

Swelling to 20μm - 40μm

By increasing the surface area of the chlorobenzene by ultraturraxing before mixing with the polymer-oligomer latex it turned out that it was possible to prepare particles of 20μm to 40μm starting with particles of 2.3μm. As discussed above it was by far not possible to attain such degrees of swelling when the chlorobenzene was added in bulk and the droplets formed are large and few in number.

The equilbrium swelling capacity ($\overline{\Delta G}_1 = 0$) is calculated from eqn 2.4.4 and shown in fig.3 giving log of swelling capacity against log γ/r_o. As calculated in section 5.4 j_2 for DOA = 4. At 2.5g NaLS/$dm^3 H_2O$, $\gamma = 4 \times 10^{-3}$ N/m. The equilbrium swelling capacity is $\sim 10^4$.

Tables 5.6E and 5.6F shows results of swelling polystyrene - DOA particles d_o = 2.32μm, (with v/v ratio $V_3:V_2$ of 1:2) with chlorobenzene V_1, in the ratios V_1: V_2+V_3 of 740:1 for E and 2500:1 for F. The chlorobenzene was mixed with water and emulsifier and ultraturraxed at 6,000 r.p.m. for ~ 1 min. The emulsifier used is 2.5g NaLS/$dm^3 H_2O$ at 308K, 140 r.p.m.

time/hr	diameter/μm	volume/μm^3
0.00	2.32	6.54
0.25	9.70	477.9
0.50	11.30	753.6
1.00	13.05	1166.2
1.38	14.47	1586.3
1.83	15.18	1830.5
4.58	19.07	3636.7
5.83	20.16	4290.2
7.00	20.33	4406.6
23.58	20.87	4766.8

Table 5.6E: Ultraturraxed chlorobenzene: polystyrene-DOA ratio of 740:1.

time/hr	diameter/μm	volume/μm^3
0.00	2.32	6.54
0.50	12.19	948.3
1.00	15.07	1792.8
1.75	16.67	2425.3
3.75	18.76	3451.6
22.00	27.35	10710.7
43.67	30.10	14279.6

Table 5.6F: Ultraturraxed chlorobenzene: polystyrene-DOA ratio of 2500:1.

Variation of volume and diameter with time of swelling polystyrene-DOA particles (v/v ratio V_3: V_2 of 1:2) with ultraturraxed chlorobenzene in the ratios shown above. Emulsifier used is 2.5g NaLS/dm^3 H_2O at a stirring rate of 140 r.p.m., temp. 308K. The diameter of polystyrene-DOA particles d_o is 2.32μm.

The results of tables 5.6E and 5.6F are shown in fig.5.6.5 giving the variation of diameter with time. Log volume variation with time at different swelling capacities, is shown in appendix A-2.

When comparing results of table 5.6E with those of table 5.3A, where the V_1 : V_2+V_3 ratio is almost the same, of 740:1, whereas in table 5.3A the chlorobenzene was not ultraturraxed, the chlorobenzene absorbed was 22% of the total added, while with ultraturraxed chlorobenzene it was ~100%.

It also appears that the rate of swelling up to a ratio of about 200 is considerable faster in the case with the ultraturraxed experiments than has ever been obtained without this treatment. However also, in the case with ultraturraxed chlorobenzene the rate of swelling at large degrees of swelling is very much reduced. This may be as discussed above to be due to the decrease in the driving force of the swelling caused by the increase in $\overline{\Delta G}_1$ in the particles. Another fact should also be brought in mind, namely that the droplets formed by the ultraturrax however will degrade by diffusion among themselves during the time of swelling giving larger chlorobenzene droplets. This effect may lead to a further decrease in the rate of swelling and may infact be the main reason for the decrease in the rate of swelling.

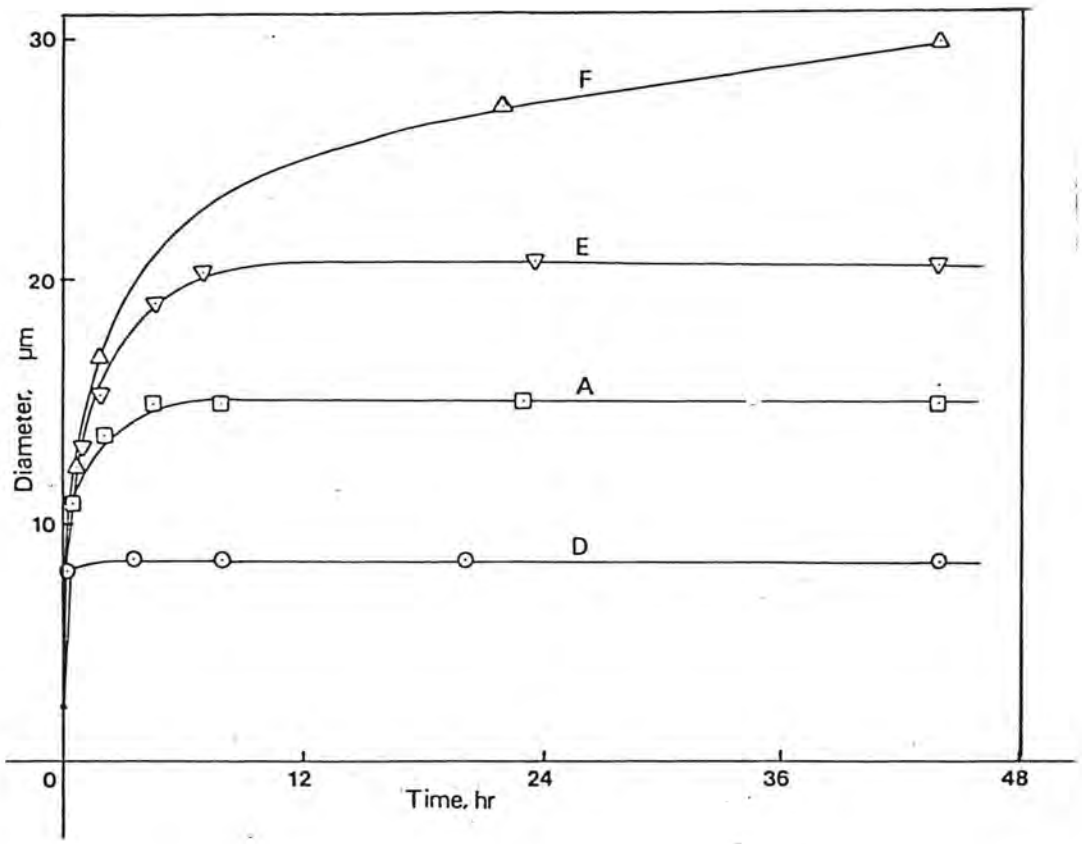


Fig.5.6.5 The variation of diameter with time of swelling polystyrene-DOA particle (v/v of 1:2) with ultra-turraxed chlorobenzene in the ratios V_1: V_2+V_3 of 290:1 for A, 46:1 for D, 740:1 for E and 2500:1 for F. Emulsifier used is 2.5g NaLS/dm^3 H_2O, at stirring rate of 140 r.p.m. and temp. 308K.

Preparation of 40 μm particles:

40 μm particles were prepared as follows. PS-DOA particles in v/v ratio of polymer to oligomer 1:2 and diameter, d_o = 2.32 μm were swollen with chlorobenzene, V_1 in the ratio $V_1:V_2+V_3$ of 4800:1 (i.e. ∿ 15,000 times the volume of the original polystyrene particles), using 4.0 g NaLS/dm^3 H_2O at 308 K, stirring rate 140 rpm. The chlorobenzene was mixed with water and enough emulsifier and ultraturraxed at ∿ 8,000 r.p.m. for 2 minutes. It should be noted that from Eqn. 2.4.4. one can calculate that with d_o ∿ 2.32 and interfacial tension $\gamma = 4x10^{-3}$ N/m, the equilibrium swelling capacity is ∿ 10,000 corresponding to particle size of ∿ 50 μm.

Figures 5.6.6, 5.6.7 and 5.6.8 show the optical micrograph of the 20 μm, 30 μm and 40 μm particles respectively, swollen with chlorobenzene.

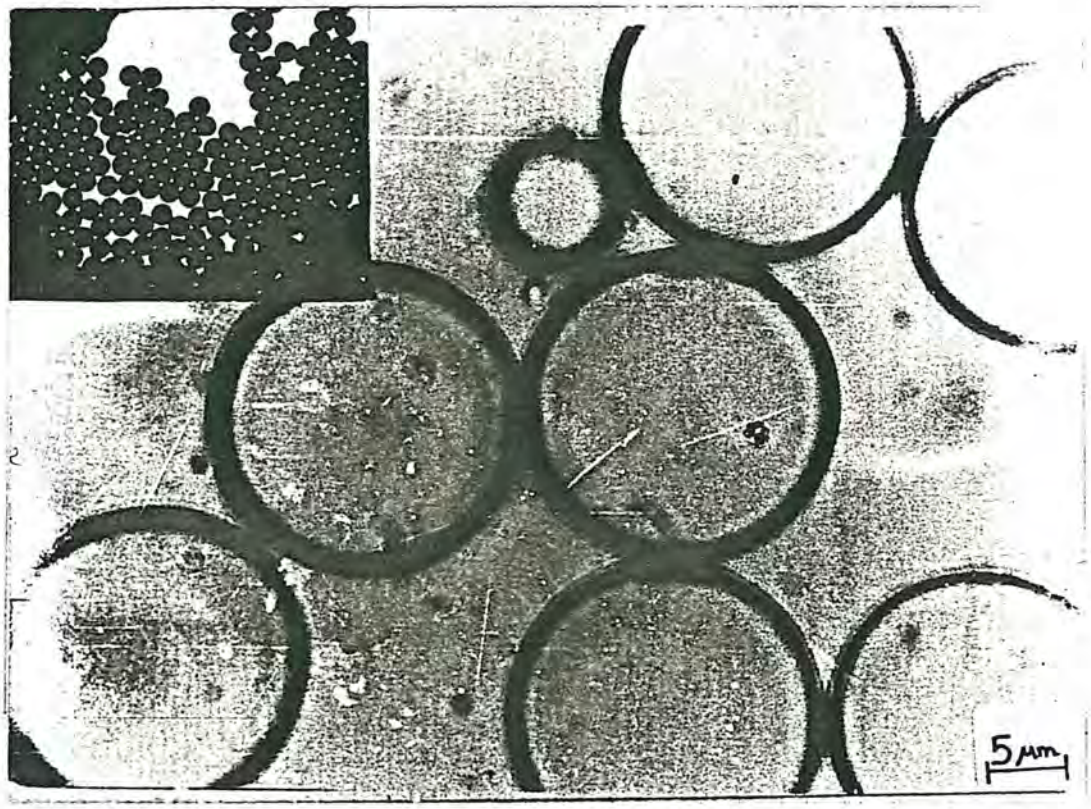


Fig.5.6.6: Optical micrograph of polystyrene - DOA particles in v/v ratio of polymer to oligomer of 1:2, swollen with ultraturraxed chlorobenzene, V_1 in the ratio $V_1:V_2+V_3$ of 740:1 (which is ∼ 2280 times volume of original polystrene in the particles). The size of the particles is ∼ 20μm. The stirring rate used is 140 r.p.m. at temp. 308K using 2.5g NaLS/dm^3H_2O. The original polystyrene seed is shown on the upper left corner. (d_3 = 1,61μm).

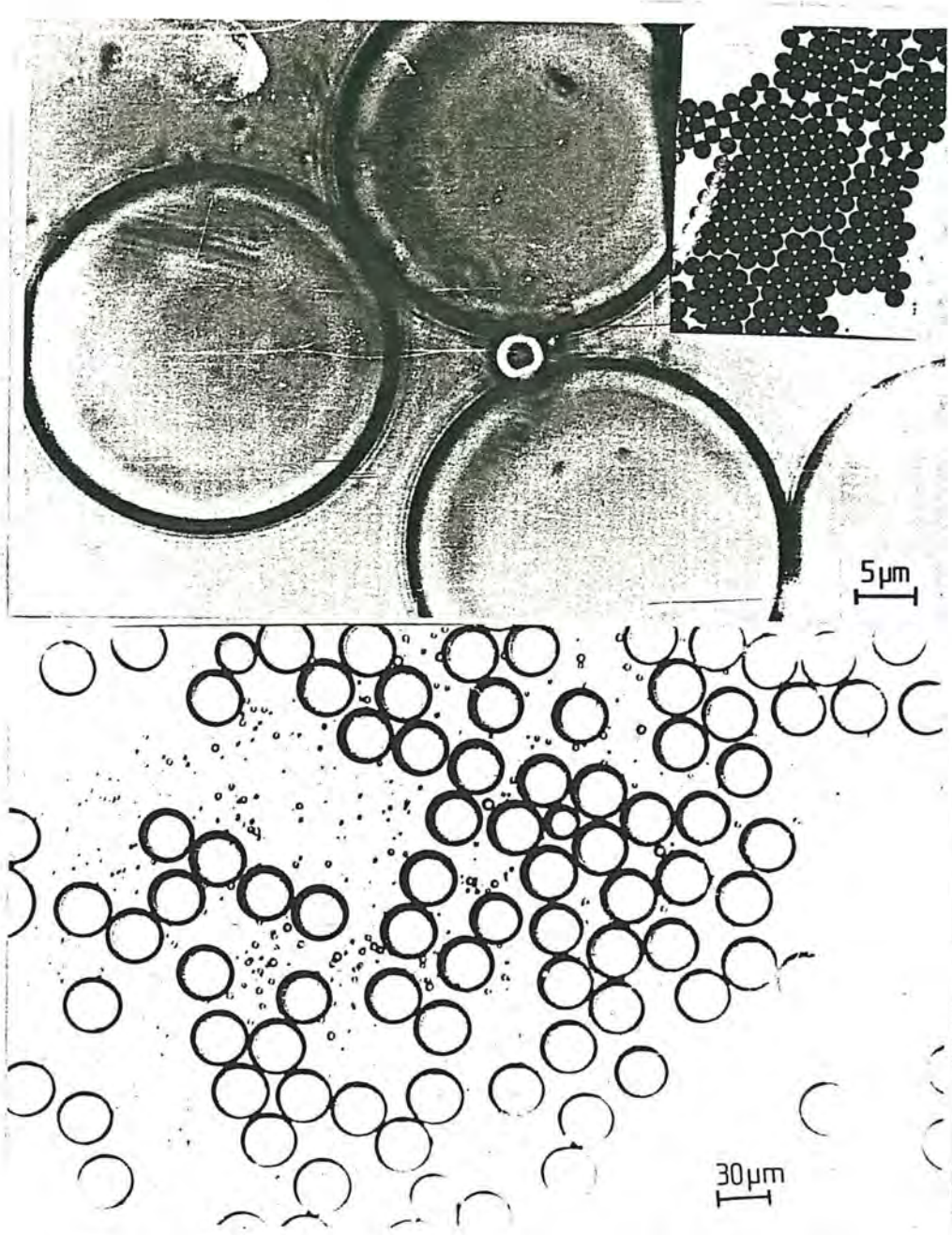


Fig.5.6.7: Optical micrograph of polystyrene - DOA particles in v/v ratio of polymer to oligomer of 1:2, swollen with ultraturraxed chlorobenzene V_1 to 30µm. The ratio of chlorobenzene to polymer - oligomer particles $V_1:V_2+V_3$ is 2500:1 (which is ~7500 times the volume of the original polystyrene particles). The stirring rate used is 140 r.p.m. at a temp. 308K using 2.5g NaLS/dm^3H_2O. The lower picture shows the 30µm particles at a lower scale, to show the monodispersity. The original polystyrene seed is shown on the upper right corner (d_3 = 1,61µm).

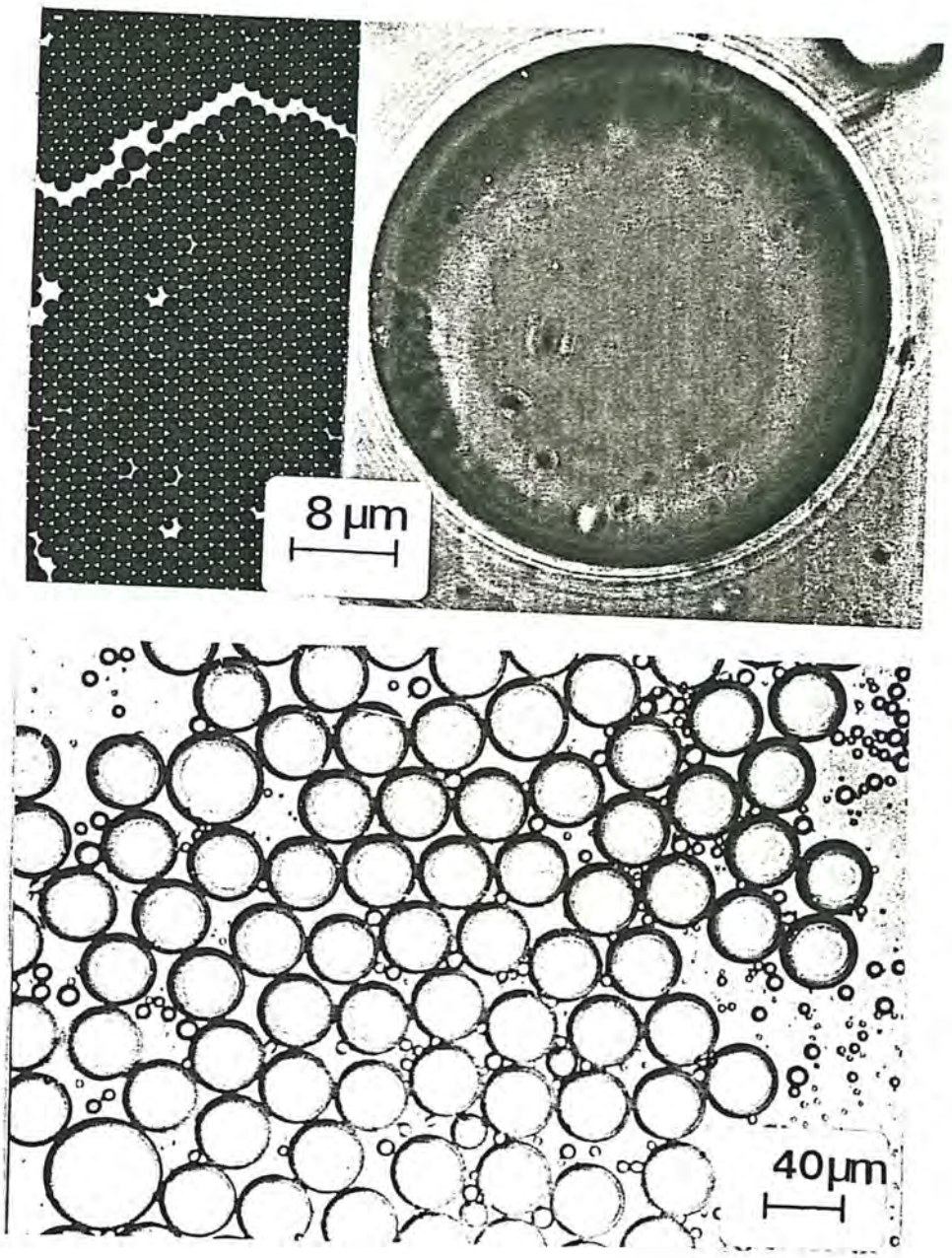


Fig.5.6.8:Optical micrograph of polystyrene - DOA particles in v/v ratio of polymer to oligomer of 1:2, swollen with ultraturraxed chlorobenzene V_1 to 40µm. The ratio of chlorobenzene to polymer-oligomer particles, $V_1:V_2+V_3$ is 4800:1 (i.e ~ 15,000 times the volume of the original polystyrene particles). The stirring rate used is 140 r.p.m. at a temp. 308K using 4.0g NaLS/dm^3H_2O. The lower picture shows the 40µm particles at a lower scale to show the monodispersity. The original polystyrene seed is shown on the upper left corner.

It should also be noted that the fact that the absorption in cases without subdivision of compound 1 by ultraturrax treatment reduces the rate of swelling, is as discussed earlier in accordance with the theory for the rate of swelling as expressed by Eqn. 2.4.9. Generally the equilibrium swelling is given by

$$\frac{\Delta\bar{G}_1}{RT} = \ln\phi_1 + (1-\frac{1}{j_2})\phi_2 + (1-\frac{1}{j_3})\phi_3 + \phi_2\phi_3$$

$$(\chi_{12}+\chi_{13}-\chi_{23}/j_2) + \frac{2V_{1M}\gamma}{rRT} - \frac{2V_{1M}\gamma}{r_dRT}$$

r ans r_d are the radius of particles and droplets of 1 respectively. Usually I have set the expression on the left hand side of the equation equal to zero. The last expression on the right hand side of the above equation takes into account the fact that the subdivision of compound 1 would lead to an increase in free energy of compound 1 and hence lead to a larger equilibrium swelling. The droplet size of compound 1 after ultraturrax is between 0.5-20 μm, most being between 5-7 μm, and is comparable to the size of the particles after a certain degree of swelling. As long as $r_d \leqq r$, one would, when we have reasonable values of interaction energy parameters expect that the particles might swell infinitely.
A quantitative discussion of the effect of subdivision of compound 1 based upon the experiments is difficult because the droplets of compound 1 increases during the experiment as they are unstable and may degrade by coalescence and diffusion processes among themselves.

As seen from the results after prolonged swelling times, one without ultraturrax achieve a lower equilibrium value for the amount of compound 1 absorbed. A possible explanation

may be that there is desorption of compound 2 out of the particles. Without ultraturrax treatment of compound 1 the rate of swelling after some time becomes very slow, so slow that there is time for transport of some of compound 2 out of the particles to be mixed with unabsorbed compound 1. This in turn decreases both the equilibrium swelling and the rate of further swelling.

5.7 COMPETITIVE SWELLING.

As described in theoretical part, section 2.4 part (c), we would expect if in one and the same exiperiment we have two different types of particles, different in the way that they have different size, or contain different amounts of compound 2, it will be expected that the particles will compete for the compound I e.g. chlorobenzene, added. If we have chlorobenzene in excess the swelling of each type could be calculated independently. If we have a limited amount of chlorobenzene-yhe swellong of the particles would, as described in the theoretical part be determined by the condition that at equilbrium the partial free energy of chlorobenzene in the different particles a and b should be equal i.e. $\Delta\overline{G}_{ia} = \Delta\overline{G}_{ib}$. Experiments were carried out to verify the theoretical calculation.

Table 5.7A shows comparison of expected and calculated swelling diameters. In this series of experiments the starting polystyrene seed was the same. In each series of experiments the starting polystyrene seed was the same. In each, particles a and b with different amounts of DOA were swollen with chlorobenzene and the final diameter of the two types of particles after swelling were measured. In the tables, is given the ratio between compound 2 and 3 in the particles a and b and the ratio V_I/V_3 i.e. the ratio between the volume of chlorobenzene added and the total amount of polystyrene V_3 added, where $V_3 = V_{3a} + V_{3b}$. the compound I was added as a bulk.

	Composition	V_1/V_3	Experimental da/µm	Experimental db/µm	Calculated da/µm	Calculated db/µm
A	$V_{2a} = V_{3a}$ $V_{2b} = 2V_3b$	200	7.10	9.10	7.20	9.30
		750	10.30	13.50	10.90	14.00
		1700	11.80	15.80	14.20	18.20
B	$V_{2a} = 1/9\ V_{3a}$ $V_{2b} = 2V_{3b}$	200	4.1	9.5	3.7	10.0

Table 5.7A: Comparison of experimental and calculated swelling diameter in a competitive swelling. 1 = chlorobenzane, 2 = dioclytadipate, 3 = polystyrene, $d_3 = 1.4\mu m$, $V_{3a} = V_{3b} = 0.5V_3$

It appears that there is very good agreement between experimental and theoretical values of the "final" diameters of the two particles up to moderate amount of monomer added, expressed as V_I/V_3. At high values of V_I/V_3, the relative degree of swelling is still in accordance with theory while the absolute swelling of each type of particles is less than the theoretical value. This is what may be expected in view of the discussion given above (Section 5.3) i.e. the slow rate of swelling as we approach the equilbriumswelling especially in the case where we use chlorobenzene which is not subdivided.
The same excellent agreement between the experimental and calculated diameters (shown in A-3) in competitive swelling of particles is shown in Table 5.7B. In this case we started with polystyrene seeds with different size which were swollen with the same v/v ratio of compound 2 (I:I) before being mixed and used in the swelling experiment

V_1/V_3	Experimental		Calculated	
	d_a/µm	d_b/µm	d_a/µm	d_b/µm
250	2.9	9.7	3.0	9.2
470	3.7	11.8	3.7	11.5
560	3.6	12.5	3.8	12.2
750	3.9	13.0	4.2	13.6

Table 5.7B Comparison of experimental and calculated swelling diameter in a competitive swelling. 1 = chlorobenzene, 2 = dioetyladipate, 3 = polystyrene. $V_{3a} = V_{3b} = 0.5V_3$, T = 308K. The staring diameters of polystyrene seeds, $da_o = 0.5$µm, $d_{bo} = 1.4$µm.

The following tables, 5.7C, 5.7D, and 5.7E describe in more detail the results of competitive swellings as a function of time under different conditions. The values of d_a/d_{ao} and d_b/d_{bo} may be taken as a measure for the rate of swelling. Note that d_{ao} and d_{bo} are the diameter of the particles after swelling with compound 2. Table 5.7C give results where we have out with two polystyrene seeds with different particle size but with the same V_2/V_3 ratio and therefore correspond to Table 5.7B.

It will appear from the results given in Tables 5.7A and 5.7B that the ratio of swelling capacity between particles b with the largest swelling capacity and the particles a increases with increasing amount of chlorobenzene added. It should of course as an upper limit reach a value which would be the one obtained if so much chlorobenzene was added that we got maximum swelling of each type of particles. As an example of this may look upon the results given in Table 5.7B. In this case we have a value of $\gamma = 4 \times 10^{-3}$ N/m,
and a value of $d_{oa} = 6.3 \times 10^{-7}$ m, $d_{ob} = 1.76 \times 10^{-6}$ m.
This gives $\gamma/r_{oa} = 4.1$, and $\gamma/r_{ob} = 3.66$.
From eqn. 2.4.4 we calculated that the ratio S,

$$S = \frac{V_{1b}/V_{2b}+V_{3b}}{V_{1a}/V_{2a}+V_{3a}} = 4.$$

The values of S from Table 5.7B and at different values of V_1/V_3 are as follows,

V_1/V_3	Experimental S	Calculated S
250	1.72	1.32
470	1.49	1.38
560	1.92	1.52
750	1.70	1.58

The experimental values vary a little, but within experimental error. In the case of the experiment in Table 5.7A case A the difference in the swelling ratio between the two types of particles is expected to be at maximum value i.e. S = 1.6 and therefore the increase in swelling with increasing values of chlorobenzene is not easily observed.

time/hr	d_a/d_{ao}	d_b/d_{bo}	$V_a/\mu m^3$	$V_b/\mu m^3$
0.00	I.0	I.0	0.I3	2.85
1.91	4.3	4.68	10.5	291.9
18.83	5.7	6.60	24.3	816.8
23.00	5.91	6.87	27.2	927.4
25.50	5.91	6.94	27.2	950.9
28.00	5.91	7.01	27.2	974.3
43.25	6.04	7.16	28.9	1047.2
48.00	6.04	7.39	28.9	1147.7
66.00	6.13	7.31	30.2	1113.4

Table 5.7C. Variation of relative diameters ,and volumes, V's of swelling two kinds of polystyrene-DOA particles (V_2/V_3 of I:I) together. The starting diameters were d_{oa} =0.63μm and d_{ob} = I.76μm for a and b particles. The rotio of chlorobenzene to the total amount of polystyrene in a and b particles is $V_I:V_{3a}+V_{3b}$ of 746:I, using 4g NaLS/dm^3 water. the stirring rate used was 250 r.p.m.,at a temperature of 308K.

The results of Table 5.7C are plotted in fig. 5.7.I showing variation of relative diameters with time. Variation of log. volume of particles with time is shown in A-2.

It appears from Table 5.7C and from fig. 5.7.I that the rate of increase of relative diameters of the two particles is very fast in the beginning. As the swelling continues, the rate is faster for b particles than a particles. The b particles are bigger than a particles. As was discussed earlier this is expected since the fact that the swelling capacity for b particles is bigger than for a particles, also involves a higher rate of swelling. This is because the driving force $\Delta\bar{G}/RT$, is bigger for smaller γ/r_o ratio. (fig. 5 in the theoretical part.)

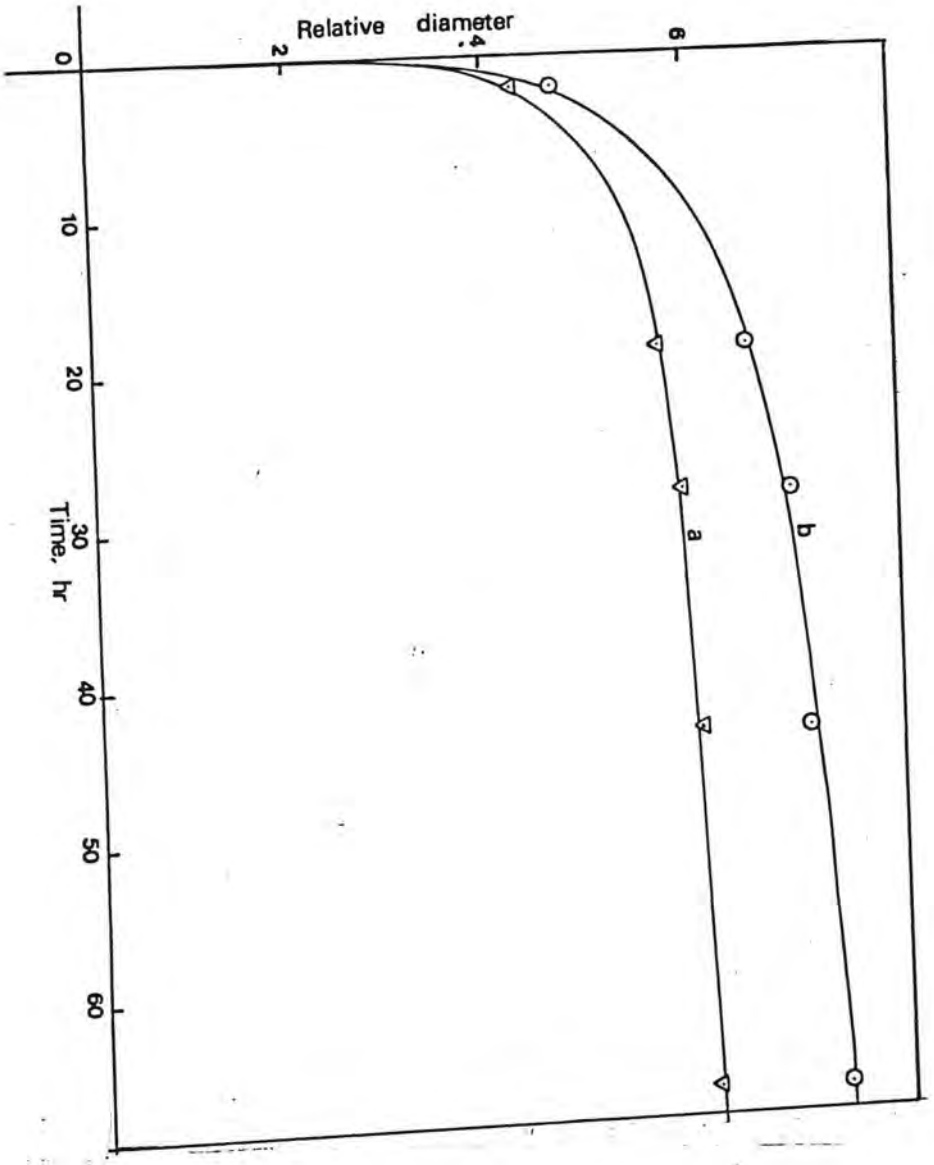


Fig.5.7.1 Variation of relative diameter with time for two kinds of particles swollen competitively. The polystyrene - DOA particles were both swollen in v/v ratio of 1:1. The starting diameters of polystyrene-DOA particles is 0.63μm and 1.76μm for a and b particles respectively. The ratio of the chlorobenzene V_1, to the total amount of polystyrene in a and b particles, $V_1 : V_{3a}+V_{3b}$ is 746:1, using 4g NaLS/dm^3 H_2O at a stirring rate 250 r.p.m., temp 308K. The volume of polystyrene used is $V_{3a} = V_{3b} = 0.67 cm^3/dm^3$ H_2O.

Fig. 5.7.2 shows the optical micrograph of the particles discussed above.

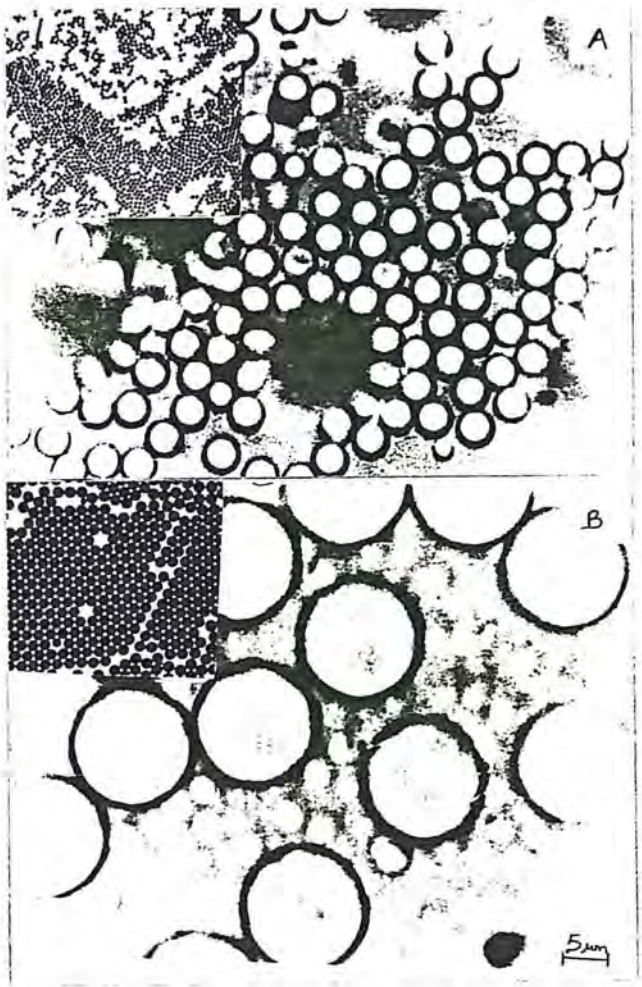


Fig.5.7.2 Optical micrograph of polystyrene-DOA particles swollen competitively, polystyrene-DOA particles in v/v ratio V_3 : V_2 of 1:1 in both kinds, where A particles has starting diameter d_{oa} = 0.63μm while B particles d_{ob} = 1.76μm. The ratio of chlorobenzene, V_1 to the total amount of polystyrene V_1: V_{3a} + V_{3b} is 746:1, using 4g NaLS/dm^3 H_2O, at 308K, stirring rate 250 r.p.m. The original polystyrene seed are shown in the upper left corner of each particles, A, d_3 = 0.5μm, B, d_3 = 1.4μm.

time/hr	d_a/d_{oa}	d_b/d_{ob}	$V_a/\mu m^3$	$V_b/\mu m^3$
2.50	2.84	4.37	36.4	237.9
4.42	3.03	5.23	44.4	408.8
6.25	3.60	5.47	74.6	466.2
32.25	3.60	6.40	74.6	749.4

Table 5.7D: Variation of relative diameter and volume with time of swelling polystyrene-DOA particles in v/v ratio of $V_3:V_2$ of 9:1 for a particles, d_{oa} = 1.45μm and 1:1 for b particles, d_{ob} = 1.76μm. The starting polystyrene seed, d_3 = 1.4μm was the same. The particles were competitively swollen with chlorobenzene V_1 in the ratio $V_1 : V_{3a} + V_{3b}$ of 200:1. The volume of polystyrene used is 2.5 cm^3/dm^3 H_2O of each. The emulsifier used is 0.95g NaLS/ dm^3 H_2O at 308K, stirring rate of 250 r.p.m.

The results of table 5.7D are plotted in fig.5.7.3 variation of relative diameter with time and volume variation with time is shown in appendix A-2.

As already discussed above, the rate is faster for the b particles which are bigger. Also the values of V_2 are different, setting $V_2 + V_3 = I$, we have for the b particles $V_2 = 0.5$, for a particles $V_2 = 0.I$. As discussed in section 5.5, the swelling capacity, and hence the rate is faster when V_2 is bigger.

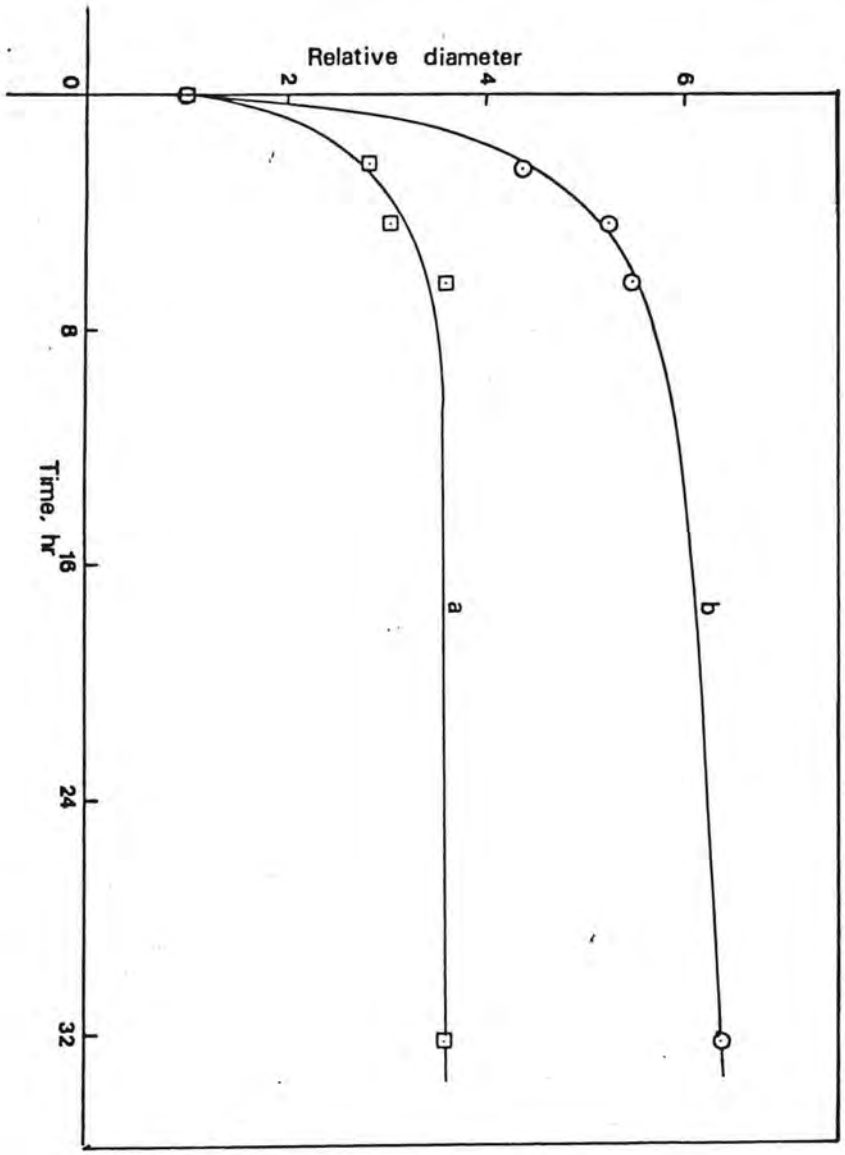


Fig. 5.7.3 Variation of relative diameter with time of swelling polystyrene-DOA particles in v/v ratio of 9:I for a particles, curve a, d_{oa} = I.45μm and the ratio of I:I for b particles, curve b, d_{ob} = I.76μm. The particles were competitively swollen with chlorobennene, V_I, in the ratio $V_I : V_{3a} + V_{3b}$ of 200:I. Experimental conditions are shown in Table 5.7D.

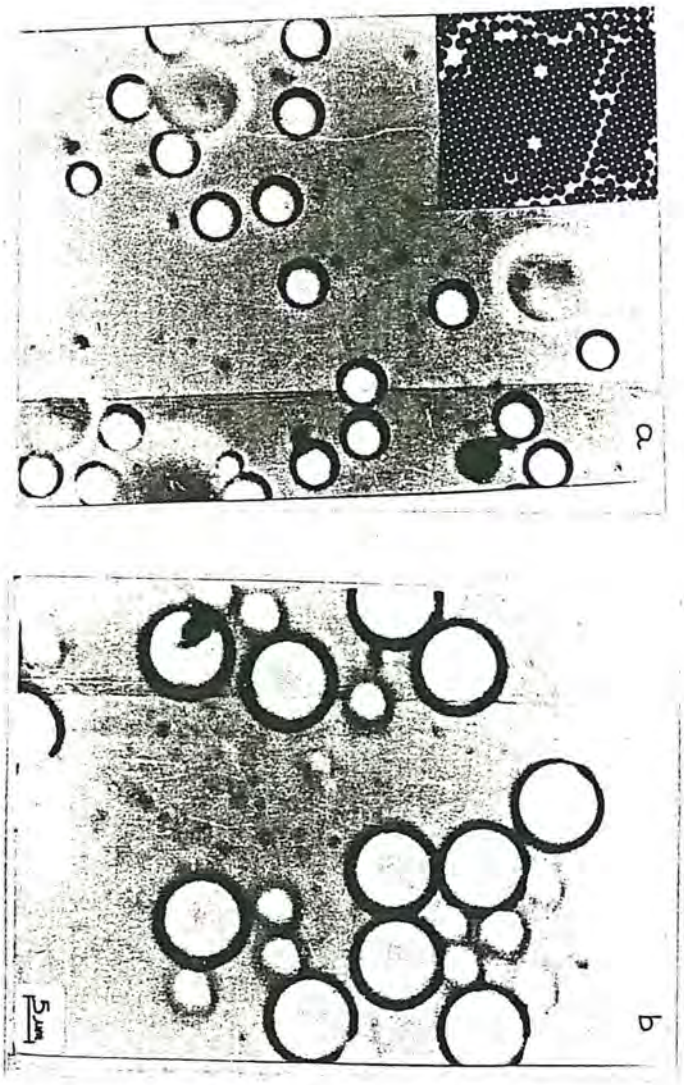


Fig. 5.7.4. Optical micrograph of particles swollen competitively where the polystyrene-DOA ratio is 9:I for a particles and I:I for b particles. The chlorobenzene, V_I, is added in the ratio V_I : V_{3a} + V_{3b} of 200:I. Experimental conditions corresponds to those given in Table 5.7D. The original polystyrene seed with d_3 = I.4μm is shown in the upper left corner.

Table 5.7E and figures 5.7.5 and 5.7.6 shows the results of swelling competitively polystyrene-DOA particles where a particles are swollen in a ratio V_2:V_3 of I:I, while for b particles the ratio is 2:I with chlorobenzene V_I in a ratio V_I:V_{3a} + V_{3b} of 755:I.

time/hr	d_a/d_{oa}	d_b/d_{ob}	$V_a/\mu m^3$	$V_b/\mu m^3$
1.17	4.67	5.25	290.7	606.5
2.43	5.40	6.24	450.3	1018.3
6.00	5.70	6.66	527.8	1239.0
29.00	5.88	6.75	580.6	1286.0
52.20	5.88	6.75	580.6	1286.0

Table 5.7E: Variation of volume and relative diameter with time of swelling polystyrene-DOA particles in v/v ratio $V_3:V_2$ of 1:1, d_{oa} = 1.76μm and 1:2, d_{ob} = 2.0μm for a and b particles respectively, with chlorobenzene V_1 in a ratio $V_1:V_{3a} + V_{3b}$ of 755:1, using 15.9g NaLS/dm^3 H_2O at a stirring rate of 250 r.p.m, temp.308K. The volume of polystyrene used 2.65cm^3/dm^3 H_2O for each.

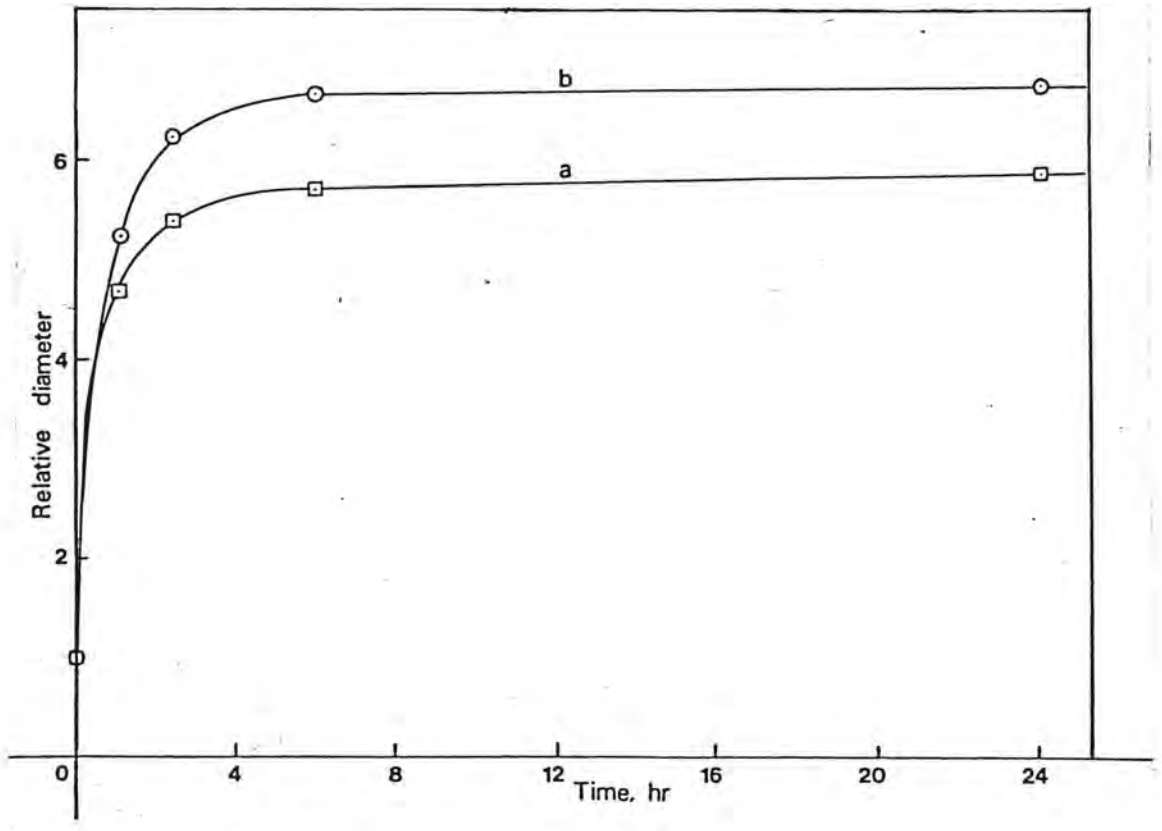


Fig.5.7.5 Variation of relative diameter with time of polystyrene-DOA particles in v/v ratio $V_3:V_2$ of 1:1 for a particles, curve a, d_{oa} = 1.76μm and 1:2 for b particles, curve b, d_{ob} = 2.0μm. The paritcles were competitively swollen with chlorobenzene, V_1 in a ratio V_1: V_{3a}+ V_{3b} of 755:1. Experimental conditions are the same as those in table 5.7E.

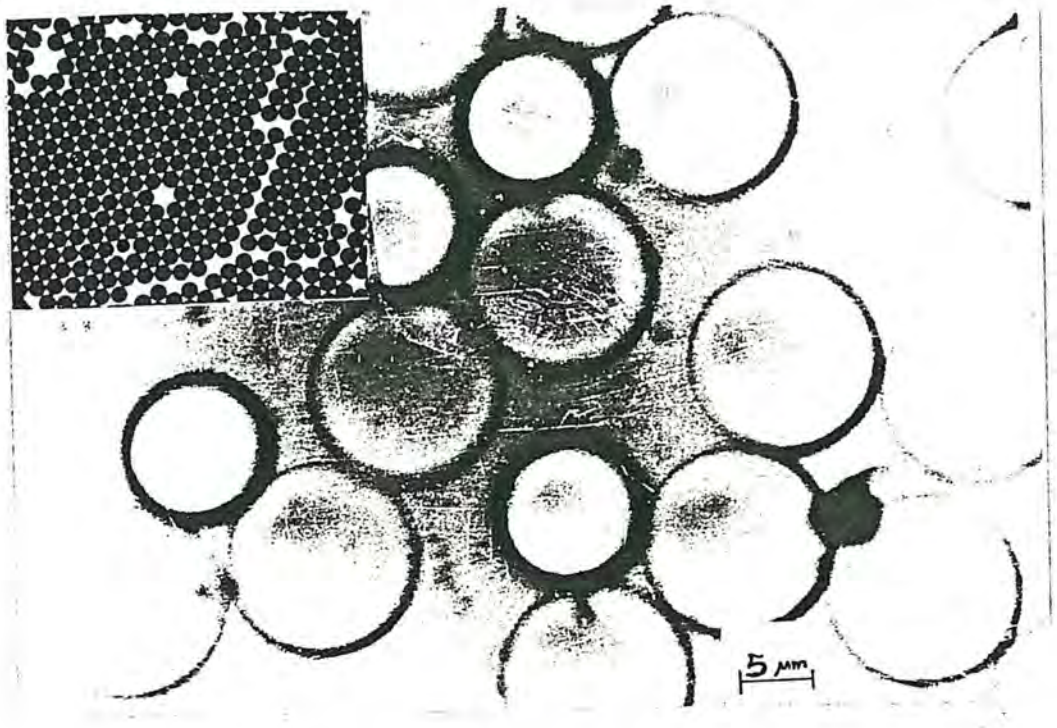


Fig.5.7.6 Optical micrograph of particles swollen competitively with chlorobenzene, V_1. The polystyrene-DOA ratio for a particles is 1:1, hence d_{oa} = 1.76µm, b particles 1:2, d_{ob} = 2.0µ. The particles are swollen in a ratio $V_1 : V_{3a} + V_{3b}$ of 755:1. Experimental conditions correspond to those on table 5.7E. The original polystyrene seed, (d_3 = 1.4µm) is shown on the upper left corner.

It is also seen that the larger particles swell at a higher rate than the smaller particles. Teh equilbrium swelling capacity (as calculated from fig.4 in theory), of a particles with d_{oa} = 1.76 is 5925, while for b particles, d_{ob} = 2.0µm it is 10.000.

The above results of swelling by competition are summarized below.

	$d_3/\mu m$	$V_3:V_2$	S.C	Fig. No.
I	0.5	1:1	1250	5.7.1
	1.4	1:1	5.925	5.7.3
II	1.4	9:1	650	5.7.3
	1.4	1:1	5.925	
III	1.4	1:1	5.925	
	1.4	1:2	10.000	5.7.5

Table 5.7F: Summary of results of 3 competitive swelling experiments discussed above, where d_3 is the starting polystyrene seed diameter, the polystyrene-DOA ratio is $V_3:V_2$, S.C. is the equilbrium swelling capacity as calculated from fig.4.

In all the above pairs, the one with smaller swelling capacity has a lower rate. In I, the S.C. of the bigger particles is ~ 5 times that of smaller particles. In II it is 10 times while in III it is ~ 2 times. This can be analysed from figures 5.7.1 for I, 5.7.3 for II, and 5.7.5 for III, using the same scale, the difference kinds of particles followers the order, III < I < II in relative diameter of the two. Meanwhile the difference in the volume absorbed between the two kinds of particles depends on the difference in starting diameters of the particles (A-2). It was also noted that while II and III above, the diameters of the swollen particles competitively did not change much after about standing for 6½ months, there was diffusion from the small to big particles in case I. This is expected because of diffusion of DOA from small to big particles is greater the bigger the difference in size. Section 2.2 part d, from eqns 2.217 and 2.2.18. It is noted that the diameters reached for polystyrene - DOA particles (v/v ratio 1:1 in both kinds) with d_{oa} = 0.63 and d_{ob} = 1.76μm, was 12.86μm corresponding to using 519 cm^3 chlorobenzene, V_1 for 'b' particles and 3.86μm, corresponding to using 308 cm^3 v_1 for a particles, hence total amount of V_1 is 827 cm^3, and the total amount of V_1 added was 1000cm^3.

After 6½ months, the sizes were 15.23μm, corresponding to using 862cm^3 V_1 for b particles, and 0.5μm ~ 1.0μm, corresponding to a volume V_1 of 0.7 ~ 5.4cm^3. Henche the total amount used is ~ 867cm^3 of the 1000cm^3 added. Another possibility could be due to more DOA left in the small particles for case I, than II and III. But from calculation of the amount of DOA left in both cases it was almost the same e.g for the 0.63μm particles in I, the volume of one particle is 0.131μm^3, and after swelling to 3.86μm, the volume is 30.1μm^3. Since the DOA before swelling was 50%, after swelling it was $\frac{0.131}{30.1} \times 50 = 0.22\%$.

5.8 HIGH OIL/WATER CONTENT

High o/w emulsion has been prepared with 70-87% o/w. Polystyrene-DOA particles (v/v ratio V_3:V_2 of 1:2) were swollen 133-400 times with chlorobenzene. The diameter of PS-DOA particles was 2.0μm. The results are shown in table 5.8. Since the viscosity was high, low stirring rate was used.

	time/hr	diameter/μm	volume/μm
	1.33	9.13	397.9
I	2.58	9.43	439.8
	5.00	9.48	446.1
	5.25	Add chlorobenzene	to 80% o/w
II	6.25	10.20	550.8
	6.58	10.33	578.0
	7.75	10.39	586.4
	7.83	Add chlorobenzene	to 85% o/w
III	8.92	11.82	862.9
	9.17	Add chlorobenzene	to 90% o/w
IV	9.58	12.64	1056.8
	10.92	13.74	1357.2

Table 5.8: Variation of diameter and volume with time of polystyrene-DOA particles v/v ratio of 1:2, (d_o=2.0μm) swollen with chlorobenzene V_1, in the ratio V_1: V_2 + V_3 of 133:1, 178:1, 252:1 and 400:1 for I, II, III, and IV respectively. The emulsifier used is 23g NaLS/dm^3 H_2O, at temp.308K. The volume of polystyrene used is 7.5cm^3/dm^3 H_2O.

The above results are shown in fig.5.8.1 and 5.8.2.

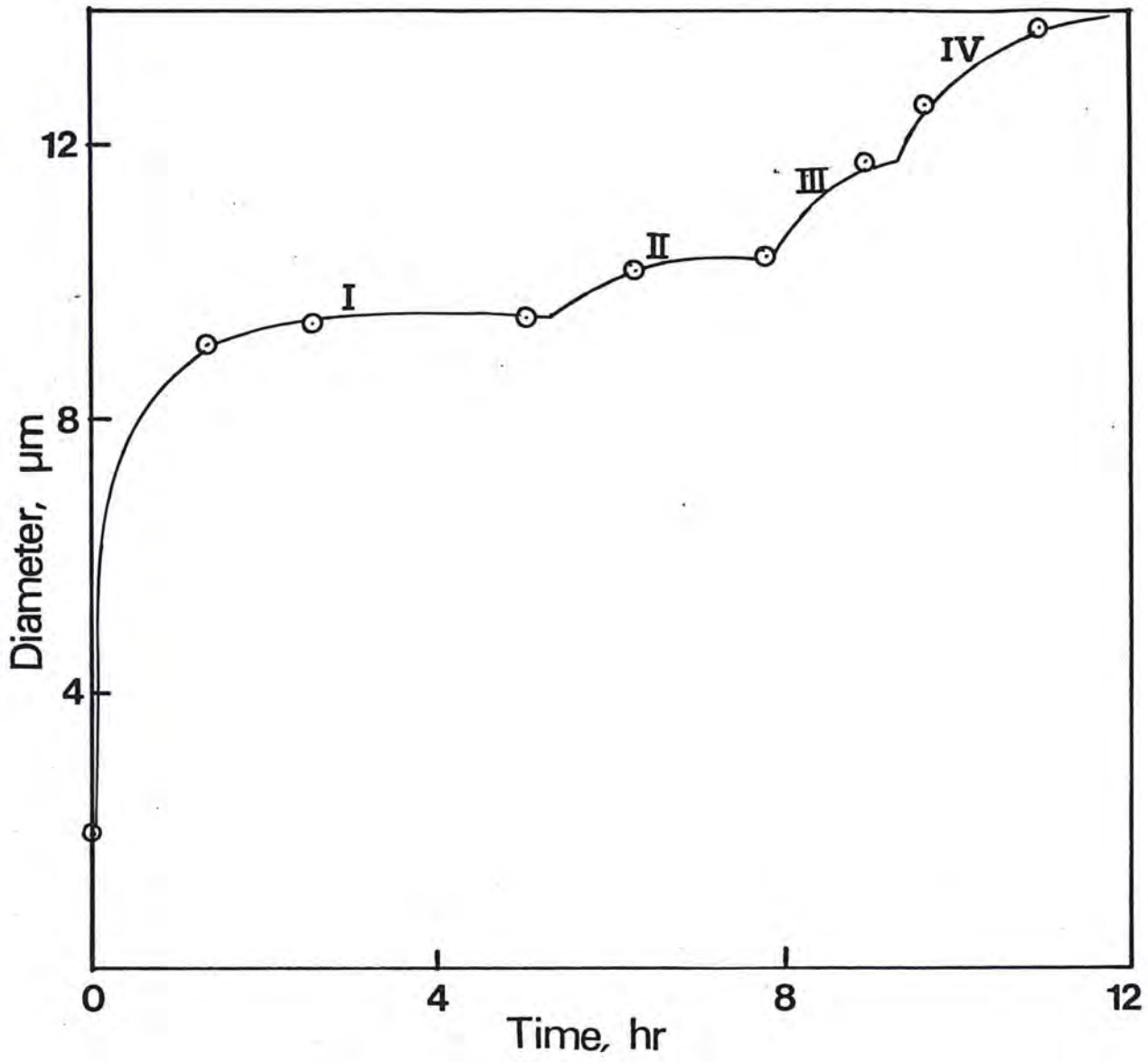


Fig.5.8.1: Variation of diameter with time for polystyrene-DOA particles in v/v ratio $V_3:V_2$ of 1:2, d_o = 2.0µm swollen with chlorobenzene V_1 to high oil content in the ratios $V_1:V_2+V_3$ of 133:1, 178:1, 252:1 and 400:1 corresponding to % oil of 70%, 75%, 82% and 87% respectively for I, II, III, and IV respectively. Experimental conditions are shown on table 5.8.

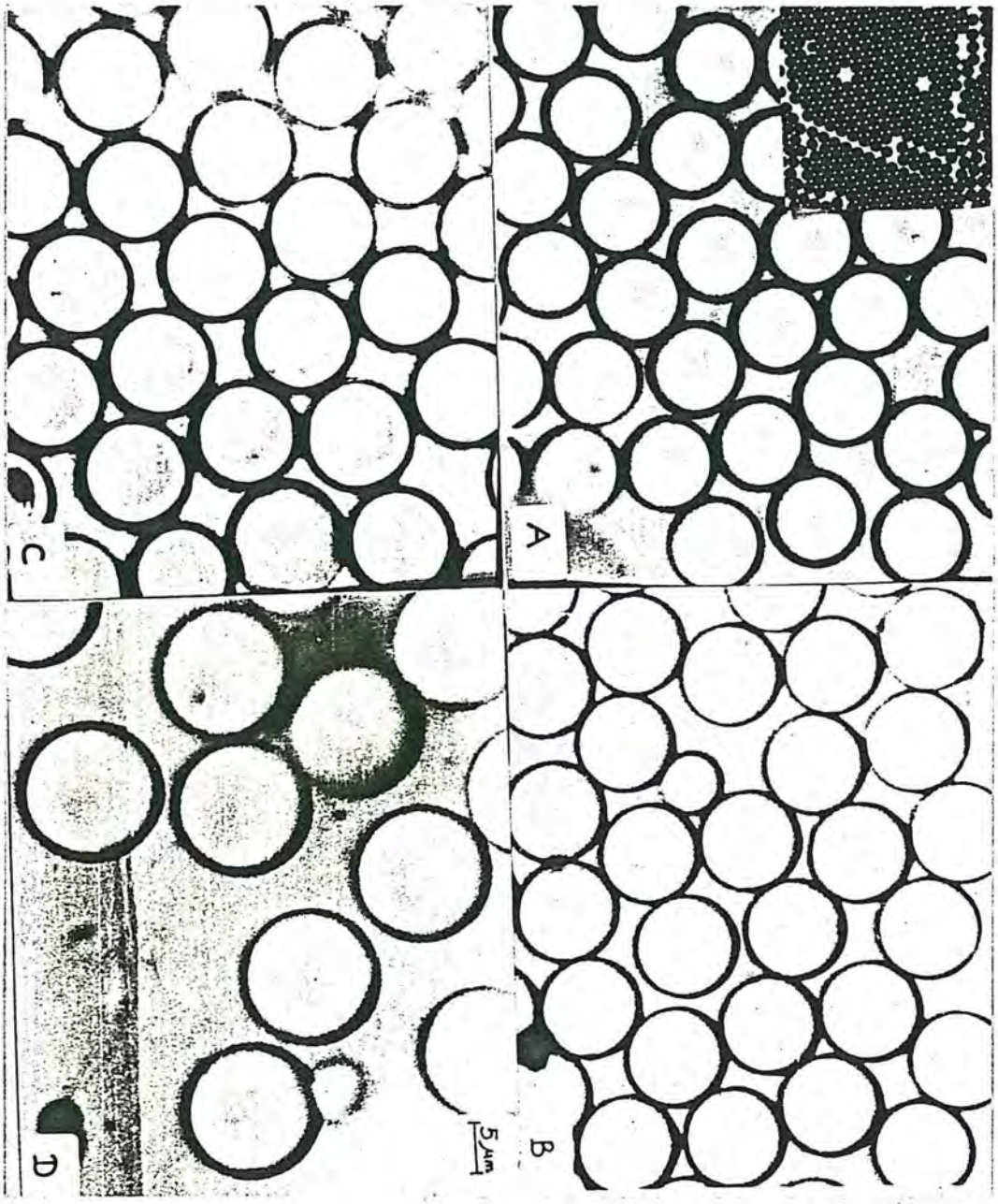


Fig.5.8.2: Optical micrograph of polystyrene-DOA particles (v/v ratio 1:2) swollen to high o/w content with chlorobenzene. The ratios of chlorobenzene to polystyrene-DOA are 133.1 corresponding to 70% o/w for A, 178:1, corresponding 75% o/w for B, 252:1 corresponding to 82% o/w for C and 400:1 corresponding to 87% o/w for D. The samples were with water before looking in the microscope. The emulsifier used is 23g NaLS/dm^3 H_2O at temp of. 308K.

From the volume of chlorobenzene added, the expected percentage o/w was 90%, but managed to reach 87%. This was discussed earlier as that swelling increases the rate becomes very low and hence the absorption of the chlorobenzene becomes very, very slow, (since it can remain constant for about 48 hrs. etc) unless chlorobenzene is added in droplets (section 5.6).

After standing a sample for ~ 6 2/3 months, the diameter changed to ~ 11.77μm corresponding to 82% o/w.

5.9 DIFFUSION EXPERIMENTS

The rate of diffusion of chlorobenzene from polystyrene-DOA particles ((v/v ratio of 1:2) swollen with chlorobenzene, V_1 to ~ 8.0μm.) to polystyrene-DOA particles alone, was very fast. Even when the diffusion process was done under very low speed using a magnetic stirrer, the diffusion was over after 1 minute only.

The following are results of diffusion experiments. Polystyrene-DOA particles (v/v ratio of 1:2, d_o = 2.2μm) were swollen with chlorobenzene V_1 to 8.2μm. These are A particles. B particles are the polystyrene-DOA particles not swollen with chlorobenzene. The emulsion was 9% o/w so that is is dilute enough for the distance between the two kinds of particles to be much larger than the radius of the swollen particle.

The number of particles was the same i.e $N_A = N_B$, hence expected dimeter

$$d = \left(\frac{d_A^3 + d_B^3}{2}\right)^{1/3} = 6.55\mu m$$

Experimental value of diameter was ~ 6,4μm

Several attemts were made in order to slow the rate of diffusion from one particle type to the other.

(i) The number of B particles was made twice the number of A particles. This did not effect the rate to the degree that it would be experimentally observed.

(ii) Very small amounts of cetyl alcohol (heated to 70°C) was added. Amounts of cetyl alcohol added was just enough to cover the particles, so as to form a mechanical barrier and it was calculated to be ∿ 0.1 g COH/dm^3 H_2O. To avoid solubilisation of the COH in the NaLS micelles, the emulsifier was added just below its critical micelle concentration. When the alcohol was added to the A particles, many small particles ∿ 0.5 µm were formed, hence the alcohol was drawing chlorobenzene out of the particles rather than form a layer around the particles to reduce diffusion rate. When the alcohol was added to the small particles B, no particles ∿ 0.5 µm were formed, but the alcohol was seen in the microscope in its crystal form, hence it did not form a layer in this case. Alcohol was stirred for 15 minutes before the other kind of particles was added.

(iii) The amount of alcohol was increased to 1.3 g COH/dm^3 H_2O.

(iv) The time of stirring the alcohol with one kind of particles was increased to about 12 hours.

None of the experiments with COH did lead to any observable change in the rate of diffusion.

The results given above with the high rate of equilibrium by the chlorobenzene between the A and B particles is in agreement with the previously discussed effect of subdivision of chlorobenzene droplets (Section 5.6). The chlorobenzene is in this case distributed to a large number of particles with a very high total surface.

The fact that the rate of transport of chlorobenzene from A to B particles is so high also supports an assumption that tran-

sport within the polymer-oligomer particles even at start is not seriously hindered by the relative high viscosity in these particles.

6. CONCLUSIONS

The present study has confirmed that the swelling capacity of aqueous dispersions of particles containing polymer molecules with a slightly water soluble compound 1, e.g. chlorobenzene, increases drastically if the particles in addition to polymer molecules contain some oligomer molecules of relatively low molecular weight. The degree of swelling obtained agrees well with what would be predicted by equation 2.4.4 which is a combination and a modification of the Flory-Huggins equation and the Morton equation of swelling setting the partial molar volume of mixing of compound 1, $\Delta\bar{G}_1$, equal to zero. Previous studies indicated that even if the swelling capacity of the particles increased drastically due to the presence of the oligomer molecules, the swelling capacity did not by far reach the swelling predicted from theory.

The increased swelling capacity of polymer-oligomer particles obtained in the present work may be due to two effects which are to some degree connected. First, the increased swelling capacity as compared to previous work was obtained in cases where compound 1 was subdivided. It is shown that this may in principle lead to a much higher value of the equilibrium swelling with compound 1. Furthermore, it seems that one in previous studies and as was in the beginning of this study, were not sufficinetly aware of the importance of the kinetics of swelling and have worked with conditions when the rate of swelling as the swelling proceeded has become so reduced that one has not by far reached equilibrium swelling within reasonable time. The prolonged swelling time necessary when compound 1 is added as a bulk, may have lead to that some of the oligomer, compound 2, may get time to desorb from the particles, which in turn leads to a decrease in swelling capacity and rate of swelling.

Therefore it became evident as the present work proceeded that emphasis, both theoretical and practical should be given

to the kinetics of the swelling procedure.

From the present study one can conclude that the most important factor in determining the rate of transport of slightly water soluble compound 1, e.g. chlorobenzene, through the aqueous phase to the polymer-oligomer particles is the degree of subdivision of 1. If the droplet size of compound 1 is sufficiently small, the rate depends on the number and radius of the polymer particles. On the other hand, when 1 is added as a bulk phase, the rate is very low and depends on the number and radius of droplets of 1.

It was found that, when compound 1 was subdivided, particles up to 40 μm were obtained from polymer-oligomer particles of ∿ 2.5 μm with a v/v ratio of oligomer to polymer of 2:1 in a relatively short time. In cases where compound 1 was added as a bulk phase, the size reached with the same polymer-oligomer particles was ∿ 16 μm, even after moderate stirring for 72 hours.

The rate of swelling also depends on the stirring intensity, the rate being higher, the higher the stirring rate because the number of droplets of 1 formed is greater for higher stirring speed. On the other hand, a disadvantage of using faster stirring speed is the break-up of the particles.

It is also concluded that the swelling capacity depends on the amount of oligomer and the type of emulsifier used. These dependences was in accordance with theory. The larger amount of oligomer used, the better swelling. However, using low amounts of oligomer led to a surprisingly high degree of swelling as compared to the swelling reached when higher amounts of oligomer was used. It will be of great interest to do more work on the swelling using low amounts of oligomer.

The different emulsifiers have different interfacial tension γ, and the higher the γ, the lower was the swelling at otherwise equal conditions, as predicted by the theory.

It was also possible to make bidisperse emulsions by competitive swelling. A mixture of polymer seeds containing different amounts of oligomer were swollen with compound 1. Alternatively, one could start with seeds with different diameters, but with equal volume ratios of oligomers, and swell the mixture with compound 1. High o/w emulsion were also prepared, up to 87% o/w oil in water.

When polymer-oligomer particles already swollen with compound 1 were mixed with unswollen polymer-oligomer particles, the diffusion process was found to be very fast. The high rate is in agreement with the previously discussed effect of subdivision of the chlorobenzene droplets. The chlorobenzene is in this case distributed on a large number of particles with a very high total surface. Thus the rate of transport of chlorobenzene from the "reservoir" to the water phase would not be expected to be the rate determining step, as is the case if the chlorobenzene is only dispersed by ordinary stirring. This fact that the rate of transport is very high supports the assumption that transport within the polymer-oligomer particles even at start is not seriously hindered by the relative high viscosity in these particles.

REFERENCES

1. Becher, P., "Emulsions Theory and Practise", 2nd ed., p 2 Reinhold Publishing Corp. 1966.

2. Cobb, R.M.K., International Soc. of leather Trades chemistry, Emulsion technology, 2nd ed. p 10, Chemical Publ. Co., Inc. Brooklyn 1946.

3. Sherman, P., "Emulsion Science." p 4, Academic Press Inc. London, 1968.

4. Ibid 3, p.14-15.

5. Shaw D.J., "Introduction to Colloid and Surface Chemistry" 2nd.ed., p. 206. Butterworths London (1978).

6. Lissant, K.J., "Emulsions and Emulsion technology" Vol 6, pt.II p. 664, Marcel Dekker, Inc. 1974 N.Y.

7. Becher, P., "Emulsions Theory and Practise," 2nd ed., p.152-153 Reinhold Publ. Corp. 1966.

8. Howland, L.H. and Nisonoff, A., Ind.Eng.Chem., 46, p.2580 (1954)

9. Becher, P., "Emulsions Theory and Practise", 2nd ed., p 158-164, Reinhold Publ. Corp.1966.

10. Ibid 9, p. 172-178.

11. Sherman, P., "Emulsion Science". p.97, Academic Press Inc. London.

12. Shaw, D.J., "Introducton to Colloid and Surface Chemistry" 2nd.ed, p.169 Butterworths London 1978.

13. Ottewil, R.H., J. of Colloid and Interface Science, 58, No.2 p. 357 (1977)

14. Napper, D.H., Ibid 13, 58, No 2, p.390 (1977).

15. Napper, D.H., NATO advance Study institue: Polymer Colloids. Preprints, June 30 - July 11.,1975, University of Trondheim, NTH.

16. Higuchi, W.I., Misra, J., J. Pharm. Sci., 51, p.459 (1962).

17. Nielsen, A.E., J. Phys.Chem. 65, p.46 (1961)

18. Lewis, G.N., and Randall, M., "Thermodynamics", Revised by Pitzer K.S., and Brewer, L., 2nd ed., p. 483 McGraw Hill book Co., 1961.

19. Cowie, G.M.J., "Polymers: Chemsitry and Physics of Modern Materials" p.131 Billing and Sons Ltd. London (1973).

20. Denbigh, K., "The principles of chemical equilbrium" 3rd ed. p.247, Cambridge University Press 1966.

21. Flory, P.J., J. of Chem.Phys., 10, p.51-52 (1942).

22. Huggins M.L., J. of Am. Chem. Soc., 64, p.1712-1719 (1942)

23. Scatchard, G., Chem Rev. 8 p.321 (1931)

24. Harris F.W. and Seymour R.B., "Structure Solubility Relations in Polymers, p.112, Academic Press, N.Y. (1977).

25. Morton M. Kaizerman, S. Altier M.W., J.Colloid Sci.,9 p.300 (1954).

26. Gardon, J.L., J.Polym. Sci. A-1 6, p. 2859 (1968)

27. Ugelstad J., Makromol. Chem. 180 (1979)

28. Ugelstad, J., Kaggerud K.H., Hansen, F.K., Berge, A., Makromol Chem., 180 p.737, (1979).

29. Ugelstad, J., Kaggerud, K.H., Fitch, R.M., ACS meeting, Miami Beach 1979. Polymer Colloids, in press.

30. Ugelstad, J., Mørk, P.C., Kaggerud, K.H., Ellingsen, T., Berge, A., Advances in Colloid and Interface Sci. To be published.

31. Shaw, D.J., "Introduction to Colloid and Surface Chemistry" 2nd ed., p.21. Butterworths London-Boston (1978).

32. Becher, P., "Emulsions Theory and Practise," 2nd. ed., p.95, Reinhold Publ. Corp. 1966.

33. Serralach J.A., Jones, G., Ind.Engng Chem. 23, p 1016. (1931).

34. Ibid 33, 25, p.816 (1933)

35. Graham, D.E., Phillips M.C., "Theory and Practise of Emulsion technology" Symp. Brunel University, sept.16-18,1974, p.75-98.

36. Schulman, J.H., Cockbain E.G., "Trans.Faraday Soc." 36, p.651 (1940).

37. Tallman, F.A.J. et al. J.Pharm. Pharmac. 25, p.393 (1973)

38. Barry, B.W., Saunders G.M., J. Colloid and Interface Sci., 35, p.689-705 (1971)

39. Ibid 38, J4, p.300-315 (1970)

40. Barry B.W., J. Pharm. Pharmacol. 21, p.533-540. (1969)

41. Ibid 40, 25, p.393 (1973)

42. Davies, J.T., Haydon, A.D., Proc.Intern. Congr. Surface Activity 2nd, London 1, p.417 (1957)

43. Hallworth, G.W., Carless, E.J., "Theory and Practise of Emulsion technology" Symp. Brunel University, Sept.16.-18.-1974, p.305.

44. Davis, S.S., Smith, A., Ibid 43, p.325.

45. Hansen, F.K., Ofstad, B.E., Ugelstad, J., Ibid 44, p.13.

46. Ugelstad, J. Hansen, F.K., Lange, S., Macromol. Chem. 175 p.507-521, (1974)

47. Azad A.R.M., Ugelstad, J., Fitch R.M., Hansen, F.K., ACS symposium series 1, 24 p.1-23 (1976)

48. Private communications with Kari H. Kaggerud, SINTEF, Trondheim, Norway.

49. Friberg, Stig., "Food Emulsions" p.321 Marcel Dekker, Inc. New York 1976.

50. Harkins, W.D., J. Am.Chem. Soc. 69, p.1428 (1947) "Physical Chemistry of Surface films" Ch.5, Reinhold Publ. Corp. 1952.

51. Smith, W.V., Ewart, R.H., J. of Chem. phys., 16 No.6 p. 592 (1946).

52. Ugelstad, J., Mørk, P.C., Br. Polym. J., Vol.2, p.31-39 (1970)

53. Ugelstad, J., Mørk, P.C., Dahl, P. and Rangnes, P., J. Polym. Sci. C27, p.49 (1969).

54. Ugelstad, J., Mørk, P.C., Aasen, J. O., J.Polym. Sci., 5 (A1), p. 2281 (1967).

55. Matsumoto, T., Ochi, A., Kobunski Kagaku 22, p.481 (1965).

56. Goodwin, J.W., J. Hearn C.C.Ho, Ottewil R.H., Br.Polymer J.5, p. 347 (1973).

57. Goodwin, J.W., J. Hearn C.C.Ho, Ottewil R.H., Colloid and polymer Sci. 252, p. 464 (1974)

58. Hearn, J., Ottewil R.H., Shaw J.N., Br. Polymer J.2 p.116 (1970).

59. Goodwin, J.W., Chung-Li, Y., Ottewil, R.H., Progr. Colloid and Polymer Sci.60, p.163-175 (1976)

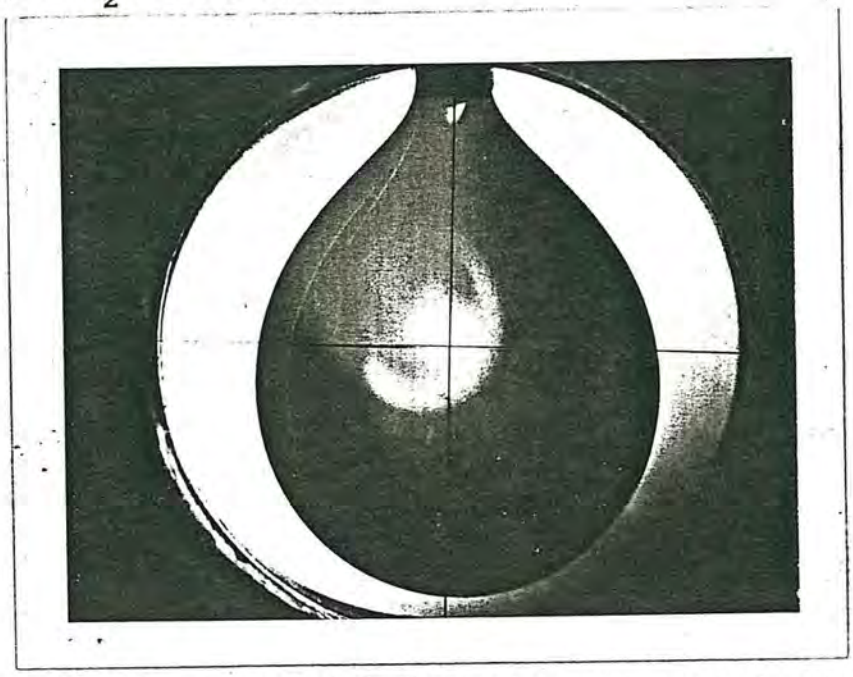
60. Report on large size monodisperse latexes as a commercial space product by Dale M. Kornfeld, Space Science Laboratory.

61. Adamson, W.A., "Physical Chemsitry of Surfaces," 2nd. ed. p.30, Interscience publ.1967.

62. Perry, H.J., "Chilton.,"Chemical Engineers Handbook" 5th Ed., p.3-230.

APPENDIX:

To find interfacial tension, γ by the pendant drop method. Below is picture of a drop of chlorobenzene into a 2·0g whey protein/$dm^3 H_2O$ solution



By measuring the equtorial diameter, de, and ds which is diameter measured a distance de up from the bottom of the drop, one can calculate γ.
Magnification of the contact gonimeter is 15·7.

$$S = \frac{ds}{de} \quad , \text{ where } de = \frac{de\,(\text{measured})}{15{\cdot}7}$$

γ can be calculated from equation,[61]

$$\gamma = \frac{\Delta\rho g de^2}{H} \quad \text{where}$$

g is gravitational constant, = 981 in dynes/g
$\Delta\rho$ is density difference between chlorobenzene and water in g/cm^3
H is correction factor found from tables A-1-1 of $\frac{1}{H}$ vs S below.
The density of chlorobenzene at different temperatures is found from,[62]

Table A-1·1

Numerical Tabulation of $1/H$ versus S Function for Calculation of Boundary Tensions by Pendant Drop Method
(Linear interpolation warranted)

S	0	1	2	3	4	5	6	7	8	9
0.30	7.09837	7.03966	6.98161	6.92421	6.86746	6.81135	6.75586	6.70099	6.64672	6.59306
0.31	6.53998	6.48748	6.43556	6.38421	6.33341	6.28317	6.23347	6.18431	6.13567	6.08756
0.32	6.03997	5.99288	5.94629	5.90019	5.85459	5.80946	5.76481	5.72063	5.67690	5.63364
0.33	5.59082	5.54845	5.50651	5.46501	5.42393	5.38327	5.34303	5.30320	5.26377	5.22474
0.34	5.18611	5.14786	5.11000	5.07252	5.03542	4.99868	4.96231	4.92629	4.89061	4.85527
0.35	4.82029	4.78564	4.75134	4.71737	4.68374	4.65043	4.61745	4.58479	4.55245	4.52042
0.36	4.48870	4.45729	4.42617	4.39536	4.36484	4.33461	4.30467	4.27501	4.24564	4.21654
0.37	4.18771	4.15916	4.13087	4.10285	4.07509	4.04759	4.02034	3.99334	3.96660	3.94010
0.38	3.91384	3.88786	3.86212	3.83661	3.81133	3.78627	3.76143	3.73682	3.71242	3.68824
0.39	3.66427	3.64051	3.61696	3.59362	3.57047	3.54752	3.52478	3.50223	3.47987	3.45770
0.40	3.43572	3.41393	3.39232	3.37089	3.34965	3.32858	3.30769	3.28698	3.26643	3.24606
0.41	3.22582	3.20576	3.18587	3.16614	3.14657	3.12717	3.10794	3.08886	3.06994	3.05118
0.42	3.03258	3.01413	2.99583	2.97769	2.95969	2.94184	2.92415	2.90659	2.88918	2.87192
0.43	2.85479	2.83781	2.82097	2.80426	2.78769	2.77125	2.75496	2.73880	2.72277	2.70687
0.44	2.69110	2.67545	2.65992	2.64452	2.62924	2.61408	2.59904	2.58412	2.56932	2.55463
0.45	2.54005	2.52559	2.51124	2.49700	2.48287	2.46885	2.45494	2.44114	2.42743	2.41384
0.46	2.40034	2.38695	2.37366	2.36047	2.34738	2.33439	2.32150	2.30870	2.29600	2.28339
0.47	2.27088	2.25846	2.24613	2.23390	2.22176	2.20970	2.19773	2.18586	2.17407	2.16236
0.48	2.15074	2.13921	2.12776	2.11640	2.10511	2.09391	2.08279	2.07175	2.06079	2.04991
0.49	2.03910	2.02838	2.01773	2.00715	1.99666	1.98623	1.97588	1.96561	1.95540	1.94527
0.50	1.93521	1.92522	1.91530	1.90545	1.89567	1.88596	1.87632	1.86674	1.85723	1.84778
0.51	1.83840	1.82909	1.81984	1.81065	1.80153	1.79247	1.78347	1.77453	1.76565	1.75683
0.52	1.74808	1.73938	1.73074	1.72216	1.71364	1.70517	1.69676	1.68841	1.68012	1.67188
0.53	1.66369	1.65556	1.64748	1.63946	1.63149	1.62357	1.61571	1.60790	1.60014	1.59242
0.54	1.58477	1.57716	1.56960	1.56209	1.55462	1.54721	1.53985	1.53253	1.52526	1.51804
0.55	1.51086	1.50373	1.49665	1.48961	1.48262	1.47567	1.46876	1.46190	1.45509	1.44831
0.56	1.44158	1.43489	1.42825	1.42164	1.41508	1.40856	1.40208	1.39564	1.38924	1.38288
0.57	1.37656	1.37028	1.36404	1.35784	1.35168	1.34555	1.33946	1.33341	1.32740	1.32142
0.58	1.31549	1.30958	1.30372	1.29788	1.29209	1.28633	1.28060	1.27491	1.26926	1.26364
0.59	1.25805	1.25250	1.24698	1.24149	1.23603	1.23061	1.22522	1.21987	1.21454	1.20925
0.60	1.20399	1.19875	1.19356	1.18839	1.18325	1.17814	1.17306	1.16801	1.16300	1.15801
0.61	1.15305	1.14812	1.14322	1.13834	1.13350	1.12868	1.23389	1.11913	1.11440	1.10969
0.62	1.10501	1.10036	1.09574	1.09114	1.08656	1.08202	1.07750	1.07300	1.06853	1.06409
0.63	1.05967	1.05528	1.05091	1.04657	1.04225	1.03796	1.03368	1.02944	1.02522	1.02102
0.64	1.01684	1.01269	1.00856	1.00446	1.00037	0.99631	0.99227	0.98826	0.98427	0.98029
0.65	0.97635	0.97242	0.96851	0.96463	0.96077	0.95692	0.95310	0.94930	0.94552	0.94176
0.66	0.93803	0.93431	0.93061	0.92693	0.92327	0.91964	0.91602	0.91242	0.90884	0.90528
0.67	0.90174	89822	89471	89122	88775	88430	88087	87746	87407	87069
0.68	86733	86399	86067	85736	85407	85080	84755	84431	84110	83790
0.69	83471	83154	82839	82525	82213	81903	81594	81287	80981	80677
0.70	80375	80074	79774	79477	79180	78886	78593	78301	78011	77722
0.71	77434	77148	76864	76581	76299	76019	75740	75463	75187	74912
0.72	74639	74367	74097	73828	73560	73293	73028	72764	72502	72241
0.73	71981	71722	71465	71208	70954	70700	70448	70196	69946	69698
0.74	69450	69204	68959	68715	68472	68230	67990	67751	67513	67276
0.75	67040	66805	66571	66338	66107	65876	65647	65419	65192	64966
0.76	64741	64518	64295	64073	63852	63632	63414	63196	62980	62764

(continued)

Table A-1·1 (cont·)

S	0	1	2	3	4	5	6	7	8	9
0.77	62550	62336	62123	61912	61701	61491	61282	61075	60868	60662
0.78	60458	60254	60051	59849	59648	59447	59248	59050	58852	58656
0.79	58460	58265	58071	57878	57686	57494	57304	57114	56926	56738
0.80	56551	56364	56179	55994	55811	55628	55446	55264	55084	54904
0.81	54725	54547	54370	54193	54017	53842	53668	53494	53322	53150
0.82	52978	52808	52638	52469	52300	52133	51966	51800	51634	51470
0.83	51306	51142	50980	50818	50656	50496	50336	50176	50018	49860
0.84	49702	49546	49390	49234	49080	48926	48772	48620	48468	48316
0.85	48165	48015	47865	47716	47568	47420	47272	47126	46980	46834
0.86	46690	46545	46401	46258	46116	45974	45832	45691	45551	45411
0.87	45272	45134	44996	44858	44721	44585	44449	44313	44178	44044
0.88	43910	43777	43644	43512	43380	43249	43118	42988	42858	42729
0.89	42600	42472	42344	42216	42089	41963	41837	41711	41586	41462
0.90	41338	41214	41091	40968	40846	40724	40602	40481	40361	40241
0.91	40121	40001	39882	39764	39646	39528	39411	39294	39178	39062
0.92	38946	38831	38716	38602	38488	38374	38260	38147	38035	37922
0.93	37810	37699	37588	37477	37367	37256	37147	37037	36928	36819
0.94	36711	36603	36495	36387	36280	36173	36067	35960	35854	35749
0.95	35643	35538	35433	35328	35224	35120	35016	34913	34809	34706
0.96	34604	34501	34398	34296	34195	34093	33991	33890	33789	33688
0.97	33587	33487	33386	33286	33186	33086	32986	32887	32787	32688
0.98	32588	32489	32390	32290	32191	32092	31992	31893	31793	31694
0.99	31594	31494	31394	31294	31194	31093	30992	30891	30790	30688
1.00	30586	30483	30379							

$$\frac{(\rho_l - \rho_v)_2}{(\rho_l - \rho_v)_1} = \frac{T_c - T_2}{T_c - T_1}^{0.31}$$

ρ_v's are ignored.

T_c for chlorobenzene = 359·2°C

$\rho_{20°C}$ for chlorobenzene = 1·106 g/cm^3

From the drop of chlorobenzene above at 22°C,

$\rho_{22°C}$ = 1.104g/cm^3

ρ_{H_2O} at 22°C = 0.9978g/cm^3

de = 5.29cm

ds = 3.21cm

S = 0.6068, and from tables, 1/H = 1.169.
Substituting all the values to the equation for γ,

$$\gamma = 0.0969 \times 981 \times (5.29/15.7)^2 \times 1.169$$

$$= 12.6 \text{ dynes/cm.}$$

γ was also found for different concns of NaLS, a graph below of γ vs concentration of NaLS is plotted and one can find γ at any concentration.

Below is a graph showing the interfacial tension, γ, as a function of concentration of NaLS.

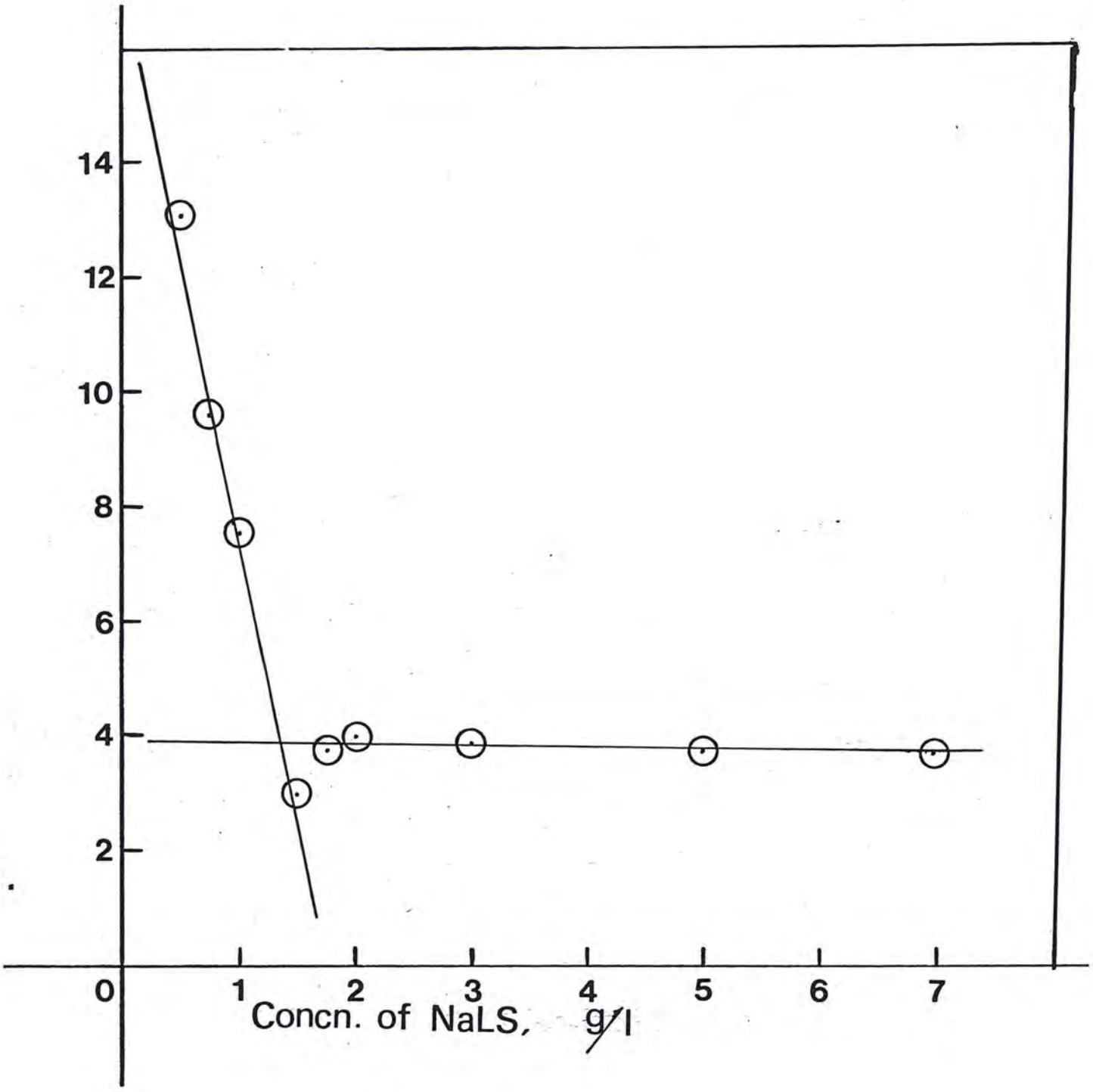


Fig.A-1.1: Variation of γ with concentration of NaLS.

The following are graphs of volume/diameter against time corresponding to tables discussed in section 5.1 - 5.7.

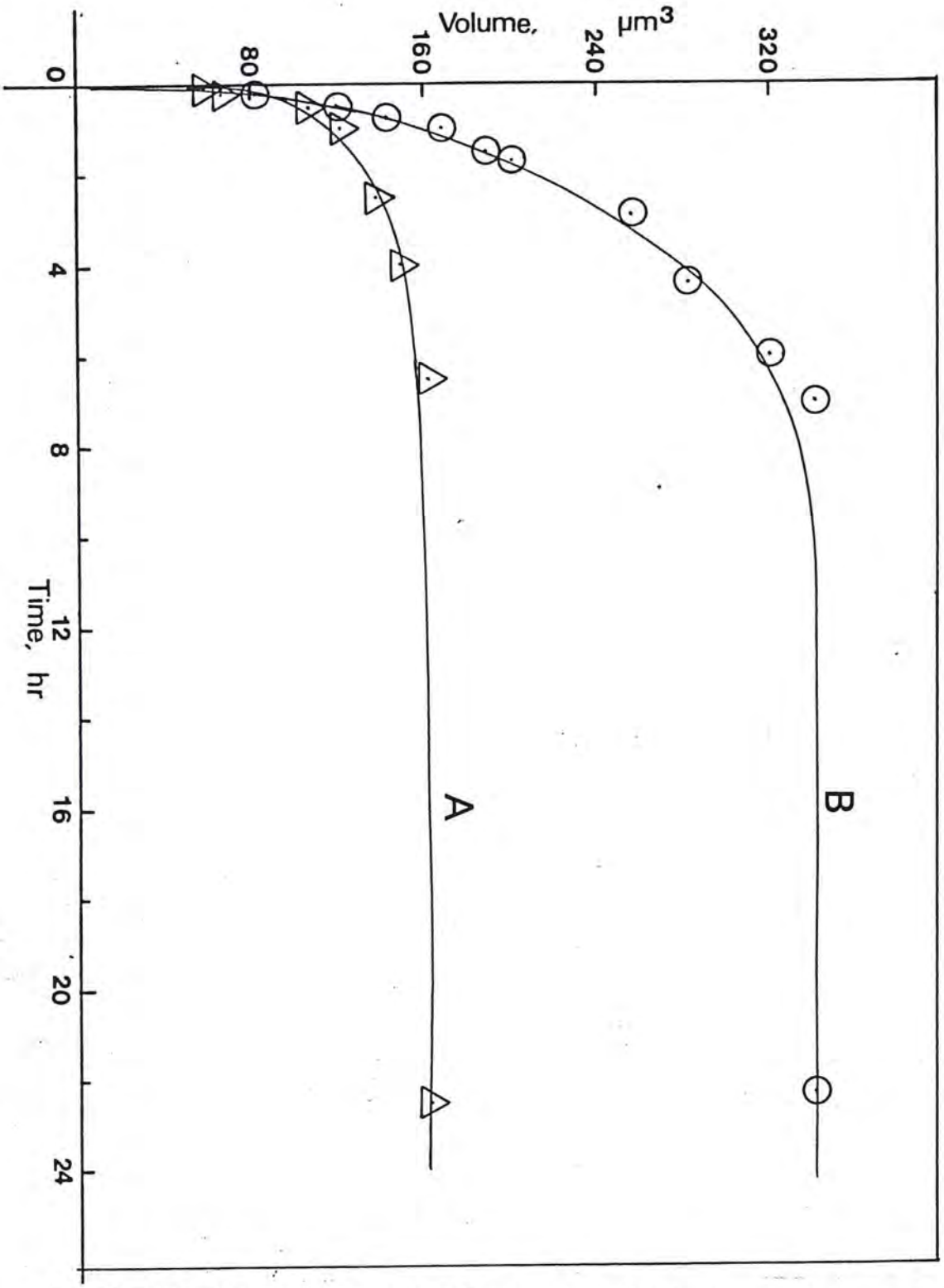


Fig.A-2.1: Variation of volume of polystyrene-DOA particles with time at different stirring speeds, 250 r.p.m. for curve A, 500 r.p.m. for curve B. Experimental conditions correspond to tables 5.2A and 5.2B.

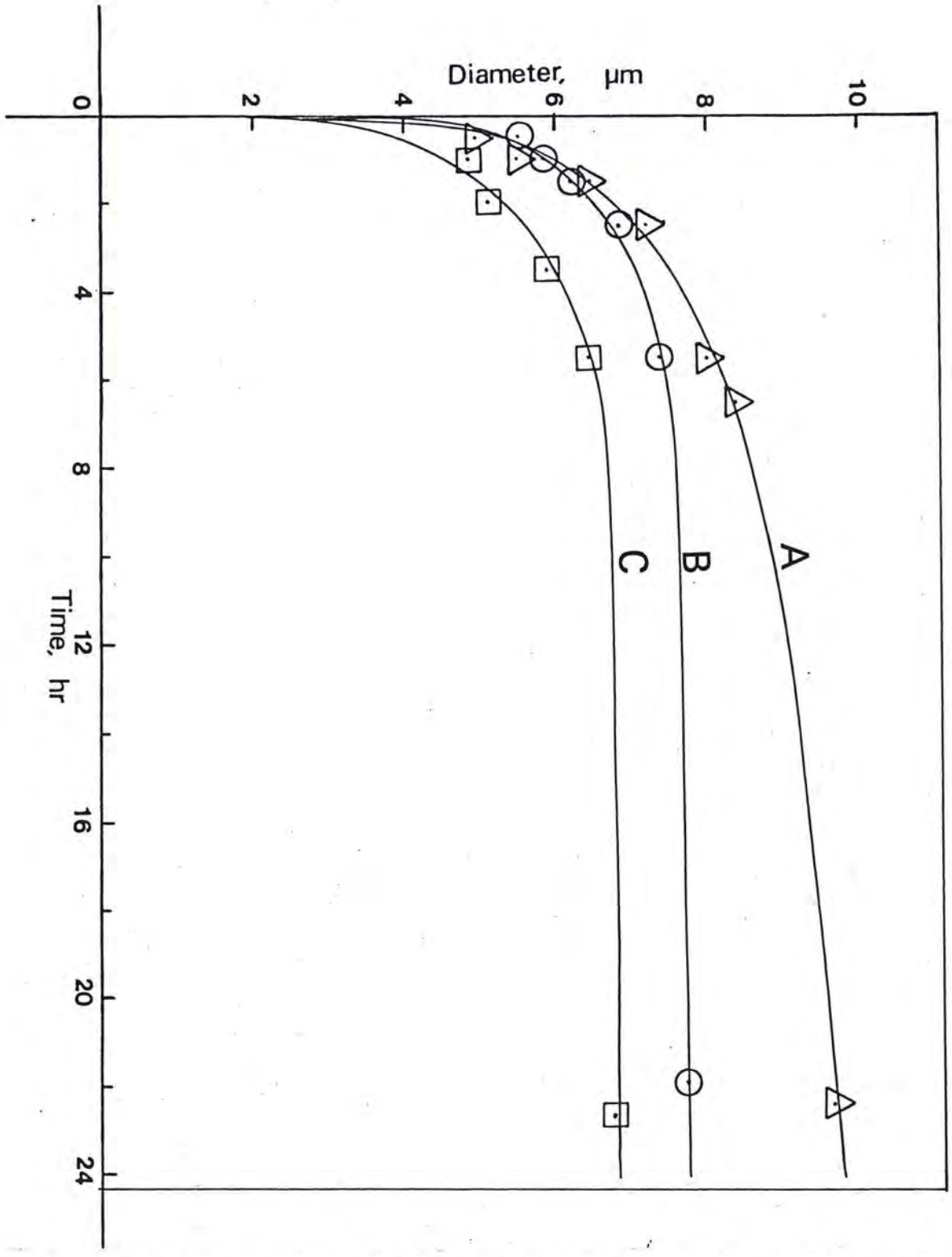


Fig.A.2.2: Variation of diameter with time of swelling polystyrene chlorododecan particles with different amounts of chlorobenzene V_1, in ratios $V_1:V_2+V_3$ of 746:1, 373:1 and 149:1 for curves A, B and C respectively. Experimental conditions correspond to tables 5.3A, 5.3B and 5.3C.

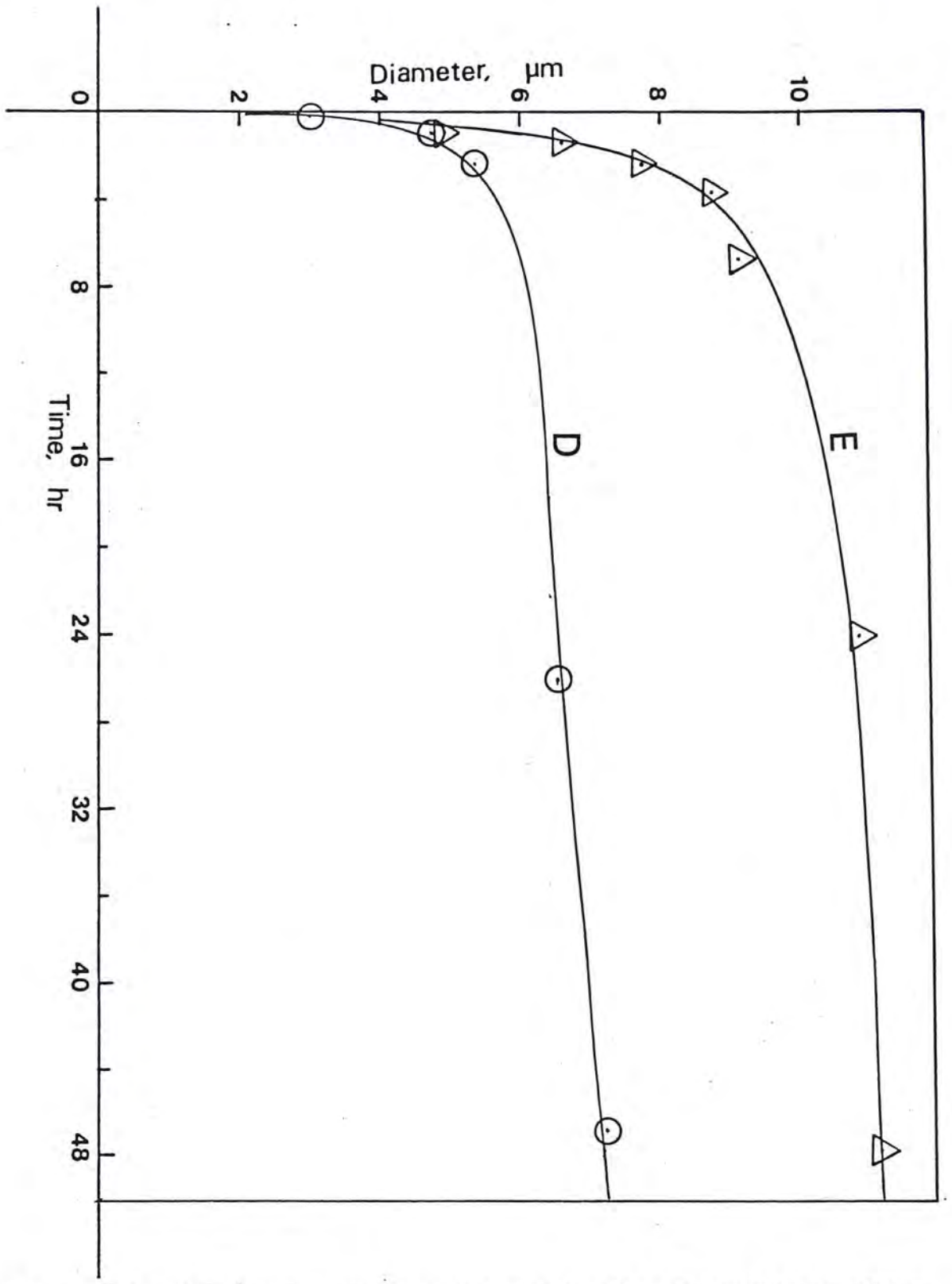


Fig.A.2.3: Variation of diameter with time of swelling polystyrene-DOA particles with different amount of chlorobenzene V_1, in ratios $V_1:V_2+V_3$ of 500:1 for curve E and 87:1 for curve D.
Experimental conditions correspond to those in tables 5.3E and 5.3D.

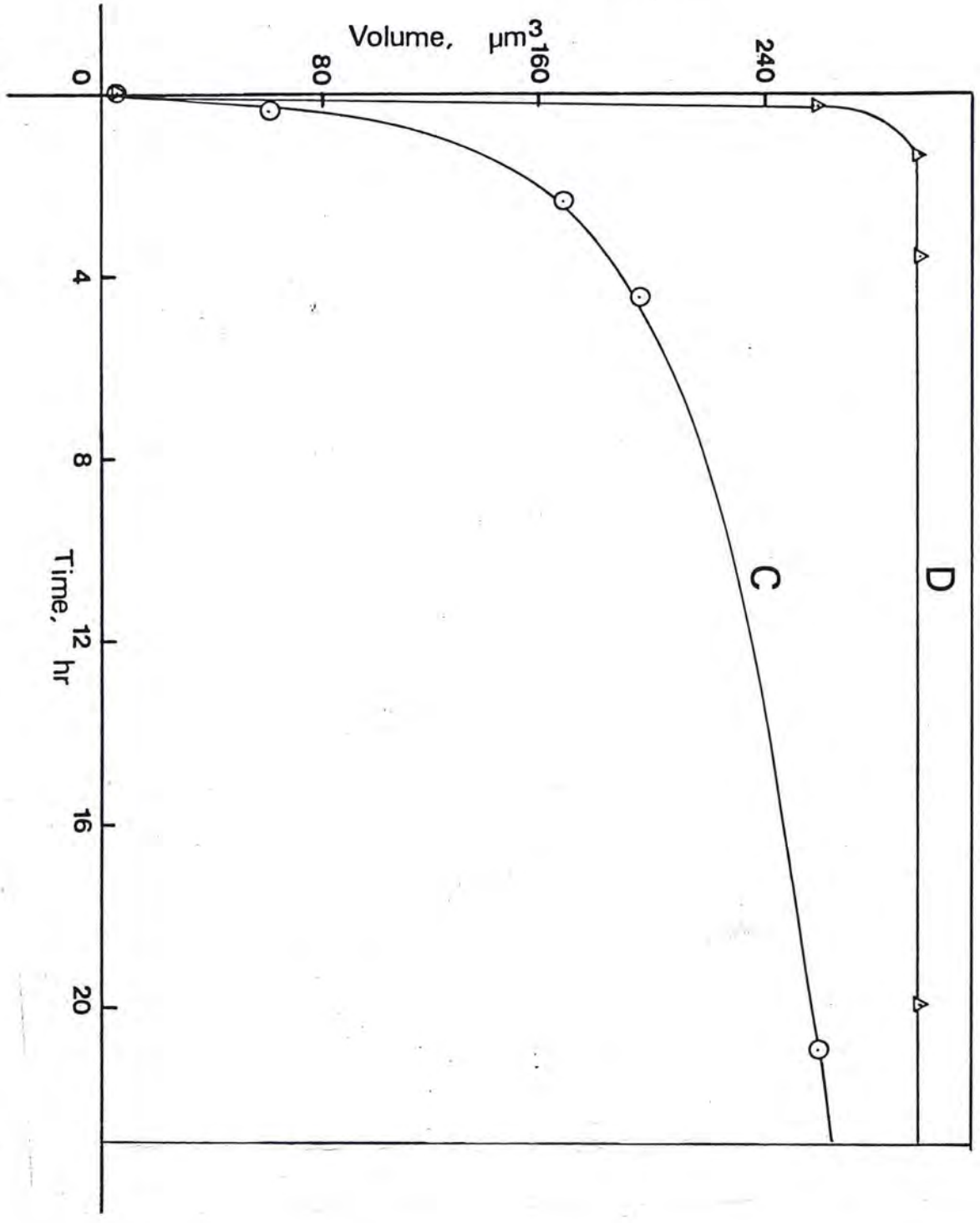


Fig.A.2.4: Variation of volume with time of swelling polystyrene-DOA particles with chlorobenzene, V_1. Curve C is where chlorobenzene was added as bulk, while in curve D, the chlorobenzene was ultraturraxed. Experimental conditions correspond to tables 5.6C and 5.6D.

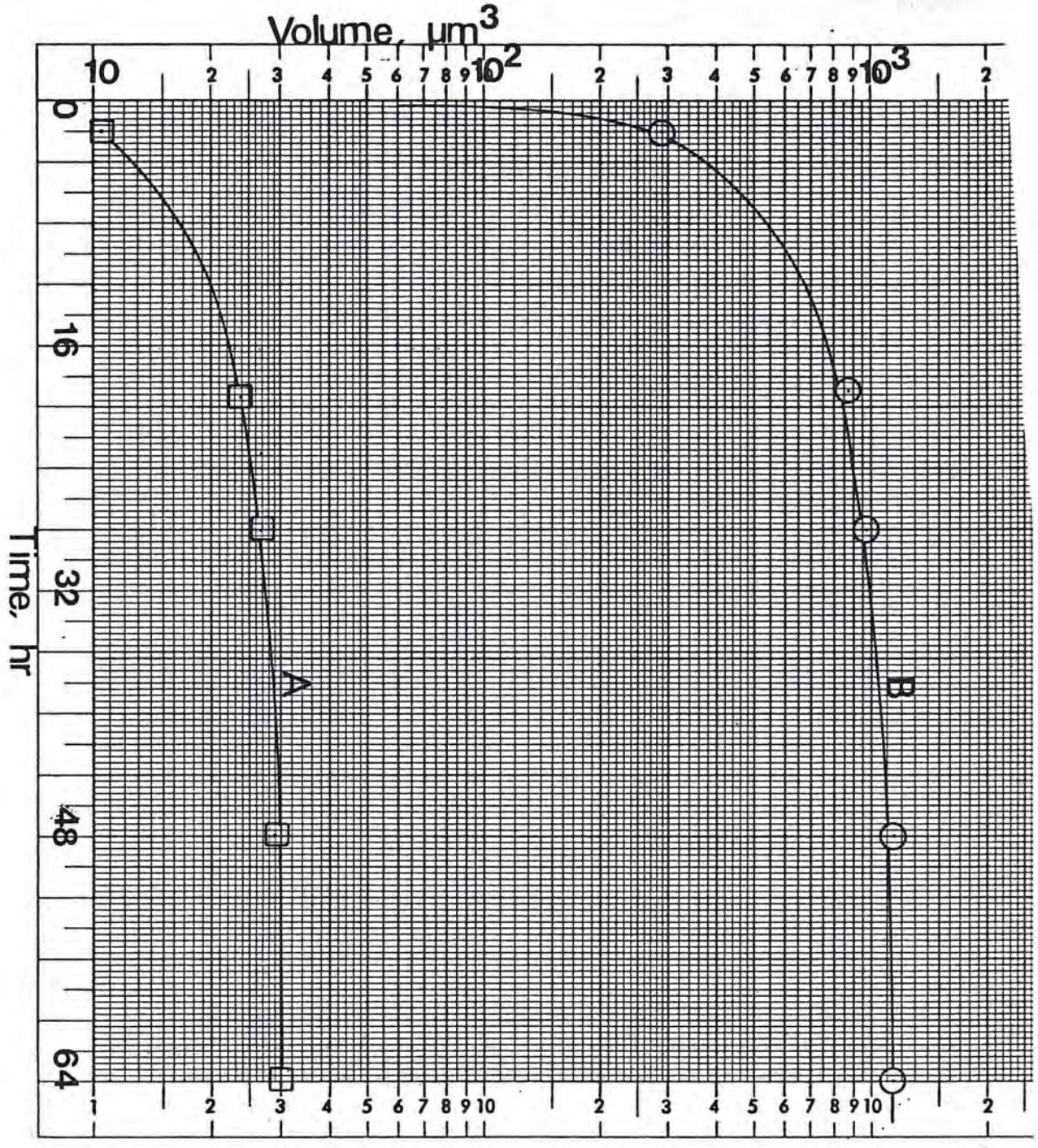


Fig.A.2.5: Variation of log.volume with time of PS-DOA particles swollen competitively with chlorobenzene PS-DOA particles were both swollen in v/v ratio of 1:1, while the starting diameters of the polystyrene was 0,63μm for curve a, and 1,4μm for curve B. Experimental conditions correspond to table 5.7C.

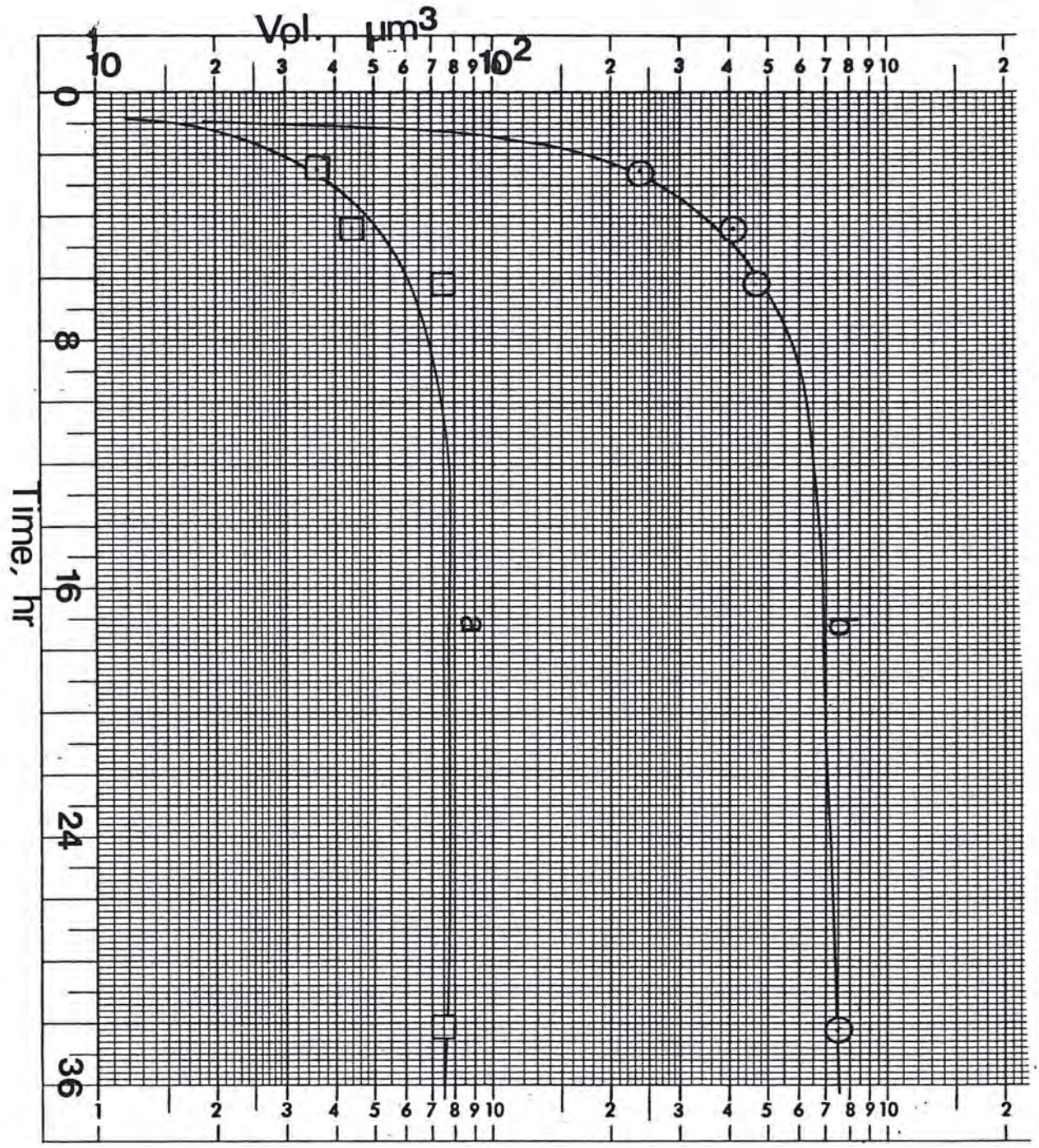


Fig.A.2.6 Variation of log.volume with time of the same Polystyrene seed (d_3=1,4µm) (Swollen with DOA in the ratios PS:DOA of 9:1 for curve a, and 1:1 for curve b), with chlorobenzene. Experimental conditions correspond to table 5.7D.

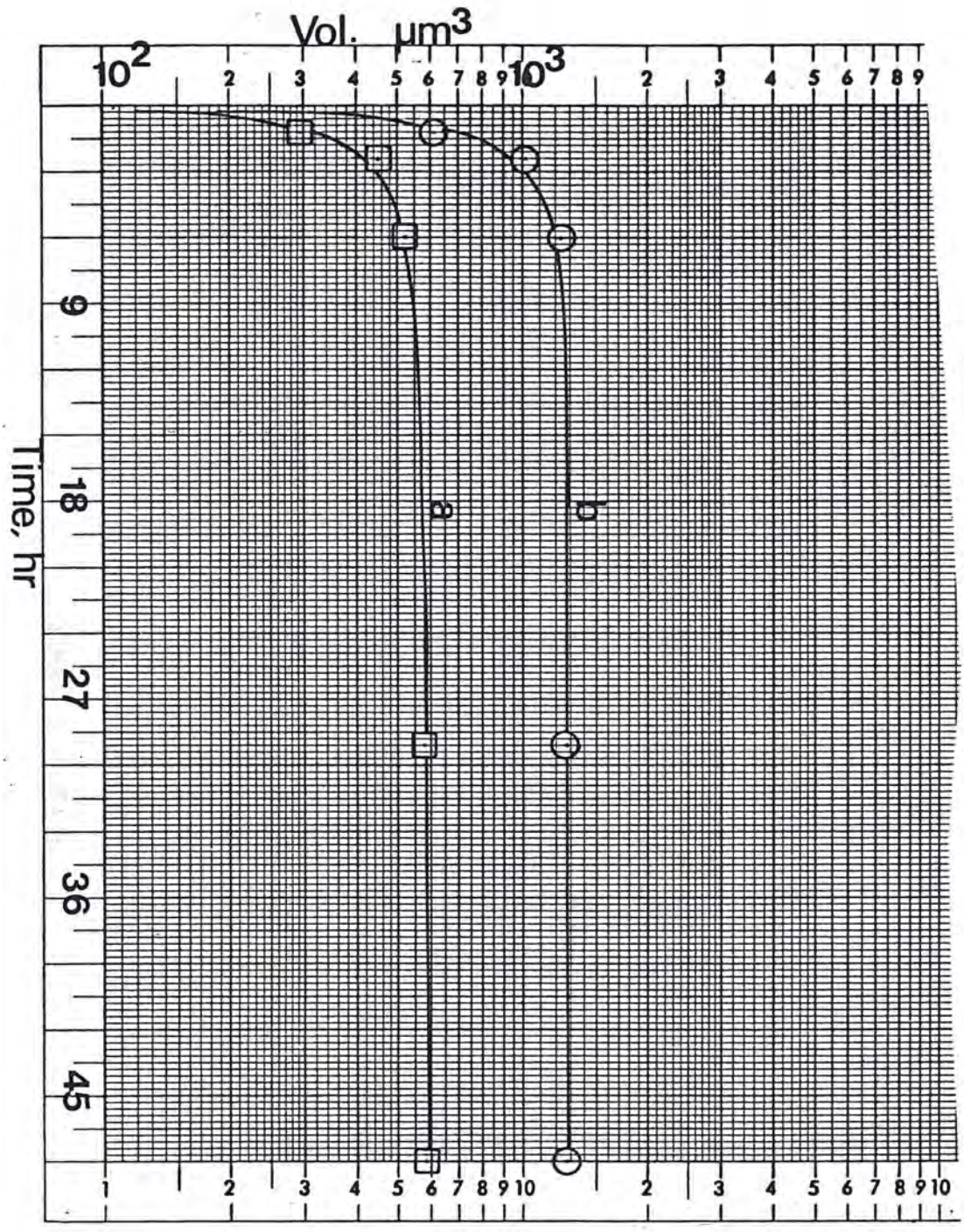


Fig.A.2.7: Variation of log. volume with time of the same polystyrene seed (d_3=1,4μm) (swollen with DOA in the ratios PS:DOA of 1:1 for curve a and 1:2 for curve b), with chlorobenzene, V_1, in the ratio $V_1:V_3+V_{3b}$ of ~ 750:1. Experimental conditions correspond to table 5.7E.

The following is a table of results of competitive swelling of particles of 0.5 μm (a) and 1.4 μm (b), each swollen with DOA in the ratio PS:DOA of 1:1 (so that $V_2/V_3 = 1$), as calculated from equation 2.4.13.

V_1: Total chlorobenzene added in cm^3
V_b: Chlorobenzene in the b particles in cm^3
V_a: Chlorobenzene in the a particles in cm^3
r_b: Radius of the b particles in m
r_a: Radius of the a particles in m
S_b: Swelling of the b particles
S_a: Swelling of the a particles

γ used is 5 N/m, and $V_{1a}/V_{1b} = 1$, where $V_{1a} = V_{2a}+V_{3a}$, $V_{1b} = V_{2b}+V_{3b}$.
2 is DOA and 3 is polystyrene

V_1	V_b	V_a	r_b	r_a
10.00	5.064	4.936	.1608-05	.5705-06
50.00	25.94	24.06	.2644-05	.9218-06
100.0	52.90	47.10	.3331-05	.1146-05
200.0	109.2	90.76	.4229-05	.1421-05
300.0	168.4	131.6	.4880-05	.1606-05
400.0	229.9	170.1	.5411-05	.1749-05
500.0	293.7	206.3	.5869-05	.1864-05
600.0	359.6	240.4	.6277-05	.1961-05
700.0	427.5	272.5	.6649-05	.2045-05
800.0	497.3	302.7	.6992-05	.2117-05
900.0	568.9	331.1	.7312-05	.2181-05
1000.	642.1	357.9	.7613-05	.2238-05
1100.	717.4	382.6	.7899-05	.2289-05
1200.	793.5	406.5	.8169-05	.2335-05
1300.	871.1	428.9	.8426-05	.2377-05
1400.	950.0	450.0	.8673-05	.2415-05
1500.	1030.	469.8	.8910-05	.2450-05
1600.	1112.	488.4	.9139-05	.2482-05
1700.	1194.	505.9	.9359-05	.2511-05
1800.	1273.	522.3	.9573-05	.2538-05
1900.	1362.	537.7	.9779-05	.2563-05
2000.	1448.	552.2	.9980-05	.2586-05
2100.	1534.	565.8	.1017-04	.2607-05
2200.	1621.	578.6	.1036-04	.2626-05
2300.	1709.	590.6	.1055-04	.2644-05
2400.	1798.	601.9	.1073-04	.2661-05
2500.	1887.	612.6	.1090-04	.2677-05
2600.	1977.	622.7	.1107-04	.2691-05
2700.	2068.	632.2	.1124-04	.2705-05
2800.	2161.	639.5	.1140-04	.2715-05
2900.	2251.	648.7	.1156-04	.2728-05
3000.	2343.	657.4	.1171-04	.2740-05

Calculation of amount of NaLS to use.

$$\text{Number of particles, } N_p = \frac{V}{V_o} = \frac{V \cdot 3}{4\pi r_o 3}$$

where V is the volume used, and V_o is the volume of one particle.

Consider particles of diameter 2.2μm swollen with chlorobenzene to diameter 30.0μm.
Volume used = $0.025 cm^3$.

$$N_p = \frac{0.025 \times 3}{4\pi (1.1 \times 10^{-4})^3}$$

Total area occupied by the particles after swelling is

$$A_p = N_p . 4\pi r^2, \quad r = 15 \times 10^{-4} cm.$$

$$= 4\pi (15 \times 10^{-4})^2 . N_p .$$

Molecular layer occupied by NaLS = $50 \dot{A}^2 = 50 \times 10^{-16}$ cm^2/molecule

$$\text{Hence, moles covered by NaLS} = \frac{A_p}{50 \times 10^{-16} \times N_o}$$

N_o = Avogadros Number.

Amount of NaLS = No. of moles x Molecular weight of NaLS

$$= \frac{A_p}{50 \times 10^{-16}} = \frac{288.4}{N_o} .$$

Hence, Amount of NaLS, needed to cover the particles is,

$$= \frac{0.025x3 \cdot 4\pi(15x10^{-4})^2 x\ 288.4}{4\pi(1.1x10^{-4})^3(50x10^{-16})x6.023x10^{23}}$$

$$= 0.012g.$$

The critical micelle concentration, cmc of NaLS is $1.8g/dm^3 H_2O$ Since amount of water used in experiment was $235cm^3$ hence, amount of NaLS needed for cmc is 0.423g.

The total amount of NaLS needed is then

$$0.012g + 0.423 = 0.435g = [1.85g/dm^3 H_2O]$$

Hence in all experiments, 2.5g-4.0g NaLS/$dm^3 H_2O$ was used, which is enough.

A-5. SYMBOLS

a : Activity

Rate determining constant in Smoluchowski's equation, $\sim 10^{-11}$ cm^3/s

a_{12} : Parameter expressing deviation from ideal solution behavious in Scatchard equation

A : Hamaker's constant

B : Constant in Reerink and Overbeck expression for electrostatic repulsion between two particles, = 3.93×10^{39} $A^{-2}s^{-2}$

C : Concentration in moles/dm^3

Compound 1: Slightly water soluble compound

Compound 2: Water insoluble, low molecular weight compound or oligomer

Compound 3: Polymer

C_r : Solubility in water of oil in droplets of radius r in g/cm^3

C_∞ : Solubility of an unfinitely large droplet in g/cm^3

C_w^∞ : Equilibrium constant of compound 1 in water

d : Diameter of particles or droplets

D : Diffusion coefficient in dm^2/s

E : Energy of vaporisation

g : Acceleration of gravity, = 980.665 cm/sec^2

G : Gibb's free energy

Rate of dissolution

h_o : Shortest distance between spheres

H : Enthalpy

j : Number of segments of polymer molecule

k : Boltzmann constant = 1.38046×10^{-6} erg/deg/mol

K : Measure of rate of coalescence

m : Average number of separate particles in aggregate at time t

n : Number of moles

n_o : Number of particles at t = 0

n_v : Number of aggregates

N : Number of particles or droplets

N_o : Avogadro's number, = 6.0229×10^{23} molecules/mole

P : Pressure in kg/cm^3

r : Radius of particles or droplets in m

R : Molar gas constant = 8.314 Joule/deg/mol

S	:	Surface area in m^2
		Entropy in J/K
t	:	Time in sec
T	:	Absolute temperature in K
U	:	Rate of sedimentation in cm/sec
V	:	Volume in dm^3
V_A	:	Energy of attraction in Joule
V_{1M}	:	Molar volume of compound 1
V_M	:	Molar volume
V_R	:	Repulsive energy in Joule
V_T	:	Total potential energy in Joule
W	:	Work done in ergs
X	:	Mole fraction
z	:	Charge number
γ	:	Interfacial tension in N/m
ε	:	Permitivity of medium
η	:	Viscosity
κ	:	Debye parameter
μ	:	Chemical potential in Joule/mol
ρ	:	Density in g/cm^3
ϕ	:	Volume fraction
χ	:	Flory-Huggin's interaction parameter