Preparation and properties of dispersions of colloidal boehmite rods

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Abstract: Dispersions of colloidal boehmite (γ-A1OOH) rods (of controllable length) are prepared from alkoxide precursors. A polyisobutene grafting procedure leads to sterically stabilized dispersions. In the organophilic system ($L \approx 200$ nm ± 50%; $D \approx 10$ nm ± 25%) an isotropic-nematic phase separation is observed for boehmite volume fractions between 3.8% and 14.6%. The effect of polydispersity on the phase diagram is well predicted qualitatively by Onsager's theory extended to bidisperse mixtures.

Key words: Boehmite rods — organophilic — isotropic-nematic — phase separation

Introduction

Concentrated dispersions of colloidal particles of rodlike shape may show interesting physical-chemical behavior, like the formation of an ordered nematic phase. The phenomenon of rod alignment has been observed in several aqueous dispersions, like V_2O_5 [1], β-FeOOH [2], γ-AlOOH [3], cellulose microcrystals [4] and tobacco mosaic virus [5]. These species show a hard-core interaction with an additional soft repulsion due to the surface charge.

Systematic phase studies of rodlike colloids were, until now, hindered by the lack of suitable systems. Further, it is desirable to study a system of rods showing a hard repulsion. Recently, we were able to prepare aqueous dispersions of boehmite (γ-AlOOH) particles of controllable rodlength in the range 100-500 nm and a width of around 15 nm [6]. These particles were sterically stabilized in cyclohexane by a polyisobutene grafting procedure [7].

This study concerns the isotropic-nematic phase separation as observed in the organophilic boehmite system of rods which are assumed to model a hard interparticle potential.

Isotropic-nematic phase separation

Concentrated dispersions of the organophilic boehmite rods ($L \approx 200$ nm ± 50%, $D \approx 10$ nm ± 25%) show an isotropic-nematic phase separation for boehmite volume fractions between $\phi = 3.8\%$ and $\phi = 14.6\%$. The nematic phase nucleates as a tactosol of spindle-shaped droplets (tactoids) in the isotropic phase which settle under gravity to form the continuous nematic phase. The experimental phase diagram of the measured volume fractions of the coexisting isotropic and nematic phases is shown in Fig. 1. Clearly, the phase behavior deviates from that expected for the monodisperse system, where the boehmite volume fractions of the coexisting isotropic and nematic phases would be constant with increasing overall volume fraction.

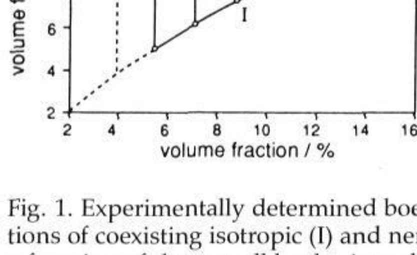

Fig. 1. Experimentally determined boehmite volume fractions of coexisting isotropic (I) and nematic (N) phases as a function of the overall boehmite volume fraction. From these values, the phase diagram is constructed.

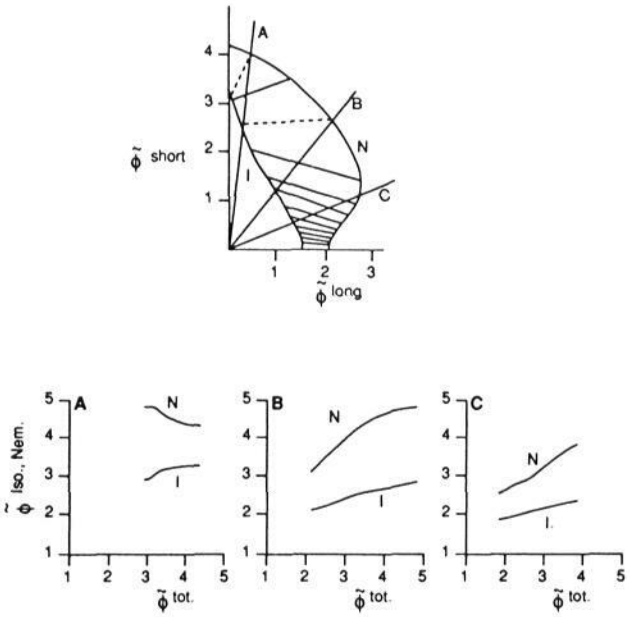

Fig. 2. Upper plot: Theoretical phase diagram for the isotropic (I) to nematic (N) phase separation of the bidisperse system of short (L_1) and long (L_2) rods with $L_2/L_1 = 2$, based on calculations of Lekkerkerker et al. [8]. The tielines imply a fractionation effect: the long rods go preferentially into the nematic phase. The presented volume fractions are scaled ($\tilde{\phi} = (L_1/D)\phi$). Lower plots: Theoretical scaled volume fractions of coexisting isotropic and nematic phases as a function of the overall volume fraction, constructed from the tielines in the upper plot

To investigate the effect of polydispersity on the phase diagram, we took the model of the bidisperse mixture. Figure 2 gives the theoretical phase diagrams for a bidisperse mixture of short (L_1) and long (L_2) particles having the same diameter D. The diagrams are constructed for $L_2/L_1 = 2$, using the calculations of Lekkerkerker et al. [8], who extended the Onsager [9] approach to the bidisperse case. The qualitative trends in the experimental phase diagram can be well explained by a large ϕ^{short}/ϕ^{long} ratio. The dispersions of the boehmite rods indeed contain a minor amount of very long particles (see [6]).

Concluding remarks

This is the first time, to our knowledge, that the I-N phase transition is observed and studied accurately in a system of rodlike particles where the interparticle potential is assumed to be hard. The effect of polydisperity on the phase diagram is qualitatively predicted by the theory for bidisperse hard rods.

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