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Comparative study on magnetic nanoparticles colloids stability

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Advanced soft magnetic materials in the form of stable concentrated suspensions of magnetic nanoparticles in either organic or inorganic solvents are called magnetic fluids or ferrofluids. The complex structure of the magnetic colloids involves the assurance of their stability as required by both technical and biomedical applications. In order to prevent ferrophase particles agglomerations, good quality coating of small size particles need to be carried out. Small size ferrophase is essential not only for the homogeneity of the magnetic colloid but also for the efficient penetration of biological structures. In this respect, we carried out a comparative study regarding one magnetic fluid prepared in our laboratories (one based on petroleum) as well as other similar products presented in the literature reports. The ferrophase of our magnetic fluid was prepared by chemical co-precipitation. In all cases, the physical diameter of the ferrophase nanoparticles was measured using transmission electron microscopy (TEM) data. The average values were first considered but the whole distribution histogram was also analyzed. The dimensional distribution of the ferrophase physical diameter was comparatively presented using the box-plot statistical method. The percentage of relatively small particles (under 5 nm) was compared with the percentage of relatively large particles (over 10 nm). The presence of exceptionally large aggregates was also discussed in order to assess the quality of the magnetic colloids prepared by us in comparison with the products from several other countries.

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1. Introduction

Ferrofluids are soft magnetic materials prepared in the form of colloidal solutions of magnetic particles suspended within a carrier fluid [1]. The magnetic particles, are usually ferrites, having the general composition MFe_2O_4 (M being a bivalent metal cation such as Ni, Co, Mg or Zn), the magnetite, Fe_3O_4 being frequently present in combination with the maghemite γ-Fe_2O_3). Initially produced by grinding large particles in suitable organic solvents and sieving [1], ionic ferrofluids are now prepared chemically, mostly by following the Massart method [2].

To prevent the agglomeration of ferrophase particles, good quality coating of small size particles need to be carried out. The small size of ferrophase particles in ferrofluids intended for biological applications is needed for the good penetration of biological tissue but larger particle aggregates are not necessarily dangerous if their biodegradability is considered.

Many efforts of the physicists from Iassy (Romania) University (1978–2005) were dedicated to the production of stable magnetic colloids and successful projects have opened new promising ways for both technical and biological applications. Significant results in ferrofluid preparation, ferrofluid characterization and biological applications (experiments with plants and microorganisms) have been obtained [3-5].

In the future the applications of the magnetic fluids will be focused more toward the biological uses where the ultra fine ferrophase is particularly important the size distribution of the magnetic colloids remaining a major problem.

2. Experimental

We carried out a comparative study regarding one ferrofluid prepared in our laboratories (based on petroleum) for technical purposes [3] and some other ferrofluids used in biological applications accordingly to in the literature reports mentioned below. The ferrophase (about 5% volume) was obtained by chemical precipitation from autocatalytic reactions of $FeSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$ in the presence of the NaOH aqueous solution, according to Massart's project. Oleic acid (10% volume) has been used to stabilize the ferrophase particles while petroleum (85% volume) was the carrier liquid. Particle size distribution was studied using transmission electron microscopy (Tesla TEM device with a resolution of 1.0 nm) on collodion sheet, the ferrofluid being diluted 10^{-4} in toluene. The box-plot technique, proposed by Koopmans [6], was applied to get comparative picture of this ferrofluid size distribution and some other similar products.

The box-plot representation is able to represent a distribution curve by means of a draw box, being recommended for both large and small data series, since practically all the values are shown. This representation method is consistent with the transformation of any distribution curve into a "box" provided with two "tails" and certain "outliers". The range of experimental data is divided into three subintervals defined as follow:

- The box length limited by Q_1 and Q_3 i.e. the data corresponding to cumulative percentile frequencies between 25% and 75%. This subinterval contains about 50% of the total data points of the studied series.
- The subinterval contained within the box tails, A_1 and A_3, given by relations (1) and (2)

$$Q_1 - 1.5(Q_3 - Q_1) < A_1 < Q_1 \quad (1)$$

$$1.5(Q_3 + Q_1) > A_3 > Q_3 \quad (2)$$

(About 80% of the total data points in the studied series can be found within this larger subinterval, which includes the box length);

- Exceptionally large or small values (which are represented as white circles placed near the box), according to relations (3) and (4):

$$Q_1 - 3(Q_3 - Q_1) < \circ < A_1 \quad (3)$$

$$Q_3 + 3(Q_3 - Q_1) > \circ > A_3 \quad (4)$$

A "median" M, corresponding to the cumulative percentile frequency of 50%, is plotted as a vertical line within the box (Fig. 1).

For symmetrical curves, this line overlaps the average value. In other cases, M is able to indicate curve asymmetry, as do the box tails.

Comparisons between related or similar data point set can be successfully carried out in a very convenient manner using the box-plot representation, no matter if symmetrical or nonsymmetrical, monomodal or multimodal, ranging from large to small size intervals.

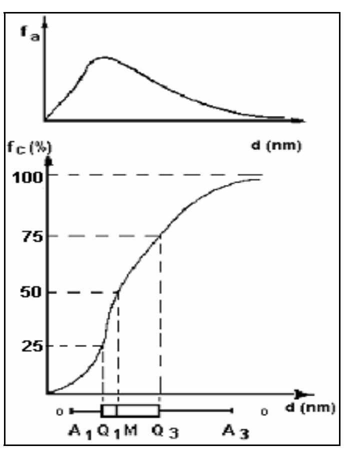

Fig. 1. The transformation of the absolute frequency curve of the analyzed data series into the cumulated frequency curve and further into the box plot; f_a – Absolute frequency, d (nm) – Particle diameter, f_c (%) – Cumulated frequency, A1 – The box left tail, Q1 – The box left edge (fc=25%), M – The median (fc=50%), Q3 – The box right edge (fc=75%), A3 – The box right tail. Exceptional values are plotted by white circles.

3. Results and discussion

The visual inspection of the box-plot representation corresponding to the particle size distribution for sample S (petroleum based ferrofluid synthesized in our laboratory), led to the next issues:

- About 50% of the data points are smaller than Q_3=5.5 nm but not smaller than Q_1=3.0 nm; box length are 2.5 nm.
- At least 80% of the data points are not smaller than A_1=2.0 nm but not larger than A_3=11.0 nm.
- The exceptionally large size aggregates "outliers", were found at 17.0 nm and 25.5 nm.
- The asymmetry is accentuated: the median position is closer to the left edge where the most values are concentrated.
- The right tail (A_3-Q_3) is longer than the left one (Q_1-A_1), consequently the small particles are dominated (no smaller than 2.0 nm) in comparison to the large ones (not larger than 11.0 nm).

The comparison (Fig. 2) of the analyzed sample "S" with other six ferrofluids used in biological applications: S_1 – water based ferrofluid (stabilized with carboxidextran) [7], S_2 - water based ferrofluid (stabilized with dimercaptosuccinic acid) [8], S_3 - water based ferrofluid (stabilized with dodecanoic acid) [9], S_4 – iron oxides in aqueous suspension (stabilized with polyvinylic alcohol) [10], S_5 – iron oxides in petroleum (stabilized with oleic acid) [11], S_6 – hydrocarbon based ferrofluid (stabilized with oleic acid) [12], led to the following results.

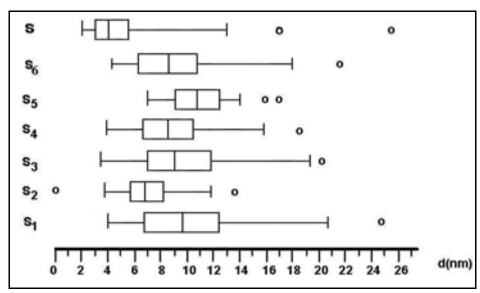

Fig. 2. Comparison analysis between samples S and S_i (i = 1..6).

After the application of box-plot technique to these six samples the characteristic parameters presented in the Table 1 are obtained.

Table 1. Statistical analysis by means of box-plot technique

F	A_1 (nm)	Q_1 (nm)	M (nm)	Q_3 (nm)	A_3 (nm)	Exceptional values (nm)	
S	2.0	3.0	4.00	5.5	11.0	17.0	25.5
S_1	4.0	6.6	9.45	12.2	20.7	24.93	
S_2	3.8	5.6	6.80	8.1	11.8	0.1	13.7
S_3	3.3	7.0	8.96	11.8	19.1	20.19	
S_4	3.9	6.7	8.50	10.3	15.8	18.57	
S_5	7.0	9.0	10.7	12.5	14.0	16.0	17.0
S_6	4.3	6.2	8.57	10.9	17.9	21.5	

Regarding the comparison picture (Fig. 2) and Table I, we may see that the sample S has the smallest A_1 value from all data. All the Q_1 values for samples S_i (i=1.. 6) are the larger than Q_3 value for sample S. In the Table II are presented the box length values, right tail (A_3-Q_3) values and left tail (Q_1-A_1) values for sample S and samples S_i.

Table 2. Box-plot parameters.

Sample	Box length (Q_3-Q_1) (nm)	Left tail (Q_1-A_1) (nm)	Right tail (A_3-Q_3) (nm)
S	2.50	1.00	5.50
S_1	5.63	2.64	8.44
S_2	2.50	1.86	3.72
S_3	4.88	3.64	7.30
S_4	3.65	2.73	5.47
S_5	3.50	2.00	1.50
S_6	4.70	1.93	7.05

Sample S has the smallest box length. One may see that the ferrofluid S_2 has the same box length value as the sample S, analyzed inhere, but its A_1, Q_1, Q_3 and A_3 values are the smallest. So, we might say that the sample S is representing a more stable ferrofluid than the samples S_i. Also, the ferrophase size distribution of the sample S is characterized by preponderantly small particles, with small number of large aggregates, which is making it suitable for both technical and biological applications.

4. Conclusion

The soft magnetic material prepared by us is characterized by small ferrophase particles and narrow distribution of physical diameter when compared with literature data. The box-plot representation method seems to be a convenient analytical method for the comparative study of ferrophase dimension regarding the special importance of this ferrofluid feature in the assurance of stability and biocompatibility. The revealing of exceptionally large diameter particles or agglomerations is useful in the microstructural analysis imposing the further improvement of preparation procedure.

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