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Adsorption of Polyethylene-Glycols by Nanosized Iron Oxides Particles in Iron Oxides/Polyethylene-Glycol/Water/ Dispersions

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Abstract

The successful application of dynamic light scattering and electron magnetic resonance spectroscopy technique to control the formation of nanosized particles of iron oxides in iron oxides containing aqueous polyethylene-glycol dispersions is shown. The formation of the pegylated iron oxides particles with superparamagnetic properties in this system is established.

Keywords: water-polyethyleneglycol; nanoparticle; iron oxide; EMR, DLS; microcalorymetry.

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Introduction

Currently, nanosized particles of iron oxides are successfully used in various fields of science and technology, including biotechnology and medicine [1]. However, there are the problems preventing their widespread clinical use, including lack of sufficient studies on biocompatible polymers useful as stabilizing of the nanoscale magnetic iron oxide particles [2]. To expand the area of application of magnetic iron oxides it is necessary to use oligomeric polyfunctional stabilizers and study their interaction with iron oxides particles, the properties of obtained complexes, to develop methods for producing biocompatible polymeric compositions.

In recent years the most widely used biocompatible polymer is polyethylene-glycol (PEG). This paper presents the results of the study of nanoscale particles in the system FeCl2-FeCl3/H2O/PEG/NH4OH. using dynamic light scattering (DLS), electron magnetic resonance (EMR) methods in combination with microcalorimetric measurements of adsorption of polyethylene-glycol by these particles from water-polyetylene-glycol solutions..

Experimental part

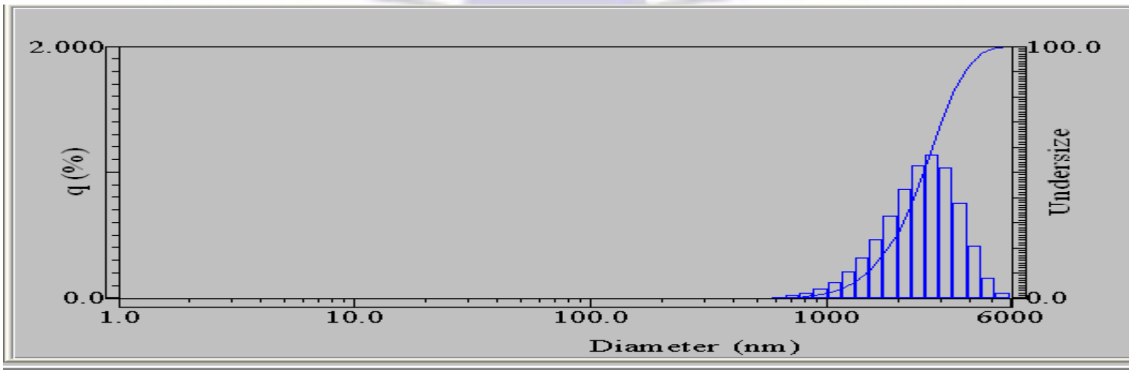
The polyethylene-glycol HO-(CH2-CH2-O-)$_n$H with molecular weight of 300, 600, 1500 and ethylene-glycol (EG) HO-CH2-CH2-OH from “LOBA-CHEMIE” (Austria), iron chlorides(II,III) qualification “Chemically pure”, Russia, 25% aqueous ammonia solution qualification “Chemically pure”, Russia, are used in this work. As the solvent bidistilled water obtained using a glass distiller is used. Aqueous polyethylene-glycol dispersions containing magnetic iron oxides particles were obtained by adding 25 % aqueous solution of NH4OH on to aqueous solutions of polyethylene-glycol with di-and tri-valent iron chlorides. In both cases the resulting precipitate was washed with distilled water until pH = 7 and air dried. The washed and air dried powder was analyzed by XRD and formation of magnetite crystallites was established. After the synthesis and wash on his way without drying the magnetite samples ethylene-glycol (EG) and PEG were added and the dispersions with different concentrations of EG and PEGs were obtained. As shown by infrared spectroscopy control of the sample processing EG and PEG led to the modification of the surface of magnetite, by substituting surface adsorbed water molecules with EG and PEG molecules. Amount of adsorbed PEG determined from calorimetric measurements. The linier dimensions of the particles formed in solutions and their size distribution were investigated using dynamic light scattering (DLS) method using an apparatus LB550, Horiba, Japan. The characteristic features of the analyser: accurate particle size measurements from 1nm to 6µm; wide concentration range - from 1ppm to 40wt.%, depending on the sample; temperature controle: 5-70 ^{o}C, with integrated Peltier temperature controller system. The Fourier-Transform/Iterative Deconvolution technique provides accurate results for average particle size and for distribution shape and identification of multiple modes. Light source - 650 nm diode laser [3].

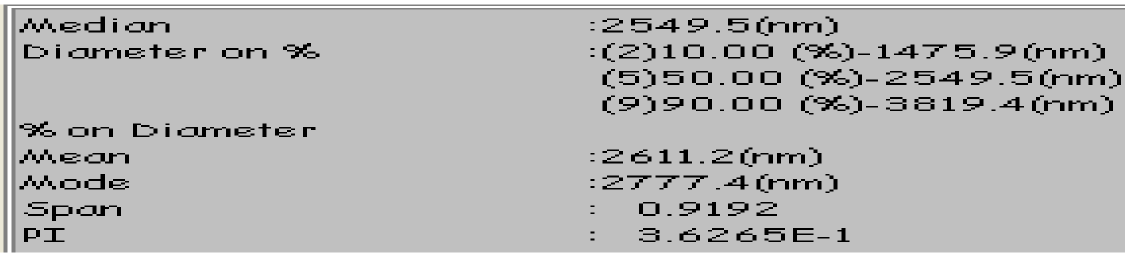
Sizes of the magnetic particles was estimated by using EMR method. EMR measurements were carried out using JES-PE-3, Jeol spectrometer operating at 9.3 GHz (X band) and modulation frequency of 100 kHz. The JES-VT-3A variable temperature controller is used to vary the temperature when observing EMR spectra at other than room temperature (variable temperature range: -170 ^{o}C - +300 ^{o}C). The desired temperature is obtained by applying hot or cold air to the vicinity of the specimen. For low temperature measurements, nitrogen gas evaporated from liquid nitrogen in a metal dewar is used, the evaporating rate being controlled automatically. For the high temperature measurements, air from an air compressor passed through a heat blasting pipe is used, the temperature of the air being automatically controlled by regulating the heater power.

Calorimetric measurements were done using a differential automatic microcalorimeter DAK-1-1, Institute of Chemical Physics, Russia.

Results and Discussion

Figure1 shows the spectrum of DLS for dispersion FeCl2-FeCl3/H2O/PEG/NH4OH. As seen from the Fig.1 in the polymer -aqueous solution at a ratio of PEG/iron salt = 1:1 (mole/mole) particles with the linear dimensions from 1,4 to 2,6 µm are coexist in dynamic equilibrium. The number and distribution of particles in size essentially depends on the ratio of PEG/iron salt and measuring temperature.





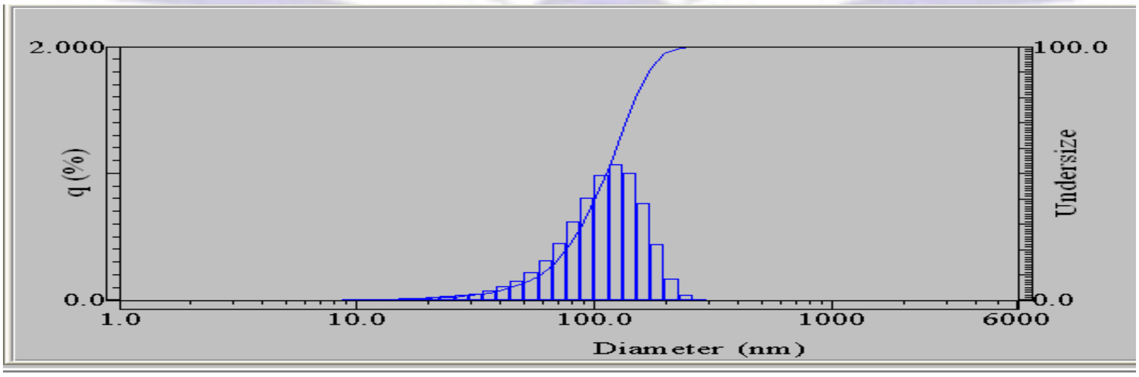
Median :2549.5(nm)
Diameter on % :(2)10.00 (%)-1475.9(nm)
(5)50.00 (%)-2549.5(nm)
(9)90.00 (%)-3819.4(nm)
% on Diameter
Mean :2611.2(nm)
Mode :2777.4(nm)
Span : 0.9192
PI : 3.6265E-1

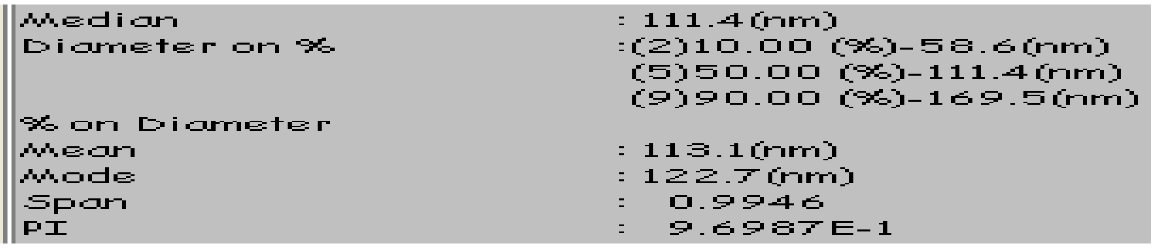
Fig.1. Particle size distribution in aqueous polymer solutions at a ratio of PEG/iron salt = 1:1 (mole to mole) in the system FeCl2-FeCl3/H2O/PEG600/NH4OH (before washing and drying).

Diffusion Coefficient 1.6942 E^{-13} (m^2/s)

X (nm)	q*	Q	X (nm)	q*	Q	X (nm)	q*	Q	X (nm)	q*	Q
0.0011	0.000	0.000	0.0100	0.000	0.000	0.0873	0.000	0.000	0.7660	0.019	0.368
0.0013	0.000	0.000	0.0114	0.000	0.000	0.1000	0.000	0.000	0.8773	0.039	0.895
0.0015	0.000	0.000	0.0131	0.000	0.000	0.1145	0.000	0.000	1.0048	0.073	1.889
0.0017	0.000	0.000	0.0150	0.000	0.000	0.1312	0.000	0.000	1.1509	0.127	3.615
0.0020	0.000	0.000	0.0171	0.000	0.000	0.1503	0.000	0.000	1.3182	0.206	6.416
0.0022	0.000	0.000	0.0196	0.000	0.000	0.1721	0.000	0.000	1.5099	0.317	10.722
0.0026	0.000	0.000	0.0225	0.000	0.000	0.1971	0.000	0.000	1.7294	0.466	17.050
0.0029	0.000	0.000	0.0257	0.000	0.000	0.2258	0.000	0.000	1.9808	0.654	25.929
0.0034	0.000	0.000	0.0295	0.000	0.000	0.2586	0.000	0.000	2.2687	0.866	37.688
0.0038	0.000	0.000	0.0338	0.000	0.000	0.2962	0.000	0.000	2.5985	1.055	52.010
0.0044	0.000	0.000	0.0387	0.000	0.000	0.3393	0.000	0.000	2.9763	1.138	67.450
0.0050	0.000	0.000	0.0443	0.000	0.000	0.3886	0.000	0.000	3.4090	1.034	81.480
0.0058	0.000	0.000	0.0507	0.000	0.000	0.4451	0.000	0.000	3.9045	0.749	91.652
0.0066	0.000	0.000	0.0581	0.000	0.000	0.5098	0.000	0.000	4.4721	0.410	97.217
0.0076	0.000	0.000	0.0666	0.000	0.000	0.5839	0.000	0.000	5.1223	0.161	99.406
0.0087	0.000	0.000	0.0762	0.000	0.000	0.6687	0.008	0.112	6.0000	0.038	100.000

The results from LB550 measurements for magnetite/PEG600/water solution with different dilution (1:4 and 1:50) are shown in Fig.2 and 3, respectively.





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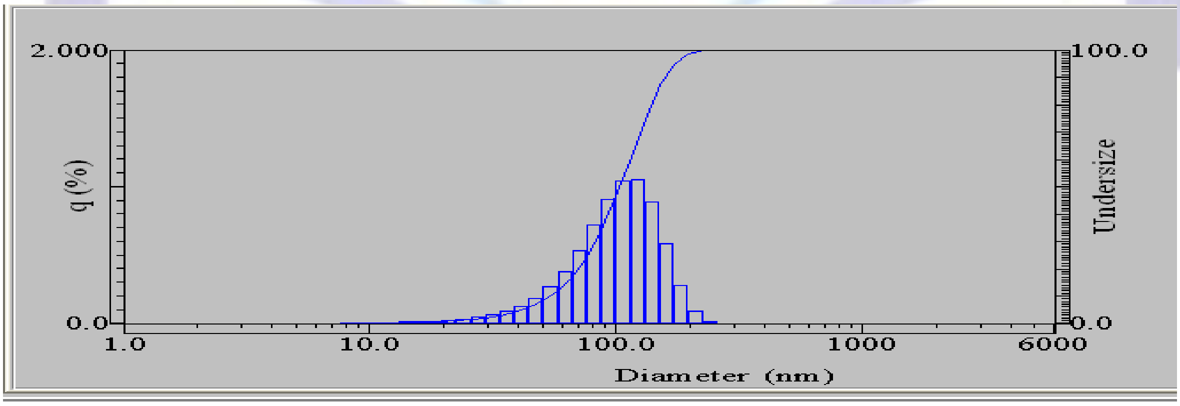
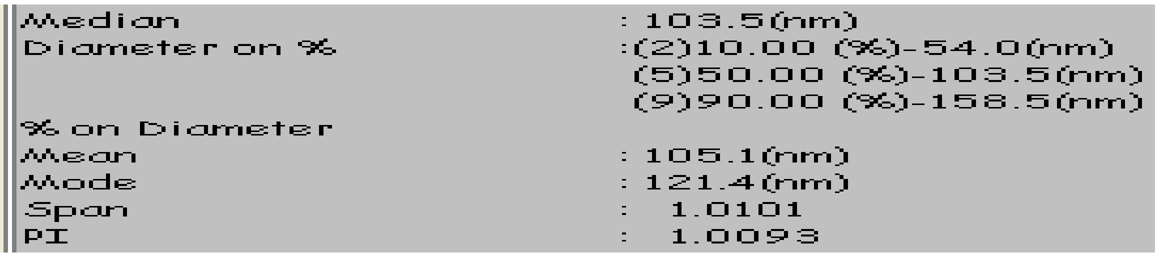
Median                                  : 111.4(nm)
Diameter on %                           :(2)10.00 (%)-58.6(nm)
                                         (5)50.00 (%)-111.4(nm)
                                         (9)90.00 (%)-169.5(nm)
% on Diameter
Mean                                    : 113.1(nm)
Mode                                    : 122.7(nm)
Span                                    :   0.9946
PI                                      :   9.6987E-1
```

Fig.2. Particle size distribution in aqueous magnetite/PEG600 solutions at a ratio of PEG/iron salt = 1:1 (mole to mole) (after washing the system $FeCl_2$-$FeCl_3$/H_2O/PEG/NH_4OH and drying in air at 45-50 °C the product of washing; dilution 1:4).

Diffusion Coefficient 4.1808 E^{-8} (m^2/s)

X (nm)	q*	Q	X (nm)	q*	Q	X (nm)	q*	Q	X (nm)	q*	Q
0.0011	0.000	0.000	0.0100	0.005	0.113	0.0873	0.719	34.170	0.7660	0.000	100.000
0.0013	0.000	0.000	0.0114	0.006	0.190	0.1000	0.906	46.466	0.8773	0.000	100.000
0.0015	0.000	0.000	0.0131	0.007	0.289	0.1145	1.041	60.600	1.0048	0.000	100.000
0.0017	0.000	0.000	0.0150	0.009	0.416	0.1312	1.051	74.860	1.1509	0.000	100.000
0.0020	0.000	0.000	0.0171	0.012	0.583	0.1503	0.885	86.879	1.3182	0.000	100.000
0.0022	0.000	0.000	0.0196	0.016	0.806	0.1721	0.585	94.820	1.5099	0.000	100.000
0.0026	0.000	0.000	0.0225	0.022	1.108	0.1971	0.279	98.611	1.7294	0.000	100.000
0.0029	0.000	0.000	0.0257	0.031	1.524	0.2258	0.087	99.790	1.9808	0.000	100.000
0.0034	0.000	0.000	0.0295	0.043	2.106	0.2586	0.015	100.000	2.2687	0.000	100.000
0.0038	0.000	0.000	0.0338	0.061	2.933	0.2962	0.000	100.000	2.5985	0.000	100.000
0.0044	0.000	0.000	0.0387	0.087	4.119	0.3393	0.000	100.000	2.9763	0.000	100.000
0.0050	0.000	0.000	0.0443	0.127	5.837	0.3886	0.000	100.000	3.4090	0.000	100.000
0.0058	0.000	0.000	0.0507	0.184	8.336	0.4451	0.000	100.000	3.9045	0.000	100.000
0.0066	0.000	0.000	0.0581	0.267	11.959	0.5098	0.000	100.000	4.4721	0.000	100.000
0.0076	0.000	0.000	0.0666	0.383	17.152	0.5839	0.000	100.000	5.1223	0.000	100.000
0.0087	0.004	0.050	0.0762	0.535	24.416	0.6687	0.000	100.000	6.0000	0.000	100.000





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Median                        : 103.5(nm)
Diameter on %                 :(2)10.00 (%)-54.0(nm)
                               (5)50.00 (%)-103.5(nm)
                               (9)90.00 (%)-158.5(nm)
% on Diameter
Mean                          : 105.1(nm)
Mode                          : 121.4(nm)
Span                          :  1.0101
PI                            :  1.0093
```

Fig.3. Particle size distribution in aqueous magnetite/peg600 solutions at a ratio of PEG/iron salt = 1:1 (mole to mole) (after washing the system FeCl2-FeCl3/H2O/PEG/NH4OH and drying in air at 45-50 ^{o}C the product of washing; dilution 1:50).

Diffusion Coefficient 3.8855 E^{-8} (m^2/s)

X (nm)	q*	Q	X (nm)	q*	Q	X (nm)	q*	Q	X (nm)	q*	Q
0.0011	0.000	0.000	0.0100	0.004	0.056	0.0873	0.615	28.394	0.7660	0.000	100.000
0.0013	0.000	0.000	0.0114	0.005	0.124	0.1000	0.807	39.353	0.8773	0.000	100.000
0.0015	0.000	0.000	0.0131	0.006	0.211	0.1145	0.982	52.688	1.0048	0.000	100.000
0.0017	0.000	0.000	0.0150	0.008	0.321	0.1312	1.072	67.236	1.1509	0.000	100.000
0.0020	0.000	0.000	0.0171	0.011	0.464	0.1503	1.003	80.853	1.3182	0.000	100.000
0.0022	0.000	0.000	0.0196	0.014	0.654	0.1721	0.761	91.182	1.5099	0.000	100.000
0.0026	0.000	0.000	0.0225	0.019	0.908	0.1971	0.434	97.079	1.7294	0.000	100.000
0.0029	0.000	0.000	0.0257	0.026	1.254	0.2258	0.170	99.385	1.9808	0.000	100.000
0.0034	0.000	0.000	0.0295	0.035	1.735	0.2586	0.040	99.932	2.2687	0.000	100.000
0.0038	0.000	0.000	0.0338	0.050	2.411	0.2962	0.005	100.000	2.5985	0.000	100.000
0.0044	0.000	0.000	0.0387	0.071	3.376	0.3393	0.000	100.000	2.9763	0.000	100.000
0.0050	0.000	0.000	0.0443	0.103	4.768	0.3886	0.000	100.000	3.4090	0.000	100.000
0.0058	0.000	0.000	0.0507	0.149	6.791	0.4451	0.000	100.000	3.9045	0.000	100.000
0.0066	0.000	0.000	0.0581	0.217	9.733	0.5098	0.000	100.000	4.4721	0.000	100.000
0.0076	0.000	0.000	0.0666	0.314	13.988	0.5839	0.000	100.000	5.1223	0.000	100.000
0.0087	0.000	0.000	0.0762	0.446	20.042	0.6687	0.000	100.000	6.0000	0.000	100.000

In the Fig.2,3 the particle size distribution and the average particle size of a aqueous magnetite/peg suspension with different dilution are shown. As can be seen, different range of the size distribution is found. Of course, the viscosity and temperature can significantly affect the measurement results. However, as follows from the above data, significant changes were not observed with significant dilution of the solutions with water. Both parameters can be monitored during measurements using LB550. This allows to get more accurate and reproducible results in the case of varying concentrations, which is illustrated by the example of a prepared dispersion.

EMR spectra of the system FeCl2-FeCl3/H2O/PEG/NH4OH at different ratios (mol to mol) PEG:iron salt are shown in Fig.4. As can be seen the EMR experimental spectra are asymmetrical single lines with effective g-factor of 2.16-2.31 and a width of 750-1350 gauss. Sizes of the magnetic iron oxide particles in the test systems and their complexes with PEG were determined by EMR method, as described in [4]. Particle sizes estimated by EMR for different experimental conditions ranged from 3 to 22 nm. It was established the stabilization of small magnetite particles in the system when the PEG with low molecular weight at certain concentration is used. Comparison of results using dynamic light scattering and electron magnetic resonance shows that although these results are not identical, the similarity confirms the ability of the EMR to operate in this size range. The modes of the distributions are reported as 105-111 nm using DLS and 3-22 nm using EMR, for the magnetite/aquaeous-PEG600 dispersions indicating the different, but in general the same range of distribution. The differences in the results are not surprising since the used measuring techniques based on different physical principles. It is quite rare that different particle size determination techniques gives identical results.

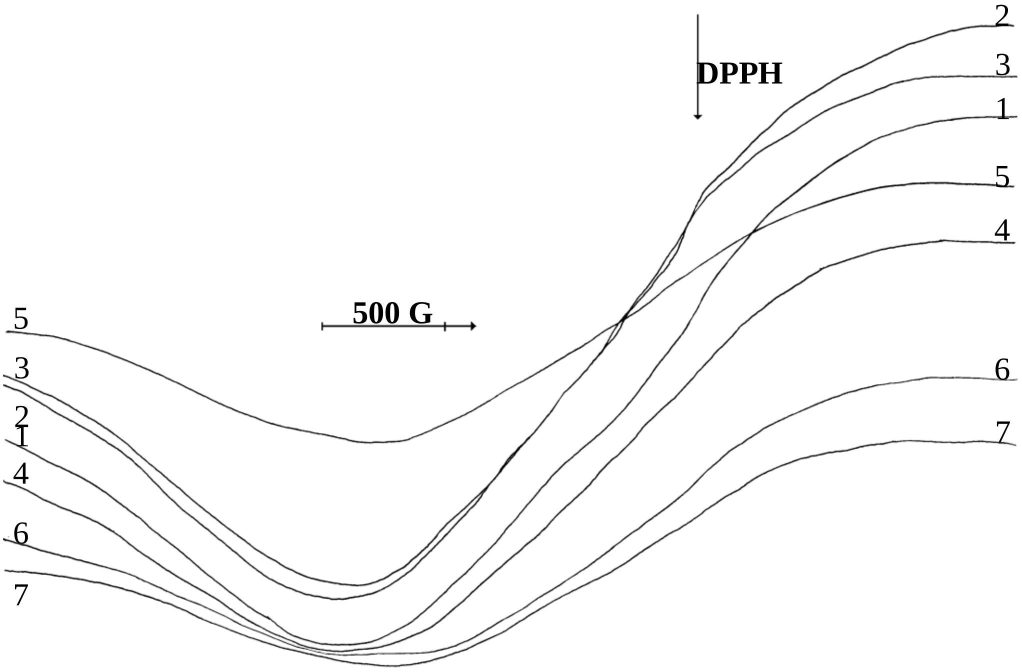

Fig.4. EMR spectra at 293K of oxide nanoparticles/hydroxides of iron in the hydrosol with different ratios (mole to mole) of PEG:iron salt , where: 1 - 1:1; 2 – 3:1;3–5:1;4-10:1;5-20:1;6-50:1;7-100:1

The observed wide EMR spectra are characteristic to concentrated magnetic phases. Study the concentration dependence of the signal indicates that with the changing of the ratio of PEG: iron salt complex pattern associated with the shifting of the position of the resonance line is observed. In general, the shift of the resonance line toward lower fields with increasing ratio iron salt:PEG is observed. The reason of the shifting is the formation, probably, the linear aggregates of magnetite in the magnetic field of the spectrometer.

With increasing the temperature of measuring the width and g-factor of the spectra are decreasing and the temperature behavior of the intensity of the spectra is characteristic to the superparamagnetic particles. The same results for the temperature behavior of the width and resonance position of EMR spectra obtained for the nanoparticles of iron oxides stabilized in oxide, zeolite and polymer matrix [5]. The width and resonance line position as a function of temperature for the magnetite in polyethylene aqueous dispersion are given in Fig.5 and 6.

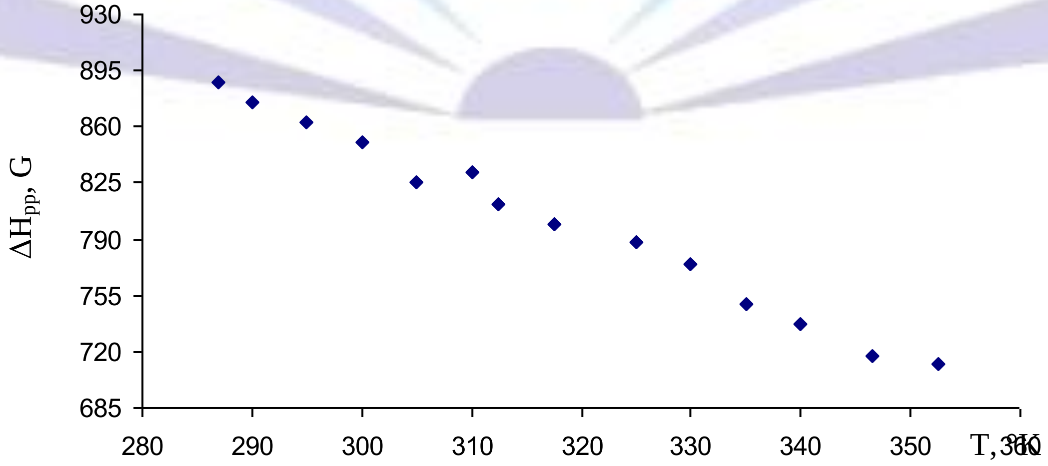

Fig.5. The width of EMR spectrum of magnetite/water/PEG600 dispersion as a function of temperature measuring

The fig.5 shows that with increasing measurement temperature of samples the line width is decreased. Such behavior may indicate that in this system particles with superparamagnetic properties are stabilized and for these particles the temperature dependence of the width of the signal obeys to Curie law.

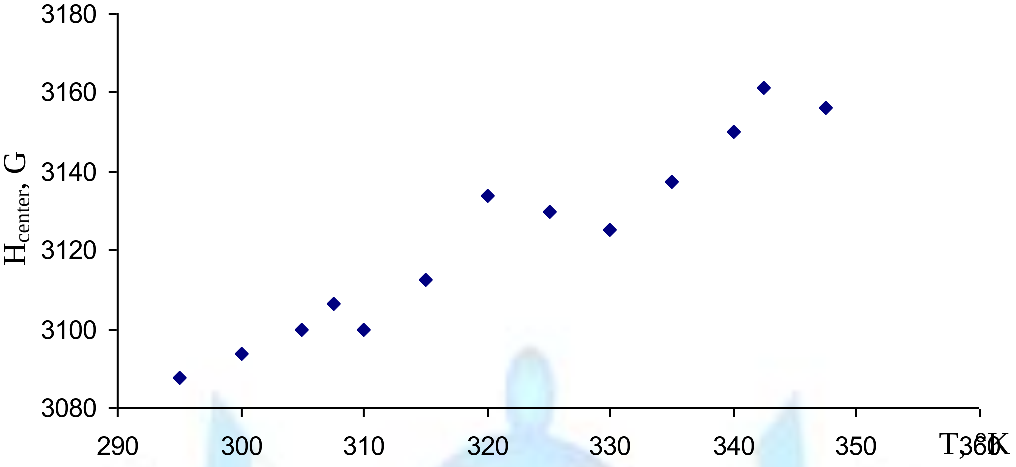

Fig.6. The resonance position of EMR line of magnetite/water/PEG600 dispersion as a function of temperature measuring

In the table parameters of adsorption isotherms of ethylene-glycol (EG) and poly-ethylene glycols PEGs 300,600,1500 by iron oxides in aqueous dispersion are given. These parameters are evaluated using the approach, described in [6]. .

Table 1. Parameters of adsorption isotherms EG and PEGs for the aqueous dispersions of magnetite/EG(PEG).

Adsorbate	Equilibrium concentration of adsorbate, C, M	The value of adsorbate adsorption, **A**,mmole/g_{Fe3O4}	Characteristic activation energy,E_a, kJ/mole	volume of pore space, V_p, sm^3/sm^3 (Fe_3O_4)
EG	3.3	2.0+_0.1	11.9+_0.2	3.1+_0.2
PEG-300	2.8	1.4	12.4	2.2
PEG-600	2.9	1.6	12,9	2.3
PEG-1500	2.5	1.3	13.3	2.7

As the table shows the amount of adsorbed per gram of iron oxide ethyleneglycole is much larger than the PEG -300, 600.1500. This may be due to the fact that the EG has higher reactivity as compared to PEG. EG chemisorbed on iron oxides with higher heats of adsorption. For PEG unlike EG physical adsorption and consequently less heat of adsorption are more characteristic. It is likely that in the adsorption of PEG initially its chemisorption, followed by physical adsorption of PEG molecules from the solution takes place. Strong adsorption of ethylene glycol (EG) monomer at the surface of iron oxide as compared with PEG, is explained by greater quantity of adsorption heat of EG relative to PEG. This in turn can be explained by the formation of stable complexes of EG with iron ions on the oxide surface during the adsorption. The coordinated EG can form directly the chelate type structure with surface -Fe-O-Fe-O- moieties. With the formation of such type structure the magnetic state of iron oxide particles can vary greatly. For PEG the formation of such structures on the surface of the iron oxide particles is not characteristic. PEG enveloping nanoparticles loosely forms the surface layers. These particles with nanoscale iron oxide core are clearly observed in the DLS spectra, which was mentioned above.

References

1. Q.A. Pankhurst., J. Connolly, S.K.Jones, J. Dobson // J.Phys.D.Appl.Phys.vol. **36**, 2003. p.167; Y.Qiang, J.Antony, S A.Harma, J.Nutting, D.Sikes, D. Meyer,vol. **8**, 2006,p .489; V.S. Kalambur, E.K. Longmire, Langmuir,vol. **23**, 2007**, p.**12329.

2. E.A. Masimov., B.Yu. Zaslavsky, T.O. Bagirov., A.A. Borovskaya., A.A. Gasanov., N.D Gulaeva., Levin Yu. Colloid and Polymer Science, vol. **264**, №12, 1986, p.354; X-H. Peng,X.Qian et al.International Journal of Nanomedicine 3(3) 2008, p.311.

3. http://www.horiba.com/scientific/products/particle-characterization/download-center/brochures/;http://www.horiba.com/scientific/products/particlecharacterization/particle-size-analysis/details/lb-550- 112/;http://www.titanex.com.tw/doc/tecsupport/TN-LB DynamicLightScatteringTechnique.pdf

4. R.Berger. J.C.Bissey, and J.Kliava, //J.Phys:Condens.Matter 12(44),99347-9360 (2000); R.Berger. J.C.Bissey, J.Kliava, H.Daubric, and C Estournes//J.Magn.Magn.Mater.234(3),535-544 (2001).

5. R. J. Usselman, M. Klem, M. Allen, E. D. Walter, K. Gilmore, T. Douglas,M. Young, Y. Idzerda, and D. J. Singel, J. Appl. Phys. 97(10), 10M523(2005); J. L. Dormann, D. Fiorani, and E. Tronc, “Magnetic Relaxation in Fine-Particle Systems,” in Advances in Chemical Physics, Vol. 98, edited by I.Prigogine and S. A. Rice (Wiley, Hoboken, NJ, 2007), pp. 283–494.; K. Gilmore, Y. Idzerda, M. Klem, M. Allen, T. Douglas, and M. Young, J. Appl. Phys. 97(10), 10B301 (2005).

6. Blinov A.V., Ramazanova A.G., Korolyov V.V. // Jurn.Fiz.Khimii (Russia), 2002. v.76. №5. pp.909-911.; Korolyov V.V., Ramazanova A.G., Blinov A.V.// Izv.Akademii Nauk (Russia), Seriya Khimicheskaya. 2002. № 11. pp. 1888-1893.