Coagulation of luminescent colloid nGdVO$_4$:Eu solutions with inorganic electrolytes

V.K.Klochkov

Institute for Scintilaltion Materials, STC "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60 Lenin Ave., 61001 Kharkiv, Ukraine

Aqueous colloid solutions of europium-doped gadolinium orthovanadates have been prepared. The nanoparticles of about 20 nm diameter show a bright luminescence. The aqueous nGdVO$_4$:Eu solutions are transparent in the visible region and maintain the unchanged properties for more than two months. The presence of inorganic salts causes a reduction of the solution aggregative stability. The aggregation threshold values are in a close correspondence with the Schultze-Hardy rule and the 6th power Deryagin-Landau law for "negative" lyophobic sols.

Получены водные коллоидные растворы ортованадатов гадолиния активированных европием. Наночастицы диаметром около 20 нм обладают яркой люминесценцией. Растворы nGdVO$_4$:Eu в воде прозрачны в видимом диапазоне и обладают неизменными свойствами более 2^x месяцев. Снижению агрегативной устойчивости растворов способствует присутствие неорганических солей. Соотношения значений порогов коагуляции находятся в близком соответствии с правилом Шульце-Гарди и законом 6^{й} степени Дерягина-Ландау для "отрицательных" лиофобных золей.

Inorganic luminescent materials are used widely in modern engineering and electronics [1]. Today, luminescent nanomaterials for novel composites and electronic devices take a special actuality. The great hopes are pinned on the use thereof in biology and medicine [2, 3]. In particular, the luminescent organic dyes are used for a long time as biological probes and labels. The use of those materials, however, is limited by their low photostability and toxicity. The use of inorganic materials will provide an expanded monitoring possibility for biochemical processes, mainly due to high photostability and unique chemical properties of the materials.

The semiconductor nanocrystals (nano-points) and RE-doped dielectric nanocrystals are among the objects being considered as the most promising materials for inorganic probes [2, 4, 5]. Today, there are numerous publications aimed at the study of biological probes and labels based on nano-points, while an insufficient attention is given to use of luminescent dielectric nanocrystals to that end.

In this work, the synthesis of aqueous solutions of doped nGdVO$_4$:Eu is presented as well as the study results of some physico-chemical and colloidal properties of the solutions.

The aqueous colloid solutions of orthovanadates doped with various rare-earth elements are prepared using solid phase synthesis [6], wet ultrasound [7], sol-gel [8] and colloid chemistry [9−11] techniques. However, the solutions obtained by the above methods have not find use in biology. It was our end to prepare the aqueous solution of controlled compositions using non-toxic materials.

To prepare the nGdVO$_4$:Eu colloidal solution, an original technique was used based on thermal decomposition of a RE element complex with EDTA and formation of water-insoluble RE orthovanadates as
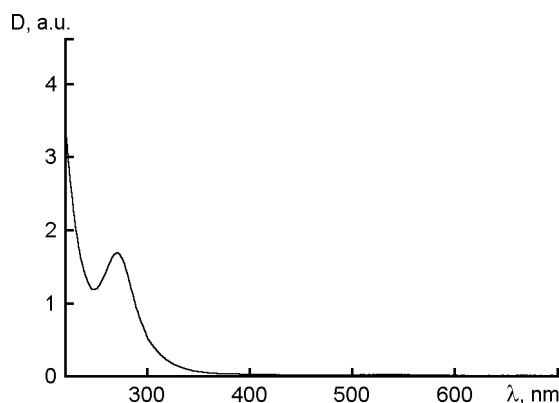
Fig. 1. Absorption spectrum of colloid solution nGdVO$_4$:Eu.

Fig. 2. Excitation (λ_{vis} = 618 нм) and emission (λ_{ex}=394нм) spectra of colloid solution nGdVO$_4$:Eu.

nanoparticles. The aqueous solutions of gadolinium and europium chlorides were mixed with EDTA disodium salt in the equivalent ratio, then the equivalent amount of Na$_3$VO$_4$ solution (pH = 13) was added to the above mixture. Then the mixture was subjected to dialysis for 24 h using a 12 KDa membrane (pore size about 2.5 nm). The dialysis run was monitored using the dialysate electric conductivity. The absorption spectra were measured using a SPECORD 200 spectrophotometer. To obtaine the luminescence spectra, an MDR-23 monochromator was used combined with the control and data collection system within the CAMAC standard. It has been found in experiment that the particles containing the RE elements in the Gd:Eu molar ratio of 9:1. The coagulation thresholds were determined as is described in [12, 13]. The error of the fast coagulation threshold values did not exceed 15 %. The transmission electron microscopy was carried out using a PEM-125K microscope. The samples for microscopy were applied onto carbon film substrates by immersion in diluted solutions and drying.

The colloid system under study is a colorless solution transparent in transmitting light. The colloidal character of the solution is confirmed by the presence of the Tyndall cone. The colloid particles pass easily through a 100 nm pore diameter nitrocellulose filter. The solid phase concentration is 12.6 g/L. The solution pH values are 6.8 to 7.4. Under UV irradiation with a wideband filter, a red luminescence is observed in the solution. The solution properties remain unchanged during storage for over 2 months in normal conditions.

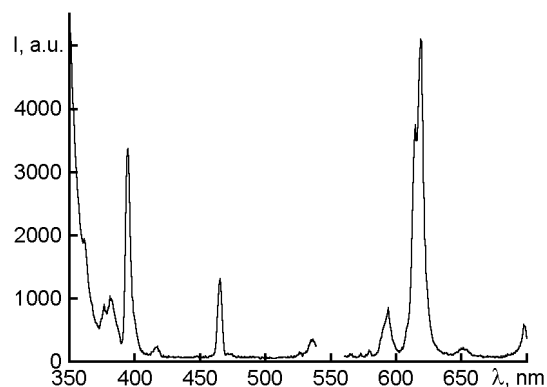In the absorption spectrum of the colloid solutions, a wide band peaked at 271 nm is observed (Fig. 1) related to the energy transfer from oxygen ligands to the central vanadium atom in VO$_4^{3-}$. Note that for ionic solutions of salts containing VO$_4^{3-}$, the absorption maximum is near 268 nm. The band shift towards longer wavelengths shows that VO$_4^{3-}$ is in the crystalline state. That band was observed by various authors [10, 11, 14] within the 272 to 282 nm range. The maximum position scatter is explained by differences in the crystal lattice type and the crystalline phase particle size [14]. In our case, the absorption maximum position of the solution corresponds most closely to the monozite nanocrystal type [14], however, the solid phase crystalline state was not studied.

The excitation and luminescence spectra of the colloid solutions (Fig. 2) contain narrow bands typical of europium dopant in the orthovanadate matrix composition. The spectra obtained are analogous to those of similar systems and are described in detail in [6–11, 14].

Fig. 3 presents the electron-microscopic image of the solid phase from the aqueous nGdVO$_4$:Eu colloid solution. The solid phase is seen to be a polydisperse system of spherical particles. The average particle diameter is 19 nm ($\pm$5 nm standard deviation). It is to note especially the well visualizable layers surrounding the nanoparticles and having a reduced density under electron microscopy conditions. Those layers are obviously an organic phase consisting of EDTA and playing the part of the potential-forming protective layer. The presence of that layer influences to a considerable extent the solution stability and colloid-chemical properties. That is, EDTA provides simultaneously two functions at the synthesis of nanoparticles. At the synthesis stage, it
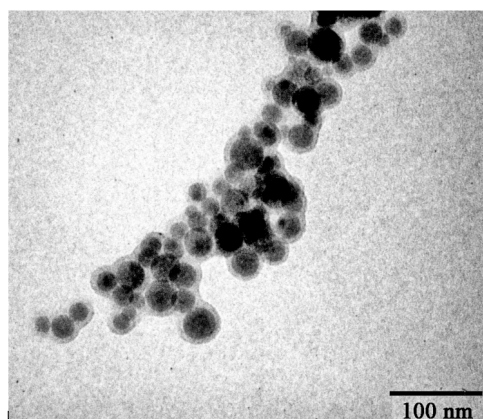
Fig. 3. TEM image data of solid phase of colloid solution nGdVO$_4$:Eu.

Table. Coagulation thresholds of nGdVO$_4$:Eu hydrosol in the presence of inorganic electrolytes.

Salt	Z	Y (mol·dm-3)	Y(NaCl):Y(salt)
NaCl	1	0.32	1
KCl	1	0.32	1
KJ	1	0.28	1.1
KBr	1	0.28	1.1
MgCl2	2	0.00257	125
CaCl2	2	0.00185	173
SrCl$_2$	2	0.00163	196
BaCl$_2$	2	0.00104	308
LaCl$_2$	3	0.00034	940

is the lanthanide complexing agent favoring the slow formation of the heterogeneous system during the thermal decomposition of the complex. On the other hand, the EDTA molecules form chelate complexes with cations at the solid phase surfaces, thus forming the protective layers that hinder the colloid system coagulation.

The hydrosol stability against electrolyte admixtures is an important characteristics of the surface properties of an aqueous dispersion. In this work, the colloid dispersion stability was studied by measuring the fast coagulation threshold Y. The coagulation was found to follow the "threshold" character typical of the lyophobic systems. The coagulation thresholds are defined by the cation nature, the anion influences only slightly the Y value (Table).

The coagulation threshold Y of nGdVO$_4$:Eu hydrosol by sodium chloride solution has been found to amount 0.32 mmoles/L. The inverse coagulation thresholds (Y^{-1}) proportional to the coagulating action
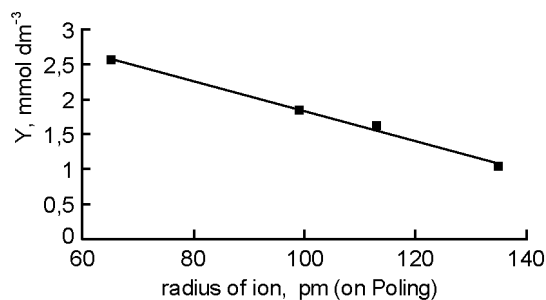

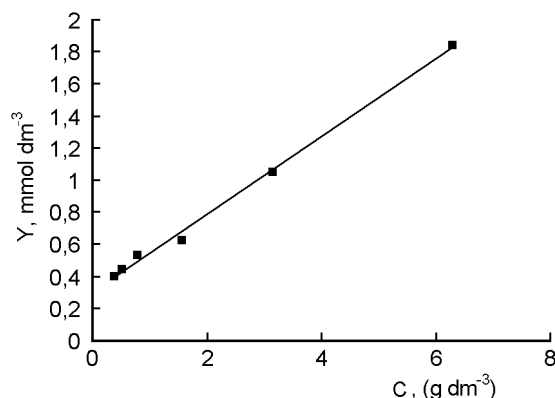Fig. 4. Dependence of coagulation threshold values on radius of double coagulant cations.

Fig. 5. Dependence of coagulation threshold values on hydrosol concentration (coagulant CaCl$_2$).

are in proportion 1:200:940 for cations K$^+$, K^{2+}, K^{3+}. Such correlations correspond closely to the classic Schultze-Gardy rule and the Deryagin-Landau-Fairway-Overbeck (DLFO) theory for lyophobic "negative" sols [13, 15−17]. The deviation from the 6th power Deryagin-Landau law (requiring the relation 1:11:730) seems to be associated with the increased role of specific adsorption at multicharged ions that is not taken into account in the DLFO theory. The largest deviations from the 6th power law are observed for doubly charged cations. The neutralization coagulation mechanism of doubly charged cations is related to the specific interaction of the latter with the colloid particle environment. The coagulating ability of doubly charged cations, in its turn, depends heavily on the cation nature and is reduced linearly at increasing cation size (Fig. 4), thus corresponding fully to the classic concept of lyotropic series for irreversible systems [15]. The Y dependence on the hydrosol concentration is also linear, thus typical of lyophobic sols of constant composition (Fig. 5).

To conclude, the synthesized aqueous nano-dispersions exhibit the properties of hydrophobic sols with negatively charged surfaces. The micelle structure can be represented as $n[GdEuVO_4]mEDTA^-(m–x)Na^+\}^{x-}xNa^+$. The results obtained in the study of the solid phase surface properties in aqueous solutions are to be taken into account when carrying out the biological experiments with that object.

References

1. G.G.Elenin, *Inform. Tekhnologii Vychislit. Sistemy*, No.2, 32 (2002).
2. G.Schmid (ed.), Clusters and Colloids. From Theory to Applications, VCH Verlagsgesellschaft, Weinheim (1994).
3. F.Wang, W.B.Tan, Y.Zhang et al., *Nanotechnology*, **17**, R1 (2006).
4. I.Nabiev, S.Mitchell, A.Davies et al., *Nano Letters*, **7**, 3452 (2007).
5. C.R.Patra, R.Bhattacharya, S.Patra et al., *Clinical Chemistry*, **53**, 2029 (2007).
6. U.Rambabua, D.P.Amalnerkara, B.B.Kalea et al., *Mater. Res. Bull.*, **35**, 929 (2000).
7. A.Huignard, T.Gacoin, J-P.Boilot, *Chem. Mater.*, **12**, 1090 (2000).
8. M.Yu, J.Lin, Z.Wang et al., *Chem. Mater* **14**, 2224 (2002).
9. A.Huignard, V.Buissette, A-C.Franville et al., *J. Phys. Chem. B*, **107**, 6754 (2003).
10. K.Riwotzki, M.Haase, *J. Phys. Chem. B*, **102**, 10129 (1998).
11. A.Huignard, V.Buissette, G.Laurent et al., *Chem. Mater.*, **14**, 2264 (2002).
12. N.O.Mchedlov-Petrossyan, V.K.Klochkov, G.V.Andrievsky, *J. Chem. Soc., Faraday Trans.*, **93**, 4343 (1997).
13. R.E.Neuman, in book: Water in Disperse Systems, ed. by B.V.Deryagin et al., Khimia, Moscow (1989), p.188 [in Russian].
14. W.Fan, Y.Bu, X.Song, S.Sun, *Cryst. Growth Des.*, **7**, 2361 (2007).
15. G.R.Croyt, Colloid Science, Vol.1, Moscow (1955) [in Russian].
16. S.S.Voyutsky, Course of Colloid Chemistry, Khimia, Moscow (1976) [in Russian].
17. B.V.Deryagin, Stability Theory of Colloids and Thin Films, Nauka, Moscow (1986) [in Russian].

Коагуляція люмінесцентних колоїдних розчинів nGdVO4:Eu неорганічними електролітами

В.К. Клочков

Отримано водні колоїдні розчини ортованадатів гадолінію, активованих європієм. Наночастинки діаметром близько 20 нм мають яскраву люмінесценцію. Розчини $nGdVO_4$:Eu у воді прозорі у видимому діапазоні й мають незмінні властивості більше 2^x місяців. Зниженню агрегативної стійкості розчинів сприяє присутність неорганічних солей. Співвідношення значень порогів коагуляції перебувають у близькій відповідності із правилом Шульце-Гарді й законом 6-го ступеня Дерягіна-Ландау для "негативних" ліофобних золей.