

# Stable concentrated emulsions as precursors for hydrophilic–hydrophobic polymer composites

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A new method to prepare polymer composites based on concentrated emulsions was developed in this laboratory. The composite is synthesized starting from a concentrated emulsion of a hydrophobic phase, containing a hydrophobic monomer, dispersed in a continuous hydrophilic phase, containing a hydrophilic monomer. Of course, inverted dispersions in which the hydrophilic phase is dispersed in a hydrophobic phase are also possible. The concentrated emulsions have the same appearance and behaviour as a gel; the volume fraction of their dispersed phase is very large (it can be as large as 0.99). Not all pairs of monomers can lead to concentrated emulsions. In addition, concentrated emulsions prepared and stable at room temperature may not remain stable at the polymerization temperature of 50°C. The present paper contains a large number of experiments whose goal is to identify the conditions under which a coupling between two monomers can lead to hydrophilic–hydrophobic or hydrophobic–hydrophilic composites. The nature of the hydrophilic and hydrophobic monomers (particularly their polarity), the pH and the ionic strength are found to be important factors in the formation at room temperature and stability at 50°C of the concentrated emulsions. It is found that the instability at 50°C of the concentrated emulsions (expressed as weight per cent of bulk phases separated from the emulsion after heating for a certain time) can be correlated with the interfacial tension at 25°C between the hydrophilic and hydrophobic phases free of surfactant. The larger this interfacial tension, the higher the stability of the concentrated emulsion. Hence, the lower the polarity of the hydrophobic monomer and the higher the polarity of the hydrophilic monomer, the more stable the emulsion. The film-forming capability of the surfactant is also important. Improved mechanical strength of the interfacial film is achieved using blends of non-ionic surfactants or mixtures of ionic surfactants and long-chain alcohols as dispersants. Increased stability is exhibited by adding methyl cellulose in the aqueous continuous phase when hydrophobic monomers with higher polarity are employed in the dispersed phase. High temperatures and higher volume fractions of the dispersed phase decrease the stability of the emulsion. Several hydrophilic–hydrophobic polymer composites have been prepared on the basis of the above observations.

(Keywords: polymer composites; concentrated emulsions; synthesis; hydrophobic monomer; hydrophilic monomer; stability of concentrated emulsions)

## INTRODUCTION

Emulsions are mixtures of two immiscible liquids, one being dispersed in the other in the form of droplets. The presence of surfactant molecules adsorbed upon the interface between the two phases is responsible for their stability, which has a kinetic and not a thermodynamic origin. Depending upon the nature of the dispersed phase, they can be either of the oil-in-water (o/w) or water-in-oil (w/o) type. In conventional emulsions, the volume fraction of the dispersed phase is in general lower than 0.74, which represents the volume fraction of the most compact arrangement of spheres of equal radius. By increasing the volume fraction of the dispersed phase above 0.74, a concentrated emulsion, which has the appearance of a gel and the structure of a liquid–liquid foam, is generated. In concentrated emulsions, the spheroidal droplets of the conventional dispersed phase are deformed into polyhedral cells and the small volume

fraction of the continuous phase, which can be as small as 0.01, is in the form of a network of thin liquid films that separate the polyhedral cells of the dispersed phase (*Figure 1*)<sup>1–5</sup>. A surfactant dissolved in the continuous phase and adsorbed upon the interface between the two phases as an oriented interfacial film ensures the stability of the concentrated emulsion. If the oil phase is replaced by a hydrophobic monomer, or the water phase by a hydrophilic monomer, an emulsion is obtained that can be employed as a precursor for the preparation of polymers. Similarly, if both phases are replaced, the oil phase by a hydrophobic monomer and the water phase by a hydrophilic monomer, the generated emulsion could be employed as a precursor in the preparation of polymer composites. Experiment shows, however, that such emulsions cannot be generated. In order to produce stable emulsions, the hydrophilicity of one of the monomers and/or the hydrophobicity of the other monomer must be increased by using their solutions in strong hydrophobic (such as decane) and/or hydrophilic liquids (such as water).

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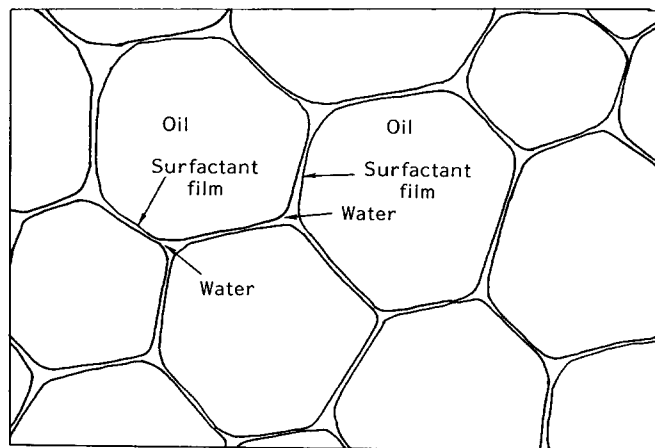


Figure 1 Sketch of a concentrated emulsion

Concentrated emulsions have been employed in this laboratory to synthesize polymers<sup>6,7</sup> and polymer composites<sup>8-15</sup>. The polymerization of the monomer cells that constitute the dispersed phase of the concentrated emulsion was found to lead to higher molecular weights than polymerization in bulk<sup>6,11,12</sup>. A hydrophilic-hydrophobic polymer composite was prepared by polymerizing simultaneously both the dispersed and continuous phases of a concentrated emulsion containing a hydrophilic (hydrophobic) monomer in the dispersed phase and a hydrophobic (hydrophilic) monomer in the continuous phase<sup>8</sup>. These composites contain particles of one polymer dispersed in a continuum of the other polymer. Membranes prepared from these polymer composites could be used to separate toluene from cyclohexane<sup>9</sup> and water from ethanol<sup>10</sup>. The concentrated emulsion polymerization method was employed to prepare polymeric latexes, which were subsequently used to prepare hydrophilic-hydrophobic polymer composites<sup>11</sup> and hydrophobic-hydrophobic polymer composites<sup>12</sup>. In addition, submicrometre-sized inorganic powders were encapsulated using the concentrated emulsion polymerization method<sup>13</sup>, and a highly porous polymer, obtained via the concentrated emulsion polymerization method, was used as host in the preparation of a thick conducting polymer composite<sup>14,15</sup>.

As already noted, concentrated emulsions form when one of the phases is sufficiently hydrophobic and the other sufficiently hydrophilic. In addition, concentrated emulsions that are generated and stable at room temperature may become unstable at the polymerization temperature. In order to be suitable for the preparation of polymers and polymer composites, the concentrated emulsion must first form and, subsequently, it must remain stable at the temperature at which polymerization takes place. The objective of the present study is to investigate the factors that influence the formation and stability of concentrated emulsions at the preparation and polymerization temperatures in order to identify the physico-chemical conditions that ensure their stability.

Stability of emulsions usually refers to the resistance to the formation of two separate phases<sup>5,16-18</sup>. The coalescence of the colliding droplets is responsible for the phase separation. The film-forming capability of the surfactant, which is adsorbed on the surface of the droplets, plays a part in this process<sup>19-22</sup>. The mechanical properties of this interfacial film depend in addition upon the cohesive forces among the adsorbed

surfactant molecules, and also upon the electrostatic repulsion among the head-groups when they are charged or the steric repulsion among the polar head-groups of non-ionic surfactants. In addition, double-layer repulsive forces and/or steric repulsion as well as van der Waals attractive forces between globules are involved in the rate of coalescence. There exists another mechanism by which the large droplets grow in size at the expense of the smaller ones, which decrease in size, namely Ostwald ripening.

The stability of concentrated emulsions is affected by the chemical nature of the dispersed and continuous phases as well as of the surfactant, the viscosities of the continuous and dispersed phases, the temperature and the volume fraction of the dispersed phase.

First, the effect of the chemical nature of the dispersed and continuous phases on the stability of concentrated emulsions is investigated. Experiment indicates that the higher the hydrophobicity of one of the phases and the hydrophilicity of the other phase, the more stable is the concentrated emulsion. Because the interactions between strong hydrophobic and hydrophilic phases are relatively weak, the interfacial free energy between the two phases is expected to be large. In other words, the concentrated emulsion is expected to form more easily when the interfacial free energy between the two phases free of dispersant is larger. The effects of the polarity of the hydrophobic phase, of the pH and of the ionic strength are investigated to gain some understanding regarding the formation and stability of concentrated emulsions.

Secondly, the effects of the nature of the surfactant and its concentration are investigated. To achieve a mechanically strong interfacial film, which can ensure the stability of the emulsion, the interfacial film of adsorbed surfactant molecules should be condensed, in order to have strong lateral intermolecular interactions. A blend of two surfactants rather than an individual surfactant can be used to prepare a close-packed and mechanically strong interfacial film. The effect of the nature and concentration of such blends of surfactants on the formation and stability of concentrated emulsions is examined.

Thirdly, the effect of the viscosity of the continuous phase on the stability of the concentrated emulsion is investigated. Particularly, the formation of a liquid-crystalline structure in the continuous phase when the surfactant concentration is sufficiently large can increase the stability of the emulsion. However, a too high viscosity of the continuous phase caused by an increased surfactant concentration hinders the formation of a concentrated emulsion. The effect of the viscosity of the continuous phase on stability is studied by adding thickeners or by increasing the surfactant concentration.

Fourthly, the effect of the volume fraction of the dispersed phase on the stability of the concentrated emulsion is investigated to show that too small volume fractions of the continuous phase decrease the stability.

Fifthly, the effect of temperature on the concentrated emulsion stability is studied. A change in temperature causes changes in the solubilities of the two phases and of the surfactant as well as in the characteristics of the interfacial film.

Various examples of monomer pairs that can form concentrated emulsions and can lead to hydrophilic-hydrophobic polymer composites conclude the paper.

## EXPERIMENTAL

### Materials

In the experiments carried out to examine the stability of concentrated emulsions, the chemical compounds were used as received. Those used for polymerization were first purified to remove the inhibitors before use. Toluene, benzene, ethylbenzene, nitrobenzene, divinylbenzene, styrene, methyl methacrylate, n-butyl methacrylate, ethyl methacrylate, butyl acrylate, methyl acrylate, ethyl acrylate, vinyl acetate, acrylic acid, 2-hydroxyethyl methacrylate, methyl cellulose (2 wt% solution in water, 15 cP), sodium chloride, sodium hydroxide and styrene-sulphonic acid salt were purchased from Aldrich. Chloroform, decane and isopropyl ether were purchased from Kodak. Acrylamide (Polysciences) was purified by recrystallization in methanol. The initiators such as azobisisobutyronitrile (AIBN, Alfa) and potassium persulphate (Aldrich) were used after recrystallization. Water was deionized and distilled. All the surfactants were used as received. Sodium dodecylsulphate (SDS), cetyl alcohol (CA) and oleyl alcohol (OA) were purchased from Aldrich. Span 20 (sorbitan mono-laurate), Span 40 (sorbitan monopalmitate), Span 65 (sorbitan tristearate), Span 80 (sorbitan monooleate), Span 85 (sorbitan trioleate), Tween 20 (polyoxyethylene(20) sorbitan laurate), Tween 40 (polyoxyethylene(20) sorbitan monopalmitate), Tween 60 (polyoxyethylene(20) sorbitan monostearate) and Tween 85 (polyoxyethylene(20) sorbitan trioleate) were purchased from Fluka.

### Preparation of the concentrated emulsion

A small amount of continuous phase containing a suitable surfactant was placed in a three-necked flask equipped with a mechanical stirrer and an addition funnel. The dispersed phase located in the addition funnel was added dropwise to the continuous phase under vigorous stirring. This process was conducted at room temperature. Surfactant blends composed of one of the Spans and a long-chain alcohol, which are oil-soluble, were dissolved in the hydrophobic phase, and SDS and Tweens, which are water-soluble, were dissolved in the aqueous phase, prior to emulsification.

### Preparation of hydrophilic-hydrophobic polymer composites

Oil- and water-soluble initiators were dissolved in the two phases before emulsification at room temperature. The prepared concentrated emulsions were packed in glass tubes by mild centrifugation. The polymerization of the concentrated emulsion was carried out in a temperature-controlled water bath at 50°C.

### Measurement of the concentrated emulsion stability

The concentrated emulsion prepared at room temperature and free of initiators was packed in a sealed glass tube and stored in a temperature-controlled water bath for various lengths of time at 50°C. The stability was characterized by decanting and weighing the amount of bulk phases that separated from the concentrated emulsion. The volume fraction of the dispersed phase in the concentrated emulsions employed for the stability test was 0.9.

### Measurement of the interfacial tension

All the interfacial tension measurements were carried out by the drop weight method, using the correction of Harkins and Brown<sup>23</sup>. The density of the solutions was measured by employing Mohr's Mechanical Balance (Fisher Science). All measurements were conducted at room temperature.

### Electron microscopy

The samples of polymer composites were first cooled (-120°C) and sectioned by employing an ultramicrotome (Reichert-Jung Ultracut 43-E, Cambridge Instruments), which was equipped with a FC-4D cryo-ultramicrotomy stage. Microtomed samples (~900 Å thick) were shadowed with carbon in a vacuum evaporator and examined by transmission electron microscopy (TEM, Hitachi HS-8).

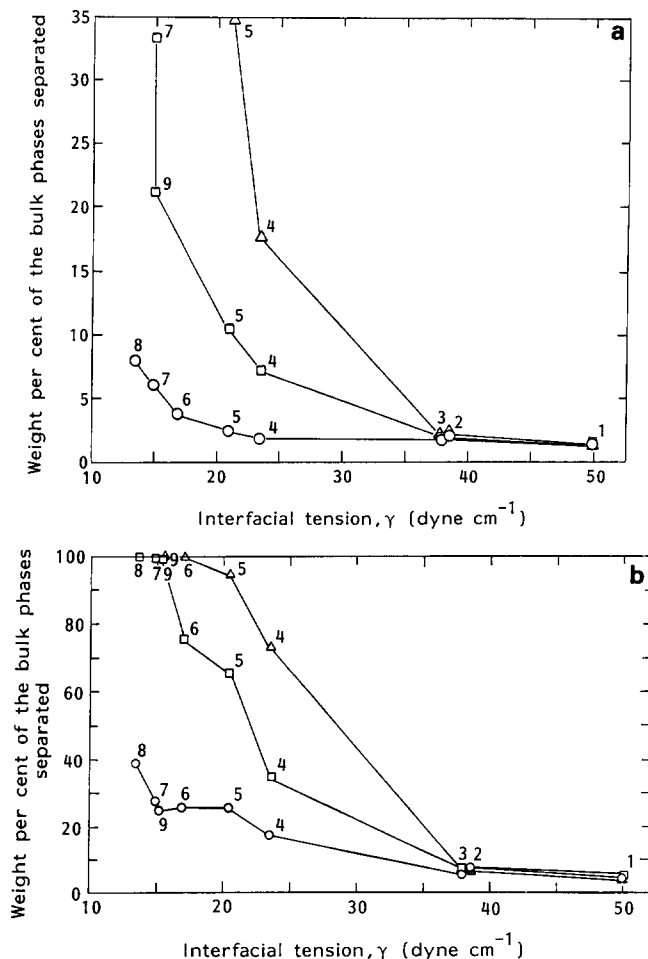
## RESULTS AND DISCUSSION

### Effect of the nature of the hydrophobic liquid on the formation and stability of concentrated emulsions in which the other phase is water

Figures 2a and 2b show that the stability of the concentrated emulsion prepared at room temperature and heated subsequently at 50°C can be correlated with the interfacial tension between the hydrophobic liquid and water measured at 25°C, in the absence of surfactant. A striking increase in stability is observed with increasing interfacial tension between the hydrophobic liquid and water. Phase separation can occur because of (i) the coalescence of the droplets of the dispersed phase and (ii) the Ostwald ripening process, in which large globules grow in size at the expense of the small globules, which decrease in size. The rate of Ostwald ripening is probably determined by the diffusion of the molecules of the dispersed phase through those of the continuous phase. An increase in the polarity of the hydrophobic organic liquid produces a fall in stability; a too high polarity hinders the formation of the concentrated emulsion. The surfactant employed in the preparation of the concentrated emulsion affects both the formation and the stability. For the hydrophobic organic liquids with high polarity, for which the interfacial tension at 25°C is less than about 35 dyn cm<sup>-1</sup>, the formation at 25°C and the stability at 50°C are strongly dependent upon the nature of the surfactant employed. For instance, the non-ionic surfactant Tween 20 is more effective than the ionic surfactant SDS for o/w concentrated emulsions, which are more stable than the w/o concentrated emulsions. The stability of the concentrated emulsions can also be correlated with the solubility of the hydrophobic organic liquid in water. (The interfacial tension and water solubility can be related as shown in the Appendix.) The relatively high polar hydrophobic liquids whose interfacial tensions with water and water solubilities are less than 15 dyn cm<sup>-1</sup> and higher than 1.5 g/100 g of water at 25°C, respectively, do not form w/o concentrated emulsions at room temperature when Span 80 is used as surfactant.

### Effect of the nature of the hydrophilic phase on the formation and stability of the concentrated emulsions

Figures 3-7 contain plots correlating the stability of the concentrated emulsions at 50°C with the interfacial



**Figure 2** Weight per cent of bulk phases separated from the concentrated emulsions by heating at 50°C plotted against the interfacial tension between the hydrophobic liquid and water. The concentrated emulsions were prepared at 25°C and had a volume fraction of the dispersed phase of 0.9. Weight per cents of bulk phases separated after (a) 3 h of heating and (b) 24 h of heating. ○ and □ denote o/w concentrated emulsions prepared using Tween 20 ( $8.15 \times 10^{-2}$  mol/l water) and SDS ( $3.47 \times 10^{-1}$  mol/l water) as surfactant, respectively. △ denotes w/o concentrated emulsions prepared using Span 80 ( $2.5 \times 10^{-1}$  mol/l styrene) as surfactant. Numbers are as follows: 1, decane; 2, ethylbenzene; 3, styrene; 4, n-butyl methacrylate; 5, butyl acrylate; 6, ethyl methacrylate; 7, vinyl acetate; 8, ethyl acrylate; 9, methyl methacrylate

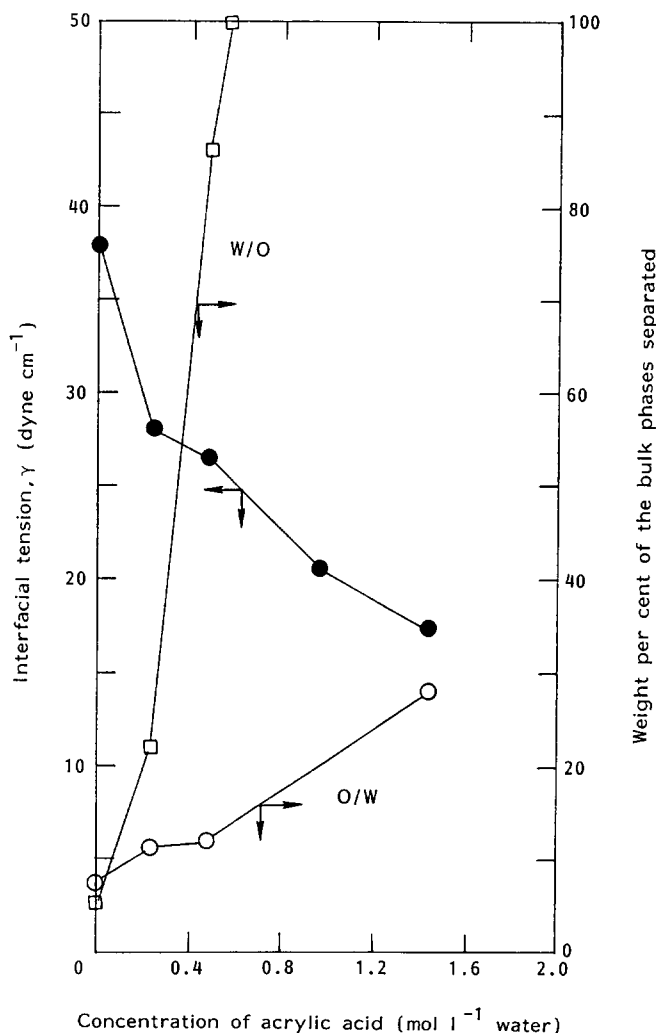
tension at 25°C between the two phases, aqueous monomer solution and styrene.

In Figure 3 the interfacial tension between styrene and aqueous acrylic acid solution as well as the stability of the concentrated emulsion is plotted against the concentration of acrylic acid in water. As the concentration of this polar monomer increases, the concentrated emulsion becomes more unstable, and finally the entire concentrated emulsion separates into the bulk phases. The presence of the acrylic acid in the aqueous phase destabilizes more strongly the w/o concentrated emulsions than the o/w concentrated emulsions. When SDS is used as surfactant, the o/w concentrated emulsions do form under stirring at 25°C above a monomer concentration of  $2.3 \text{ mol l}^{-1}$ . However, they separate into the two bulk phases as soon as stirring ceases. When Span 20 is used and the monomer concentrations are greater than  $0.25 \text{ mol l}^{-1}$ , the o/w concentrated emulsions do not even form under stirring at 25°C. When Span 80 is used as surfactant and the

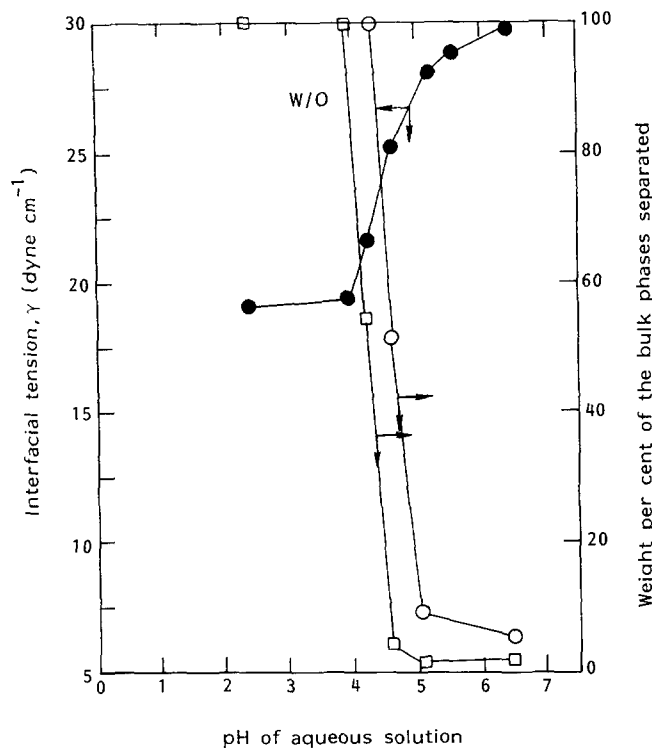
monomer concentrations are higher than  $0.94 \text{ mol l}^{-1}$ , the w/o concentrated emulsions formed at 25°C under stirring separate into bulk phases as soon as stirring ceases.

The effect of the pH of the aqueous monomer solution on the stability of the concentrated emulsion was examined by partially neutralizing the aqueous solution of acrylic acid with sodium hydroxide. The results are plotted in Figure 4. As the pH of the aqueous solution increases, the interfacial tension and the stability of the concentrated emulsion sharply increase. The amount of bulk phases that separates is greater for longer heating times.

The effect of the concentration of 2-hydroxyethyl methacrylate in the aqueous phase on the stability of the concentrated emulsion and interfacial tension is shown in Figure 5. The interfacial tension and the stability of the emulsion decrease with increasing concentration of the polar monomer in the aqueous phase. This polar monomer destabilizes both the o/w and w/o concentrated



**Figure 3** Interfacial tension between styrene and aqueous acrylic acid solutions and weight per cent of the phases separated from concentrated emulsions by heating for 24 h at 50°C plotted against the concentration of aqueous acrylic acid solution. The concentrated emulsions were prepared at 25°C and had a volume fraction of the dispersed phase of 0.9. ● denotes interfacial tension. ○ denotes o/w concentrated emulsions prepared using SDS ( $3.47 \times 10^{-1}$  mol/l water) as surfactant. □ denotes w/o concentrated emulsions prepared using Span 80 ( $2.5 \times 10^{-1}$  mol/l styrene) as surfactant. The w/o concentrated emulsions do not form at 25°C when Span 20 is used as surfactant and the concentration of acrylic acid is greater than  $2.3 \text{ mol l}^{-1}$



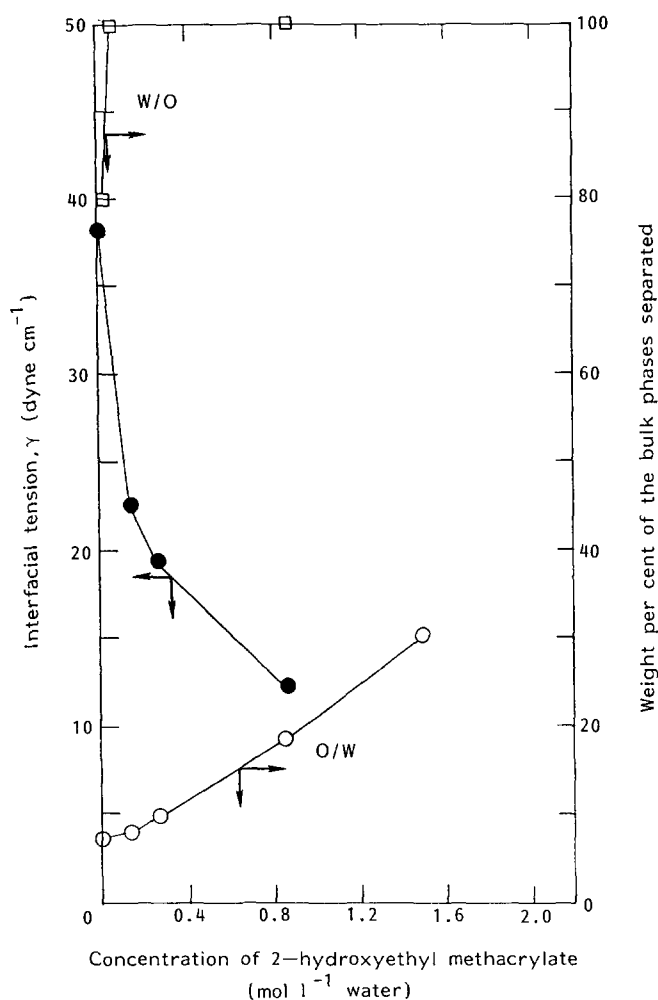
**Figure 4** Interfacial tension between styrene and aqueous acrylic acid solution and weight per cent of bulk phases separated from concentrated emulsions by heating at 50°C plotted against the pH of the aqueous acrylic acid solution. The concentrated emulsions were prepared at 25°C and had a volume fraction of the dispersed phase of 0.9. Aqueous acrylic acid solutions (0.94 mol/l water) were partially neutralized with NaOH. The w/o concentrated emulsions were prepared using Span 80 ( $2.5 \times 10^{-1}$  mol/l styrene) as surfactant. ● denotes the interfacial tension. □ and ○ denote weight per cent of bulk phases separated from concentrated emulsions by heating at 50°C for 3 and 24 h, respectively

emulsions. At high concentrations of 2-hydroxyethyl methacrylate in the aqueous phase (above  $2.0 \text{ mol l}^{-1}$ ), both the o/w and w/o concentrated emulsions form under stirring at room temperature; however, they separate into bulk phases as soon as stirring ceases. The o/w concentrated emulsions do not form at 25°C at a monomer concentration above  $2.6 \text{ mol l}^{-1}$  even under stirring.

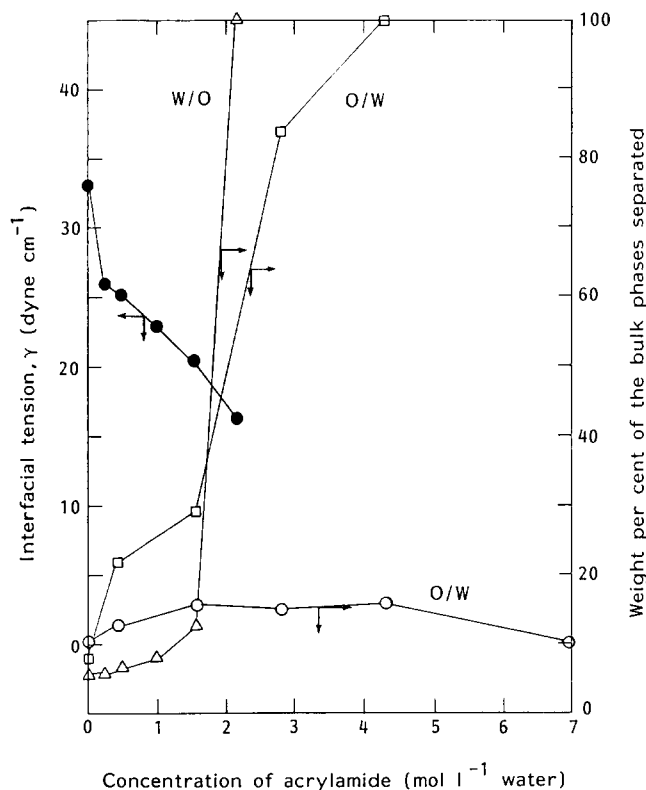
Figure 6 shows that the interfacial tension between styrene and aqueous solution of acrylamide decreases with increasing acrylamide concentration. Owing to the high viscosity of the aqueous solution, inaccuracies in the measurement of the interfacial tension between styrene and aqueous acrylamide solution are very likely to occur for high acrylamide concentrations. For this reason, the interfacial tensions for high acrylamide concentrations are not included in Figure 6. As expected from the decrease of the interfacial tension with increasing concentration of acrylamide, the stability of the concentrated emulsion decreases with increasing acrylamide concentration in both o/w and w/o systems. Unexpectedly, the stability of the o/w concentrated emulsions prepared using Span 20 (sorbitan mono-laurate) as surfactant does not decrease with increasing acrylamide concentration in the aqueous phase. This might be due to the interactions between the sorbitan ring of the surfactant and acrylamide at the interface.

Figure 7 correlates the interfacial tension and the stability of the concentrated emulsions containing styrene

as one of the phases and an aqueous styrenesulphonic acid salt solution as the other phase. Except for the steep decrease of the interfacial tension in the low concentration range of the aqueous monomer solution, a moderate decrease of the interfacial tension is observed with increasing styrenesulphonic acid salt concentration. The o/w concentrated emulsion prepared using SDS as surfactant becomes extremely unstable at 25°C with increasing monomer concentration in the aqueous solution. At monomer concentrations above  $0.62 \text{ mol l}^{-1}$ , o/w concentrated emulsions do form at room temperature under stirring, but separate into two bulk phases when stirring ceases. The o/w concentrated emulsions do not even form at room temperature when the non-ionic Span 20 is used. However, the w/o concentrated emulsion prepared using the non-ionic Span 80 as surfactant is relatively stable at 50°C and almost independent of the concentration of the monomer in the aqueous solution. The instability of the o/w concentrated emulsion at relatively high monomer



**Figure 5** Interfacial tension between styrene and aqueous 2-hydroxyethyl methacrylate solution and weight per cent of bulk phases separated from concentrated emulsions by heating for 24 h at 50°C plotted against the concentration of aqueous 2-hydroxyethyl methacrylate solution. The concentrated emulsions were prepared at 25°C and had a volume fraction of the dispersed phase of 0.9. The o/w concentrated emulsions were prepared using SDS ( $3.47 \times 10^{-1}$  mol/l water) as surfactant and w/o concentrated emulsions using Span 80 ( $2.5 \times 10^{-1}$  mol/l styrene) as surfactant. ● denotes interfacial tension. ○ and □ denote o/w and w/o concentrated emulsions, respectively. The o/w concentrated emulsions do not form at all at 25°C for monomer concentrations greater than  $2.6 \text{ mol l}^{-1}$



**Figure 6** Interfacial tension between styrene and aqueous acrylamide solution and weight per cent of bulk phases separated from concentrated emulsions by heating for 24 h at 50°C plotted against the concentration of aqueous acrylamide solution. The concentrated emulsions were prepared at 25°C and had a volume fraction of the dispersed phase of 0.9. ● denotes interfacial tension. ○ and □ denote o/w concentrated emulsions prepared using Span 20 ( $2.89 \times 10^{-1}$  mol/l water) and SDS ( $3.47 \times 10^{-1}$  mol/l water) as surfactant, respectively. △ denotes w/o concentrated emulsions prepared using Span 20 ( $2.89 \times 10^{-1}$  mol/l styrene) as surfactant

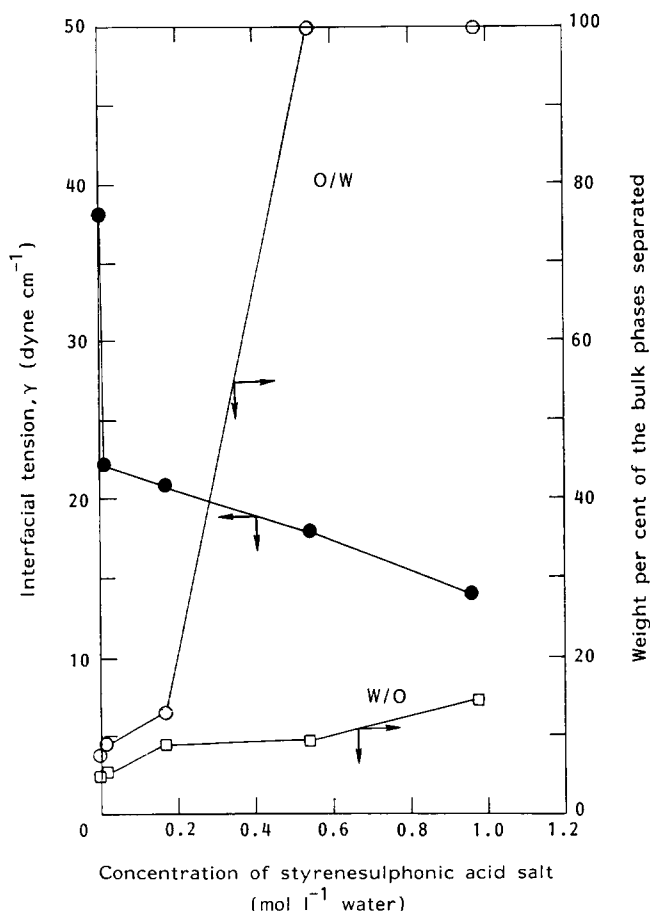
concentrations may be caused by the organization of water by the salt monomer to such an extent that the hydrophilic head-group of the surfactant has no longer more favourable interactions with water than with styrene. As a result, the surfactant molecules are salted out from the aqueous into the styrene phase and the amount adsorbed on the interface between the two phases becomes small. The stabilizing effect of the adsorbed surfactant molecules is thus tremendously decreased. The o/w concentrated emulsions prepared using SDS as surfactant have some stability at low concentrations of styrenesulphonic acid salt probably because of the repulsive double-layer forces among globules generated by the molecules of surfactant adsorbed upon the interface of the network of thin liquid films. However, as the concentration of styrenesulphonic acid salt (ionic strength) in the aqueous continuous phase increases, the double-layer repulsion is increasingly shielded and the concentrated emulsion becomes unstable. The fact that the concentrated emulsion maintains some stability for salt concentrations at which the electrostatic repulsion is completely shielded ( $0.3 \text{ mol l}^{-1}$ ) may be due to the existence of hydration repulsive forces<sup>5</sup>. The complete instability for large salt concentrations is due, as noted above, to the salting-out effect.

In Figure 8 the interfacial tension and the stability of concentrated emulsions containing styrene and an aqueous sodium chloride solution are plotted against the concentration of sodium chloride. In contrast to

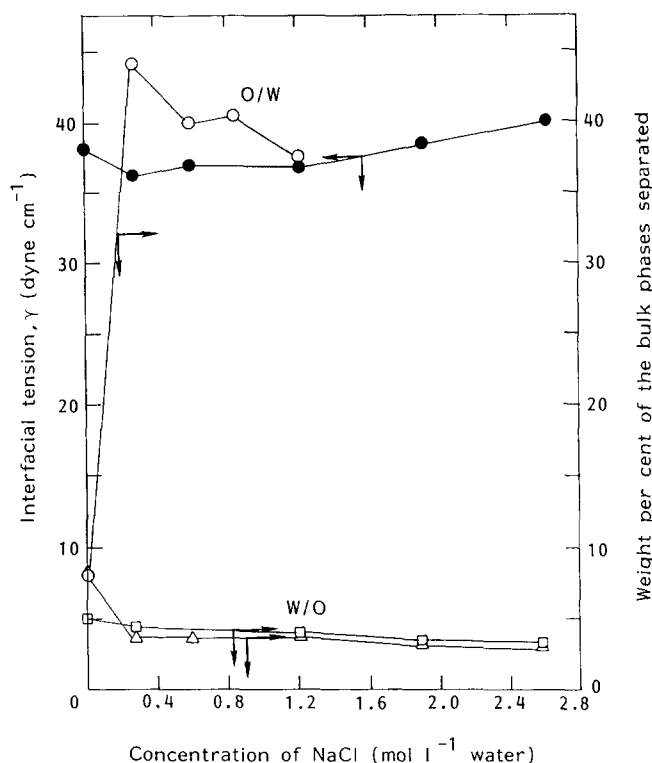
Figure 7, no noticeable change in interfacial tension with salt concentration is observed. The w/o concentrated emulsions are stable for both Span 20 and Span 80. When SDS is used as surfactant, the o/w concentrated emulsions are more unstable at 50°C than the above w/o concentrated emulsions and do not form at room temperature above a salt concentration of  $1.2 \text{ mol l}^{-1}$ , probably because of the salting-out effect. The o/w concentrated emulsion does not form at all at 25°C when Span 20 is employed as surfactant. These results are similar to those in Figure 7.

#### Effect of the surfactant and its concentration on the formation and stability of concentrated emulsions

Figures 9 and 10 show the effect of surfactant and its concentration on the stability of o/w and w/o concentrated emulsions, when styrene is employed as the hydrophobic monomer and water as the hydrophilic liquid. As already noted, the surfactant is expected to affect the formation and stability of concentrated emulsions. At low concentrations of SDS (below  $1.0 \times 10^{-3} \text{ mol l}^{-1}$ ) or of Tween 20 (below  $5.0 \times 10^{-4} \text{ mol l}^{-1}$ ) in the o/w systems, and of Span 80 (below  $1 \times 10^{-2} \text{ mol l}^{-1}$ ) in the w/o systems, concen-



**Figure 7** Interfacial tension between styrene and aqueous styrenesulphonic acid salt solution and weight per cent of bulk phases separated from concentrated emulsions by heating for 24 h at 50°C plotted against the concentration of aqueous styrenesulphonic acid salt solution. The concentrated emulsions were prepared at 25°C and had a volume fraction of the dispersed phase of 0.9. The o/w concentrated emulsions were prepared using SDS ( $3.47 \times 10^{-1}$  mol/l water) as surfactant and w/o concentrated emulsion using Span 80 ( $2.5 \times 10^{-1}$  mol/l styrene) as surfactant. ● denotes interfacial tension. ○ and □ denote the o/w and the w/o concentrated emulsion, respectively



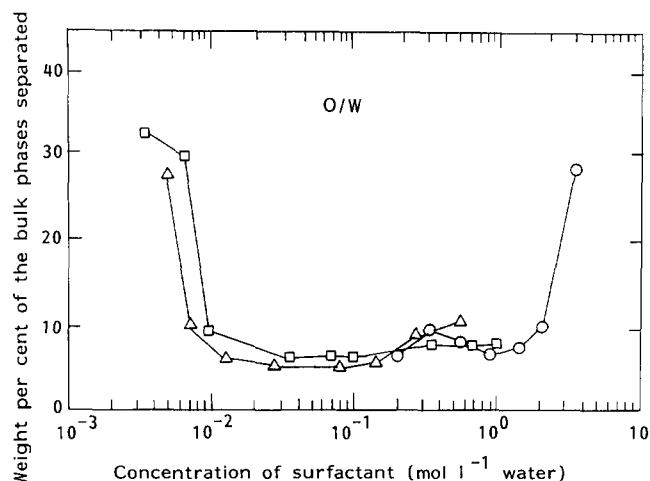
**Figure 8** Interfacial tension between styrene and aqueous NaCl solutions and weight per cent of bulk phases separated from concentrated emulsions by heating for 24 h at 50°C plotted against the concentration of aqueous NaCl solution. The concentrated emulsions were prepared at 25°C and had a volume fraction of the dispersed phase of 0.9. ● denotes interfacial tension. ○ denotes o/w concentrated emulsions prepared using SDS ( $3.47 \times 10^{-1}$  mol/l water) as surfactant. □ and △ denote w/o concentrated emulsions prepared using Span 80 ( $2.5 \times 10^{-1}$  mol/l styrene) and Span 20 ( $5.77 \times 10^{-1}$  mol/l styrene) as surfactants, respectively. The o/w concentrated emulsions do not form at room temperature above a salt concentration of  $1.2 \text{ mol l}^{-1}$  with SDS as surfactant

trated emulsions do form at room temperature under stirring; they separate, however, into two bulk phases as soon as stirring ceases. When Span 20 is employed as surfactant, the o/w and w/o concentrated emulsions do not form at room temperature (even under stirring) below  $9.6 \times 10^{-2}$  and  $4.8 \times 10^{-2} \text{ mol l}^{-1}$  surfactant concentration, respectively. Similarly, at high surfactant concentrations, above  $2.0 \text{ mol l}^{-1}$  for SDS,  $2.0 \text{ mol l}^{-1}$  for Tween 20 and  $8.5 \text{ mol l}^{-1}$  for Span 20 in o/w systems, and above  $4.0 \text{ mol l}^{-1}$  for Span 80 and above  $8.0 \text{ mol l}^{-1}$  for Span 20 in w/o systems, concentrated emulsions do not form, because of the high viscosity of the continuous phase. A too high viscosity of the continuous phase prevents the incorporation of the dispersed phase into the continuous phase and thus prevents the formation of the concentrated emulsion. The stability of o/w concentrated emulsions, when styrene is employed as the hydrophobic liquid, can be slightly improved by using the non-ionic surfactant Tween 20 instead of (the ionic surfactant) SDS (see Figure 9). The nature of the surfactant does not affect stability for the less polar hydrophobic liquids, but does affect stability for the more polar hydrophobic liquids (see Figure 2). The non-ionic surfactant Tween 20 is found to be a more efficient surfactant than the ionic surfactant SDS. The Tween 20 molecule, which has a long hydrophilic polyoxyethylene head-group, is more bulky and covers a larger surface area than the SDS molecule<sup>24</sup>. In addition, the steric

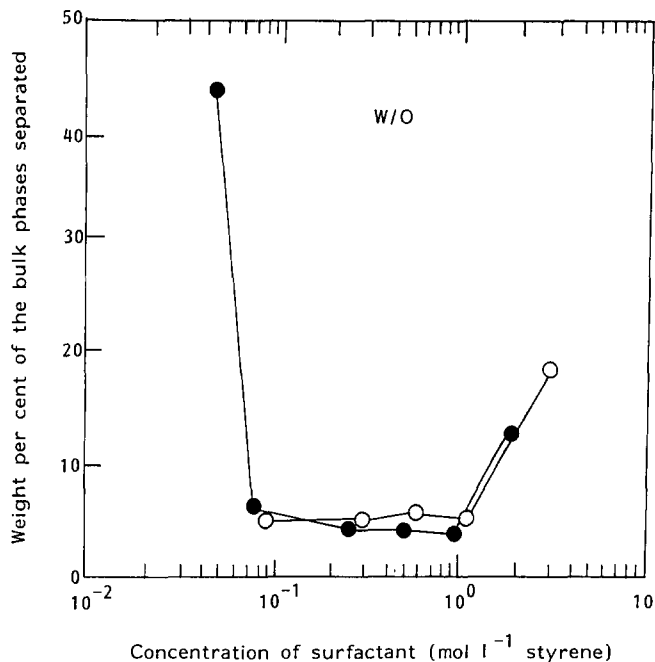
repulsion among the head-groups of the adsorbed molecules of Tween 20 is probably smaller than the electrostatic repulsion among the charged groups of SDS. As a result, the interfacial film is mechanically stronger for Tween 20.

In Figure 11, the interfacial tension between styrene and an aqueous ionic surfactant (SDS) solution and the concentrated emulsion stability are plotted against the logarithm of the concentration of surfactant. The break observed in the interfacial tension curve occurs when the concentration of surfactant in the continuous phase equals the critical micelle concentration (CMC), the concentration at which a large number of surfactant aggregates (micelles) form. The stability of the o/w concentrated emulsion increases with increasing surfactant concentration until the equilibrium concentration of the surfactant in the continuous phase reaches the CMC. When the concentration of surfactant in the continuous phase is below about  $1.0 \times 10^{-3} \text{ mol l}^{-1}$ , the concentrated emulsion formed under stirring becomes very unstable at room temperature as soon as the stirring ceases, and rapidly separates into the two bulk phases. Above the CMC, the interfacial tension remains essentially constant, since only the adsorption of the monomeric form of the surfactant contributes to the decrease in the interfacial tension and any further addition of surfactant above the CMC increases only the number of micelles. No changes in stability and interfacial tension occur for moderate increases in the surfactant concentration in the continuous phase above the CMC. However, no concentrated emulsions form at room temperature for surfactant concentrations larger than  $2.0 \text{ mol l}^{-1}$ . The high viscosity of the continuous phase prevents in such cases the incorporation of the dispersed phase into the continuous phase.

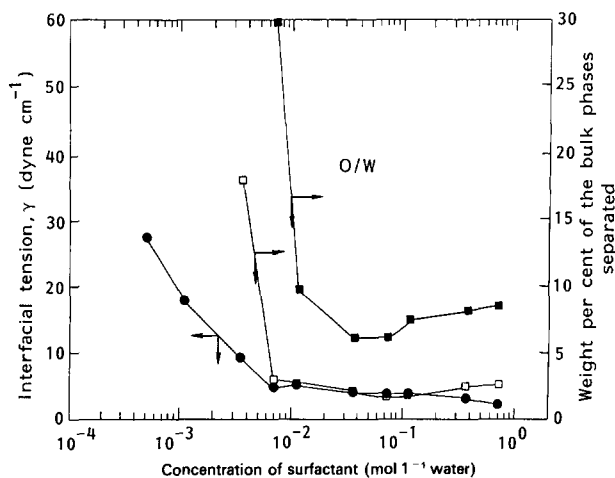
Figure 12 presents plots of the interfacial tension between styrene and aqueous Tween 20 solution and of the stability of the o/w concentrated emulsions against the logarithm of concentration of surfactant in the aqueous solution. As in Figure 11, both the interfacial tension and the emulsion stability do not change above the CMC for moderate increases in surfactant



**Figure 9** Weight per cent of bulk phases separated from o/w concentrated emulsions by heating at 50°C for 24 h plotted against the concentration of aqueous surfactant solutions. The concentrated emulsions were prepared at 25°C and had a volume fraction of the dispersed phase of 0.9. △, ○ and □ refer to Tween 20, Span 20 and SDS, respectively



**Figure 10** Weight per cent of bulk phases separated from w/o concentrated emulsions by heating at 50°C for 24 h against the plotted concentration of surfactant in styrene. The concentrated emulsions were prepared at 25°C and had a volume fraction of the dispersed phase of 0.9. ● and ○ refer to Span 80 and Span 20, respectively



**Figure 11** Interfacial tension between styrene and aqueous SDS solution and weight per cent of bulk phases separated from o/w concentrated emulsions by heating for 3 h (□) and for 24 h (■) at 50°C plotted against the concentration of aqueous SDS solution. The concentrated emulsions were prepared at 25°C and had a volume fraction of the dispersed phase of 0.9. ● denotes the interfacial tension

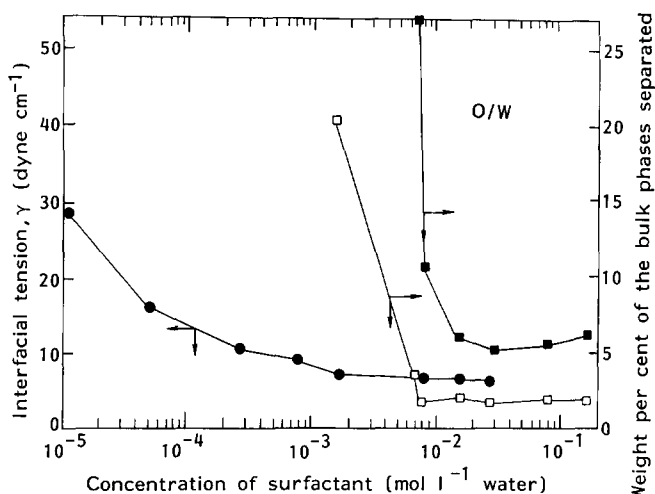
concentration. Below a surfactant concentration of  $5.0 \times 10^{-4} \text{ mol l}^{-1}$ , the concentrated emulsion obtained under stirring at 25°C rapidly separates into the two bulk phases when stirring ceases. At high surfactant concentrations, larger than  $2.0 \text{ mol l}^{-1}$ , concentrated emulsions do not form at 25°C because of the high viscosity of the continuous phase.

The interfacial free energy between water and a solution of Span 80 in styrene and the stability of w/o concentrated emulsions is plotted in Figure 13 against the concentration of Span 80. No concentrated emulsion is formed at room temperature until the concentration of Span 80 in the continuous phase reaches

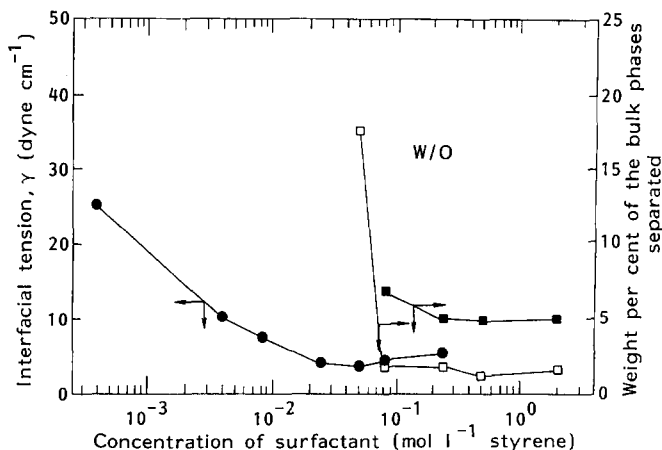
$1 \times 10^{-2} \text{ mol l}^{-1}$ . When the concentration of surfactant becomes higher than  $4.0 \text{ mol l}^{-1}$ , again no concentrated emulsion is formed because of the high viscosity of the continuous phase. For surfactant concentrations between about  $10^{-1}$  and  $2.0 \text{ mol l}^{-1}$ , the concentrated emulsions are relatively stable at 50°C.

*Effect of the HLB of the surfactant and of the surfactant blends on the stability of the concentrated emulsions*

Table 1 summarizes the relation between the hydrophilic-lipophilic balance (HLB) of surfactants and their ability to form concentrated emulsions. As expected from the definition of the HLB<sup>1,19</sup>, surfactants with low HLB values are oil-soluble and can therefore generate w/o concentrated emulsions, while those with high HLB values are water-soluble and can lead to o/w concentrated emulsions. Span 20, whose HLB is 8.6, can generate both w/o and o/w concentrated emulsions.



**Figure 12** Interfacial tension between styrene and aqueous Tween 20 solution and weight per cent of bulk phases separated from the o/w concentrated emulsions by heating for 3 h (□) and 24 h (■) at 50°C plotted against the concentration of aqueous Tween 20 solution. The concentrated emulsions were prepared at 25°C and had a volume fraction of the dispersed phase of 0.9. ● denotes the interfacial tension



**Figure 13** Interfacial tension between water and a solution of Span 80 in styrene and weight per cent of bulk phases separated from w/o concentrated emulsions by heating for 3 h (□) and 24 h (■) at 50°C plotted against the concentration of Span 80 in styrene. The concentrated emulsions were prepared at 25°C and had a volume fraction of the dispersed phase of 0.9. ● denotes the interfacial tension



**Table 1** Effect of the *HLB* of the surfactant on the formation and stability of concentrated emulsions. The concentrated emulsion contains styrene and water as the two phases and the volume fraction of the dispersed phase is 0.9. The concentrated emulsion was prepared at room temperature and its stability test was conducted by heating the emulsion at 50°C for 3 h and 24 h, respectively

Surfactant <sup>a</sup> ( <i>HLB</i> value)	Weight per cent of the bulk phases separated from the emulsion			
	w/o conc. emulsion		o/w conc. emulsion	
	3 h	24 h	3 h	24 h
Span 85 (1.5)	100	100	no emulsion formed	
Span 80 (4.3)	1.8	4.9	no emulsion formed	
Span 40 (6.7)	1.2	4.3	no emulsion formed	
Span 20 (8.6)	1.4	5.6	2.3	10.5
Tween 60 (14.9)	no emulsion formed		1.9	8.0
Tween 40 (15.5)	no emulsion formed		1.7	7.5
Tween 20 (16.6)	no emulsion formed		1.8	6.9
SDS (> 30)	no emulsion formed		2.4	9.1

<sup>a</sup>The concentrations of Spans and Tweens were  $2.5 \times 10^{-1} \text{ mol l}^{-1}$  and  $8.1 \times 10^{-2} \text{ mol l}^{-1}$ , respectively. The concentration of SDS was  $3.5 \times 10^{-1} \text{ mol l}^{-1}$

The effect of the *HLB* of surfactant blends (calculated as the weight average) on the stability of the concentrated emulsions is presented in Figure 14. It shows that both *HLB* and the chemical nature of the surfactant have an effect on the stability of the o/w concentrated emulsions. (No w/o concentrated emulsion could be prepared using the surfactant blends employed in Figure 14 because of the phase inversion that occurs at the beginning of the emulsification process.) The o/w concentrated emulsions exhibit minimum coalescence at a *HLB* of about 12. The stability of the concentrated emulsions prepared using surfactant blends is higher than that of concentrated emulsions prepared with individual surfactants. When Span and Tween are used together, they can cover the interface in a more compact manner because their areas per surfactant molecule are different and hence they can better fill the space. Thus, the van der Waals forces between the hydrocarbon chains of the surfactants become greater and the interfacial film becomes mechanically stronger. Figure 14 also shows that not only the type of surfactant blends, but also the polarity of the hydrophobic phase affects stability.

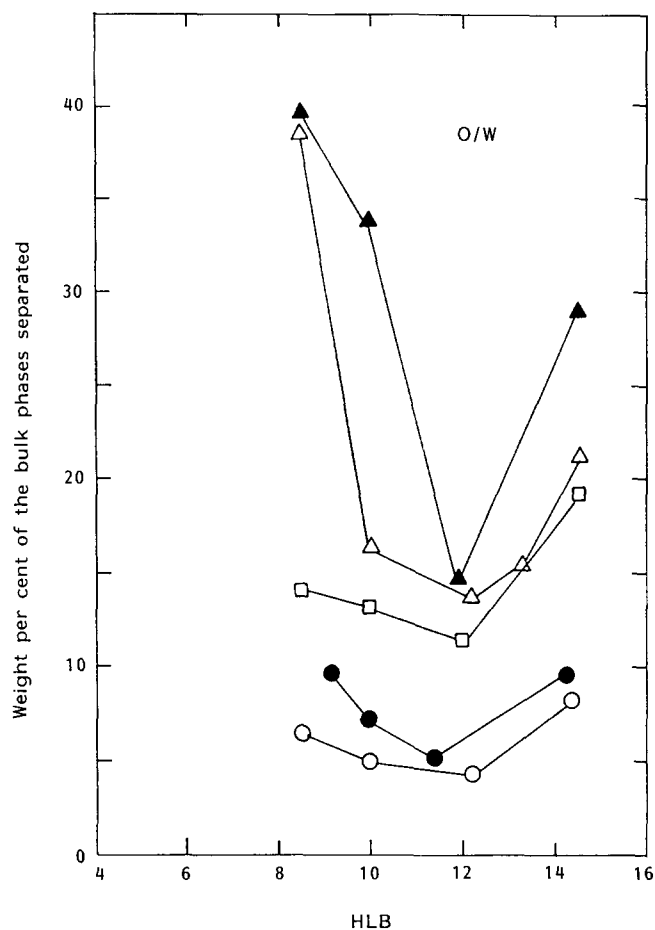
#### Effect of a mixture of ionic surfactant and long-chain alcohol on the stability of concentrated emulsions

The results listed in Table 2 indicate a pronounced effect of the long-chain alcohols on the stability of the concentrated emulsions prepared using a mixture of SDS and long-chain alcohols. The concentration of SDS of  $1.74 \times 10^{-1} \text{ mol l}^{-1}$  that was employed in the mixtures is well above the *CMC* of the single surfactant. It is interesting to note that the ionic surfactant SDS provides better stabilization when it is coupled with a long-chain alcohol than when it is used alone. The most likely cause of the increased stabilization brought by the long-chain alcohols is the increased cohesion in the interfacial film. The presence of the alcohol molecules among those of SDS increases the distance between the charged head-groups of SDS molecules, thus decreasing the electrostatic repulsion among them and hence increasing

the cohesion. The cohesion is additionally increased by the more compact packing of the two different species, which occupy different areas on the interface and thus can better fill the space. As a result, the film acquires a higher viscoelasticity than the interfacial film free of alcohols and is thus able to stabilize the cells of the dispersed phase against coalescence. Table 2 also shows that the concentrated emulsions prepared using hydrophobic liquids of higher polarity are less stable than those prepared using less polar hydrophobic liquids.

#### Effect of the viscosity of the continuous phase on the stability of concentrated emulsions

In Figure 15 the stability of the concentrated emulsions is plotted against the concentration of methyl cellulose in the aqueous continuous phase. Of course, the viscosity of the continuous phase increases with increasing concentration. Concentrated emulsions do not form for high concentrations of methyl cellulose owing to the difficulty of incorporating the dispersed phase into the

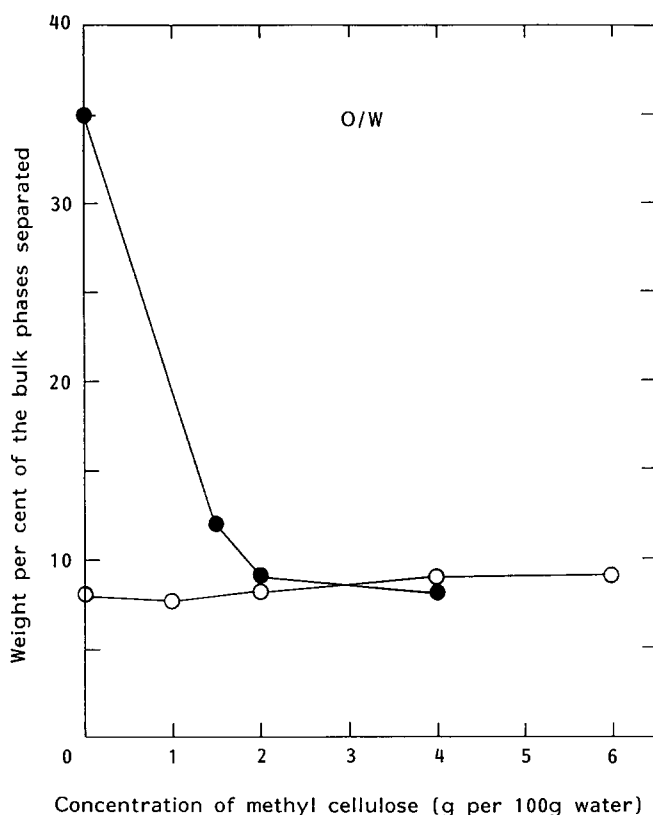


**Figure 14** Weight per cent of bulk phases separated from o/w concentrated emulsions by heating at 50°C for 24 h plotted against *HLB* values of surfactant blends. The concentrated emulsions were prepared at 25°C and had a volume fraction of the dispersed phase of 0.9. The total surfactant blends concentration in each emulsion was held constant at  $6.5 \times 10^{-2} \text{ mol l}^{-1}$ . ○ and ● denote o/w concentrated emulsions of styrene and water prepared using surfactant blends of Tween 20-Span 85 and Tween 40-Span 85, respectively. □ denotes o/w concentrated emulsions of butyl acrylate and water prepared using surfactant blends of Tween 20-Span 85. △ and ▲ denote o/w concentrated emulsions of methyl methacrylate and water prepared using surfactant blends of Tween 20-Span 20 and Tween 20-Span 85, respectively

**Table 2** Effect of mixtures of ionic surfactant and long-chain alcohols on the stability of the o/w concentrated emulsions. The concentrated emulsion contains a hydrophobic monomer and water as the two phases. The volume fraction of the dispersed phase is 0.9. The concentrated emulsions were prepared at room temperature and their stability tests were conducted by heating the emulsions at 50°C for 3 and 24 h, respectively

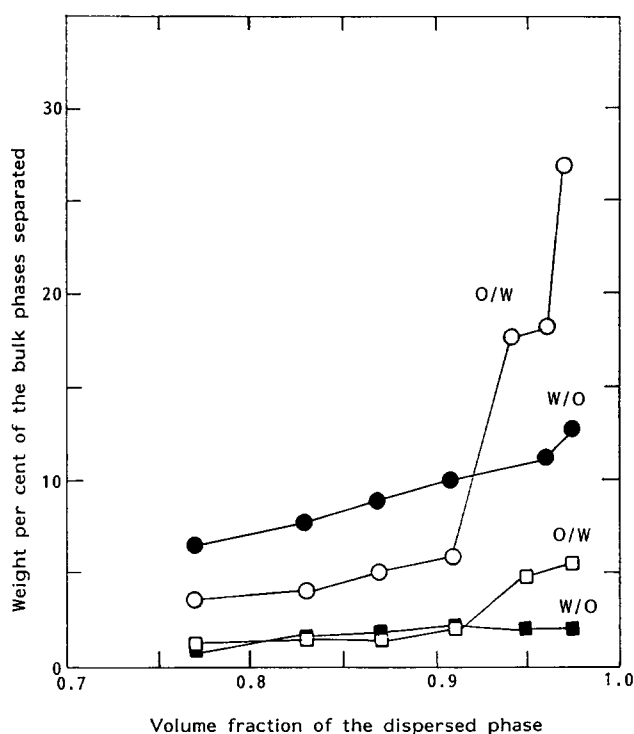
System	Surfactant <sup>a</sup> /alcohol	Weight per cent of bulk phases separated from the emulsion	
		3 h	24 h
Styrene/water	SDS	2.4	9.1
	SDS/CA	3.2	8.0
	SDS/OA	1.9	6.3
n-Butyl methacrylate/water	SDS	7.0	44.5
	SDS/CA	3.3	29.1
	SDS/OA	2.7	19.4
Ethyl methacrylate/water	SDS	21.4	100
	SDS/CA	17.6	100
	SDS/OA	13.5	100

<sup>a</sup>When used alone, the concentration of SDS was  $3.47 \times 10^{-1} \text{ mol l}^{-1}$ ; in the mixtures of SDS/CA and SDS/OA, the concentrations of SDS, CA and OA were  $1.74 \times 10^{-1} \text{ mol l}^{-1}$ , respectively



**Figure 15** Weight per cent of bulk phases separated from o/w concentrated emulsions by heating for 24 h at 50°C plotted against the concentration of methyl cellulose in the aqueous phase containing SDS ( $3.47 \times 10^{-1} \text{ mol l}^{-1}$  water). The concentrated emulsions were prepared at 25°C and had a volume fraction of the dispersed phase of 0.9. ○ and ● denote styrene and n-butyl methacrylate as the dispersed phases of concentrated emulsions, respectively

continuous phase. For instance, styrene–water and n-butyl methacrylate–water do not form concentrated emulsions for methyl cellulose concentrations in the aqueous continuous phase higher than 6.2 and 4.5 g/100 g water, respectively. Compared with the relatively non-polar monomer styrene, the stability of the concentrated emulsions containing slightly higher polar hydrophobic monomers, such as n-butyl methacrylate, is increased by the addition of methyl cellulose to the aqueous continuous phase. This might be due to the

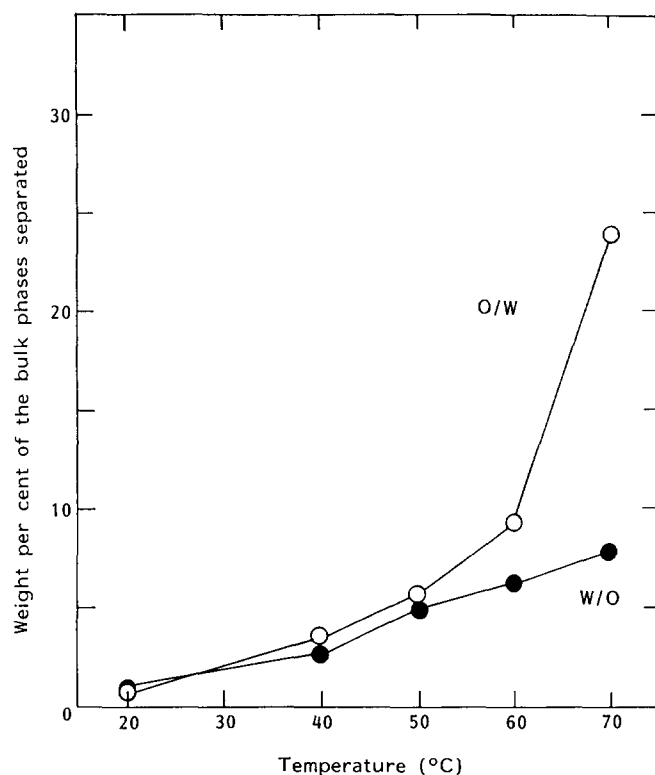


**Figure 16** Weight fraction of bulk phases separated from concentrated emulsions of water and styrene containing either SDS ( $3.47 \times 10^{-1} \text{ mol l}^{-1}$  water) or Span 80 ( $2.5 \times 10^{-1} \text{ mol l}^{-1}$  styrene) by heating at 50°C plotted against the volume fraction of the dispersed phase. The concentrated emulsions were prepared at 25°C. □ and ○ denote 3 and 24 h of heating time for the o/w concentrated emulsions, respectively. ■ and ● denote 3 and 24 h of heating time for the w/o concentrated emulsions, respectively.

interactions between methyl cellulose and n-butyl methacrylate.

*Effect of the volume fraction of the dispersed phase on the stability of the concentrated emulsions*

Figure 16 shows that the stability at 50°C of concentrated emulsions is affected by the volume fraction of the dispersed phase. As the volume fraction of the dispersed phase increases, the stability decreases. The increased instability of the concentrated emulsion is caused by the increased expansion of the interfacial film that surrounds the cells of the dispersed phase.



**Figure 17** Weight per cent of bulk phases separated from concentrated emulsions by heating for 24 h plotted against temperature. The concentrated emulsions were prepared at 25°C and had a volume fraction of the dispersed phase of 0.9. ○ and ● denote the o/w and w/o concentrated emulsions of styrene and water prepared using Tween 20 ( $8.1 \times 10^{-2}$  mol/l water) and Span 80 ( $2.5 \times 10^{-1}$  mol/l styrene) as surfactant, respectively

#### Effect of temperature on the stability of concentrated emulsions

The effect of temperature on the stability of the concentrated emulsions is examined in *Figure 17*. Both the o/w and w/o concentrated emulsions become unstable with increasing temperature, because this changes the mutual solubilities of the two phases, the interfacial tension between the two phases and the solubilities of the surfactant. When the temperature increases, the mutual solubilities of the two phases increase and the surfactant of the interfacial film becomes more soluble in the bulk liquid phases. This stimulates the surfactant molecules to migrate away from the interface, allowing the droplets to coalesce.

#### Preparation of hydrophilic-hydrophobic polymer composites

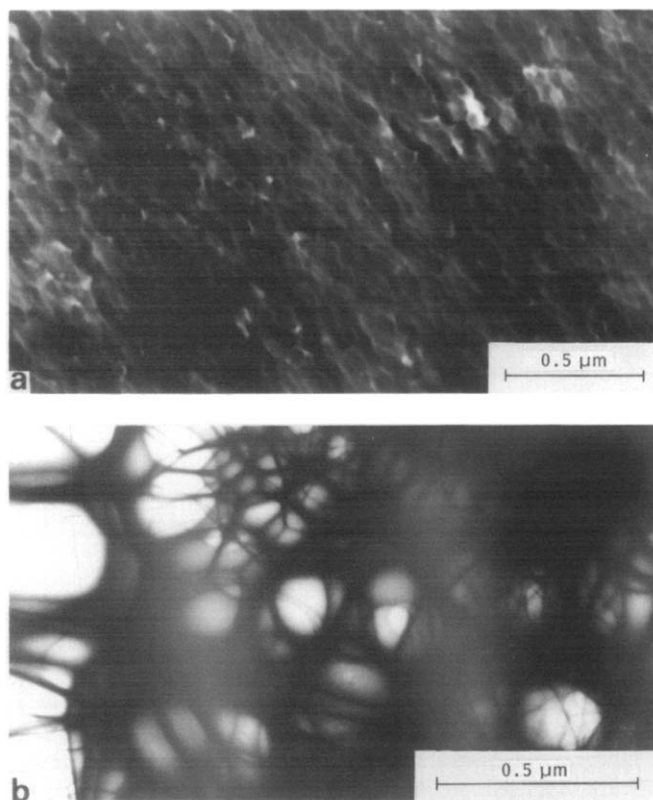
*Table 3* lists several hydrophilic-hydrophobic polymer composites that were synthesized using the concentrated emulsion pathway. The composites obtained from o/w systems were rigid solids; the membranes prepared from these composites had high permselectivity to toluene from a mixture of toluene and cyclohexane<sup>9</sup>. The composites prepared by polymerizing the w/o concentrated emulsions had poor mechanical strength; their mechanical strength could be improved, however, by crosslinking either the hydrophobic polymer in the continuous phase and/or the hydrophilic polymer in the dispersed phase. The membranes prepared from the latter composites had high permselectivity to water from

**Table 3** Hydrophilic-hydrophobic polymer composites. The concentrated emulsion was prepared at room temperature and heated at 50°C for 24 h to obtain the polymer composite. The volume of the dispersed phase is 30 ml and the volume of the continuous phase 3 ml. AIBN was used as initiator for the hydrophobic monomer and potassium persulphate for the hydrophilic monomer<sup>a</sup>. The hydrophilic phase was a solution of monomer in water

Polymer composites	Compositions	
	o/w system	w/o system
Polystyrene/polyacrylamide	Styrene: 30 ml Acrylamide: 2.4 mol/l water SDS <sup>b</sup>	Acrylamide: 0.24 mol/l water Styrene: 3 ml Span 80 <sup>b</sup>
Crosslinked polystyrene/polyacrylamide	Styrene: 27 ml Divinylbenzene: 3 ml Acrylamide: 2.4 mol/l water SDS <sup>b</sup>	Acrylamide: 0.24 mol/l water Styrene: 2.7 ml Divinylbenzene: 0.3 ml Span 80 <sup>b</sup>
Polystyrene/poly(acrylic acid)	Styrene: 30 ml Acrylic acid: 0.1 mol/l water SDS <sup>b</sup>	Acrylic acid: 0.167 mol/l water Styrene: 3 ml Span 80 <sup>b</sup>
Polystyrene/poly(acrylic acid) salt	Styrene: 30 ml Acrylic acid salt: 0.082 mol/l water SDS <sup>b</sup>	Acrylic acid salt: 0.167 mol/l water Styrene: 3 ml Span 80 <sup>b</sup>
Polystyrene/poly(2-hydroxyethyl methacrylate)	Styrene: 30 ml 2-Hydroxyethyl methacrylate: 0.13 mol/l water SDS <sup>b</sup>	
Polydivinylbenzene/polyacrylamide	Divinylbenzene: 30 ml Acrylamide: 2.4 mol/water Span 20 <sup>b</sup>	Acrylamide: 0.24 mol/l water Divinylbenzene: 3 ml Span 80 <sup>b</sup>
Poly(butyl methacrylate)/polyacrylamide	n-Butyl methacrylate: 30 ml Acrylamide: 1.6 mol/l water Tween 20 <sup>b</sup>	Acrylamide: 0.18 mol/l water n-Butyl methacrylate: 3 ml Span 80 <sup>b</sup>

<sup>a</sup> The concentrations of AIBN and potassium persulphate were 0.02 g/ml monomer and 0.015 g/ml monomer solution, respectively

<sup>b</sup> The concentration of Span 20, Span 80, SDS and Tween 20 were 0.29 mol/l water, 0.25 mol/l monomer, 0.35 mol/l water and 0.09 mol/l water, respectively



**Figure 18** Transmission electron micrographs of hydrophilic-hydrophobic polymer composites. The black regions represent polystyrene and the white regions are polyacrylamide. The compositions of these composites are given in the first row of *Table 3*. (a) Polystyrene constitutes the dispersed phase and polyacrylamide the continuous phase. (b) Polyacrylamide constitutes the dispersed phase and polystyrene the continuous phase

aqueous solutions of alcohol because of the high affinity of the hydrophilic polymer for water<sup>10</sup>.

Figures 18a and 18b are TEM micrographs of hydrophilic-hydrophobic polymer composites made of polystyrene and polyacrylamide. The polymer composites obtained by polymerizing the concentrated emulsion have a foam-like structure, containing sub-micrometre-sized polyhedral particles of polystyrene (polyacrylamide) separated by a network of thin polyacrylamide (polystyrene) films. The structure of the polymer composites prepared by the concentrated emulsion polymerization method can be controlled by controlling the structure of the precursor gel.

## CONCLUSIONS

A number of factors are found to be important in the formation at room temperature and stability at the polymerization temperature of 50°C of concentrated emulsions. They are: the chemical nature of the monomers employed in the dispersed and continuous phases; the capability of the surfactants used as dispersants in forming mechanically strong viscoelastic interfacial films at the interface; the viscosity of the continuous phase; the volume fraction of the dispersed phase; and the temperature. The chemical nature of the hydrophilic and hydrophobic monomers, particularly their polarity, is a major factor. The stability is increased

when the interfacial tension between the two phases containing the monomers and free of surfactant is higher. The factors that decrease this interfacial tension, such as strong acidity and high concentrations of the hydrophilic monomer in the aqueous phase, have a negative effect on stability. The presence of salt in the continuous phase of the o/w concentrated emulsions destabilizes or even prevents the formation of a concentrated emulsion. Above the CMC, the concentration of the surfactant, if it is not too high, does not affect the stability of the concentrated emulsions. A too high concentration of surfactant in the continuous phase, however, prevents the inclusion of the dispersed phase in the continuous one because it increases the viscosity of the continuous phase. The non-ionic surfactants such as the Tweens can be more effective surfactants than the ionic surfactant SDS. Blends of non-ionic surfactants and mixtures of ionic surfactant and long-chain alcohols are more efficient dispersants than the single surfactants. Increases in temperature and volume fraction of the dispersed phase can destabilize the system.

A number of hydrophilic-hydrophobic polymer composites have been prepared on the basis of the above considerations. By analysing the factors that affect the stability of concentrated emulsions, it is possible to design the hydrophilic-hydrophobic polymer composites by a more proper selection of the monomers and surfactants.

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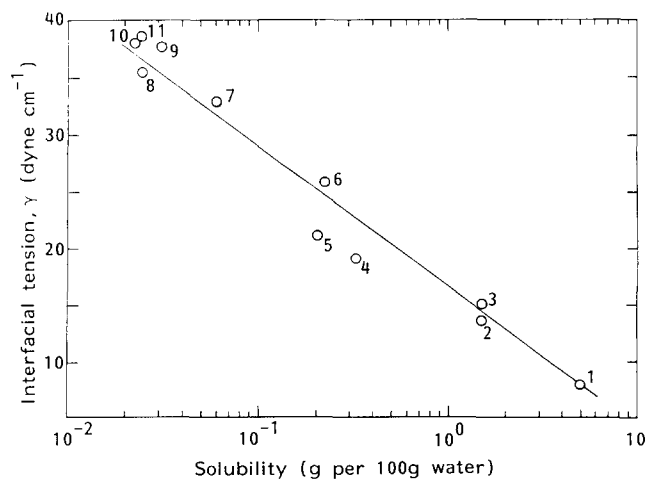


Figure 19 Relation between interfacial tension and water solubility. See text of Appendix for details

## APPENDIX

Interfacial tensions between hydrophobic liquids and water are plotted against the solubility of the hydrophobic liquid in water (g/100 g water) at 25°C in Figure 19. The data for the interfacial tensions and solubilities were obtained by the drop weight method<sup>23</sup> and from the literature<sup>25,26</sup>, respectively. The points in Figure 19 are numbered and refer to the following: 1, methyl acrylate; 2, ethyl acrylate; 3, methyl methacrylate; 4, isopropyl ether; 5, butyl acrylate; 6, nitrobenzene; 7, chloroform; 8, benzene; 9, styrene; 10, toluene; 11, ethylbenzene.