

Structure of colloidal particles in water oil mixtures stabilized by polymeric emulsifiers: 1. Phase diagrams and electron microscope studies

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The phase diagrams of toluene/water mixtures, stabilized by amphiphilic graft copolymers in the presence of an alcohol, show two domains in which these systems are optically clear. The composition of the continuous phase of the polymeric microemulsions was determined by dialysis experiments. The results indicate a preferential solvation of the copolymer sequences by the ternary solvent mixture. The micellar particles were observed by electron microscopy on carbon replicas of freeze-fractured samples. Depending on the copolymer composition and the location of the system in the phase diagram, the micrographs reveal either individual particles ($50\text{Å} < \text{radius} < 250\text{Å}$), well-dispersed in the continuous medium, or inter-particle clusters.

The colloid behaviour of block and graft copolymers in many respects resembles that of soaps and non-ionic surfactants. For example, dissolution of a copolymer in a medium which is a good solvent for one of its sequences and a non-solvent for the other leads to the formation of structures in which unlike copolymer sequences are micro-separated. Particles are formed which, in analogy to soaps, are called micelles. The simplest model of micelles consists of a compact core of the least soluble polymer component surrounded by the solvated sequences which prevent macroscopic flocculation of the polymer.¹⁻³

Recently, Riess and coworkers⁴ proposed the use of amphiphilic copolymers instead of soaps, for the formation of *microemulsions*. The latter are true colloidal systems with a solubilized dispersed phase. These apparently homogeneous transparent systems contain high percentages of oil and water with, in addition, 15 to 25% of an emulsifying mixture. Microemulsions are considered to be made of spherical or cylindrical droplets of 100 to 800 Å.

In previous papers,⁵ we have reported preliminary results on the structure of transparent water and oil dispersions stabilized by polymeric emulsifiers. More specifically, the ability of poly(ethylene oxide)-polystyrene graft copolymers to solubilize a water-toluene mixture in the presence of 2-propanol as a cosurfactant was investigated and compared with that of microemulsions prepared from conventional surfactants such as soaps. In particular, it was shown that polymeric microemulsions exist only when they involve three solvents which are mutually soluble (at least in a certain composition range).

In the present paper, the phase diagrams of quaternary systems water/toluene/PS-PEO copolymer/2-propanol are described. Our previous results⁵ have been completed by varying the copolymer concentration over a wide range. Parts of this paper are also concerned with the characterization of the continuous phase outside the droplets in these systems and with electron microscopic investigations on the morphology of the dispersed particles.

In subsequent papers (parts 2 and 3), additional information is presented on the size and the structure of the droplets using small-angle neutron scattering, quasi-elastic light scattering and viscosity measurements.

MATERIALS AND METHODS

Surfactants

We have used a homologous series of graft copolymers composed of an hydrophobic polystyrene backbone and hydrophilic poly(ethylene oxide) grafts. The grafting reaction proceeds via anionic deactivation of a 'living' poly(ethylene oxide) onto a partly chloromethylated polystyrene.⁶ By this method, the length of the backbone, as well as the number and length of branches can be varied almost at will. Furthermore, the resulting samples are homogeneous in composition and have a narrow molecular weight distribution. Their characteristics are listed in Table 1.

Formation of transparent systems (turbidimetry)

Milky emulsions containing variable amounts of water, toluene and graft copolymer were converted to stable microemulsified systems by titration to clarity with 2-propanol.

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Table 1 Structural characteristics of PS-PEO graft copolymers

Sample	M_w (PS backbone)	M_w (PEO graft)	\bar{P} (average number grafts)	M_w (copolymer)	$R = \frac{M_w, PS}{M_w, PS + M_w, PEO}$
A3	135 000	4 750	61	425 000	0.32
A4	18 200	2 100	9	38 400	0.49
A5	18 200	3 700	10	55 000	0.33
A7	18 200	7 800	6.5	75 000	0.26

Weight-average molecular weights have been determined by light scattering except for $M_w, A3$ calculated from the numerical data for M_w, PS and M_w, PEO ⁶

Dialysis experiments

Rather elaborate methods are needed⁷ to determine the composition of the continuous phase of conventional microemulsions. In contrast, a simple dialysis equilibrium between the quaternary system and the ternary solvent mixture is sufficient when polymeric surfactants are involved, since the semipermeable membranes are impervious to macromolecules.

The dialysis equilibrium is reached after a few hours, when the composition of the ternary mixture is equal to that of the continuous phase of the microemulsion.

The weight composition of the ternary solvent mixture is analysed before and after dialysis by gas chromatography, following a procedure described in detail elsewhere.⁸ This technique allows a precise determination of the composition of the continuous phase after equilibrium. As the volume of the microemulsion is large compared to that of the ternary mixture (ratio of 7 to 1 between the two compartments of the cell), the fluctuations of composition in the microemulsion during the dialysis process can be neglected and the equilibrium composition taken equal to that of the initial microemulsion.

Freeze-etching

The freeze-etching technique has recently been successfully applied to the preparation of polymer lattices,^{9,10} copolymer micellar aggregates,^{11,12} or classical microemulsions¹³ for electron microscopy (EM) studies.

Best results were obtained using the following operative procedure.¹⁴ A droplet of the solution, deposited on a small gold plate was rapidly quenched in liquid nitrogen in equilibrium with its own solid phase (rather than liquid Freon held at liquid nitrogen temperature). The replicas of the fracture surfaces, prepared at -150°C in a 'Balzer Baf 301' unit, were obtained in the classical way, i.e. by C/Pt shadowing followed by carbon coating, without prior etching of the exposed surface. The replicas were allowed to warm up to room temperature and then washed several times in pure tetrahydrofuran to dissolve away the remaining polymer. After mounting on a copper grid, the replicas were examined with a Philips EM 300 or a Hitachi HU 11 CS transmission electron microscope.

RESULTS AND DISCUSSION

Phase diagrams

For the sake of simplicity, pressure and temperature were kept constant (atmospheric pressure and room temperature). Under these conditions, the phase diagram of the quaternary systems may be represented by a tetrahedron in which each corner corresponds to one component of the system (Figure 1).

Furthermore, we will consider sections of the tetrahedron; this amounts to imposing an additional parameter. We chose to study diagrams corresponding to different values of the wt percent copolymer with respect to the total weight of (water + toluene). Such diagrams are described by triangular sections like ABC, $A_1 B_1 C_1$, etc. . . of the tetrahedron (Figure 1) whose area decreases gradually as the proportion of copolymer is increased.

Clearly, with no copolymer the phase diagram is represented by the basal equilateral triangle ABC in Figure 1. This diagram is divided into two domains separated by the mutual solubility curve of the three solvents water/toluene/2-propanol (as shown in Figure 2a). Above this line, there is a transparent solution while below phase separation occurs.

By addition of the copolymer, the mutual solubility line is lowered in proportion to the polymer concentration^{4, 5, 15} (Figure 2b) which implies that the copolymer enhances the mutual solubility of the three solvents.

Above a given copolymer concentration typically of the order of 12%, a new monophasic domain appears in the diagram (part M in Figure 2b). This domain is located on the left, the toluene-rich area. Its size increases gradually as the copolymer concentration increases (Figures 2c and 2d).

The above results indicate that, for fixed copolymer concentration and water/toluene ratio, it is possible to obtain two transparent systems, presumably of different structure, since they require amounts of 2-propanol which vary within a ratio of about 3 to 1.

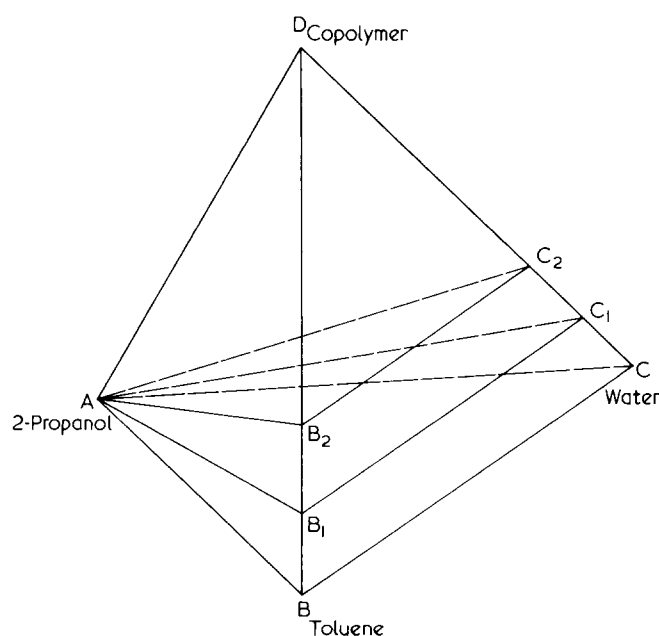


Figure 1 Spatial model used for the representation of the phase diagram of a quaternary system

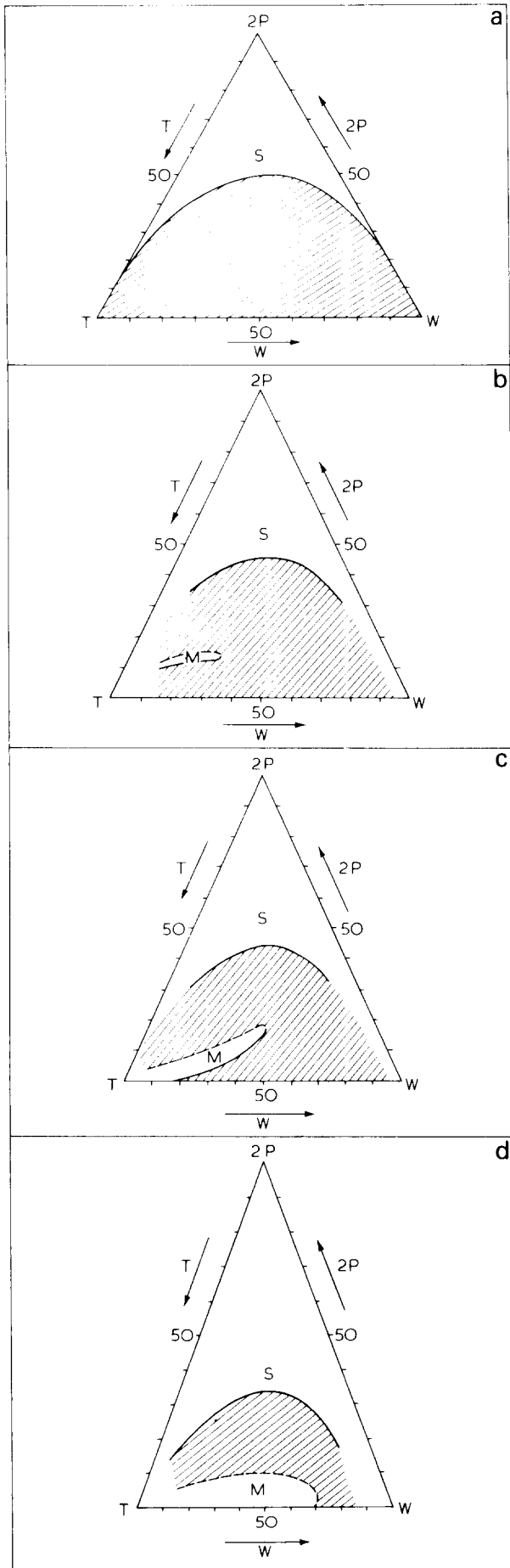


Figure 2 Pseudo-ternary phase diagrams at room temperature of water/toluene/sample A4/2-propanol for different values of the copolymer weight percentage $Y = m_{\text{cop}}/(m_{\text{T}} + m_{\text{W}})$. (a) $Y = 0$; (b) $Y = 0.20$; (c) $Y = 0.30$; (d) $Y = 0.60$

The influence of the copolymer composition on the formation of transparent systems is shown in Figure 3 where the weight percentage, Z , of 2-propanol with respect to the total weight of (water + toluene) $Z = m_{2\text{P}}/(m_{\text{T}} + m_{\text{W}})$ is plotted versus the percentage of copolymer $Y = m_{\text{cop}}/(m_{\text{T}} + m_{\text{W}})$. It should be emphasized that the copolymer concentration required for the formation of systems M is a decreasing function of the hydrophobic nature of the copolymer, characterized by the weight percentage of PS $R = M_{\text{w,PS}}/(M_{\text{w,PS}} + M_{\text{w,PEO}})$. This result suggests that in these toluene-rich systems, the water is trapped in micelles in which the PEO grafts of the copolymer molecules lie on the inside layer of the shell and the PS backbones on the outside layer. An increasing amount of PS favours the shielding of the hydrophobic interactions between the trapped water and the toluene outside of the micelles.

Alternatively, systems S, located on and above the upper transition line behave differently since the amount of 2-propanol required to obtain transparency increases with the hydrophobic character of the copolymer (see Figure 3). In this case, the micelles presumably exhibit the reverse structure, with the PEO grafts directed outwards. This structure will be discussed in more detail in paper 2.

Nature of the continuous phase

A quantitative description of micellar systems first requires the determination of their continuous phases. Dialysis experiments have yielded accurate ponderal compositions of the phase located outside of the droplets. Results for systems formed with sample A5 are represented on the pseudo-ternary diagram of Figure 4 where two distinct sections of the tetrahedron have been superposed. The broken and solid lines represent the mutual solubility curve of the ternary solvent mixture ($Y = 0$) and the transition from milky emulsions to transparent systems S, respectively. In the phase diagram, each arrow joins a pair of points of which one corresponds to the overall composition of the system at the transition and the other to the composition of its continuous phase. It is noteworthy that the compositions of the continuous phases of the systems S, given by the tip of the arrows, all lie on the mutual solubility curve of the ternary solvent mixture.

These results confirm a previous model⁵ according to which the solubilization is due to a preferential solvation of the copolymer sequences by the ternary solvent mixture, in contrast to classical models where one component is entirely trapped within the micelle.

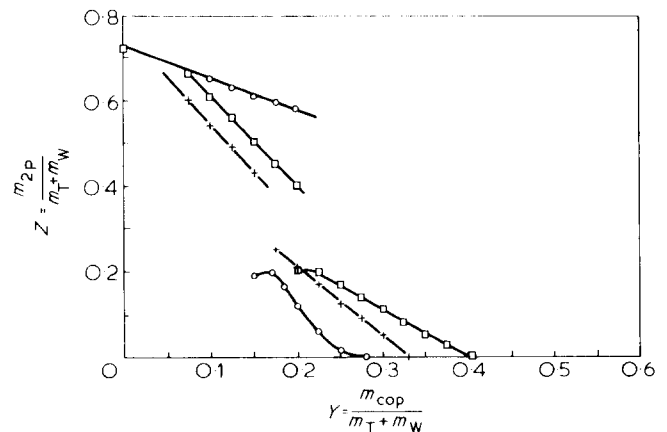


Figure 3 Influence of the copolymer composition on the formation of the transparent systems, water/toluene graft copolymer/2-propanol: \circ , sample A4; $+$, sample A5; \square , sample A7

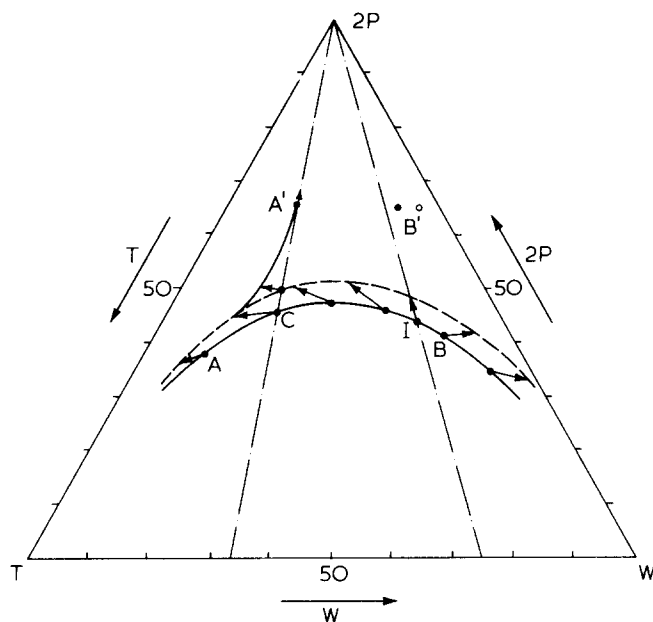


Figure 4 Pseudo-ternary phase diagram for the system, water/toluene/sample A5/2-propanol: ———, $Y = 0$; ———, $Y = 0.083$. Points A, B, A', B' are relative to the overall compositions of solvent mixtures in the corresponding systems (the copolymer concentration is kept constant $Y = 0.083$):
Systems A, water, 10.1; toluene, 49.9; 2-propanol, 40.0;
Systems B, water, 46.3; toluene, 9.4; 2-propanol, 44.3;
Systems A', water, 11.7; toluene, 23.4; 2-propanol, 64.9
Systems B', ●, samples A4, A3 and A5: water, 29; toluene, 5.8; 2-propanol, 65.2; ○, sample A7: water 31.9; toluene, 2.9; 2-propanol, 65.2

When the amount of 2-propanol is increased progressively, (see *Figure 4* curve CA'), the composition of the continuous phase tends rapidly towards that of the overall composition of the system, as could be expected. Closer inspection of *Figure 4* reveals the existence of an 'invariant' point (I in the phase diagram). At this specific composition, the toluene/water ratios of the system, of the continuous phase and consequently of the dispersed phase are identical. The invariant point corresponds presumably to an 'optimal' composition of the solvent mixture absorbed by a given copolymer. In fact, there is a clear correlation between this 'optimal' composition and the amphiphilic nature of the copolymer, as evidenced by an increase of the weight percentage of toluene at the invariant point with the parameter R (*Table 2*). This behaviour expresses the affinities of PS and PEO for toluene and water, respectively.

For any other system on the transition line, one can reasonably assume that the copolymer absorbs a solvent mixture whose composition is very close to that at the invariant point. When passing from one side of I to the other on the transition line, the direction of the arrows reverses (*Figure 4*), indicating opposite variations of the toluene/water ratio of the continuous phases with respect to the overall compositions.

This reasoning is confirmed when studying the influence of copolymer concentration on the composition of the continuous phase, the toluene/water ratio being kept constant in the different systems. At the invariant point, the composition of the external phase is not affected when the copolymer concentration is changed (*Figure 5a*). On the contrary, for any other composition, a variation of the copolymer concentration results in a variation of the composition of the continuous phase, and this is more pronounced the higher the copolymer concentration (*Figure 5b*).

Electron microscopy

As a general rule, the morphology of the micelles, as observed by electron microscopy, strongly depends on the location of the systems in the phase diagram and on the nature of the copolymer.

In the following we will consider, as illustrated in *Figure 4*, four systems *S* of varying compositions: two systems A' and B' containing high percentages of alcohol and located far above the transition line. These systems are toluene-rich and water-rich, respectively; two systems A and B located in the vicinity of the transition line.

Systems with high percentages of 2-propanol (A' and B'). *Figures 6a* and *6b* show micrographs obtained with two different systems. *Figure 6a* corresponds to a system prepared from copolymer A3 (overall composition B', water-rich area) and *Figure 6b* to a system prepared from copolymer A7 (overall composition A', toluene-rich area). As clearly shown by the micrographs, both systems display particles widely dispersed over the whole fracture surface. At first sight, the particles appear to be spherical in shape and approximately monodisperse in size.

It should be noted that the shadow of each droplet is much more elongated than expected for spherical particles. Furthermore, the direction of the shadows is not unique but varies slightly from one particle to the other. These observations strongly suggest that considerable distortion occurred during the fracture process, resulting in the formation of thin, rod-like protusions visible inside circular imprints.

Similar features have already been pointed out by several authors^{9,10,16} and discussed in detail by Sleytr and Robards⁹ in the case of polymer latex spheres and poly(β -hydroxybutyrate) (PHB) granules. They have been interpreted as due to plastic deformation of the spheres or granules during the freeze-cleaving. The fracture of the frozen droplets can proceed along two different paths:

- (i) the fracture goes along the particle/matrix interface. In this case, the particles can be either removed from the surface or remain embedded in the continuous medium resulting in a depression or a protuberance on the fracture surface;
- (ii) the fracture plane passes straight through the particles. As underlined by Menold *et al.*,¹⁷ this generally occurs for colloidal particles, in which the dispersed phase is made of a polymer. This is what is observed for the present systems. During the process, part of the particle becomes highly stretched until fracture occurs. This finally gives rise to the observed rod-like spike which collapses more or less back onto the surface and to a circular imprint probably corresponding to a cross-section of the initial particle.

Table 2 Influence of the copolymer composition on the location of the invariant point I in the phase diagram (characterized by the weight of toluene with respect to the total weight of water and toluene X_I)

Copolymer	A4	A5	A3	A7
$R = \frac{M_{W,PS}}{M_{W,PS} + M_{W,PEO}}$	0.49	0.33	0.32	0.26
$X_I = \frac{m_T}{m_T + m_W}$	0.70	0.25	0.25	0.13

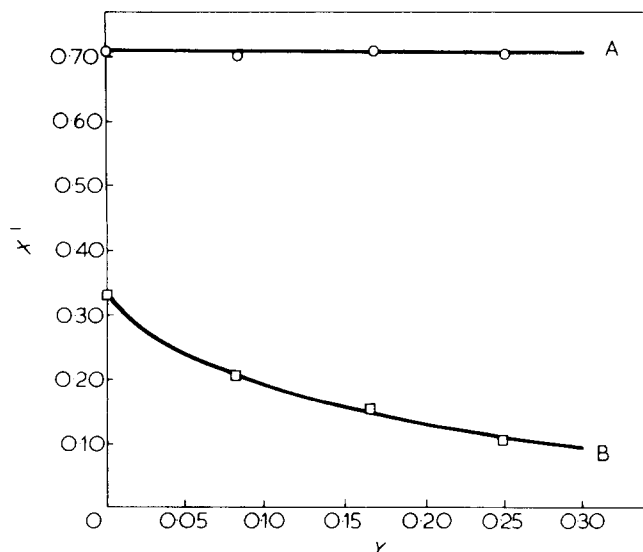


Figure 5 Influence of the copolymer concentration on the composition $X^1 = [m_T/(m_T + m_W)]_{\text{cont}}$ of the continuous phase for systems: water/toluene/sample A4/2-propanol. A, O, at the invariant point. The overall composition $X = m_T/(m_T + m_W) = 0.72$; B, □, for an overall composition $X = 0.33$

It should be mentioned that the circular imprints exhibit an unusually high contrast, since they are fairly opaque in the electron beam. A similar observation has already been made by Reed and Barlow^{10a} who conclude that the polymer might adhere firmly to the film, due to a failure of the solvent to enter the small fissures of the replica. This seems unlikely in the present case, since tetrahydrofuran is a very good solvent of the PS-POE graft copolymer, but no alternative more satisfactory explanation is at hand.

Systems in the vicinity of the transition line (A and B). A systematic study carried out with samples A3, A4, A5 and A7 has shown that different morphologies could be observed for systems located near the transition line.

Figures 6c and 6d show two types of morphology observed for the same copolymer (A3) in two regions of the phase diagram, the water-rich area (point B) and the toluene-rich area (point A), respectively.

In the first case (Figure 6c) individual particles are again dispersed in the continuous medium, with a density somewhat higher than in Figures 6a and 6b, due to an increase of the copolymer concentration (4.4% as compared to 2.8% w/w).

The plastic deformation undergone by these particles is much less pronounced. This fact can be attributed to a greater softness of the particles, as confirmed by neutron scattering experiments and discussed later on (part 2). A striking feature found for systems located in the toluene-rich area, is the formation of compact network-like clusters made of individual particles (Figure 6d). Price and Woods¹¹ have observed a similar clustering effect on block and graft copolymers. These authors suggested that these clusters were formed during the preparative process and were therefore not representative of solution behaviour. In the present case, this phenomenon is certainly not an artifact due to the freezing technique, since quasi-elastic light scattering experiments have confirmed the presence of inter-particle packings in solution at room temperature (part 3).

A more detailed study undertaken on systems prepared from the same sample (A3) has shown that clusters appear for T/W phase ratios higher than 0.30. This value corresponds

Table 3 Radii (Å) of the dispersed particles in quaternary systems (type S) measured by electron microscopy

	Toluene-rich side (A and A')	Water-rich side (B and B')
Systems A and B (transition line):		
A4	55	Clusters
A5	Clusters ($R_i^* \sim 105$)	200
A7	Clusters	200
A3	Clusters ($R_i^* \sim 175$)	230
Systems A' and B' (upper domain):		
A4	60	150
A5	95	—
A7	220	250
A3	180	210

R_i^* is the radius of an individual particle

approximately to the 'invariant' point of the system shown by dialysis experiments. For lower values of the T/W phase ratio, the particles are well dispersed as shown in Figure 6c.

The region in the phase diagram where these clusters appear depends also on the nature of the copolymer. For the predominantly hydrophilic samples A5, A7 as well as A3, this region lies on the toluene side while for the more hydrophobic sample, A4, it lies on the water side of the phase diagram. This phenomenon may well be due to a pre-transitional effect occurring before the flocculation of the solution.

In Table 3, we have reported for both types of systems (A, A' and B, B'), and in the absence of cluster formation, the sizes of the circular imprints observed on the micrographs, sizes which are directly related to the initial dimensions of the droplets. Their radii range approximately 50 to 250 Å. They appear to vary not only with the structure of the copolymers but also with the location of the systems in the phase diagram. These dimensions will be compared with the values obtained from small-angle neutron scattering and quasi-elastic light scattering measurements and discussed in paper 3.

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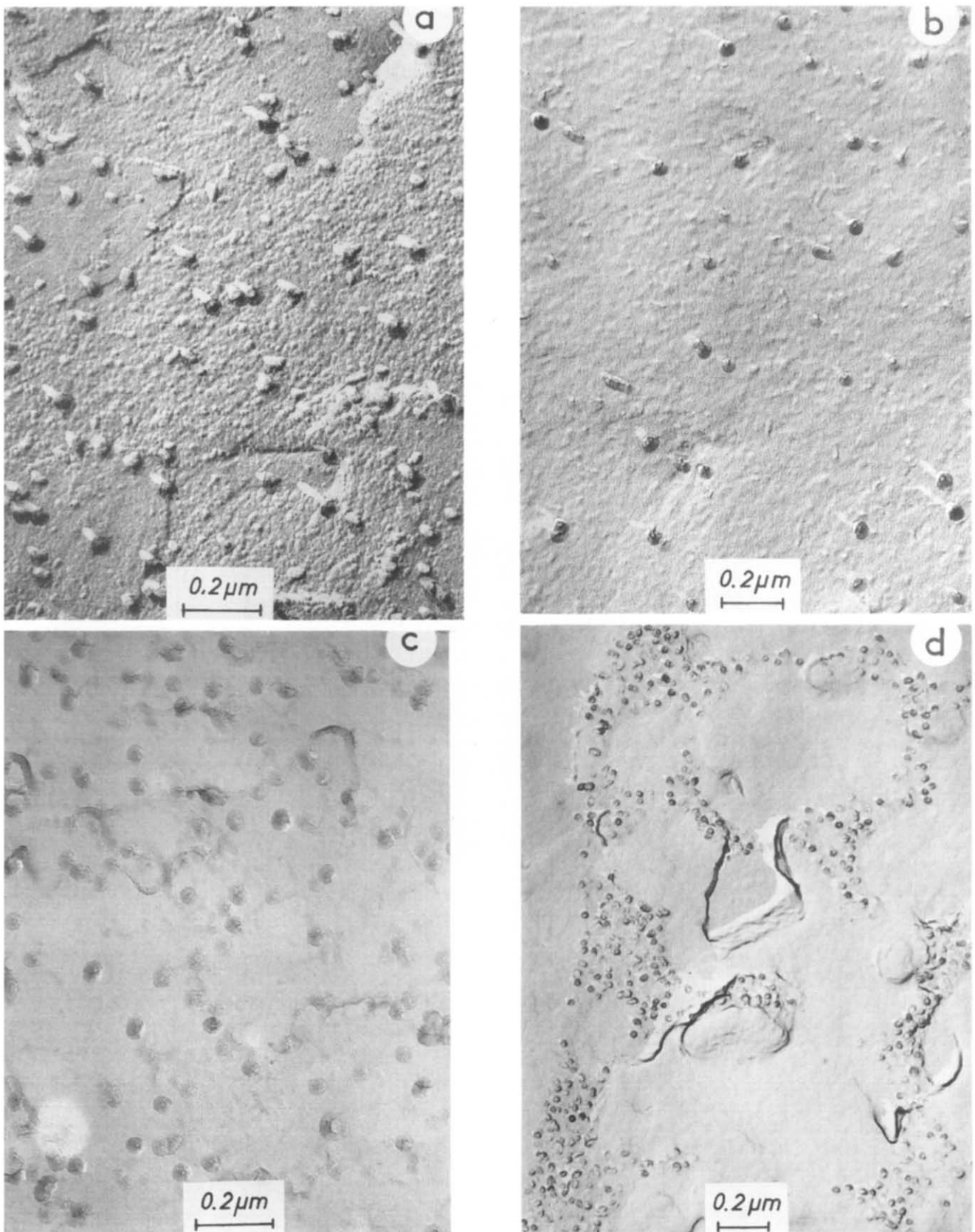


Figure 6 Electron micrographs of freeze-fracture replicas of quaternary systems ($Y = 0.083$). (a) sample A3 (system B'); (b) sample A7 (system A'); (c) sample A3 (system B); (d) sample A3 (system A)

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