

Nematic ordering *vs.* gelation in suspensions of charged platelets

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Abstract. – We study aqueous suspensions of charged gibbsite platelets that show the isotropic (I) to nematic (N) phase transition. This is the first case where the I-N transition in a dispersion of charged colloidal platelets is not impeded by gelation since Langmuir's classic work on dispersions of clay particles more than sixty years ago (*J. Chem. Phys.*, **6** (1938) 873). On increasing particle concentration, our dispersions subsequently show an isotropic, nematic and gel phase. We attribute the shift of the gelation boundary from below to above the I-N transition to the surface modification of the gibbsite platelets with aluminium polycations, which are known to enhance the stability of gibbsite colloids significantly.

In a remarkable paper [1] Irving Langmuir reported in 1938 on sols of California bentonite clay particles that, after standing for several 100 hours, separated into two distinct phases. This separation was found to occur for sols containing between 2.0 and 2.2 wt% clay particles. The phase-separated system can be identified as an isotropic phase (I) in equilibrium with a nematic liquid-crystal phase (N). Prior to the observations of Langmuir, I-N phase separation was observed by Zocher in suspensions of rod-like vanadium pentoxide (V_2O_5) [2] and by Bawden *et al.* in solutions of Tobacco Mosaic Virus (TMV), a rod-like virus [3]. The phase separation in suspensions of such highly anisometric colloidal particles —plates or rods— into an isotropic and a nematic phase was addressed theoretically by Lars Onsager in the 1940s [4]. He recognised that the anisometric particle shape has major implications on the phase behaviour of suspensions of such particles. In particular, he demonstrated that the stability of the nematic phase can be explained on a purely entropic basis by considering the competition between orientational entropy (favouring the isotropic state) and the entropy of excluded volume (which favours the nematic state). As the latter becomes more important at higher concentrations, a first-order phase transition from an isotropic to a nematic phase may occur if the concentration of plates or rods is sufficiently high. Thus, even hard plates

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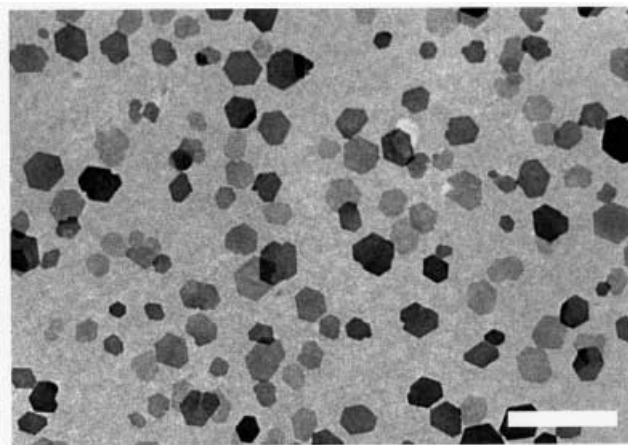


Fig. 1 – A Transmission Electron Micrograph of the aluminium-chloro-hydrate-treated colloidal gibbsite platelets. The scale bar denotes 500 nm.

and rods without any interaction whatever may form a nematic phase. Computer simulations have confirmed the validity of this notion [5–7].

Since the discovery of a nematic phase in suspensions of vanadium pentoxide [2, 8] and TMV [3], several other suspensions of rods have been found to exhibit the I-N phase transition: inorganic colloidal rods (boehmite (γ -AlOOH) [9, 10] and goethite (α -FeOOH) [11]), organic colloidal rods (microcrystalline cellulose [12] and poly-(tetrafluoroethylene) [13]) and rod-like virus particles (fd virus [14, 15]). In the case of plate-shaped colloids however, the observation of an I-N transition remained until recently restricted to Langmuir's experiment on a suspension of smectite clay platelets to which Onsager refers. Recently, extensive experiments have again been performed on the phase behaviour of smectite clays like montmorillonite [16] and Laponite (a synthetic form of hectorite produced by Laporte Industries Ltd.) [16–18]. Upon increasing the concentration, these (initially isotropic liquid) suspensions become isotropic gel and finally birefringent gel. Thus it appears that the gel concentration is lower than the isotropic-to-nematic transition concentration. The mechanism of gel formation in these smectite clay systems is a matter of considerable debate [17–25] but appears to be intimately related to the I-N transition, as the microscopic textures of these concentrated gels closely resemble nematic ones [16].

Given the propensity of clay systems to form gels rather than displaying the I-N phase transition, it is natural to focus on other systems of inorganic platelets. Such a strategy was recently applied to the study of phase transitions of suspensions of sterically stabilised nickel hydroxide [26] and gibbsite platelets [27]. Concentrated suspensions of the nickel hydroxide platelets show an ordered phase (columnar) but not an I-N transition, most likely because the diameter-to-thickness ratio of these particles is too small [5, 26]. The sterically stabilised gibbsite platelets, however, show the full range of liquid-crystal phases predicted for hard platelets [5, 6], *i.e.* isotropic, nematic and columnar [27, 28].

This still leaves open the issue of the I-N phase transition in a system of charged colloidal platelets. Here we report on a study of an aqueous dispersion gibbsite platelets. These colloidal platelets were synthesised following a procedure developed earlier in our laboratory [27, 29]. It involves a hydrothermal treatment of an acidified aluminium alkoxide mixture, yielding a dispersion of hexagonal gibbsite (γ -Al(OH)₃) platelets with an average diameter (defined as

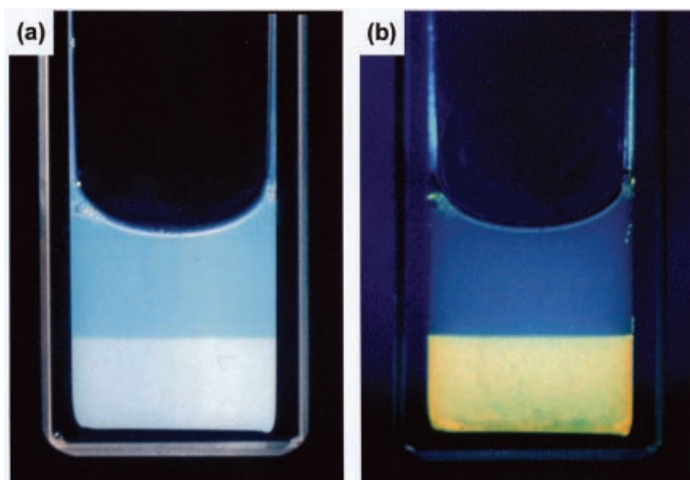


Fig. 2 – Equilibrium between the isotropic upper phase and the birefringent, nematic lower phase. (a) As observed with the naked eye and (b) between crossed polarisers. Particle concentration is 241 g/l, ionic strength 10^{-3} M.

the average of the three corner-to-corner cross-sections) of 148 nm and a diameter polydispersity (defined as the standard deviation of the average diameter) of 26%. A Transmission Electron Micrograph of the particles is shown in fig. 1. As the particle thickness is not readily obtained from such images, the thickness is estimated at 11 ± 3 nm based on previous experiments with the same kind of particles [29]. The dispersion contained 6.8 g/l gibbsite; at this low concentration, the particles display colloidal stability and sediment slowly over months. However, on centrifuging (*i.e.* to raise the particle concentration) the particles flocculate.

It has been observed that the presence of Al_{13} -ions ($\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$) has a stabilising effect on colloidal boehmite particles [9, 10, 30–32]. Recently, Hernandez [33] presented a systematic study of the adsorption of aluminium polycations, in particular Al_{13} , on colloidal iron and aluminium oxy-hydroxides and hydroxides. He used ^{27}Al -NMR to study the reaction of the Al_{13} species with the surface of these particles. From this he concluded that the adsorption leads to an increased surface charge, which in turn appears to enhance the stability of the particles. In view of this, we decided to use Al_{13} ions (as produced by hydrolysis of aluminium chloro hydrate, $\text{Al}_2(\text{OH})_5\text{Cl} \cdot 2-3 \text{H}_2\text{O}$ [10]) to stabilise our gibbsite particles.

Dispersions of the aluminium-chloro-hydrate-treated gibbsite platelets were subjected to phase separation experiments at 10^{-2} M and 10^{-3} M NaCl, for which samples were prepared in small absorption cells. After thorough homogenisation, samples were left to phase separate macroscopically. They were observed between crossed polarisers and the relative amount of nematic phase was measured. Furthermore, a sample was prepared in a flat capillary (concentration 146 g/l) and studied using a polarisation microscope.

The dispersions are isotropic up to a particle concentration c_1 of 95 g/l (at 10^{-3} M NaCl) and 114 g/l (at 10^{-2} M NaCl). At higher concentrations, the dispersions show birefringent spots immediately after homogenisation. These spots grow into birefringent droplets (tactoids), that sediment on a timescale of days to form a liquid-crystalline nematic phase on the bottom of the cell, in equilibrium with a non-birefringent isotropic upper phase, see fig. 2. Such a two-phase equilibrium is stable for months. Figure 3 depicts a polarisation micrograph of the capillary, showing the I-N interface and the sedimenting tactoids. The relative amount

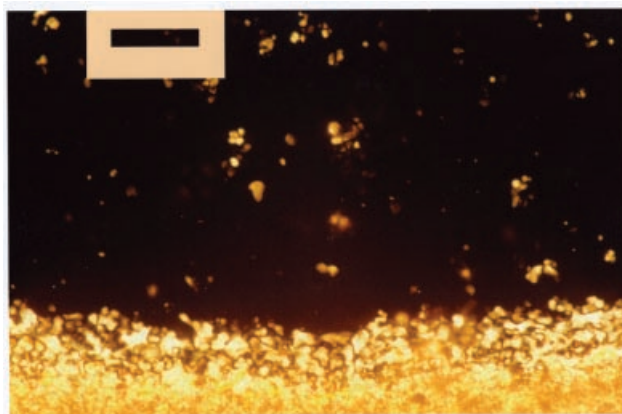


Fig. 3 – Polarisation microscope photograph of the suspension at 146 g/l and 10^{-3} M. This picture of the I-N interface is taken 24 days after homogenisation of the sample. The scale bar corresponds to 200 μm .

of nematic phase decreases with ionic strength and increases with particle concentration, corresponding to a repulsion-driven phase transition. Above a certain particle concentration, the dispersions do not phase separate any more. At this point, the amount of nematic phase jumps from typically 80% to an apparent amount of 100% and the texture of the birefringent phase changes markedly: the typical nematic graininess is replaced by a more cloudy pattern of birefringent and non-birefringent patches. On the basis on these observations, we call the point where the amount of nematic phase suddenly jumps to 100% the gel concentration c_G . This is depicted in the phase diagram, fig. 4.

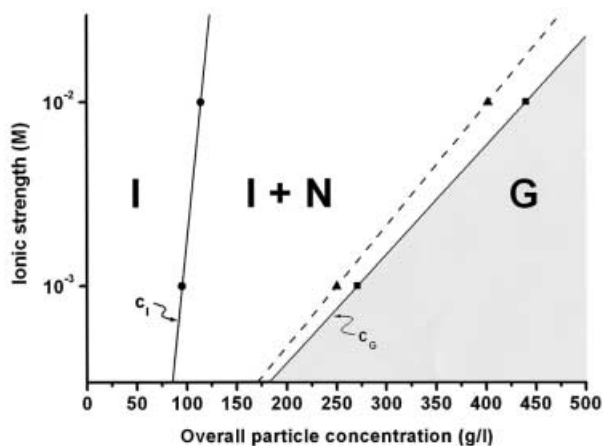


Fig. 4 – Phase diagram of the charged colloidal platelets. The left solid line is a fit through the points (\bullet) at the isotropic phase transition concentrations c_I . The dashed line indicates at which concentrations (\blacktriangle) equal amounts of isotropic (I) and nematic (N) phase are formed. The solid line on the right side of the diagram shows the concentrations c_G (\blacksquare) above which the dispersions become a gel (G).

In conclusion, our work demonstrates that it is possible to synthesise charged colloidal platelets that systematically display the I-N phase transition, dispelling the mystery of the I-N transition in such systems. Just as in the case of boehmite rods [9,10], modification of the particle surface with cationic aluminium tridecamers appears to play an essential role in facilitating liquid-crystal formation. Our assumption that the modification renders the particles highly repulsive (which, in view of the study by Hernandez [33], is reasonable) is supported by the fact that the transition is repulsion driven, as evidenced by its dependence on the salt concentration. The opposite is observed for Laponite [17,18] and Montmorillonite [16], where an increase of the salt concentration lowers the density where the gel phase appears (except at extremely low concentrations [25]). The theoretical understanding of the phase behaviour of charged colloidal platelets in an electrolyte is still in its infancy [34,35] and the appearance of a gel transition (in our case just after the I-N biphasic region) remains obscure.

Given the successful observation of the I-N phase transition in charged gibbsite suspensions, it is clear that appropriate surface treatment can delay the gel transition beyond the I-N transition concentration. Whether this is applicable in a more general way, in particular on natural clays, remains a question. Finally, one may wonder which special features the California bentonite possessed that Irving Langmuir used in his work. It has recently been noticed that from the composition of the smectite clay reported by Langmuir, he was most likely working with a California hectorite with a significant amount of calcium carbonate impurities [36]. We suggest that this particular combination has contributed to his success, since the chemically pure synthetic hectorite Laponite does not undergo the I-N phase transition, notwithstanding dedicated efforts [16–18] to achieve this goal.

REFERENCES

- [1] LANGMUIR I., *J. Chem. Phys.*, **6** (1938) 873.
- [2] ZOCHER H., *Z. Anorg. Chem.*, **147** (1925) 91.
- [3] BAWDEN F. C., PIRIE N. W., BERNAL J. D. and FANKUCHEN I., *Nature*, **138** (1936) 1051.
- [4] ONSAGER L., *Ann. N.Y. Acad. Sci.*, **51** (1949) 627.
- [5] VEERMAN J. A. C. and FRENKEL D., *Phys. Rev. A*, **45** (1992) 5632.
- [6] FRENKEL D. and EPPENGA R., *Phys. Rev. Lett.*, **49** (1982) 1089.
- [7] BATES M. A. and FRENKEL D., *J. Chem. Phys.*, **110** (1999) 6553.
- [8] DAVIDSON P., GARREAU A. and LIVAGE J., *Liq. Cryst.*, **16** (1994) 905.
- [9] BUGOSH J., *J. Phys. Chem.*, **65** (1961) 1789.
- [10] VAN BRUGGEN M. P. B., DONKER M., LEKKERKERKER H. N. W. and HUGHES T. L., *Colloids Surf. A*, **150** (1999) 115.
- [11] LEMAIRE B. J. *et al.*, *Phys. Rev. Lett.*, **88** (2002) 125507.
- [12] MARCHESSAULT R. H., MOREHEAD F. F. and WALTER N. M., *Nature*, **184** (1959) 632.
- [13] FOLDA T., HOFFMANN H., CHANZY H. and SMITH P., *Nature*, **333** (1988) 55.
- [14] LAPOINTE J. and MARVIN D. A., *Mol. Cryst. Liq. Cryst.*, **19** (1973) 269.
- [15] TANG J. and FRADEN S., *Liq. Cryst.*, **19** (1995) 459.
- [16] GABRIEL J. C. P., SANCHEZ C. and DAVIDSON P., *J. Phys. Chem.*, **100** (1996) 11139.
- [17] MOURCHID A., DELVILLE A., LAMBARD J., LÉCOLIER E. and LEVITZ P., *Langmuir*, **11** (1995) 1942.
- [18] MOURCHID A., LÉCOLIER E., VAN DAMME H. and LEVITZ P., *Langmuir*, **14** (1998) 4718.
- [19] RAMSAY J. D. F., *J. Colloid Interface Sci.*, **109** (1986) 441.
- [20] DIJKSTRA M., HANSEN J. P. and MADDEN P. A., *Phys. Rev. Lett.*, **75** (1995) 2236.
- [21] KROON M., WEGDAM G. H. and SPRIK R., *Phys. Rev. E*, **54** (1996) 6541.
- [22] PIGNON F., PIAU J. M. and MAGNIN A., *Phys. Rev. Lett.*, **76** (1996) 4857.
- [23] BONN D., KELLAY H., TANAKA H., WEGDAM G. and MEUNIER J., *Langmuir*, **15** (1999) 7534.

- [24] BONN D., TANAKA H., WEGDAM G., KELLAY H. and MEUNIER J., *Europhys. Lett.*, **45** (1999) 52.
- [25] LEVITZ P., LÉCOLIER E., MOURCHID A., DELVILLE A. and LYONNARD S., *Europhys. Lett.*, **49** (2000) 672.
- [26] BROWN A. B. D., FERRERO C., NARAYANAN T. and RENNIE A. R., *Eur. Phys. J. B*, **11** (1999) 481.
- [27] VAN DER KOOIJ F. M. and LEKKERKERKER H. N. W., *J. Phys. Chem. B*, **102** (1998) 7829.
- [28] VAN DER KOOIJ F. M., KASSAPIDOU K. and LEKKERKERKER H. N. W., *Nature*, **406** (2000) 868.
- [29] WIERENGA A. M., LENSTRA T. A. J. and PHILIPSE A. P., *Colloids Surf. A*, **134** (1998) 359.
- [30] RAMSAY J. D. F., DAISH A. R. and WRIGHT C. J., *J. Chem. Soc., Faraday Discuss.*, **65** (1978) 65.
- [31] DROUIN J. M., CHOPIN T., NORTIER P. and VAN DAMME H., *J. Colloid Interface Sci.*, **125** (1987) 314.
- [32] BEATTIE J. K., CLEAVER J. K. and WAITE T. D., *Colloids Surf. A*, **111** (1996) 131.
- [33] HERNANDEZ J., Thesis, Université Pierre et Marie Curie (1998).
- [34] ROWAN D. G. and HANSEN J. P., *Langmuir*, **18** (2002) 2063.
- [35] TRIZAC E., BOCQUET L., AGRA R., WEIS J.-J. and AUBOUY M., *J. Phys. Condens. Matter*, **14** (2002) 9339.
- [36] BIHANNIC I. *et al.*, *Langmuir*, **17** (2001) 4144.