Liquid crystal phase transitions in dispersions of rod-like colloidal particles

M P B van Bruggen, F M van der Kooij and H N W Lekkerkerker

Van't Hoff Laboratorium voor Fysische en Colloidchemie, Universiteit Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

Abstract. The isotropic–nematic (I–N) phase transition in dispersions of sterically stabilized rod-like boehmite (AlOOH) colloids is studied. We have examined the influence of the steric stabilizer, the dispersion medium and the presence of non-adsorbing polymer on the phase transition process. Dispersions in cyclohexane show an I–N phase separation that proceeds by a slow sedimentation of a pinned structure, shrinking from the meniscus, finally forming the nematic phase after weeks or months, depending on the steric stabilizer used. In toluene the onset of the I–N has shifted to higher volume fractions where individual nematic droplets grow and sediment, forming the nematic phase after one week. By adding non-adsorbing polymer to dispersions in cyclohexane the onset of the I–N phase separation shifts to lower colloid volume fractions. At polymer concentrations just above the phase boundary the same scenario as in the toluene dispersions without added non-adsorbing polymer is observed. At slightly higher polymer concentrations an abrupt change in scenario occurs. Now an interconnected network is formed which starts to sediment, resembling the process in pure cyclohexane dispersions. Clearly small variations in colloidal interactions engendered by the changes in dispersion characteristics considered in this work, have a strong influence on the I–N phase transition process.

1. Introduction

One of the most remarkable phenomena exhibited by concentrated suspensions of colloidal particles is the spontaneous transition from fluid-like structures to those exhibiting long-range spatial and/or orientational order. Such a transition was first observed and recognized as such by Zocher [1] in suspensions of rod-like colloidal V_2O_5 particles where at a volume fraction of a few percent an I–N phase transition occurs. Later more extensive studies of this phase transition were performed on dispersions of tobacco mosaic virus [2, 3]. A similar disorder to order transition was observed early on by Langmuir [4] in a dispersion of colloidal bentonite particles which are plate-like. All these transitions occur in charge stabilized colloids with long-range repulsive interactions. Onsager [5] showed that the I–N phase transition can indeed be explained as a result of repulsive forces. From his treatment of the I–N phase transition in an assembly of hard rods it follows that this transition is due to competition between the orientational entropy favouring the isotropic phase and the excluded-volume entropy favouring the nematic phase.

In the last twenty years colloidal particles approximating hard spheres have been prepared. Cores of silica or polymethylmethacrylate with thin layers of a flexible polymer grafted on their surfaces dispersed in a good solvent come close to being hard spheres. When two particles touch their polymer coatings are compressed and a repulsive force acts between them. With thin coatings this force increases rapidly with a small decrease in

interparticle separation, thus approximating the infinite hard sphere repulsion. These near hard sphere colloids have played an important role in the study of crystallization processes. Inspired by the possibilities opened up by these nearly hard sphere colloids we investigated the possibility of preparing nearly hard rod colloids following the same strategy i.e. coating a rod-like core with a thin layer of flexible polymer.

In section 2 we briefly describe the system chosen for this purpose and in sections 3 and 4 we describe liquid crystal phase transitions in dispersions of these rod-like colloidal particles without and with added non-adsorbing polymer respectively.

2. The system

The system studied is a dispersion of crystalline boehmite (AlOOH) rods with an average length of 180 nm and an average diameter of 10 nm. The polydispersity in length and diameter is about 30%. These boehmite rods are sterically stabilized by a layer of polyisobutylene (PIB) modified with a polyamine anchor group, $PIB-N-CH_2-CH_2-[NH-CH_2-CH_2-]_n-N-PIB$, which attaches to the particle surface. Details of these PIB stabilizers, which were labelled SAP 220, SAP 230 and SAP 285 by the provider Shell Research Ltd. are given in table 1.

Table 1. Structural details of the modified polyisobutylene steric stabilizers.

Stabilizer	n	MPIB ($g\ mol^{-1}$)	PIB/Polyamine molar ratio
SAP 220	3	1000	2.0–2.5
SAP 230	3	1000	1.5
SAP 285	4	2400	2.0–2.5

Both the preparation of the boehmite cores and the steric stabilization was carried out according to the methods developed by Buining *et al* [6,7]. Once the boehmite rods are coated they are dispersable in organic solvents such as toluene and cyclohexane.

3. The phase behaviour of sterically stabilized boehmite dispersions

We first present results for the phase behaviour of boehmite rods stabilized by SAP230 dispersed in cyclohexane. This system shows an I–N phase transition with a biphasic I–N region from about 5.2 vol% to 12.2 vol%. This biphasic region is much wider than is predicted by the Onsager theory for monodisperse hard rods [5] but can be explained on the basis of the polydispersity of the rods [8,9]. One can distinguish four stages in the progression of the I–N phase transition in this system.

(i) One hour after homogenization the system has become turbid and shows a light scattering ring at about 6° corresponding to a length scale of about 4 μm. We will call this stage 'microphase separated'.

(ii) After 24 hours the appearance of the system has not changed very much but the light scattering ring is replaced by a light scattering cone in the forward direction. Optical polarization micrographs at this stage show a fine pattern of dark (isotropic) and bright (anisotropic) regions (figure 1(a)).

(iii) After several days a weakly birefringent cloud is slowly separating from the meniscus leaving an isotropic supernatant.
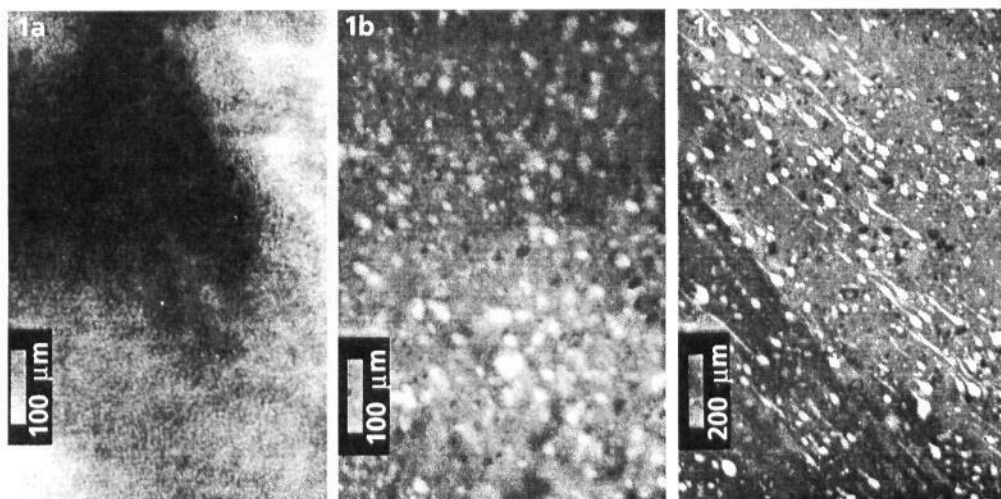
Figure 1. Polarization micrographs (between crossed polarizers) of phase separating, sterically boehmite dispersions in: (a) cyclohexane, 24 hours after homogenization; (b) toluene, 24 hours after homogenization; (c) toluene, a few days after homogenization.

(iv) After five weeks the system has separated into an isotropic upper phase and a birefringent bottom phase.

The scenario described above is also observed in dispersions of boehmite particles stabilized with SAP220 and SAP285 but the stages (iii) and (iv) proceed more slowly. It takes about six months for macroscopic phase separation in the case of SAP285 and even more than six months in the case of SAP220.

This slow phase separation scenario raises questions about its origin. At this stage we speculate that the microphase separation leads to an interconnected structure. Slow syneresis finally leads to macroscopic phase separation. The existence of an interconnected structure is supported by the observation that application of a weak centrifugal force leads to rapid sedimentation of the colloidal mass, leaving an almost clear supernatant.
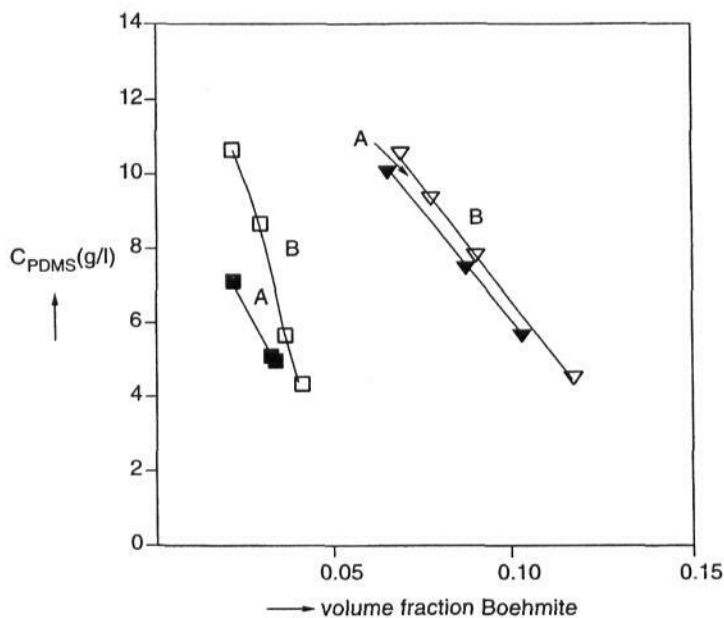
In order to investigate whether the solvent influences the phase separation process, toluene was also used as dispersion medium. The phase separation proceeds rather differently.

(i) One hour after homogenization the sample has become turbid and shows a small angle light scattering ring again indicating microphase separation.
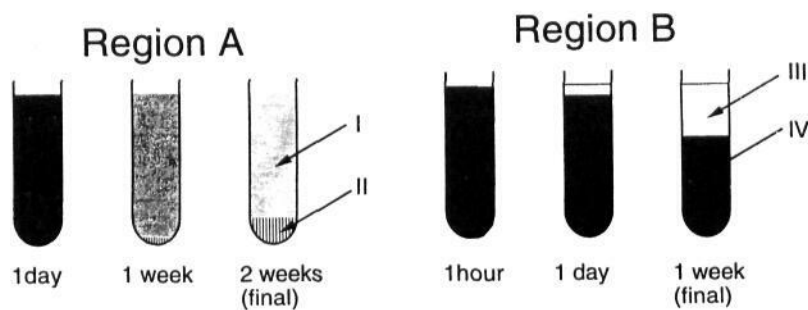
(ii) After 24 hours the light scattering ring has deformed to a horizontal ellipse. From polarization micrographs one can distinguish nematic droplets (tactoids) which are 10–30 μm large (figure 1(b)).

(iii) After several days these droplets sediment, forming a birefringent layer of the nematic phase on the bottom of the tube. Polarization micrographs show elongated tactoids (figure 1(c)).

(iv) The macroscopic phase transition is complete in a week and the biphasic region has shifted to a higher concentration. After one week small slowly sedimenting tactoids are still present in the isotropic upper phase.

Figure 2. (*a*) Phase boundaries in colloid–polymer mixtures. The solid squares and triangles indicate the minimum amount of polydimethylsiloxane required to induce phase separation in SAP220 and SAP285 stabilized dispersions. The open squares and triangles delineate the change in phase transition scenario from scenario A to scenario B. (*b*) A schematic picture of the phase separation process in region A. I: isotropic phase; II: nematic phase. (*c*) A schematic picture of the phase separation process in region B. III: isotropic supernatant; IV: weakly birefringent, turbid sediment.

4. The effect of non-adsorbing polymer on the phase behaviour of sterically stabilized boehmite dispersions

It is well known that non-adsorbing polymer induces an attractive force between colloidal particles, the so-called depletion interaction [10, 11]. This depletion interaction modifies the phase behaviour of the original colloidal dispersion. Calculations of this effect have been carried out both for dispersions of spherical colloidal particles [12, 13] and for dispersions of rod-like colloidal particles [14]. Furthermore, the depletion interaction may

significantly change the kinetics of phase separation [15, 16]. We studied the modified phase behaviour of dispersions of boehmite rods sterically stabilized with SAP 220 and SAP 285 in cyclohexane, due to the addition of polydimethylsiloxane (PDMS) with an average molecular weight of 116.500 g mol^{-1}. At polymer concentrations above the minimum required for phase separation two scenario's, indicated schematically in figures 2(*b*) and 2(*c*), can be distinguished. Just above the threshold concentration (region A in figure 2(*a*)) the system turns turbid within one day and after one week a birefringent phase starts growing from the bottom of the tube, reaching its final volume in about another week. At slightly higher polymer concentrations (region B in figure 2(*a*)) there is a sudden change to a new scenario. The system immediately turns very turbid and after one day a weakly birefringent turbid phase starts to settle, separating with a sharp interface from the almost clear supernatant. The settling visibly stops after one week while the bottom phase still occupies at least half of the total volume. So, going from scenario A to scenario B, there is a clear jump in the relative volume of the bottom phase. In accordance to recently published results of Poon *et al* [17] we speculate that scenario A and B are separated by a metastable isotropic–isotropic phase transition [14]. In agreement with the step rule of Ostwald [18] we expect that the system first explores this metastable isotropic–isotropic phase transition. The onset of this phase transition apparently prevents the I–N phase transition from reaching its equilibrium state.

5. Conclusions

From the experiments described in this paper it appears that the I–N phase transition in dispersions of rod-like particles is extremely sensitive to changes in interactions between the rods. With added non-adsorbing polymer the induced attraction results in an I–N separation, whereas slightly more polymer, i.e. slightly more attraction, prevents this transition from taking place. Similar observations in dispersions without added non-adsorbing polymer are made if the solvent is changed from toluene to cyclohexane. In toluene individual tactoids sediment, finally forming the nematic phase. In cyclohexane growing concentration gradients yield a pinned structure and no visible tactoids are formed. The phase separation process is severely retarded now. We think that attractive interactions are intervening here too. As the van der Waals interaction is enhanced with increasing optical contrast, boehmite dispersions in cyclohexane might be more attractive than in toluene. The particles coated with the different steric stabilizers used in this study require rather different times for macroscopic phase separation in pure cyclohexane. At the present time we have no explanation for this variation.

Acknowledgment

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