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## Liquid Crystals

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## PRELIMINARY COMMUNICATION

### Nematic colloidal suspensions of $V_2O_5$ in water—or Zocher phases revisited

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Vanadium pentoxide gels and sols,  $V_2O_5 \cdot nH_2O$ , exhibit a ribbon-like structure. They form colloidal suspensions (also called Zocher phases or 'tactophases') which are clearly shown here to present a homogeneous lyotropic nematic phase for concentrations larger than  $\approx 0.12 \text{ mol l}^{-1}$ . Classical threaded textures were observed in polarized light and small angle X-ray scattering patterns of oriented samples displayed a diffuse spot quite comparable to that of the Tobacco Mosaic Virus. For a sample of volume fraction  $\phi \approx 5$  per cent, the  $V_2O_5$  ribbons are separated by about  $160 \text{ \AA}$ , so that the cross sectional area of the ribbons is about  $1300 \text{ \AA}^2$ , in agreement with previous estimations by electron microscopy.

Though most liquid crystals known today are of an organic nature [1, 2], there are however several inorganic systems which do form lyotropic mesophases [3–8]. Inorganic moieties involving transition metals are particularly interesting because of their potential electrical and optical properties [9]. This perspective has led us to reconsider a system first described in the last century [10], namely the vanadium pentoxide gels:  $V_2O_5 \cdot nH_2O$ . According to different preparative methods [11], these systems can be obtained via the polymerization of molecular precursors such as vanadic acid or vanadium alkoxides. They give rise to gels or sols, depending on vanadium concentration. As early as 1925, H. Zocher [3] observed in these gels the existence of small birefringent and fluid 'spindle-like' domains floating in an isotropic liquid. He proposed a nematic-like internal organization for these domains which were called 'tactoids' (from the greek 'to assemble'), but a pure nematic phase (that is, free of isotropic liquid) was only very seldom obtained. He called 'tactophases' the dispersions of these nematic domains within the isotropic solution, but they were also sometimes called Zocher phases. In 1949, Watson, Heller and Wojtowicz performed electron microscopy upon dried tactoids and showed that they were indeed made up of parallel rods [12]. Later, however, Heller considered that tactoids should not be confused with liquid crystals, essentially on the basis that tactoids could not be obtained as a homogeneous single phase [13]. Meanwhile,  $V_2O_5$  colloidal solutions have attracted

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much interest, not only as model colloids [14–16], but also for their applications as antistatic coatings in the photographic industry [17] and as reversible cathodes for lithium batteries [11]. Nevertheless, their potential to exhibit mesomorphic properties has never been completely clarified. The aim of this preliminary communication is to describe optical and X-ray characterization experiments which prove that aqueous suspensions of  $V_2O_5$  really present a homogeneous lyotropic nematic phase.

Vanadium pentoxide gels were synthesized according to already well-described procedures [11]. Vanadic acid was obtained free of foreign cations by an ion-exchange technique: a metavanadate solution,  $NaVO_3$ , was allowed to pass through a bed of a proton exchange resin (Dowex 50W-X<sub>2</sub> 50–100 mesh). A yellow solution of decavanadic acid is first obtained that polymerizes spontaneously upon ageing at room temperature via a polycondensation process. More or less entangled, long and flat  $V_2O_5$  ribbons are formed, dispersed in the solvent. These suspensions exhibit a dark red colour. The typical dimensions of the ribbons, as estimated from electron microscopy images of dried samples [18], are a few 1000 Å long, about 100 Å wide and about 10 Å thick (see figure 1). Their internal structure is closely related to that of orthorhombic  $V_2O_5$  [19]. The curvature radius of the ribbons, is typically of the order of 1000 Å. These gels are formed around  $pH \approx 2$  and they should actually be described as polyvanadic acids,  $H_xV_2O_5 \cdot nH_2O$ . Acid ionization leads to negatively charged vanadium pentoxide ribbons that bear about 0.2 of a negative charge per vanadium. Furthermore, some reduction occurs during the synthesis, so that about 1 per cent of the vanadium ions are in the reduced  $V^{4+}$  oxidation state. These features explain the rather large electronic and ionic conductivity [11] (which ranges from  $10^{-4}$  to  $1 \Omega^{-1} \text{cm}^{-1}$ , depending on the experimental conditions) of these gels, a property used, as mentioned above, for antistatic applications. The amount of water in the gels is determined from the weight loss observed when a sample is dried in an oven at  $500^\circ\text{C}$ . The compositions of the samples will be expressed in  $\text{mol l}^{-1}$  of  $V_2O_5$  or, in an equivalent way, in terms of the number of  $H_2O$  molecules per  $V_2O_5$  unit:  $V_2O_5 \cdot nH_2O$ . Once prepared, gels and sols remain stable for years, when kept in a closed vessel. A sol–gel transition occurs at a concentration of about  $0.2 \text{ mol l}^{-1}$ , that is,  $V_2O_5 \cdot 250H_2O$ .

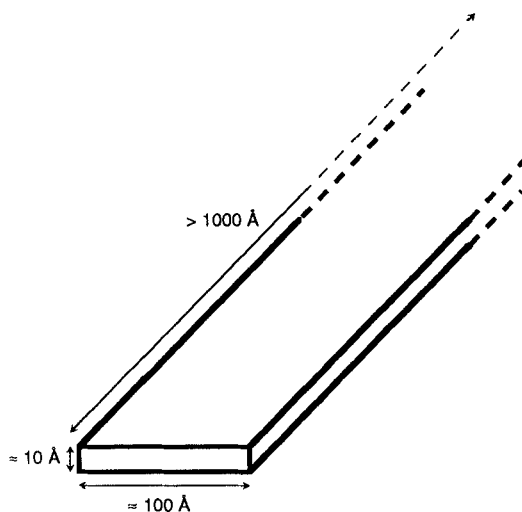


Figure 1. Schematic representation of a  $V_2O_5$  ribbon (the ribbons are not completely rigid but present curvature radii of more than 1000 Å).

Figure 2 shows the texture observed by optical microscopy, with crossed polarizers, for a rather concentrated gel (concentration  $0.85 \text{ mol l}^{-1} \text{ V}_2\text{O}_5$ ,  $65\text{H}_2\text{O}$ ). This gel exhibits a very classical threaded texture pointing to its nematic nature. The whole preparation shows the same type of nematic texture, and repeated observations gave the same results. Therefore, we clearly observe a homogeneous lyotropic nematic phase instead of 'tactoids'—nematic domains floating in an isotropic liquid.

Nematic textures were also observed for concentrations lower than that of the sol-gel transition. Indeed, colloidal solutions are very fluid, allowing easy observation of their textures. Such a texture ( $0.17 \text{ mol l}^{-1} \text{ V}_2\text{O}_5$ ,  $350\text{H}_2\text{O}$ ) is shown in figure 3; this is also indicative of a nematic phase. This photograph displays broad dark fringes, due to regions in which the director varies slowly, and sharper dark threads due to stronger singularities of the director field. Moreover, small striations of the background are often observed, but their origin is not yet understood.

At even lower concentrations, sols are optically isotropic, and the nematic phase is actually found only for concentrations larger than about  $0.12 \text{ mol l}^{-1} \text{ V}_2\text{O}_5$ ,  $500\text{H}_2\text{O}$ . No particular influence of temperature on the nematic phase stability could be observed up to  $T \approx 80^\circ\text{C}$ .

The nematic phase also appears when a concentrated gel is diluted with toluene. Adding salt (NaCl) quickly brings about flocculation of the suspension, which suggests that electrostatic interactions play a major part in the phase stability. No appreciable alignment has been obtained so far by action of either a magnetic field (1.7 T) or an electric field ( $10^6 \text{ V m}^{-1}$ ,  $f = 100 \text{ KHz}$ ). Nevertheless, the gels and sols can be oriented well by shearing.

The optical birefringence of a  $\text{V}_2\text{O}_5$  gel of concentration around  $0.3 \text{ mol l}^{-1} \text{ V}_2\text{O}_5$ ,  $200\text{H}_2\text{O}$  has been evaluated: a sample sheared between glass plates was planar oriented and observed in polarized light. A crystalline slab compensator was then used to determine the birefringence. The value obtained:  $\Delta n \approx 0.01$  is comparable to values for lyotropic nematic phases of stiff organic polymers. For instance,  $\Delta n \approx 0.003$  for the Tobacco Mosaic Virus, TMV [20].

In order to obtain information about the molecular organization in the mesophase, small angle X-ray scattering experiments were performed using an already described set-up [21]. The X-ray beam from a rotating anode generator equipped with a microfocus was monochromatized ( $\lambda \text{CuK}_\alpha = 1.541 \text{ \AA}$ ) by reflection at a curved graphite slab and collimated to a section of  $0.25 \times 0.25 \text{ mm}^2$  at the sample level. The sample was held in a sealed Lindemann glass capillary tube of 1 mm diameter. The diffracted X-rays travelled through flight tubes under vacuum and were then collected on a photographic plate. The sample-film distance was typically 0.5 m.

Figure 4 shows the small angle X-ray scattering pattern of a  $\text{V}_2\text{O}_5$  gel. The concentration was around  $1 \text{ mol l}^{-1} \text{ V}_2\text{O}_5$ ,  $60\text{H}_2\text{O}$ ; this concentration is, however, only approximate due to the slow evaporation of water, which condenses on the walls of the capillary tube. This scattering pattern is quite striking, because of its similarity to that of the nematic phase of Tobacco Mosaic Virus [22]. It shows a small angle diffuse ring which arises from the lateral interferences between ribbons. This ring is highly oriented along the capillary tube axis and reveals the radial configuration of the director in the capillary tube. This reproducible alignment is either due to anchoring on the capillary wall or to an unusual flow effect taking place when filling the capillary tube. The orientation is confirmed by the wide angle X-ray diffraction pattern, since the 010 and 020 reflections characteristic [18] of the main axis of the  $\text{V}_2\text{O}_5$  ribbons are indeed observed in the plane perpendicular to the capillary axis. Such a small angle

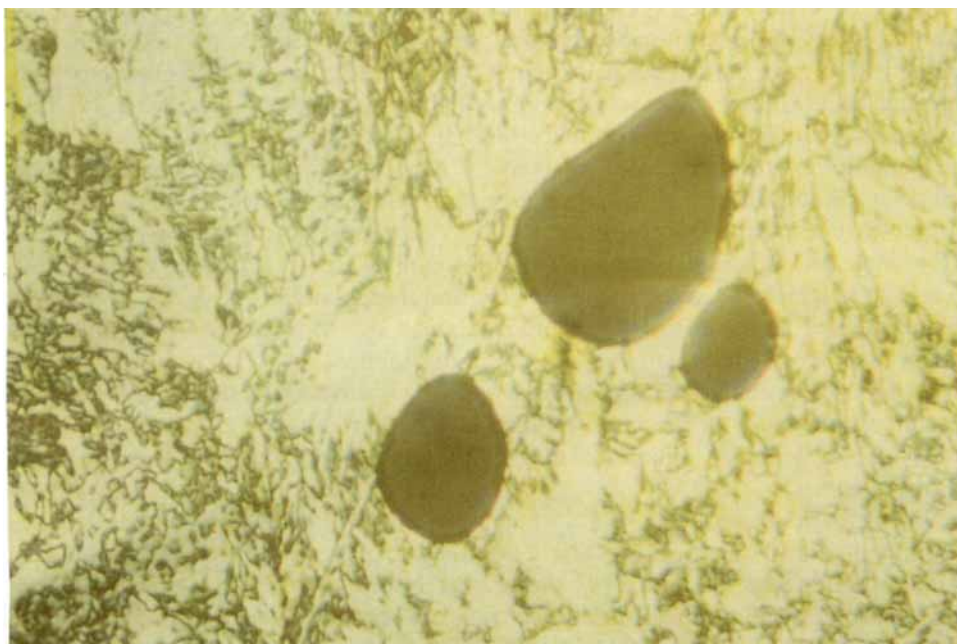


Figure 2. Texture photograph of a  $0.85 \text{ mol l}^{-1}$  gel of  $\text{V}_2\text{O}_5$  in water. (Optical microscopy with crossed polarizers, magnification  $\times 220$ : the dark areas are only air bubbles.)

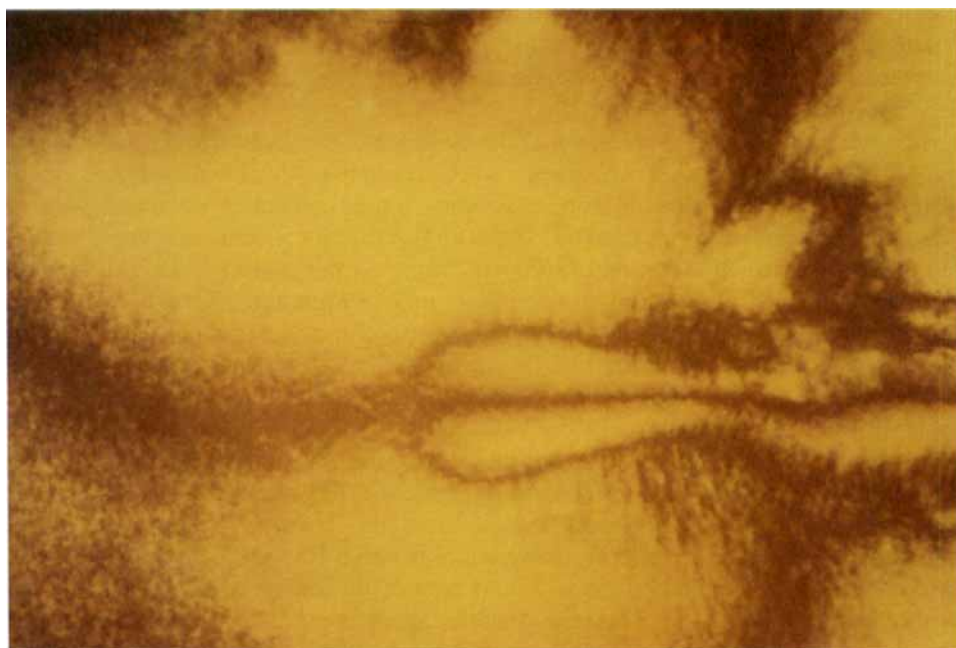


Figure 3. Texture photograph of a  $0.17 \text{ mol l}^{-1}$  sol of  $\text{V}_2\text{O}_5$  in water. (Optical microscopy with crossed polarizers, magnification  $\times 220$ .)

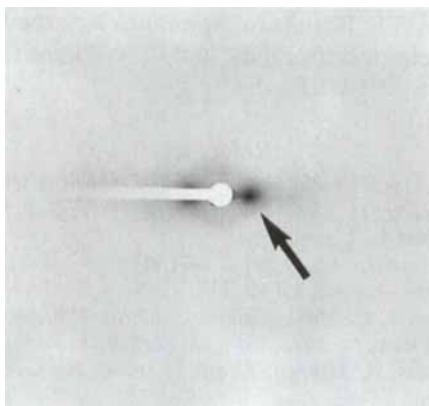


Figure 4. Small angle X-ray scattering pattern of a  $1 \text{ mol l}^{-1}$  gel of  $\text{V}_2\text{O}_5$  in water. The capillary tube axis is vertical. The arrow points to the diffuse spot at  $q \approx 2\pi/160 \text{ \AA}^{-1}$ . (The other symmetrical diffuse spot is hidden by the beam trap.)

diffuse ring had earlier been detected in small angle X-ray and small angle neutron scattering experiments on unoriented samples [23, 24]. However, it was not recognized in terms of lateral interferences among the building blocks of a lyotropic nematic phase.

The position at  $q \approx 2\pi/160 \text{ \AA}^{-1}$  of the diffuse ring in reciprocal space shows that the average lateral distance between ribbons is about  $d \approx 160 \text{ \AA}$ . From the concentration ( $1 \text{ mol l}^{-1}$ ) and the density (3.38) of the vanadium pentoxide ribbons, the molar mass of  $\text{V}_2\text{O}_5$  being 182 g, one can derive the volume fraction of the gel:  $\phi \approx 5$  per cent. This value, together with that of  $d$ , leads to a cross-sectional area of about  $1300 \text{ \AA}^2$  for the ribbon, in fairly good agreement with the ribbon dimensions mentioned above. At this point, since the ribbons are highly biaxial, one may wonder about their local packing. Indeed, the ribbons may either freely rotate around their main axis, so that they pack locally in a hexagonal way, or undergo strong, locally biaxial correlations as pointed out in previous papers [23, 24]. However, we have not yet detected at higher concentrations any hint of a hexagonal, a lamellar or a biaxial nematic phase.

Though we have clearly observed a homogeneous lyotropic nematic phase in this system, we have not so far observed Zocher's tactoids. This may be a consequence of the quite different preparative method which we used. Zocher gels were not obtained by an ion exchange technique, but by the reaction of ammonium vanadate with hydrochloric acid:  $2\text{NH}_4\text{VO}_3 + 2\text{HCl} \Rightarrow \text{V}_2\text{O}_5 + 2\text{NH}_4\text{Cl}$ . The resulting colloidal solutions were therefore polluted with foreign ions ( $\text{NH}_4^+$ ,  $\text{Cl}^-$ ) which may have destabilized the nematic suspensions.

In conclusion, Zocher phases constitute another example of lyotropic nematic suspensions of inorganic rods quite similar to those of  $\text{Li}_2\text{Mo}_6\text{Se}_6$  in *N*-methylformamide, described recently [8]. The similarity of behaviour between these two inorganic systems, though of quite a different chemical nature, suggests that any type of stiff, more or less charged, inorganic rod or ribbon system dispersed in a solvent may potentially display a nematic phase. Therefore, in this respect, purely inorganic moieties should not be considered differently from organic entities. Other experiments are presently under way to study more quantitatively the phase stability and organization of these  $\text{V}_2\text{O}_5$  colloids.

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