

REVIEW OF ELECTROSURFACE CHARACTERISTICS AND COLLOIDAL STABILITY OF DISPERSE SYSTEMS ON THE BASIS OF SILICA WITH SURFACE TITANYL NANOSTRUCTURES IN LIQUID MEDIA

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Abstract. Modern data on the production and structural properties of titania quasi-2D nanolayers onto silica particles are generalized. The special attention is paid to the methods of precise synthesis of such nanoobjects. Features of the change of electro-surface characteristics versus the number of the deposited Ti-oxo-monolayers onto silica are analyzed. The opportunity of the smart regulation of physicochemical properties of the disperse systems on the base of silica particles modified by titania nanolayers in a liquid phase and their colloidal stability are considered.

1. INTRODUCTION

Development of modern material science demands knowledge of the structure and chemical nature of an input solid material, definition of ways of its chemical transformation with the purpose of formation of a ready product with the predetermined functional properties.

In this connection it is necessary to single out an important concept in the field of the material science, connected with the chemical designing of the surface layers of future materials [1-6]. From the chemical point of view, it is a process of surface modification as a result of the appointed surface chemical reactions (SCR)) [6-10], resulting in the substantial changes of properties of the surface and the material as a whole. One of the important classes of materials is a disperse materials (catalysts, sorbents, etc.) which are a basis of majority of materials and products, such as electroinsulating covers, varnishes, and paints, plastic greasings, etc.

In this connection, the examinations of such dispersions from the point of view of colloid chemistry and processes of structurization in disperse systems (sols and suspensions) is rather actual.

Last years are characterized by increasing interest in investigations of various classes of the nanodispersed systems, including sols and suspensions with particle surfaces modified by nanosized layers (nanostructures) [7-9].

Investigations of the electro-surface phenomena in nanodispersed systems are actual for the solution of one of the fundamental problems of modern colloid science: establishment of the laws describing the distinctions in behavior of nanodispersed and macrodispersed systems[11]

Nanosized titanium dioxide was chosen as object of this review because its unique properties and widespread use in modern technologies. The electro-surface characteristics of titania quasi-2D nanolayers by thickness from 0.3 up to 5 nm deposited onto silica particles (both porous and

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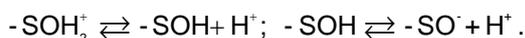
nonporous) and their colloidal stability in aqueous electrolyte solutions are generalized.

It should be noted that the titania dispersions are widespread pigments. However, production of titania nanoparticles is connected with significant difficulties because of particle agglomeration. The solution of one of the main tasks of the colloid science, paint and varnish industry - production of structures on the basis of organic and silicon organic media, various composite materials, with necessary properties (high stability, durability and resistance) - is connected with deep examination of deformation behavior of dispersed systems of the diverse nature.

2. ELECTROSURFACE CHARACTERISTICS OF OXIDE NANOLAYERS IN ELECTROLYTE SOLUTIONS

A spontaneous separation of the electric charges of opposite signs at the solid/liquid interfaces and the formation of electrical double layer (EDL) are the main cause of the various electrosurface phenomena in the dispersed and capillary systems, which manifest themselves in their corresponding electrosurface properties. Their study constitutes one of the branches of colloid science in view of variety of processes and phenomena, such as for examples electrokinetic phenomena in capillary-porous and disperse systems and their colloidal stability [11].

Main mechanisms of the charge generation at the surfaces of the metal oxides and silica in the aqueous electrolyte solutions are either the loss ($-\text{SO}^-$) or the gain ($-\text{SOH}^{+2}$) of protons by the surface hydroxilic groups ($-\text{SOH}$) due to their reactions of the acid-base interaction with water



The surface acquires an electrical charge with the density σ_0 , which can be interpreted in terms of the adsorption densities Γ_{H} and Γ_{OH} of the potential determining ions H^+ and OH^-

$$\sigma_0 = F(\Gamma_{\text{H}} - \Gamma_{\text{OH}}),$$

where F - Faraday number. The values of H^+ and OH^- activities in the bulk solution determined by its pH value at which $\sigma_0 = 0$ is called the point of zero charge (pH_{PZC}) [11].

Another electrosurface property of solid particles is their electrokinetic potential (ζ) which can be calculated from the experimental value of particle

electrophoretic mobility. The solution pH value at which $\zeta = 0$ is called the isoelectric point (pH_{IEP}).

At present, a particular attention is paid to the problem of EDL formation on the nanolayers supported by solid substrates in aqueous electrolyte solutions. The interest in this problem results from increasingly wide application of ultrathin (0.3 - 5 nm thick) oxide layers deposited onto various solid substrates for manufacturing high-efficiency catalysts, ion-selective field-effect transistors, and microelectronic devices [12-15]. Note that the peculiarities of behavior of ultrathin layers are rarely studied. Among the most studied properties are chemical composition and structural characteristics of thin layers dependent on the method of preparation and conditions of subsequent treatment. Investigations of the electrosurface properties of deposited oxide nanolayers (including nanolayers TiO_2), which, in a number of cases, determine their technological parameters, are extremely rare.

Special advantages of the synthesis of nanostructures on oxide substrates are provided by the method of molecular layer-by-layer deposition from the gaseous phase that provides a possibility to produce quasi-2D highly organized nanostructures of a given composition whose thickness is determined by the number of nanolayers [4]. As soon as both surface isoelectric point (IEP) of (hydroxide in potential-determining ions solutions (PDI) and point of zero charge (PZC) are very important surface characteristics, we are able to compare pH_{IEP} values obtained for bulk (hydr)oxides and thin element-oxide layers to analyse the changing of surface electrochemical properties when coating with nanostructures. Electrochemical characteristics changes are better noticeable when surface and bulk IEPs differ much.

During the investigation [16] Ti-O nanostructure on four SiO_2 samples (aerosil A-175 and OX-50 $\text{pH}_{\text{IEP}} = 3 \pm 0.1$), GT particles (IEP measured on the background of 10^{-2}M KNO_3 solution corresponded $\text{pH} = 2.9$) and a quartz plane-parallel capillary ($\text{pH}_{\text{IEP}} = 2 \pm 0.1$) has been studied. Electrophoretic mobility measurements for Aerosil A-175 particles covered with titanium-oxygen nanostructures showed the following. After the first cycle of molecular layering on the preliminarily dehydrated surface at $\theta = 0.1$, the isoelectric point of the modified SiO_2 surface shifts appreciably, by 0.4 pH units, to the alkaline region, and a positive region of the ζ potential appears. As θ is increased to 0.5, the isoelectric point changes to $\text{pH}_{\text{IEP}} = 4.0$. The initial Aerosil A-175 surface was not subjected to preliminary ther-

mal treatment (which, in principal, allows all silanol groups to be involved in molecular layering reactions) after the first cycle of the synthesis of the Ti-oxygen layer had $\text{pH}_{\text{IEP}} = 4.4$. This value almost did not change after several successive cycles of molecular layering (from $n = 1$ to $n = 4$) [16].

The number of cycles of the synthesis of titanium-oxygen nanolayers on the surface of GT particles was 1, 2, 6, and 11 [16]. The calculated electrokinetic potentials of the initial and modified particles on the background of 10^{-2} M KNO_3 were compared with data for the bulk sample of titanium oxide. The isoelectric point for particles covered with nanostructures is between those for the initial SiO_2 support and titanium oxide. It was also found that the isoelectric point is not affected by n (at $n = 1-11$, $\text{pH}_{\text{IEP}} \sim 4.5$) and is close to the isoelectric point for the Ti-oxygen layers on the Aerosil A-175 support at $n = 1-4$. Similar results were obtained for Aerosil OX-50 particles at $n = 1$ and 2. In this case, $\text{pH}_{\text{IEP}} = 4.2$ for modified particles [16].

Electrokinetic potential measurements for the Ti-oxygen nanostructures synthesized on the surface of a glass plane-parallel capillary at $n = 6$ and 16 gave $\text{pH}_{\text{IEP}} = 4.2-4.3$ both for HCl solutions and for those on the background of 10^{-3} M NaCl. Thus, the pH_{IEP} for plane-parallel capillaries covered with titanium-oxygen nanolayers differs from the isoelectric point of bulk titanium oxide [17]. It is also shown that the electrokinetic potentials of titanium-oxygen nanostructures of different thickness are close to each other.

It was thus shown that the deposition of titanium-oxygen nanostructures changes the electrokinetic parameters of the initial silica surface, and all of the supports modified by titanium-oxygen nanostructures have different electrokinetic parameters than bulk titanium oxide. On the other side, it is known [18] that, on complete substitution of silanol groups by Ti-oxygen ones, it is sufficient to deposit four layers to create on silica surface a titanium oxide layer with an octahedrite crystallographic structure. Therefore, six or more cycles of molecular layering would inevitably form the octahedrite structure on silica surface. The fact is that the isoelectric point of the SiO_2 surface covered with titanium-oxygen nanolayers differs from that of octahedrite ($\text{pH}_{\text{IEP}} = 5.9$) gives evidence for incomplete substitution of silanol groups, i.e. for a mosaic character of the modified surface. We also note that, in the case of Ti-oxygen nanostructures, the constancy of pH_{IEP} at increasing number of molecular layering cycles suggests that the degree

of substitution of surface groups is determined in the first cycle of the reaction.

To verify the assumption that the mosaic structure of the modified surface affects the electrokinetic characteristics of the support, we have measured the electrokinetic potential of a plane-parallel capillary formed by two different surfaces [16,17]: the initial SiO_2 surface and the SiO_2 surface covered with the titanium-oxygen nanostructure ($n = 16$). Indeed, the isoelectric point ($\text{pH}_{\text{IEP}} = 3.9$) is between the isoelectric points of the quartz glass and the titanium-oxygen nanostructure.

Potentiometric titration is another independent method for comparison of the electrokinetic characteristics of bulk oxides and ultrathin oxide layers. On the assumption that pH_{IEP} and pH_{ZPC} for titanium-oxygen nanostructures in solutions of indifferent electrolytes are equal to each other (as it was observed for bulk titanium oxide), one can compare the adsorption behavior of the nanostructures and bulk silica and titanium.

The measured adsorptions [19,20] of potential-determining ions Γ_{OH^-} on the background of 1 M NaCl for monodisperse spherical SiO_2 particles covered with the titanium-oxygen nanostructure ($n = 11$) showed no positive range of surface charge for SiO_2 particles modified with titanium-oxygen nanostructures, by contrast with electrokinetic measurements when a positive region of electrokinetic potential was observed.

The higher values of Γ_{OH^-} for modified particles as compared with bulk titanium oxide are probably related to the porosity (ion permittivity) of deposited titanium-oxygen layers. This assumption is confirmed by the results of conductivity measurements for the plane-parallel capillary covered with titanium-oxygen layers: The surface conductivity of the modified surface was higher than that of the initial one.

It is worth to note that the measurements results [16] for electrokinetic characteristics of Ti-O nanostructures on silicon oxide mounts correlate with data from [21] for SiO_2 particles covered with TiO_2 by deposition from solutions followed with calcination. It was found for the samples to possess $\text{pH}_{\text{IEP}} \cong \text{pH}_{\text{ZPC}} = 3.9 \pm 0.1$ on the background of KNO_3 solutions. Authors mention the modified particles to possess high surface charge related first of all to the porosity of the deposited oxide layer [20, 21].

The next study [22] of the adsorption and electrokinetic characteristics of one- and two-component nanostructures, which were synthesized by the ALD method ($5\text{TiO}_2/5\text{Al}_2\text{O}_3/\text{SiO}_2$), when the silica

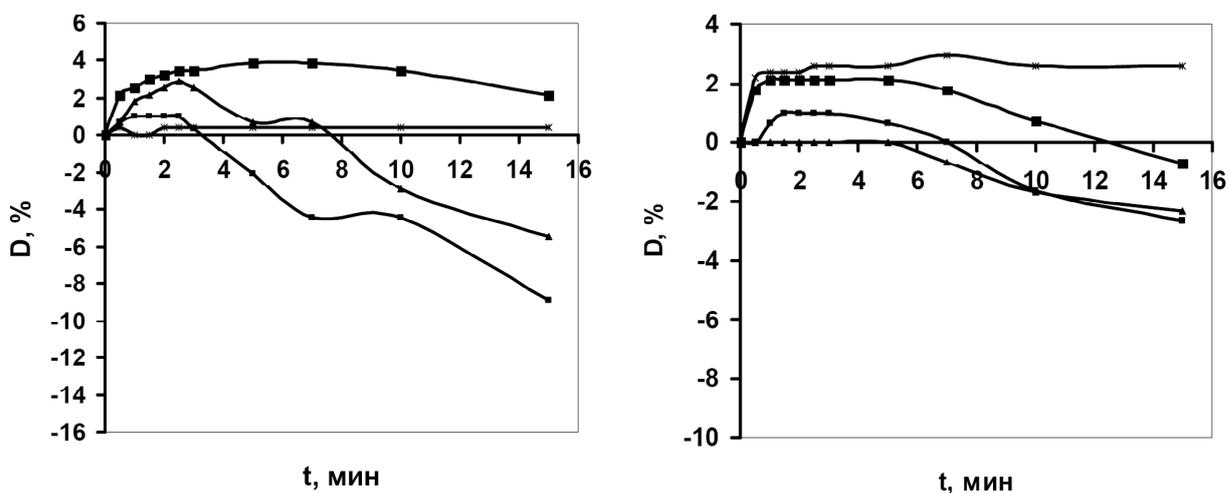


Fig. 1. Aggregative stabilities of nanostructures synthesized. Samples: (a) $[\text{SiO}_2] \setminus 1\text{Al-O} \setminus 1\text{Ti-O}$: 1 – 0.01 M KCl, 2 – 0.03 M KCl, 3 – 0.1 M KCl, 4 – 0.3 M KCl, b) $[\text{SiO}_2] \setminus 1\text{Al-O} \setminus 2\text{Ti-O}$: 5 – 0.01 M KCl, 6 – 0.03 M KCl, 7 – 0.1 M KCl, 8 – 0.3 M KCl.

surface is firstly covered with Al-O monolayers and then Ti-O monolayers, when oxide nanolayers of different chemical compositions are consecutively deposited onto a finely dispersed substrate, proved that five cycles of ALD reactions for each synthesized layer are sufficient for the electrosurface characteristics of a composite to be controlled only by an outer oxide nanostructure, the Ti-O nanolayer.

3. STABILITY OF HYDROPHOBUS COLLOID SYSTEMS OF SILICA-NANOLAYER TiO_2 IN LIQUID ENVIRONMENTS

Colloid chemistry considers dispersity as a wide range of particles starting from molecules and finishing at 10^{-2} cm, the particles that can be seen without any equipment. Systems of particles with sizes of 10^{-7} cm belong to true solutions [23]. High-dispersed (colloid) systems consist of particles with sizes 10^{-4} - 10^{-7} cm (1 μm and 1 nm). Usually high-dispersed systems are called sols. Coarsely dis-

persed systems are considered as suspensions and emulsions, depending on the character of disperse phase they consist of particles of 1 μm and more [23,24].

Under the term of stability we consider the ability of the dispersed system to keep the original particles level and their distribution in dispersive environment. Colloids are divided to two classes depending on their stability: liophilic and liophobic. Liophilic systems are self-dispersing due to thermodynamics and liophobic have to be affected from outside to be converted into disperse system, they are thermodynamically unstable.

Sedimentative (kinetics) and aggregative stabilities could be marked out. Let us consider the basis that is responsible for stability and coagulation process of disperse systems. The classical theory of liophobic colloids stability by Derjaguin-Landau-Verwey-Overbeek (DLVO) explains the coagulation process as a superposition of Van-der-Vaals forces of attraction and electrostatic repulsive forces [25,26].

Table 1. Definition of coagulation edge aerosil (OX-50).

| Sample | $[\text{SiO}_2]$ | $[\text{SiO}_2] - \text{OCH}_3$ | $[\text{SiO}_2] - \text{O-CH}_2\text{-Ca}\equiv\text{CH}$ |
|---------------------|------------------|---------------------------------|---|
| Coagulation edge, M | 0.150 | 0.114 | 0.255 |

Table 2. Definition of coagulation edge for the layered systems on OX-50

| Sample | $[\text{SiO}_2]$ | $[\text{SiO}_2] - \text{OCH}_3$ | $[\text{SiO}_2] \setminus 1\text{Al-O} \setminus 1\text{Ti-O}$ | $[\text{SiO}_2] \setminus 1\text{Al-O} \setminus 2\text{Ti-O}$ |
|---------------------|------------------|---------------------------------|--|--|
| Coagulation edge, M | 0.150 | 0.114 | 0.044 | 0.084 |

As shown in [26], the stability is affected by:

- non-electrostatic forces that appear due to formation of solvatic layers on particles' surface;
- formation of adsorbed gel-like cover that possess high durability.

Aggregative (condensation) stability is the ability of disperse phase particles to withstand aggregation. It is supported by surface charging (because of ion dissociation, ions sorption etc).

The solution for the creation of a stable suspension should be based on surface layer structure and properly changed electro-surface characteristics; this will finish for the suspension in possessing both aggregative and sedimentative high-stability (pH and electrolyte concentration influence).

Authors of [27] analyze the hydrolytic stability of the relations of the Si - O - Ti titanium-oxygen nanostructures on the surface of silica and the conditions under which titanium-oxygen nanostructures on silica resistant. Paper [28] describes the possibilities for the purposeful control and stabilization of properties of TiO₂ nanopowders and sols are analyzed.

Research [29] presents the suspensions (aerosil with Ti-organics surface groups) in KCl solution of a wide concentration range and explains the influence of surface organic groups on stability of the mounts in water environment. Aerosil surface was modified by both methyl and propargyl groups. Basing on optical density changes while coagulant (KCl) addition with different concentrations the threshold has been defined, see Table 1. The table proves that there is a tiny effect when modifying with methyl groups. Propargyl ones increase coagulation edge twice that makes the particles more stable. This may be explained with the presence of some organic fragments that increase contribution of the barrier layer into system stabilization.

The authors completed the study of kinetics of optical density changes when adding KCl in different concentrations as coagulant, (Fig.1). The presented diagrams show us that both samples behave the same at low coagulant concentrations and the increment of optical density was found to appear at KCl concentration higher than coagulation threshold.

Table 2 represents coagulation thresholds for samples modified with Ti-O monolayers; this may be explained by alteration of electro-chemical nature of the surface layer. It is well known TiO₂ suspension to be unstable at neutral pH and lower coagulation threshold may give evidence for bulk TiO₂ and nanostructures obtained to be similar this way.

4. CONCLUSION

The comparison of the data reported in scientific literature with the obtained by the authors of the present work shows that when the mount surface groups are fully modified with Ti-O nanostructures, 4-5 monolayers are enough to obtain nanostructures with electro-surface properties close to bulk TiO₂.

The same results were observed when covering silica with bi-component nanostructures (Al-O and Ti-O), sample 5x Ti-O₂/5x Al₂O₃/ SiO₂. It's worth to mention that electro-surface characteristics were defined by the outer oxide nanolayer (Ti-O).

When the mount surface was partly modified with Ti-O nanostructures (mosaic filling), electrokinetic properties of Ti-O structures possess intermediate properties (in-between silica and bulk TiO₂).

The dependence of mounts with surface organic groups modification on system stability (for aerosil A300 and OX-50) in water environment has been discussed. Surface modification with methyl alcohol does not finish in any significant mount properties changes. Aerosil modified with propargyl groups increases the coagulation threshold twice that increases particles aggregation stability. The same procedure for Ti-O modified samples doesn't affect the stability.

The results obtained contradict with some reference data, hence, some further electro-surface investigations and nanostructured suspensions stability studies are required.

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REFERENCES

- [1] V.M. Smirnov and V.B. Aleskovskii, In: *Proc. Int. Conf. IEEE-NANO, Hawaii, 2001*, p. 197.
- [2] V.B. Aleskovskii, *Khimiya Nadmolekulyamykh Soedinenil (Chemistry of Supramolecular Compounds)* (St. Petersburg State University, 1996), In Russian.
- [3] S.I. Kol'tsov, *Reaktsii Molekulyarnogo Naslaivaniya (Reactions of Molecular Layer-by-layer Deposition)* (Khimiya, St. Petersburg, 1992), In Russian.
- [4] V. M. Smirnov // *Russian Journal of General Chemistry* **72** (2002) 590.
- [5] V.M. Smirnov, V.G. Povarov, G.P. Voronkov, V.G. Semenov, I.V. Murin, V.N. Gittsovich

- and B.M. Sinel'nikov // *Journal of Nanoparticle Research* **3** (2001) 83.
- [6] V.M. Smirnov, N.P. Bobrysheva, M.G. Osmolowsky, V.G. Semenov and I.V. Murin // *Surf. Rev. Lett.* **8** (2001) 295.
- [7] G.V. Lisichkin, G.V. Kudryavtsev, A.A. Serdan, S.M. Staroverov and A.Y. Yuffa, *Modifitsirovannye Kremnezemy v Sorbtsii, Katalize i Khromatografii (Modified Silicas in Sorption, Catalysis and Chromatography)* (Khimiya, Moscow, 1986), In Russian.
- [8] A.A. Malygin, A.A. Malkov and S.D. Dubrovenskii // *Studies in Surface Science and Catalysis* **99** (1996) 213.
- [9] K. Schrijnemakers, P. Van der Voort and E.F. Vansant // *Phys. Chem. Chem. Phys.* **1** (1999) 2569.
- [10] V.A. Tertykh and L.A. Belyakova, *Khimicheskie Reaktsii s Uchastiem Poverkhnosti Kremnezema (Chemical Reactions Involving Silica Surface)* (Naukova Dumka, Kiev, 1991), In Russian.
- [11] J. Lyklema, *Fundamentals of Interface and Colloid Science, Vol. 2. Solid-liquid Interfaces* (Academic Press, London, 1995).
- [12] V.M. Smirnov, *Chemistry of Nanostructures. Synthesis, Structure, Properties*, (St. Petersburg University Press, St. Petersburg, 1996).
- [13] I.P. Suzdalev, In: *Nanotechnology. Physico-chemistry of nano-clusters, nanostructures and nanomaterials* (Komkniga, Moscow, 2006), p. 457.
- [14] I.P. Suzdalev // *Russian chemical journal* **53** (2009) 23.
- [15] *Nanotechnology research directions: IWGN Workshop Report Vision for Nanotechnology R&D in the next decade. On behalf of NSTC/CT/IWGN*, ed. by M. C. Roco, R. S. Williams and P. Alivisatos (Boston, 2000).
- [16] L.E. Ermakova, M.P. Sidorova, N.F. Bogdanova and A.V. // *Russian Journal of General Chemistry* **72** (2002) 622.
- [17] L.E. Ermakova, M.P. Sidorova and V.M. Smirnov // *Kolloidnyj Zhurnal* **59** (1997) 563, In Russian.
- [18] V.N. Pak, I.Yu. Tikhomirova, T.M. Burkat and B.I. Lobov // *Russian Journal of Physical Chemistry A* **73** (1999) 1824.
- [19] M.P. Sidorova, L.E. Ermakova, I.A. Savina, N.F. Bogdanova and S.V. Timofeev // *Colloid Journal of the Russian Academy of Sciences* **61** (1999) 768.
- [20] L. Ermakova, M. Sidorova, N. Bogdanova and A. Klebanov // *Collods & Surfaces* **192** (2001) 337.
- [21] A. Giatti and L.K. Koopal // *J. Electroanal. Chem.* **352** (1993) 107.
- [22] N.F. Bogdanova, L.E. Ermakova, P.S. Chikhachev, M.P. Sidorova, D. A. Aleksandrov and I.A. // *Colloid Journal* **67** (2005) 422.
- [23] G. R. Kroit, *Colloidal science* (Inostrannaya Literatura, Moscow, 1955).
- [24] An introduction to day colloid chemistry ed. by J.L. Parker (New York - London, 1996).
- [25] B.V. Derjgin and L.D. Landau // *Experimental and theoretical physics* **11** (1941) 802.
- [26] G. Zontag and K. Chtrenge, *Coagulation and stability of disperse systems* (Chemistry, Petersburg, 1973), In Russian.
- [27] E.A. Sosnov, A.A. Malkov and A.A. Malygin // *Russian Chemical Reviews* **79** (2010) 907.
- [28] Z.R. Ismagilov, L.T Tsikoza, N. V. Shikina, V. F. Zarytova, V.V. Zinoviev and S.N. Zagrebelnyi // *Russian Chemical Reviews* **78** (2009) 873.
- [29] E. G. Zemtsova, S. O. Kirichenko, N.F. Bogdanova and V. M. Smirnov // *Bulletin of the SPbU* **4(4)** (2011) 133.