

DOI: 10.17725/rensit.2020.12.129

## Water in Reverse Micelles

Aleksandra A. Revina

Frumkin Institute of Physical Chemistry and Electrochemistry of RAS, <http://www.phyche.ac.ru/>  
Moscow 119991, Russian Federation

E-mail: [Alex\\_revina@mail.ru](mailto:Alex_revina@mail.ru)

Received January 21, 2020; peer reviewed February 04, 2020; accepted February 10, 2020

**Abstract.** Results of the fundamental studies of chemical, radiolitic, and biochemical processes, taking place in the aqueous-organic reversed micellar solutions, suggest existence of the link between self-organization of metal nanoparticles in reverse micelles at certain synthesis stages with reductive properties of polarized water in micelle's water pool.

**Keywords:** reverse micelles, water pool, metal nanoparticles, optical, electrophysical properties, size effects, self-organization processes

UDC 54-188; 543.426

**Acknowledgments.** The studies were performed using the ULV-10-10-C-70 accelerator and the analytical equipment (AFM) of the Center for the collective use of physical research methods of Frumkin Institute of Physical Chemistry and Electrochemistry of RAS. Partial support of the RFBR grant No. 19-03-00696 A.

**For citation:** Aleksandra A. Revina. Water in Reverse Micelles. *RENSIT*, 2020, 12(1):129-134; DOI: 10.17725/rensit.2020.12.129.

### CONTENTS

1. INTRODUCTION (129)
  2. PHYSICO-CHEMICAL STUDIES OF REVERSE MICELLAR SOLUTIONS (130)
  3. CONCLUSION (133)
- REFERENCES (133)

### 1. INTRODUCTION

The unique by their characteristics systems (namely, the aqueous dispersions of the reversed micelles) allow study the complex physiological processes into the biological and living systems or organisms [1-5]. The water had and has an important role for the life origin, development and prolongation on the Earth, but this well-known chemical compound in many senses are remained poorly studied. There are many theories and models of the water nature, connected with water (and especially with a notion of so called hydrogen bonds, defining its structure, main functions and some abnormal properties, etc) [4, 6-9].

It is experimentally found and wide used in medicine, that many compounds (carotinoids, flavonoids, etc) and many medical preparations, which are *insoluble in water*, can be solved in a water micelle pool. To increase the quantum emission yield under the luminescent methods at the low metal concentrations as the initial solutions, now

the reverse micellar solutions (RMS) are often used. Under the photo-catalytic light energy transformation into the chemical energy (at the sacrifice of the electron photo-transport products recombination), the micro-emulsions "water in oil" types usage is allowing to rise the yield of the useful products, that are reserve or accumulate the light energy [10]. The key role of such aqueous systems in the non-equilibrium, but stable states for the bio-energetic processes was verified by results of work [4].

When using the nano-size particles (NP) synthesis the such reverse micelles fabrication (as the some specific micro-reactors) fabrications have demonstrated the sufficient advantages of this method, that allows us to obtain the stable nano-structural particles with the various metals and bimetals (including the rare-earth ones) with given sizes both in the liquid phase and in adsorbed state, properties and the different, earlier inaccessible poly-functional activity with the bactericide, anticorrosion, catalytic, adsorptive activity [13, 14]. But for the successive development and practical application of these results that is necessary to carry out many fundamental investigations of the method physical and chemical process kinetics (especially in fields of the NP synthesis and control), as well

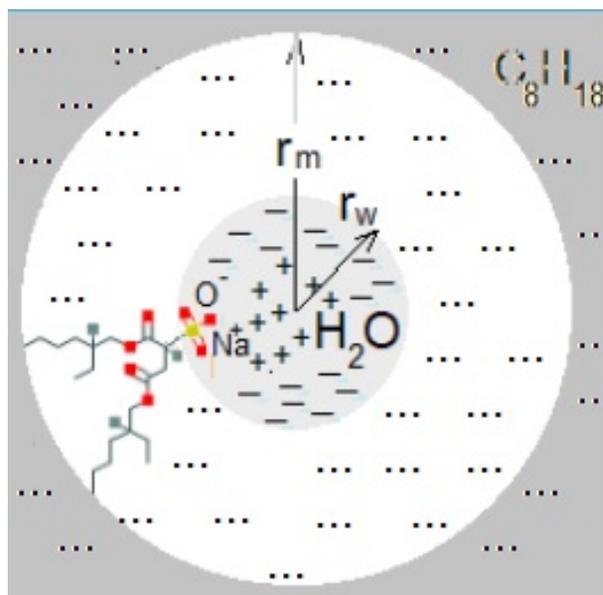
as the studies of the different water characteristics (optical, electro-dynamical, relaxation, etc) in the mentioned reverse micelle pools. There are many examples of the experimental investigations, connected with the metallic, semiconductors and polymeric particles assembling into the reverse micelle pools, but it is absent a multifold analysis of the properties and possible architecture of the nano-particles, produced in the reverse micelle pools, that are specific for their high degree of *dynamicity and self-organization* character. One another important problem is connected with the usages of the calculation and modeling methods to predict the nano-particles and colloidal self-organization behavior with accounting the lot of the scales and various factors of the environment conditions influence. In work [15] the results are presented of an imitation modeling for a nano-particle self-organization under a drying solvent drop at substrate using the self-organization process visualization and the corresponding final nano-particles distribution on the modified surface. The effects of the nano-particles self-organization or Self-Assembly under the outer factors actions in the liquid systems were studied in the work [16]. During the relatively short period the term *self-organization* become one of the most used and popular word in the modern science and practice. Many results, affirming the self-organization important role at the different metallic stable nano-particles formation into the reverse micelle pools have been obtained in [17, 18]. But the main meaning of these works is that they affirmed also the very important role of water itself in the aqueous reverse micelle pools, where the water is presented in the "polarized" state [4, 8]. The deep studies of the electromagnetic, electro-physical, optical, etc properties of the water into the aqueous-organic reverse micelle solutions, carried out by professor V.I. Ermakov investigations, allowed to select from the complex system of the experimental data information of the state and properties of water into the micelles [14,19,20].

## 2. PHYSICO-CHEMICAL STUDIES OF REVERSE MICELLAR SOLUTIONS

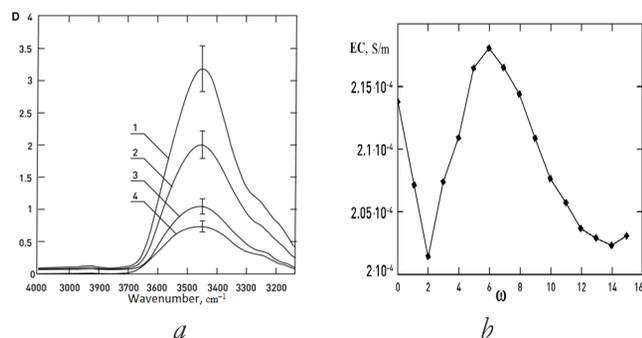
The reverse micro-emulsions of the "water-oil" types on the base of the surface active substance

AOT-bis(2-ethyl-hexyl)-sulfo succinate sodium is stabilized the big amounts of water, and the scheme of this reverse micelle is shown on **Fig. 1**, where the pool diameter  $d$  depends, naturally, on the solubilization coefficient  $\omega$ :  $d \sim k \times \omega$ , where  $\omega = [\text{H}_2\text{O}]/[\text{AOT}]$  (a molar concentration relation of water and AOT). In our works [12, 13, 17, 18] we used the values  $\omega = 1.0 \div 10.0$ ; [AOT] concentration =  $0.10 \div 0.20$  M, ions concentration  $[\text{Me}^{n+}]$  was in the range from  $10^{-3}$  M to 3.0 M; the solvent was isooctane  $\text{C}_8\text{H}_{18}$ . For the synthesis of many types NP in the water-organic RMS was selected (as a basic system the water-organic RMS was solution  $\text{H}_2\text{O}/[\text{Me}^{n+}]$   $\omega_{(i)}/0.15$  M AOT(bis(2-ethyl-hexyl)-sulfo succinate Na) in isooctane. The water content (an aqueous  $\text{Me}^{n+}$  salts solution volume) is equal corresponding to this  $\omega_{(i)}$  value.

One of the initially selected RMS systems [0.15 M AOT/isooctane], that is simultaneously the comparison solution for the optical adsorption spectra measurements) is their transparency in a wide spectral range, that allows actively use the spectrophotometric analysis methods (UV-VIS-IR). To select an information, directly related to water, from the RMS (containing water,  $\omega = 1.5 \div 4.0$ ) spectra were subtracted the AOT/isooctane solution spectra. As is seen from **Fig. 2a**), the obtained spectra include at least two adsorption lines ( $\lambda_{\text{max}} \sim 3450 \text{ cm}^{-1}$  and  $\lambda_{\text{max}}$



**Fig. 1.** The reverse micelle scheme: AOT-bis(2-ethyl-hexyl)-sulfo succinate Na,  $r_m$  and  $r_w$  – radii of the micelle and water pool,  $\text{C}_8\text{H}_{18}$  – isooctane; in the center – the state of polarized water and the positions of the sulfo-groups in the amphiphilic AOT molecules [18].



**Fig. 2.** (a) IR spectra of H<sub>2</sub>O in RMS with ω<sub>(ϑ)</sub> values: 4.0 – 1), 3.0 – 2), 2.0 – 3), 1.0 – 4); (b) Electrolytic conductivity of H<sub>2</sub>O in RMS as a function of ω<sub>(ϑ)</sub>.

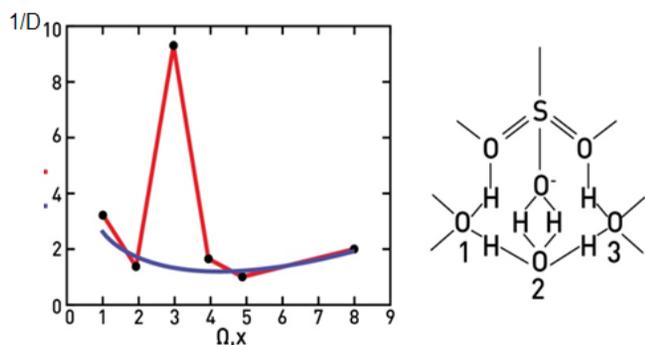
~3250 cm<sup>-1</sup>), which can be related to the different water states. More correct information about the different water states in reverse micelles, depending on ω<sub>(ϑ)</sub> value was obtained from the high-frequency electric conductivity method HF EC (Fig. 2b) [15, 20].

The optical transparency (1/D) dependence on different values of solubility coefficient ω is shown at Fig. 3.

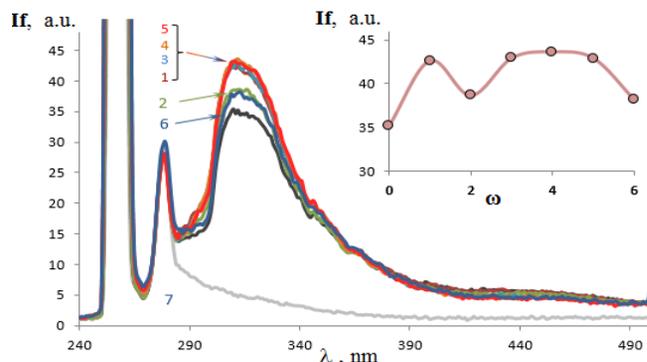
The minimal value of specific EC (Fig. 2b) into RMS at ω = 2.0 can be explained by low water content in the AOT itself. The same non-linear dependence has been obtained under the fluorescent spectra analysis for RMS system (0.15 AOT/iso-octane) after the water additions in quantities, proportional to ω values (Fig. 4).

Fig. 4 shows Fluorescence intensity (IF) spectra 1–6, respectively; isooctane – (IF) spectra 7. Insert: fluorescence intensity at λ = 312 nm as a function of RMS ω<sub>(ϑ)</sub>.

The results of the water influence investigation on the fluorescence characteristics of the RMS samples for system (H<sub>2</sub>O<sub>ω</sub>/[Me<sup>n+</sup>]/0.15M AOT/ isooctane are demonstrating the some fluorescence



**Fig. 3.** The optical transparency (1/D) of RMS and scheme of water coordination (three dimensional structure) by AOT sulfo-group in RMS at ω = 3.0.



**Fig. 4.** Fluorescence intensity (If) spectra of the 0.15 M AOT/isooctane/H<sub>2</sub>O solutions with water content in accordance with ω<sub>(ϑ)</sub> values: ω = 1...6.

intensity rise for the recombination of water charged states under light excitation of fluorometer.

On the base of the literature data and the above presented results of the electrical, physical and optical properties of the aqueous-organic solution of RMS, we could conclude, that at analysis of the synthesized metallic nanoparticles it is necessary to account the role of water in the polarized state in the reverse micelles, as the specific phase state of water.

In order to connect these results with a kinetics of the metals NP synthesized in RMS at presence of the metal ions, it was important to confirm the main point of our considerations, i.e. affirm an important role of the polarized water at the initial stages of the NP formation in RMS with metal ions presence and connect the results with a general kinetics of these processes. It was important to demonstrate the polarized water role at the initial synthesis stages for the nano-particles, obtained by different ways of the metal ions reduction. By other words, we have to give the special attention to the comparison of the plasmonic resonance spectra for the metal NP of different sizes (Fe, Re, Au, Pd), obtained in the RMS systems when using the various primary reactions for the metal ions reduction (radiolytic methods with usage of the different primary actions of the ionizing radiation, chemical, e.g. at presence of flavonol, (quercetin) as reducer [12, 13]. In all cases we have to account the water properties in a water pools of reverse micelles [17, 18]. Schematically, methods for preparing samples for different metal ion reduction reactions are shown on Table 1.

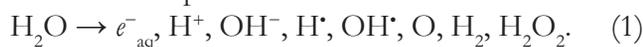
The electronic plasmon resonance spectra of RMS, containing NP of Ag RadChem after

Table 1

The methods of the metal ions reduction into the RMS  
 $[H_2O/[Me^{n+}]/0.15\text{ M/AOT/RH(isooctane)}, \omega = [H_2O]/[AOT]$ .

Radiation Chemical method (under ionizing irradiation) RadChem:	Chemical method Chem: (flavonol, Qr - reducing agent)
$Me^{n+}/H_2O \rightarrow 0.15\text{ M/AOT/RH}$ →solubilization → removal of $O_2$ →irradiation→Rad Chem H <sub>4</sub> Me	Qr → 0,15 M AOT/RH; $Me^{n+}/H_2O \rightarrow Qr/0.15\text{ M AOT/RH}$ H <sub>4</sub> Chem, ! only at $O_2$ presence
Conditions of the RMS preparation with different concentration of the metal ions $Me^{n+}$ in RMS and in the water pool, w.p.: a) $[Me^{n+}]_{RMS} = f\omega_{\theta}$ ; $[Me^{n+}]_{w.p.} = \text{const}$ , b) $[Me^{n+}]_{RMS} = \text{const}$ , $[Me^{n+}]_{w.p.} \sim 1/\omega$ .	

irradiation by electron UELV-10-10-T accelerator at the dose rate  $3 \cdot 10^3\text{ Gy/s}$  and the Dose from 5.0 kGy to 25 kGy) are presented on Fig. 5a. The spectra changes with the time of sample storage are shown. A radiation chemistry reduction of the metal ions proceeds due to the interaction with the short-lived intermediate particles of water radiolysis in the micelles water pools:



This radiation chemistry reduction can be described by the next reactions scheme:



$e^-_{aq}$  and radical  $H^{\bullet}$  – the most active reducing agents, the ionization potential ( $E$ ) is  $\sim -2.9\text{ V}$ ; the constants of the reactions are close to  $K_{diff} \sim 3.5 \cdot 10^{10}\text{ M}^{-1}\text{s}^{-1}$ .

The  $OH^{\bullet}$  – radical is the strong oxidizing agent, but due to addition the alcohol (acceptor) in RMS as the result of the reaction 3 was the formation of the hydroxyl-ethyl radical:

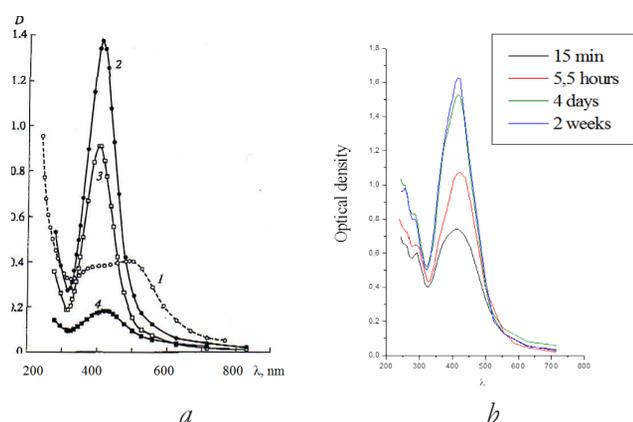


Fig. 5. The electronic plasmon resonance spectra of (a) NP Ag RadChem in RMS ( $\omega = 5$ ) at different time after irradiation,  $\Delta t$ : 1 – 40 min., 2 – 2 weeks, 3 – 3 weeks; 4 – 4 month; (b) NP Ag Chem in RMS ( $\omega = 5$ ): the storage time of samples on the insert. The concentration of Silver salt ( $AgNO_3$ ) in water solutions was 0.3 M.

which also is the strong reducer ( $k = 1.6 \cdot 10^9\text{ M}^{-1}\text{s}^{-1}$ ). The yield of the reducing agents and, respectively, the yield of metal NPs has increased. The spectra of NP AgRadChem are presented on Fig. 5b.

It has been noted, that during two weeks of post-radiation period (Fig. 5a) the optical density of studied sample solution sufficiently increase. Such increase cannot be attributed to metal ion reduction in NP AgRadChem due to presence of the radiation-induced reducing particles, which have lifetime less than several milliseconds. In the spectrum of the NP Ag Chem (Fig. 5b) the adsorption spectrum of the reducing agent Qr is absent, but in the same time is observed the growth of the adsorption intensity of NP Ag. The experimental results [14, 15] demonstrated the NP Ag Chem formation in RMS at presence of Qr and molecular oxygen but after  $O_2$  removal, in contrary to the RadChem method in anaerobic conditions, the synthesis of NPs was stopped. In this concept, Qr oxocomplex  $[nQr^{\delta+} \dots mO_2^{\delta-}]$  formation and the triple metallo-complex  $[nQr^{\delta+} \dots mO_2^{\delta-} \dots pAg^+]$  in 0.15 M/AOT/RH solution are studied. The optical spectra of Qr oxocomplex with  $\lambda_{max1} \sim 385\text{ nm}$ ,  $\lambda_{max2} \sim 265\text{ nm}$  and metal-oxocomplex with  $\lambda_{max} \sim 450\text{ nm}$  were recorded and presented on Fig. 6.

In method of quercetine Qr– 3, 5, 7, 3', 4'-pento-hydroxy flavonol and the salt  $[AgNO_3] = 0.3\text{ M}$  have used.

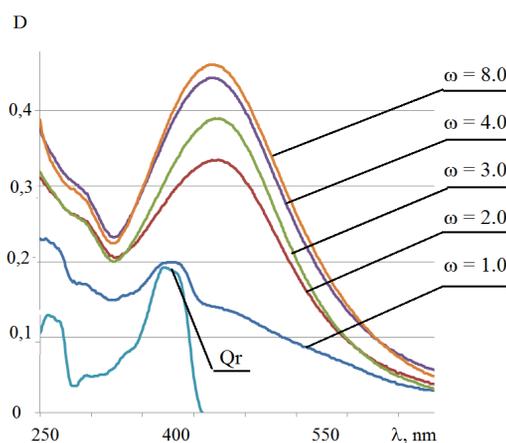


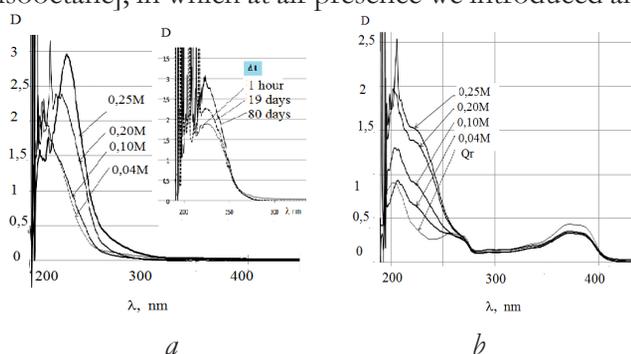
Fig. 6. The optical density spectra of the oxocomplex  $[nQr^{\delta+} \dots mO_2^{\delta-}]$  in  $150\text{ }\mu\text{M Qr}/0.15\text{ M AOT/RH}$  solution before the water solution of  $AgNO_3$  was introduced – 1; the optical band ( $\lambda_{max} \sim 450\text{ nm}$ ) appearance in the presence of Qr,  $O_2$  and  $Ag^+$  in RMS ( $\omega = 1.0$ ) is related with registration of metal oxocomplex  $[nQr^{\delta+} \dots mO_2^{\delta-} \dots pAg^+]$  during of NP syntheses; the optical spectra of the NP Ag in RMS at different  $\omega$  values: from  $\omega = 1.0$  to  $\omega = 8.0$ .

At the optical density registration of the metal NP adsorption bands on dependence on time (the results were obtained for the various primary stages of the  $Me^{n+}$  reduction reactions), there arises the question about different mechanisms of the early stages of the reduction reactions) and also the question of the “post-formation” process of metal NPs establishment and the reactions of this process during long period. An post-formation process during a “post-radiation” was detected for NP RadChem of different metals (Pd, Pt, Au, Rh, Re, and Fe [18, 19, 21].

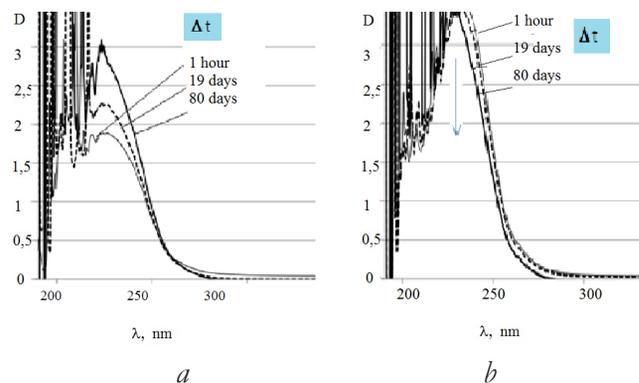
The NP Chem synthesis description is complicated by the data interpretation problem of the because the reductant  $Qr$  participates play various roles. First is the reaction with  $Me^{n+}$  as a catalyst with “regeneration“ (Fig. 7b). But in this case, the other metal ion is playing a sacrifice role, and is not detected in the spectra of RMS NP (Fig. 5b).

As shown in Fig. 7b at NP Chem Re synthesis, the  $Qr$  adsorption lines of the RSM NP spectra are nor overlapping and therefore it is easy to deduce, that there is one another mechanism of the make consideration thus the  $Me$  ions reduction by quercetin with its “regeneration”. Thus for the NP chemical synthesis in RMS was detected some of adsorption line intensity growth without an apparent changes of the form, that can testify to the NP sizes conservation.

An explanation of all these non-usual results for “the NP after-formation at the post-reaction period” was obtained after the special experiments of such NP synthesis with NP Re. As the “working” solution was used the same solution [0.15 M AOT in isoctane], in which at air presence we introduced an



**Fig. 7.** The adsorption spectra of NP Re RadChem with  $D = f[Re^{7+}]$  after irradiation at dose 27.9 kGy; Insert –  $D = f(t)$  – (a). The adsorption spectra of NP Re Chem in RMS,  $D = f[Re^{7+}]$  – (b). Salt is ammonium perenate,  $[NH_4ReO_4] = 0.02M$ .



**Fig. 8.** The adsorption spectra of Re SA NP, produced in RMS of composition [0.15 M AOT/isoctane] at different values of  $[Re^{7+}]_{RMS} = 0.5mM$  and  $\omega = 5.0$  – (a);  $[Re^{7+}]_{RMS} = 1.1 mM$  at  $\omega = 10.0$  – (b).  $[NH_4ReO_4] = 0.04M$  in the initial aqueous solution.

aqueous solution of ammonia perenate  $NH_4ReO_4$  in amounts, corresponding to the selected value  $\omega = 5.0$ . The system of spectro-photometric characteristics dependences on the time after the salt aqueous solution introducing were demonstrating the optical adsorption spectra of the NP Re for two samples of RMS at values  $\omega = 5.0$  and  $\omega = 10.0$ . The NP Re formation in RMS (Self-Assembly, SA) is proceeding at the reducer presence in aerobic conditions without any outer influence of radiation or reductant. The results are shown at Fig. 8.

From the optical spectra comparison for the NP Re, produced by different methods (Fig. 7 and Fig. 8) one can deduce, that these spectra have a complex form, but are located in the one range of spectrum (200-270 nm).

The spectrophotometric studies [18] of the Fe NP formation in RMS have revealed similar impact of self-assembly processes in the formation of NPs i.e., the processes, which do not require any targeted actions like catalysts introduction, or ionizing radiation. The X-ray diffraction and PEM data have confirmed the formation of Fe NPs with sizes from 1.0 to 3.0 nm through the SA process in RMS.

**CONCLUSION**

Thus the obtained results allow to consider, that water in aqueous pools (reverse micelles) is present in a some «polarized» state and is possible to play some a «reducer» role for the metal ions with the following construction of the spontaneously formed nanostructures into the organized ones. The reverse aqueous organic micellar systems are very near to the biological systems and therefore the fundamental

studies of their specific features, structures and the self-organization characteristics, etc are very important for establishing mechanisms and kinetics of the various processes taking place in Nature.

## REFERENCES

1. Fletcher PDI, Howe AM, Robinson BH. The Kinetics of Solubilisation Exchange between Water Droplets of a Water-in-oil Microemulsion. *J. Chem. Soc., Faraday Trans. 1*, 1987, 83:985-1006.
2. Nikolis G, Prigozhin I. *Self-Organization in non-equilibrium systems*. Moscow, Mir Publ., 1979, 512 c.
3. *Structural self-organization in solutions and at the phase RET boundary*. Ed. A.Yu. Tsivadze. Moscow, LKI Publ., 2008, 544 p.
4. Voeikov VL. The Key role of stable nonequilibrium state of aqueous systems in bioenergetics. *Ross. chem. journal*, 2009, 53(6):41.
5. Rusanov AI, Nekrasov AG. Optical activity of surfactants. *DAN*, 2010, 434(4):496-498.
6. Rodnikova MN. In: *Structural self-organisation in solutions and on phase boundary*. Ed. AYu. Tsivadze. Moscow, LKI Publ., 2008, p. 151 (in Russ.).
7. Malenkov GG. Surface of water films and droplets: Structure, dynamics and forces. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2011, 383:41-47.
8. Zheng, JM, Wexler A, Pollack GH. Effect of buffers on aqueous solute-exclusion zones around ion-exchange resins. *J. Colloid Interface Sci.*, 2009, 332:511.
9. Lymar SV, Khramov MI, Parmon VN, Zamaraev KI. Interfacial charge separation in microemulsions. Deceleration of recombination of electron phototransfer products. *Chemical physics*, 1983, 4:550-553.
10. Bulienkov NA. The role of modular design in study of the self-organization of biological systems. *Biophysics*, 2005, 50(5):811-831.
11. Voloshin VP, Zheligovskaya EA, Malenkov GG, Naberukhin YuI, Tytik DL. *Ross.Khim.Zh.*, 2001, 45(3):31.
12. Revina, A.A. *RF Patent 2312741*, 2007.
13. Revina, A.A. *RF Patent 2322327*, 2008.
14. Revina AA, Zaitsev PM. The Role of Early Stages of Dioxygen Activation in the Biological and Catalytic Activity of Phenol Natural Antioxidants. *Russian Journal of Electrochemistry*, 2012, 48(4):412-417.
15. Ermakov VI, Revina AA. *Obratnomitsellyarnye sistemy: Elektromagnitnye svoystva i struktura* [Inverse-Micellar Systems: Electromagnetic Properties and Structure]. Nizhny Novgorod, N. Novgorod Institute of Management, Russian Presidential Academy of National Economy and Public Administration Publ., 2017, 200 p.
16. Rudenko OV, Lebedev-Stepanov PV, Gusev VA, Korobov AI, Korshak BA, Odina NI, Izosimova MYu, Molchanov SP, Alfimov MV. Control of self-assembly processes in droplet of colloidal solution by the acoustic field. *Acoustical Physics*, 2010, 56(6):935-941.
17. Grzelczak Marek, Vermant Jan, Furst Eric M, et al. Directed Self-Assembly of Nanoparticles. *ACS Nano*, 2010, 4(7):3591.
18. Revina AA, Suvorova OV, Pavlov YS, Tytik DL. The role of self-assembly processes in the formation of iron nanoparticles in inverse micelles. *Fizikokhimiya poverkhnosti i zashchita materialov* [Protection of Metals and Physical Chemistry of Surfaces], 2019, 55(5):888-894 (in Russ.).
19. Revina AA, Chernyshova KF, Tabachkova NYu, Parkhomenko YuN. Gold nanoparticles in reverse micellar solutions: preparation, optical properties, and dimensional characteristics. *Russian Chemical Bulletin*, 2019, 68(6):1164-1170.
20. Tanasyuk DA, Revina AA, Ermakov VI. State of water in reverse micelles according to IR spectroscopy and PMR. *High-tech nanotechnology*, 2012, 13(2):9-15.
21. Revina AA, Kuznetsov MA, Boyakov EE, Zolotarevskii VI, Chekmarev AM. Synthesis and Physicochemical Properties of Rhenium Nanoparticles. *Fizikokhimiya poverkhnosti i zashchita materialov* [Protection of Metals and Physical Chemistry of Surface], 2018, 54(1):47-54 (in Russ.).