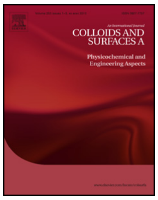
Colloids and Surfaces A: Physicochem. Eng. Aspects 506 (2016) 774–781

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa



# Stability criteria for aqueous colloidal vanadium pentoxide suspensions doped with magnetite nanoparticles

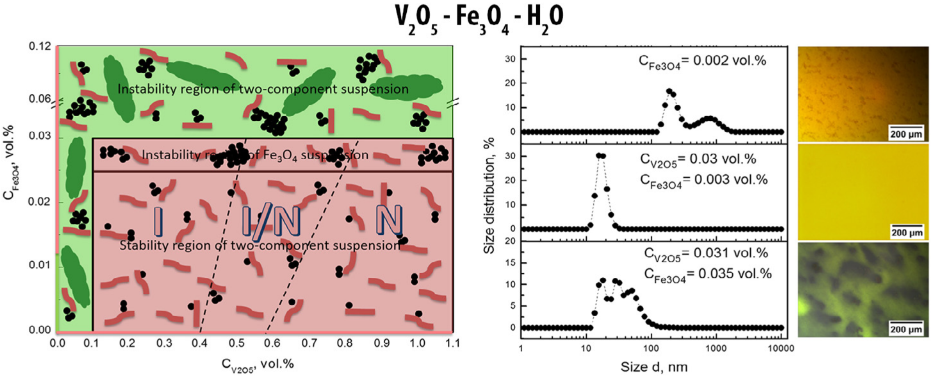
Sergey Kredentser[a,*], Lyudmila Bugaeva[a], Andrii Derzhypolski[a,b], Dmitrii Cherepanov[c], Sergiy Malynych[d], Nicolo Castro[e], Patrick Davidson[e], Yuriy Reznikov[a]

[a] Institute of Physics of National Academy of Sciences of Ukraine, Prosp. Nauky 41, Kyiv 03028, Ukraine
[b] Novations LLC, Mariny Raskovoy 23/813, Kyiv 02002, Ukraine
[c] Norma LLC, Kotelnikova 46, Kyiv 03115, Ukraine
[d] Institute for Physics of Semiconductors, of National Academy of Sciences of Ukraine, Prosp. Nauky 41, Kyiv 03028, Ukraine
[e] Laboratoire de Physique des Solides, CNRS, Univ. Paris-Sud, Université Paris-Saclay, 91405 Orsay Cedex, France

## HIGHLIGHTS

- Hybrid suspensions of $V_2O_5$ and $Fe_3O_4$ particles have outstanding magnetic properties.
- The concentration domain of colloidal stability of the suspensions was determined.
- In stable suspensions, TEM suggests that $Fe_3O_4$ particles adsorb on $V_2O_5$ ribbons.
- The nematic phase of the hybrid suspensions reorients in very weak magnetic fields.
- Oxidation of $Fe^{II}$ by $V^{V}$ induces a long-term instability of the hybrid suspensions.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

*Article history:*
Received 1 June 2016
Received in revised form 20 July 2016
Accepted 21 July 2016
Available online 22 July 2016

*Keywords:*
Nanoparticles
Liquid crystals
Colloid
$Fe_3O_4$
$V_2O_5$
Stability

## ABSTRACT

Colloidal aqueous suspensions of vanadium pentoxide ($V_2O_5$) ribbons and iron oxide ($Fe_3O_4$) nanoparticles display extreme sensitivity to magnetic fields, which promises their use in novel magneto-optic devices. However, application of these systems requires that stable colloidal suspensions can actually be achieved in a given range of concentration of each component. We explored the ($V_2O_5$, $Fe_3O_4$) stability diagram of this complex colloidal system by preparing samples of selected compositions and by studying them by visual inspection, optical microscopy, DLS, electrokinetic potential, and TEM. We found that, on the time scale of several weeks, the colloidal system is stable up to $C_{Fe_3O_4} \approx 0.025 vol.\%$ and $C_{V_2O_5} \approx 0.1 - 1.1 vol.\%$. Such concentrations are indeed suitable for applications and the high sensitivity to the magnetic field of the suspension in a stable concentration region is demonstrated. However, the system lacks chemical stability at long-term (several months) as $V^V$ eventually oxidizes $Fe^{II}$, resulting in flocculation of the dispersion.

## 1. Introduction

Colloidal suspensions of hard rods (often called Onsager liquids) are fascinating systems in which the purely steric interaction

---

[*] Corresponding author.
*E-mail address:* sergeykredenser@gmail.com (S. Kredentser).

http://dx.doi.org/10.1016/j.colsurfa.2016.07.059
0927-7757/

between rods induces a diversity of liquid-crystalline phases due to a competition between the orientational entropy of the rods and their packing entropy [1,2]. Although such liquid-crystalline colloids have been discovered long ago, they are still the focus of intense theoretical and experimental research [3]. Indeed, they are often easier to study than molecular liquid crystals due to the large dimensions ($10-100\ \ nm$) of their constituents which lead to more convenient time- and length- scales. Moreover, the use of mineral colloidal particles gives access to interesting physical properties such as ferromagnetism or ferroelectricity. Recently, we found that the orientational ordering of these Onsager liquids can be efficiently controlled by adding to them minute amounts of ferromagnetic or ferroelectric nanorods and applying an external field [4,5]. For instance, the isotropic suspension of weakly-magnetic $V_2O_5$ rods, doped with superparamagnetic $Fe_3O_4$ spherical particles that self-assemble into wires in a magnetic field, displays a large magnetically-induced birefringence. Moreover, the director of the doped nematic phase is easily reoriented by a weak magnetic field of only several tens of Oersted. The perspectives of such coupling for magneto-optical sensing, display, and data storage applications were already suggested earlier by Osterloh in reference [6] where the covalent bonding of $Fe_3O_4$ particles with optically-anisotropic perovskite nanosheets was described. Later this approach was applied by these authors for superparamagnetic colloidal nanosheets and $Fe_3O_4$ nanoparticles [7].

The unique sensitivity of the $V_2O_5-Fe_3O_4$ suspensions to a magnetic field makes this colloidal system very promising for various applications in magneto-optic devices. In particular, magnetically-sensitive colloids can represent an interesting alternative to electrically-controlled thermotropic liquid crystals thanks to the non-invasive character of magnetic-field application. Moreover, magnetically-sensitive suspensions, if used in their isotropic phase, do not require the complicated alignment techniques used to control the liquid-crystalline texture. Furthermore, producing the colloid samples is much cheaper and easier than synthesizing liquid-crystal molecules.

In this perspective, the issue of its long-term stability, both from colloidal and chemical points of view, is of crucial importance. Here, we report the effect of doping $V_2O_5$ suspensions with $Fe_3O_4$ nanoparticles on the stability of these systems. We show that, if due care is taken to keep the $pH$ around $2-3$, the stability of the doped $V_2O_5$ suspensions only depends on the fraction of $Fe_3O_4$ particles in the system. The results are qualitatively explained by changes of electrostatic repulsions between $V_2O_5$ ribbons upon doping with charged $Fe_3O_4$ nanoparticles and by slow chemical reactions between the suspension components. Moreover, electron microscopy images suggest that the coupling between both species, at the basis of the peculiar physical phenomena described above, arises from the adsorption of the $Fe_3O_4$ spherical particles onto the $V_2O_5$ rods.

## 2. Materials and methods

A highly concentrated stock $V_2O_5$ gel was produced by a well-documented chemical synthesis through the acidification of a $NaVO_3$ solution passed over an ion-exchange resin ($Dowex\ \ 50\ \ W-X2$) [8–10]. To prepare aqueous suspensions of $V_2O_5$ with different volume fractions, $C_{V_2O_5}$, the composition of the stock gel must first be determined. For this purpose, the residual water was evaporated from the gel at $300^0C$. The evaporation process was controlled by measuring the weight of the suspension and it was terminated when the weight stopped changing (approximately 2 hours). The material left was considered as pure vanadium oxide. Then, we compared the initial weight of the gel with the weight of the obtained vanadium oxide and we determined the weight fraction of $V_2O_5$ in the stock gel, $c_{V_2O_5,g}=4.221\ \ wt.\%$ and its volume fraction $C_{V_2O_5,g}=c_{V_2O_5,g}/\rho_{V_2O_5}=1.296\ \ vol.\%$ ($V_2O_5$ density, $\rho_{V_2O_5}=3.357\ \ g/cm^3$). The stock gel was then diluted with deionized water ($pH=6.5$) to produce the aqueous suspensions of required volume fractions.

The $Fe_3O_4$ (magnetite) superparamagnetic nanoparticles [11–17] were obtained by following the classical procedure of Massart [18,19]. A 1 M ferric chloride ($FeCl_3$) and $2M$ ferrous chloride ($FeCl_2$) solution in $2M$ hydrochloric acid ($HCl$) was prepared. This solution was mixed with $500\ \ ml$ of $0.7\ \ M$ ammonia solution ($NH_3(aq)$), followed by stirring for about $10\ \ $min. Upon addition of the solution of iron chlorides to the ammonia, the whole system became instantly black, indicating the formation of iron ($II$, $III$) oxide. To produce an acidic sol, the dispersion was magnetically decanted and a $2M$ perchloric acid ($HClO_4$) solution was added to the reaction flask, followed by vigorous stirring. After centrifugation, the supernatant was filtered and re-dispersed in de-ionized $H_2O$.

The two-component suspensions were prepared by directly mixing $V_2O_5$ and $Fe_3O_4$ aqueous suspensions of known volume fractions. The resulting mixtures were vortexed during 3 hours.

All suspensions were filled into flat glass optical capillaries ($VitroCom^©$) of thickness $20\ \ \mu m$ for visual inspection with the naked eye and with an optical microscope ($Olympus\ \ BX53$). The dependence of the $pH$ of the suspensions on the concentrations of the components was measured with a $pH-$meter ($HannapH-211$). The effective sizes of the particles and of their aggregates in the suspensions were investigated with a Zetasizer ($MalvernNano\ \ ZS$) using dynamic light scattering ($DLS$). The same device allowed us to measure the zeta potential of the suspensions by electrophoretic light scattering. The particles and aggregates in the dispersions are classically considered spherical in order to estimate their size with this technique. Therefore, an accurate and reliable determination of the sizes of the particles could only be achieved for the $Fe_3O_4$ suspension and such measurements for $V_2O_5$ ribbons are inappropriate.

Samples for transmission electron microscopy ($TEM$) were prepared using $300-$mesh copper grids covered with a carbon film. The grids were initially placed in a plasma for $20\ \ s$ at $5\ \ mA$ in order to enhance the hydrophilicity of the surface and favor the even coverage of the surface by the sample. The grids were then left in open air for 10 minutes, after which a drop of the sample ($\sim 1\ \ \mu l$) was cast on the grid and left to dry overnight. For the denser samples, the plastic tip of the $\mu-$ pipette was used to spread a small quantity of the sample over the grid, and the grid was then left to dry overnight. $TEM$ was done using a $JEOL\ \ 1400$ microscope at an acceleration voltage of $120\ \ kV$ and using the Gatan software for the acquisition of the images, which automatically normalized the image by subtracting a blank image acquired on the same day.

## 3. Results and discussion

### 3.1. Aqueous colloidal vanadium pentoxide suspensions

Transmission electron microscopy ($TEM$) images (Fig. 2a) show that the suspensions consist of $V_2O_5$ ribbons, which are approximately $L_{vp}=500\ \ nm$ long, $D_{vp}=25\ \ nm$ wide, in agreement with previous literature [10]. The thickness of the ribbons cannot be properly assessed by $TEM$ because most of them lie flat on the $TEM$ grid. However, the thickness, $T_{vp}=1\ \ nm$, was precisely determined by small-angle $x-$ ray scattering in a previous structural study [20]. These ribbons are known to be negatively charged with a linear charge density of $5\ \ e^-/nm$ [10], which corresponds to a surface charge density of $0.2\ \ e^-/nm^2$. This charge is compensated by $H^+$ counterions and the suspensions are acidic ($pH\approx 2$ at a vol-