

REPUBLIC OF AZERBAIJAN

On the rights of the manuscript

ABSTRACT

of the dissertation for the degree of Doctor of Science

**INTERACTIONS AND STRUCTURAL PECULIARITIES
IN AQUEOUS SOLUTIONS OF POLYETHYLENE
GLYCOLS OF VARIOUS FRACTIONS AND
IN A NUMBER OF SUSPENSIONS**

Speciality: 2204.01 – Liquid physics

Field of science: Physics

Applicant: **Hakim Fikret oglu Abbasov**

Baku – 2022

The work was performed at the section of Physics of Biological Systems of Institute of Physical Problems in Baku State University and at the laboratory of Analytical Investigations of Oil Gas Research Project Institute of SOCAR.

Scientific consultant: Doctor of physical-mathematical sciences, Professor **Eldar Ali oğlu Masimov**

Official opponents: Corr. member of ANAS, Doctor of physical-mathematical sciences, Professor **Salima Ibrahim gizi Mekhtiyeva**

Doctor of physical-mathematical sciences, Professor

Ahmed Mahammad oğlu Hajiyev

Doctor of physical-mathematical sciences, Professor

Niftali Mekhrally oğlu Godjayev

Doctor of physical-mathematical sciences, Professor

Musaver Abdusalam oğlu Musayev

Dissertation council BED 2.19 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at Baku State University

Chairman of the Dissertation Council:

Corr. member of ANAS, Doctor of physical-mathematical sciences, Professor

Aydin Gasan oğlu Kyazym-zade

Scientific Secretary of the Dissertation Council:

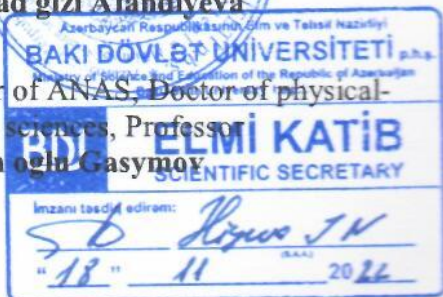
Doctor of physical sciences, Associate Professor

Izzet Mammad gizi Afandiyeva

Chairman of the scientific seminar:

Corr. member of ANAS, Doctor of physical-mathematical sciences, Professor

Oktay Kazim oğlu Gasymov



GENERAL CHARACTERISTICS OF WORK

Actuality of the work and the degree of its implementation. Fast and efficient cooling in electronic devices, automotive engines, high-power lasers, X-ray devices, computers is one of the main requirements for ensuring the quality of the device and extending its shelf life. Nanofluids, which are a colloidal dispersion of solid nanoparticles dispersed in liquids, are considered to be the most effective cooling systems with the highest thermal conductivity among those proposed for cooling fluids «Nanofluids»¹. After Maxwell's theoretical prediction of the thermal conductivity enhancement of a liquid when solid metal particles were introduced into it, for a long time it was not possible to experimentally obtain such systems because of the rapid settling of millimeter or micron-sized particles used for this purpose. In 1995, a group of scientists from the Argonne National Laboratory in the United States proposed the use of solid nanoparticles in suspension, and they managed to obtain stable nanofluids with high thermal conductivity in this way «Enhancing thermal conductivity of fluids with nanoparticles»².

Heat transfer from liquid to particles and vice versa is carried out through atoms located on the surface of the particles, the total number of which increases rapidly with decreasing particle size in the direction of the nanometer range at the same masses, which is one of the main reasons for the high thermal conductivity and stability of the nanofluid.

Classical models of thermal conductivity of suspensions, such as Maxwell, Hamilton-Crosser, etc. provide underestimated predictive values for the thermal conductivity of nanofluids compared with experimentally observed values.

These models cannot explain the thermal conductivity enhancement of nanofluids with an increase in temperature and a decrease in

¹Das S.K. Nanofluids: Science and Technology / S.K. Das, S.U. Choi, Yu.W. et al. Wiley, Hoboken, NJ, – 2007, – 416p.

²Choi S.U.S. Enhancing thermal conductivity of fluids with nanoparticles // Developments Applications of Non-Newtonian Flows, D.A. Siginer and H.P. Wang, Eds., ASME, New York, NY, USA, 1995. FED-vol. 231/MD-vol. 66, pp. 99–105.

the size of nanoparticles. To explain the new discoveries found in the study of the thermal properties of nanofluids, new approaches, the search for new concepts and mechanisms are required.

Several new concepts have been proposed in the literature to explain the high thermal conductivity of nanofluids: «Brownian motion of nanoparticles and related microconvection, the formation of a structured nanolayer of liquid in the interfacial space on the nanoparticle surface, clustering of nanoparticles, no diffusion but ballistic thermal conductivity of nanoparticles, interfacial thermal resistance, etc.»³. The values of thermal conductivity predicted by these models in some cases are consistent with some individual experimental results, but many questions still remain controversial and unresolved:

1) the role of the Brownian motion of nanoparticles in the thermal conductivity of nanofluids is not completely clarified,

2) the thickness and thermal conductivity of the structured nanolayer of the liquid in the interfacial space on the surface of the nanoparticle are not analytically determined,

3) the role of aggregation of nanoparticles in the thermal conductivity of nanofluids is still waiting for its correct answer,

4) it is necessary to find out under what conditions it is possible to achieve high thermal conductivity of microfluids with solid microparticles.

Despite the fact that «metal-string complexes were mainly developed for the creation of molecular conductors, for the construction of nanoelectronic devices»⁴, it has recently been revealed that when microparticles of these complexes are introduced into a liquid, a high thermal conductivity of the latter is achieved, comparable even with the thermal conductivity of nanofluids [8]. Therefore, it is necessary to comprehensively study the thermophysical properties of suspensions with microparticles of metal-string complexes (MSC), which are very little studied.

³Kebblinski P. Mechanisms of heat flow in suspensions of nano-sized particles (nanofluids) / P. Kebblinski, S.R. Phillpot, S.U.S. Choi [et al.] // Int. J. Heat and Mass Transfer, 2002, 45, p.855-863.

⁴Shieh S.-J. Linear pentanuclear complexes containing a chain of metal atoms: [Co II5 (5-tpda)4 (NCS)2] und [Ni II5 (5-tpda)4Cl2] / S.-J. Shieh, C.-C. Chou, G.-H. Lee [et al.] // Angew. Chem. Int. Ed. Engl., 1997, 36, p. 56-59.

Due to their unique properties, aqueous solutions of polyethylene glycols, which are molecular dispersions, are widely used in medicine, chemistry, the food industry, cosmetics, as a stabilizer, emulsifier, filler, plasticizer, binder ingredient, protective coating, surfactant, etc. Intermolecular interactions in these systems investigated by various experimental (IR, NMR spectrography, viscometry, etc.), as well as theoretical (Molecular Dynamics, Monte Carlo method) methods. Despite such studies, questions related to the «structure» of macromolecules in an aqueous medium, their flexibility, the effect on the conformations of macromolecules of various ions present in this medium, and the hydration of these ions await their answer. There are many methods for determining ion hydration numbers (density, viscosity, dielectric constant, diffusion, dissolution, conductivity - various thermodynamic and spectroscopic properties of electrolytes) whose results, in many cases, do not coincide, so the search for new universal methods for determining ion hydration numbers is relevant.

In the work, we have tried to answer all of the above questions by studying the interactions and structural features in dispersed systems of nano-, microparticle – liquid.

Object and subject of research. The object of study of the dissertation is dispersed systems of three types, differing in the size of particles of the dispersed phase: nanofluids and ferrofluids, which are colloidal dispersions of solid nanoparticles dispersed in a liquid; microfluids and suspensions of quartz, related to coarse dispersions and dilute aqueous solutions of polyethylene glycols of various fractions, related to molecular dispersions. The subject of the study is to identify the causes of high thermophysical and rheological properties of the dispersed systems studied in the work based on the creation of new approaches, models and methods.

The goal and tasks of the work. *The goal of the work* is to study the role of structural changes arising due to the interaction of particles of the dispersed phase with the dispersion medium in the thermo physical and rheological properties of various disperse systems, such as nanofluid, ferrofluid, microfluid, quartz suspension, diluted aqueous solutions of polyethylene glycols. Achieving this goal is associated with the following *tasks*:

- study of thermophysical properties of nanofluids and creation of

a model of effective thermal conductivity for these systems,

- elucidation of the role of the Brownian motion of nanoparticles in the thermal conductivity of nanofluids,
- determination of the thickness of the structured liquid nanolayer in the interfacial space on the surface of the nanoparticle,
- analysis of the role of nanoparticle aggregation in the thermal conductivity of nanofluids,
- study of thermophysical properties of microfluids, with microparticles of metal-string complexes,
- creation of a model of anisotropic thermal conductivity of ferrofluids,
- analysis of the conditions of aggregative stability of an aqueous suspension of quartz sand,
- study of rheological, refractive properties of dilute aqueous solutions of polyethylene glycols of various fractions,
- determination of the size, elasticity of macromolecules in dilute aqueous solutions of polyethylene glycols, taking into account the interaction of macromolecules, liquid molecules and ions introduced into the solutions.
- determination of the hydration numbers of ions in aqueous solutions of electrolytes by the refractometric method.

Research methods. The following research methods were used in the work: hot transient wire method, streaming method, capillary and rotational viscometric methods, low-frequency dielectric spectroscopy method, refractometric method, spectrophotometric method, dynamic light scattering (DLS) method, scanning electron microscopy (SEM) method, pendant drop method, Kohlrausch method.

Key points

- In nanofluids, when the nanoparticle radius is much greater than the nanolayer thickness, the thickness of the structured liquid nanolayer in the interfacial space on the surface of the nanoparticle depends on the Hamaker constant, surface tension, wetting angle, and the distance between the nanolayer and the nanoparticle, and does not depend on the radius of the nanoparticle,
- In nanofluids, the frequency of heat transfer of liquid molecules is two orders of magnitude higher than the heat transfer frequency of the nanoparticles themselves, as a result of which the contribution of

the Brownian motion of nanoparticles to the thermal conductivity of nanofluids can be neglected and nanoparticles in a nanofluid can be considered immobile,

- The thermal conductivity enhancement of the nanofluid at low concentrations of nanoparticles is directly proportional to their volume fraction, thermal conductivity coefficient and inversely proportional to the radius of the nanoparticles,

- Small clusters formed by the aggregation of nanoparticles and suspended in the base fluid make an increased contribution to thermal conductivity, an increase in the size of these clusters leads to a decrease in the thermal conductivity of nanofluids due to cluster settling,

- Due to the fact that, firstly, nanoparticles have a larger specific surface compared to micro- and millimeter-sized particles, and secondly, the structured liquid nanolayer formed around the nanoparticle conducts heat better compared to a pure liquid due to ordering, thirdly, the contribution of a cluster of nanoparticles suspended in a liquid to the thermal conductivity of a nanofluid is larger compared to the contribution of a nanoparticle, the nanofluid has a higher thermal conductivity compared to the base liquid,

- Under an external magnetic field, magnetic nanoparticles in a ferrofluid are oriented along the magnetic field and form chain clusters that represent an effective bridge for heat transfer along the chain and lead to an increase in thermal conductivity in this direction, while the thermal conductivity in the direction perpendicular to the chain does not depend on the magnetic field,

- Microfluids containing microparticles of metal-string complexes dispersed in a liquid have high thermal conductivity comparable to the thermal conductivity of nanofluids due to the formation of a thixotropic colloidal structure, hydrogen bonds, monocrystallinity and low density of microparticles,

- The addition of a small amount of a reagent developed on the basis of triethanolamine and orthophosphate acid to the quartz suspension leads to sand aggregation due to a decrease in the zeta potential of the suspension caused by adjunction of positively charged ions to a dense layer of counterions in the electrical double layer of sand particles,

- Molecular chains of polyethylene glycols of various fractions in their dilute aqueous solutions take the form of macromolecular coils,

- In dilute aqueous solutions of polyethylene glycols, the root-mean-square distance between the ends of the macromolecular chain increases with an increase in both the molecular weight of the polymer and the concentration of ions present in the solutions, but decreases with increasing temperature,

- Macromolecular coils in dilute aqueous solutions of polyethylene glycols, when 0.1 mol/l NaOH is added to solutions, take an unperturbed conformation, as in theta solvents,

- The hydration numbers of ions in aqueous solution of electrolytes can be determined by the refractometric method.

Scientific novelty of the work:

- a formula was proposed for determining the thickness of a structured liquid nanolayer in the interfacial space on the surface of a nanoparticle in nanofluids,

- it has been proven that the direct contribution of the Brownian motion of nanoparticles to the thermal conductivity of a nanofluid can be neglected, since the frequency of heat exchange between nanoparticles is two orders of magnitude less than the frequency of heat exchange between liquid molecules,

- a new model of effective thermal conductivity of nanofluids has been created, taking into account the aggregation of nanoparticles and the presence of a structured liquid nanolayer on the surface of a nanoparticle, which correctly predicts experimental results,

- it has been established that an increase in the thermal conductivity of a nanofluid at low concentrations of nanoparticles is directly proportional to their volume fraction, thermal conductivity coefficient and inversely proportional to the nanoparticle radius,

- a new model of anisotropic thermal conductivity of ferrofluids was created taking into account the aggregation of magnetic nanoparticles under the action of an external magnetic field,

- for the first time it was revealed that microfluids containing microparticles of metal-string complexes dispersed in a liquid have a high thermal conductivity comparable to the thermal conductivity of nanofluids,

- it has been shown that the reason for the violation of the aggregative stability of a quartz suspension under the influence of a reagent developed on the basis of triethanolamine and orthophosphate acid is

a decrease in the zeta potential, as a result of the adjunction of positively charged ions to a dense layer of counterions in the double electric layer of sand particles,

- by viscometry, low-frequency dielectric spectroscopy and refractometry methods it has been established that at low concentrations of polymer the molecular chains of polyethylene glycols of various fractions in water take the form of macromolecular coils,

- the conformational dimensions and elasticity of macromolecular coils in dilute aqueous solutions of polyethylene glycols of various fractions were determined, taking into account the interaction of macromolecules, water molecules and ions introduced into the solutions,

- it was found that in dilute aqueous solutions of polyethylene glycols, the root-mean-square distance between the ends of the macromolecular chain increases with an increase in both the molecular weight of the polymer and the concentration of ions present in the solutions, but decreases with increasing temperature,

- it was found that with an increase in the concentration of the polymer in the solution, macromolecular coils interacting with each other penetrate each other,

- a new method - the refractometric method for determining the hydration numbers of ions in aqueous solutions of electrolytes is proposed.

Scientific and practical value of the work:

- created models of effective thermal conductivity of nanofluids and ferrofluids can be used to explain and predict the experimental results of heat transfer in nano, micro and ferrofluids,

- the developed nanofluids with Cu, Al₂O₃ nanoparticles in water, glycerol and mixtures thereof, as well as microfluids with microparticles of the metal string complexes Ni₃ and Ni₅, can be recommended as a coolant with high thermal conductivity in the respective cooling systems,

- the results of the study of the aggregate stability of a suspension of silica sand can be used to control sand phenomena, to aggregate sand during fluid filtration in the oil and gas industry,

- the results of determining the size of macromolecules and their flexibility can be used when using polyethylene glycols of various fractions in medicine, pharmacology,

- the proposed refractometric method for determining the hydration number of ion can be used in the study of various ions in an aqueous medium,

- the results of the thesis can be applied, in electronics, for rapid cooling of electronic components, in the automotive industry to create effective engine cooling systems, in the energy sector to ensure the fast and efficient transfer of thermal energy in a nuclear reactor, and also in oil production for designing thermal effects on the formation .

Presentation of the work. The materials of the work were reported and discussed at the following international and republican conferences:

- The XV All-Russian Conference «Structure and Dynamics of Molecular Systems» (Yalchik, Russia, 30.06-04.07.2008);
- II Republican Conference (Baku, Azerbaijan 28.11-29.11.2008);
- XVII Russian International Conference on Chemical Thermodynamics «RCCT-2009» (Kazan, Russia, 29.06-03.07.2009);
- VI International Scientific Conference «Kinetics and Crystallization Mechanism. Self-organization during phase formation» (Ivanovo, Russia 21.09-24.09.2010);
- IV Republican Conference (Baku, Azerbaijan, 24.12-25.12.2010);
- XI International Conference «Problems of Solvation and Complexation in solutions» (Ivanovo, Russia, 10.10-14.10.2011);
- IV Congress of Biophysicists, (Nizhny Novgorod, Russia, 20.08-26.08. 2012);
- VII International Scientific Conference «Kinetics and crystallization mechanism. Crystallization and materials of a new generation» (Ivanovo, Russia, 25.09-28.09.2012);
- VI Republican Conference (Baku, Azerbaijan 14.12-15.12.2012);
- V All-Russian Scientific Conference (with international participation) «Physicochemistry of Polymer Processing» (Ivanovo, Russia 16.09-19.09.2013);
- VI All-Russian Scientific Conference (with international participation) «Physicochemistry of polymer processing processes» (Ivanovo, Russia 03.10-07.10.2016);
- XIII International Conference «Problems of Solvation and Complexation in Solutions» (Suzdal, Russia 01.07-06.07.2018);
- First Euro-Asian Conference on Nanotechnology «Nanotech Eurasia 2019», (Baku, Azerbaijan 03.10-04.10.2019).

Publications. Based on the results of the research, 32 publications were published, of which 18 articles, including 10 articles published in journals having Impact Factor (Colloids and Surfaces A: Physicochemical and Engineering Aspects (IF 4.539) – 1, Journal of Dispersion Science and Technology (IF 2.017) – 3, Journal of Polymer Research (IF 2.426) – 1, Journal of Heat Transfer (IF 2.021) – 1, Russian Journal of Physical Chemistry A (IF 0.719) – 4, and 13 materials of international and national conferences and 1 Eurasian patent.

Volume and structure of the dissertation. The dissertation (320930 characters) consists of an introduction (16280), five chapters (I chapter – 95549, II chapter – 53810, III chapter – 91896, IV chapter – 36807, V chapter – 18400), conclusions (8188) and list of references. The dissertation contains 8 tables, 30 figures and 52 graphs. The bibliography includes 374 titles.

CONTENT OF THE DISSERTATION WORK

The introduction substantiates the actuality of the work, explains its scientific novelty and practical value, provides key points, provides information on the presentation of the work.

The first chapter (literature review) presents a review of works devoted mainly to the physical properties of disperse systems, the forces of interaction in these systems, methods of obtaining and stability of disperse systems. It is indicated that the thermo physical, rheological properties of disperse systems depend on the type, concentration, shape of the particles of the dispersed phase, as well as on the type of dispersion medium and the interaction of the molecules of the dispersion medium and particles of the dispersed phase. According to the theory of the DLVO (Derjaguin, Landau, Verway and Overbeek), the structure formation in disperse systems, the stability of the disperse system itself, and its physical properties depend on the balance of forces of attraction and repulsion between particles, i.e. determined by the potential energy of interaction of two particles «Теория устойчивости коллоидов и тонких пленок»⁵. The conditions for

⁵Дерягин Б.В. Теория устойчивости коллоидов и тонких пленок / Б.В.Дерягин – М: Наука, -1986, 206с.

achieving the stability of disperse systems are analyzed. This chapter also provides detailed information on the rheological properties of disperse systems, which in many cases differ from the properties of Newtonian fluids. A literature review of experimental and theoretical works on thermo physical properties, methods for producing and stabilizing nanofluids, the most effective cooling systems with the highest thermal conductivity among those proposed for cooling fluids, is given. A critical analysis of existing models and concepts of the mechanism of thermal conductivity of nanofluids is given. This chapter also provides brief information on the rheology of polymer solutions, on the characteristic parameters of macromolecules and ion hydration.

The second chapter gives materials, equipment and research methods. All objects of investigation studied in the dissertation are dispersed systems:

- nano- and ferrofluids are suspensions (colloidal dispersion) of nanoparticles dispersed in a liquid – the particle size of the dispersed phase is 1 – 500 nm,
- microfluids and a suspension of silica sand is a coarse dispersion – the particle size of the dispersed phase exceeds 500 nm,
- aqueous solutions of polyethylene glycols is a molecular dispersion – the dispersed phase is distributed in the dispersion medium at the molecular level.

Methods for preparing samples – nano and microfluids, PEG solutions, and their testing are given.

The third chapter discusses the results obtained by studying the role of interparticle and interphase interactions in the thermo physical properties of suspensions with nano- and microparticles – nano-, ferro- and microfluids, also the quartz suspension. Despite the many models of thermal conductivity of nanofluids, there are many discrepancies between experiment and theoretical predictions. Therefore, in order to elucidate the thermal conductivity mechanism, we proposed a new model of nanofluid thermal conductivity that takes into account both the aggregation of nanoparticles and the presence of a structured liquid nanolayer around the nanoparticle [3]. We also determined the thickness of the nanolayer of the liquid by calculating the Van der Waals energy of the interaction between the liquid nanolayer and the nanoparticle and evaluated the role of the Brownian motion of nanopar-

ticles in the thermal conductivity of nanofluids.

Role of the Brownian motion of nanoparticles in the thermal conductivity of nanofluids. To clarify the role of Brownian motion in the thermal conductivity of nanofluids, we determined the average speed of nanoparticles in this medium by solving the equation of motion of a nanoparticle, which is affected by the force associated with the temperature gradient, the friction force, and gravity [3]. To find the forces associated with the temperature gradient, we used the fact that to measure the thermal conductivity of nanofluids, we mainly use the hot-wire method.

Solving the equation of motion under the above assumptions, we obtained the following formula for the velocity of a nanoparticle inside a nanofluid:

$$v_x = \frac{nk_Bqr_n}{6\pi\eta k} \left(1 - e^{-\frac{6\pi\eta r_n t}{M}}\right). \quad (1)$$

where, n is the concentration of liquid molecules, which in a first approximation can be considered constant, k_B is the Boltzmann constant, M and r_n are the mass and radius of the nanoparticle, respectively, v_x is the projection of the velocity of the nanoparticle, η is the dynamic viscosity of the liquid, t is the time, q is the heat flux per unit length of the wire, k is the coefficient of thermal conductivity of a homogeneous liquid.

Given the acceptable parameter values in formula (1), we estimated the speed of copper nanoparticles in the Cu-water nanofluid at room temperature. It was revealed that it takes the maximum value in the time $\tau = 1/b = M/6\pi\eta r_n \approx 6,25 \text{ ns}$ and does not change further: $v_{xmax} = nk_Bqr_n/6\pi\eta k \approx 1.63 \text{ m/s}$.

Note that the average Brownian motion velocity of nanoparticles is less than their average velocity associated with the temperature gradient. The average velocity of liquid molecules can be approximately estimated as: $v_f = \sqrt{3RT/M_w}$, where, R is the universal gas constant, T is the temperature, M_w is the molar mass of water. At room temperature, we obtain: $v_f \approx 645 \text{ m/s}$, t.e. $v_x \ll v_f$. Thus, we see that the average Brownian motion velocity of nanoparticles is much lower than the average velocity of liquid molecules ($v_n \leq v_{xmax} \ll v_f$).

For the ratio of the time spent on the mean free path (λ) by the nanoparticle (τ_n) to the corresponding time by the liquid molecule (τ_f) we obtain: $\tau_n/\tau_f = (\lambda/v_n) : (\lambda/v_f) = v_f/v_n \approx 400$, i.e. the frequency of heat transfer by fluid molecules is two orders of magnitude higher than the frequency of heat transfer by nanoparticles. Therefore, the contribution due to the Brownian motion of nanoparticles in the thermal conductivity of nanofluids can be neglected and nanoparticles in nanofluids, in comparison with fluid molecules, can be considered immobile.

Determination of the thickness of a ordered liquid nanolayer around a nanoparticle in nanofluids. In a number of studies the rheological, thermophysical properties of suspensions and their stability are explained by the presence of a structured liquid nanolayer around the solid particles of the dispersed phase.

To determine the thickness of this nanolayer, we calculated the Van der Waals interaction energy between the nanoparticle and the liquid nanolayer [3].

The Van der Waals interaction energy between two molecules A and B is determined by the well-known formula:

$$w = -\frac{C_{AB}}{d^6}, \quad (2)$$

where, C_{AB} is the specific interaction constant to the types of molecules in A and B, that takes into account all three contributions (Keesom, Debye, and London) and d is the distance between them.

To find the Van der Waals attraction energy between two macroscopic bodies, consisting of these molecules A and B correspondingly one has to sum over all pairs of molecules with one in A and the other in B. For this purpose we need to calculate a six-dimensional integral:

$$W_{AB} = - \int \int \frac{C_{AB} n_A dV_A n_B dV_B}{((x_A - x_B)^2 + (y_A - y_B)^2 + (z_A - z_B)^2)^{3/2}}, \quad (3)$$

where, n_A and n_B are the densities of media A and B expressed as a number of molecules per unit volume, in such a way that $n dV_A$ and $n dV_B$ are the number of molecules in the elementary volumes.

To calculate the interaction energy between a solid particle (A) of radius r_n (A) and a liquid nanolayer (B) of the thickness λ (B), for simplicity, we propose to replace the real situation (fig. 1a) with two flat

media separated by a distance D as shown in (fig. 1b) and (fig. 1c). The value of D that is universally accepted for most liquids and solids alike for this type of calculation is $D \cong 0.165 \text{ nm}$.

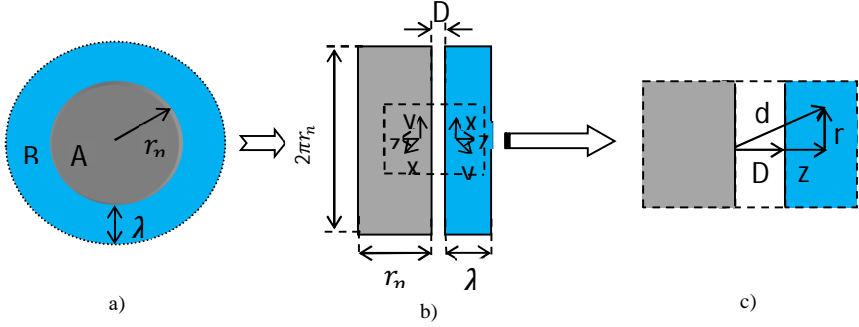


Fig. 1. a) Van der Waals interaction between a solid particle and a liquid nanolayer, b) the interaction between a single molecule of a solid particle and a liquid nanolayer separated by the distance D , and c) the area marked by a dashed rectangle in (b) in an enlarged form.

Integral (3) was solved in two steps, first by calculating the interaction between a single A-type molecule and a medium of type B of the thickness λ , and then by integrating that energy over all molecules in medium A.

We assume that the intermolecular attraction between a solid particle and the surrounding liquid extends only over the distance λ . The first step is equivalent to computing a three-dimensional integral on volume B, which is best calculated in cylindrical coordinates as (fig. 1c).

Integration taking into account the condition $r_n \gg \lambda \gg D$ leads to the following expression for the Van der Waals energy between a solid nanoparticle and a liquid nanolayer, per unit area:

$$W_{AB} = -\frac{A_{AB}}{12\pi} \left(\frac{1}{D^2} + \frac{1}{(r_n + \lambda)^2} - \frac{1}{r_n^2} - \frac{1}{\lambda^2} \right). \quad (4)$$

Equating this energy to the work of adhesion of two media (A and B), we obtain:

$$\sigma(1 + \cos\theta) = \frac{A_{AB}}{12\pi} \left(\frac{1}{D^2} + \frac{1}{(r_n + \lambda)^2} - \frac{1}{r_n^2} - \frac{1}{\lambda^2} \right). \quad (5)$$

An approximate solution to this equation can be expressed as follows:

$$\sigma(1 + \cos\theta) = \frac{A_{AB}}{12\pi} \left(\frac{1}{D^2} + \frac{1}{(r_n + \lambda)^2} - \frac{1}{r_n^2} - \frac{1}{\lambda^2} \right). \quad (5)$$

In equation (6), when $r_n \gg \lambda$, the term $1/r_n^2$ can be neglected compared to the term $1/D^2$, which leads to the independence of the nanolayer thickness from the radius of the nanoparticle:

$$\lambda \approx D \left(1 - \frac{12\pi D^2 \sigma (1 + \cos\theta)}{A_{AB}} \right)^{-1/2}. \quad (7)$$

This is understandable, since the interaction between two media occurs in close proximity to the medium surfaces, therefore, when the radius of the nanoparticles is much greater than the nanolayer thickness the contribution of the parts far from the surface to the interaction can be neglected.

As it follows from the formula (7), the thickness λ of an ordered liquid nanolayer around a solid particle in nanofluids determines by the interaction of the given liquid and solid particle through the parameters $D, \sigma, \theta, A_{AB}$ and is independent on the radius of the solid particle r_n , in the case $r_n \gg \lambda$. The better the wetting, the greater the nanolayer thickness.

As follows from formula (7) the values of parameters of the dispersed phase (solid) and the dispersion medium (liquid) in nanofluids must satisfy the following condition: $12\pi D^2 (1 + \sigma \cos\theta) / A_{AB} < 1$. The advantage of formula (7) is that this formula establishes a relationship between the microscopic characteristic (λ) and macroparameters, such as the Hamaker constant (A_{AB}), which characterizes two interacting media A and B, the surface tension (σ), and the wetting angle (θ), which can be easily measured.

Effect of nanoparticle aggregation on the thermal conductivity of nanofluids. To identify the role of nanoparticle aggregation in the thermal conductivity of nanofluids, we have developed a model that takes into account the contributions of nanoparticles, clusters formed as a result of aggregation of nanoparticles and molecules of the base fluid itself to the thermal conductivity of nanofluids [12]. According to our model, the heat from the surface of a linear heat source (a platinum wire) is transferred by the base liquid's molecules, nanoparticles

and clusters immediately adjacent to its surface.

Single nanoparticles (n) and clusters (cl) formed by nanoparticle aggregation and base fluid molecules (f) contribute to the rate of heat (Q) transferred through nanofluid according to Fourier's law:

$$Q = -(k_n A_n + k_{cl} A_{cl} + k_f A_f) \frac{\partial T}{\partial r} = -k_f A_f \left(1 + \frac{k_n (A_n + A_{cl})}{k_f A_f} \right) \frac{\partial T}{\partial r'} \quad (8)$$

where, k_n и k_f are the thermal conductivity coefficients of the nanoparticles and base fluid, respectively, and A_n , A_{cl} and A_f are the cross-sectional areas of single nanoparticles, clusters, and base fluid molecules adjacent to the cylindrical surface of the wire, respectively.

Using the determination of the volume fraction φ of nanoparticles, denoting the aggregation coefficient by $c = n_{cl}/n_n$ and taking into account that the ratio of the cross sections of the corresponding particles adjacent to the cylindrical surface of the wire is proportional to the ratio of the total surface areas of these particles in a unit volume for the thermal conductivity enhancement $(k_{ef} - k_f)/k_f$ of nanofluids we obtain the following formula:

$$\frac{k_{ef} - k_f}{k_f} = \frac{k_n \varphi r_f \left(1 + c \left(\frac{r_{cl}}{r_n} \right)^2 \right)}{k_f (1 - \varphi) r_n \left(1 + c \left(\frac{r_{cl}}{r_n} \right)^3 \right)}. \quad (9)$$

where, n_n and n_{cl} – and are the numbers of single nanoparticles and clusters in the unit volume, respectively, r_n , r_{cl} и r_f are the radii of a nanoparticle, a cluster, and a fluid molecule, respectively.

Hence, the thermal conductivity enhancement of nanofluids at low concentrations of nanoparticles ($\varphi \ll 1$) is in direct proportion to the volume fraction and thermal conductivity coefficient k_n of nanoparticles and is inversely proportional to the their radii r_n .

In extreme cases with strong aggregation $c \geq 1$ and $r_{cl}/r_n \gg 1$, formula (9) becomes

$$k_{ef} = k_f \left(1 + \frac{k_n \varphi r_f}{k_f (1 - \varphi) r_{cl}} \right). \quad (10)$$

In the case of complete aggregation of nanoparticles ($n_n \rightarrow 0$) we obtain: $c = n_{cl}(t)/n_n(t) \rightarrow \infty$ and again the same formula (10) is

obtained.

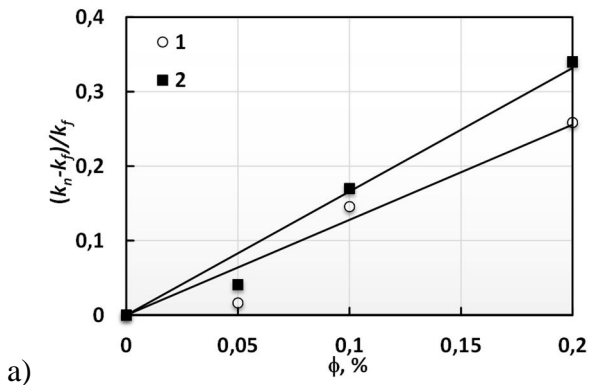
In the case of no aggregation of nanoparticles formula (9) takes the form determined by «Kumar et al. (2004)»⁶:

$$k_{ef} = k_f \left(1 + \frac{k_n}{k_f} \frac{\varphi r_f}{(1 - \varphi) r_n} \right). \quad (11)$$

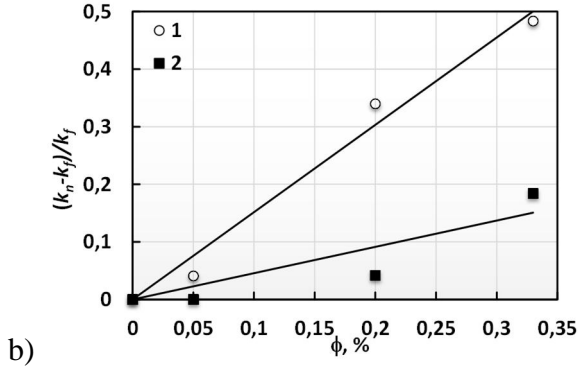
The thermal conductivity enhancement of Cu + glycerol (curve 1) and Cu + water (curve 2) systems versus the volume fraction of Cu is shown in Graph 1a. We can see that at a 0.2% copper nanoparticle concentration, the thermal conductivity enhancement for the Cu + glycerol system is about 25%, while for the Cu + water system it is 35%.

Graph 1b shows the effect of nanoparticle aggregation on Cu + water system's thermal conductivity. We can see that the nanoparticle aggregation and coagulation considerably lowers the nanofluid's thermal conductivity coefficient, starting at certain nanoparticle cluster sizes. For example, at a 0.33% copper nanoparticle concentration, the thermal conductivity enhancement for this system falls from 48% to 18% after one day.

SEM micrographs of Cu nanoparticles (0.1%) in glycerol were obtained with the JEOL JSM-7600F scanning electron microscope and are shown in fig. 2. Upon seeing the SEM micrographs of copper nanoparticles, the presence of nonhomogenous aggregates of copper nanoparticles was clear.



⁶Kumar D. H. Model for heat conduction in nanofluids / D.H. Kumar, H.E. Patel, V.R.R. Kumar et al. // Phys. Rev. Lett., 2004, 93, №14, p.144301.



Graph 1. (a) Dependence of the thermal conductivity enhancement of Cu + glycerol (1, $R^2=0.981$) and Cu + water (2, $R^2=0.951$) on the Cu nanoparticle volume fraction; (b) effect of aggregation on the thermal conductivity in the system Cu + water (1) for a freshly prepared dispersed system and (2) after one day, subsequent to nanoparticle sedimentation as a result of aggregation.

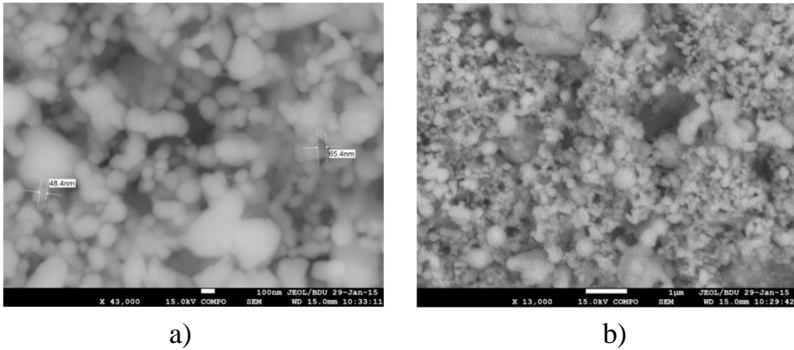


Fig. 2. SEM images of Cu nanoparticles (0.1%) in glycerol. Magnification: (a) $\times 43000$, (b) $\times 13000$.

The model of effective thermal conductivity of nanofluids, taking into account the presence of an ordered liquid nanolayer around the nanoparticle and the aggregation of nanoparticles. We determined the effective thermal conductivity of a nanofluid for the static case, when nanoparticles can be assumed to be immobile [3]. Nanofluid can be schematically represented as a periodic structure of nanoparticles and clusters formed by aggregation of nanoparticles distributed in a liquid, as shown in fig. 3.

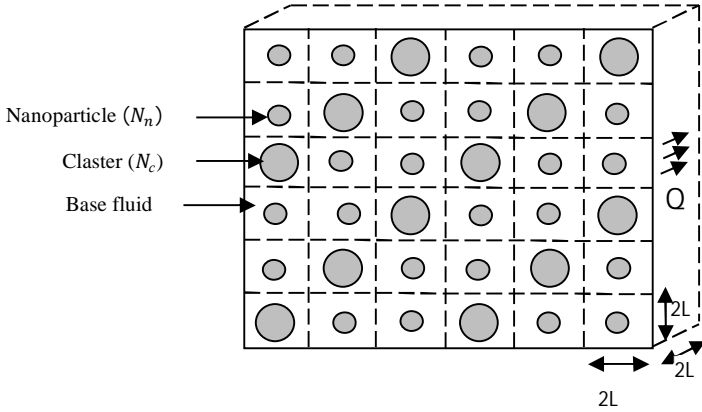


Fig. 3. Schematic cross-section of nanofluid structure consisting of nanoparticles, clusters and base fluid.

Thermal resistance of an elementary array consisting of N_n nanoparticles and N_c clusters formed from nanoparticles included in a continuous medium-into the fluid can be calculated as for parallel connected elements (fig. 3):

$$\frac{1}{R} = \frac{N_n}{R_1} + \frac{N_c}{R_2'} \quad (12)$$

where, R_1 and R_2 are resistance of cubes with the corresponding inclusions – nanoparticle and cluster.

The thermal resistance of the section shown in fig. 4 can be determined by the fragmentation method of an elementary cell by adiabatic planes (fig. 5). In this case, the thermal resistance of the cube can be found as the resistance of parallel-connected columns with resistance R_{11} and of the rest of the cube with resistance R_{12} :

$$\frac{1}{R_1} = \frac{1}{R_{11}} + \frac{1}{R_{12}}. \quad (13)$$

As shown in fig. 4 the quarter of the column of length $2L$ is divided into many infinitesimal layers with thickness dy for each layer. The thermal resistance of the layer is in series dR_p (the thermal resistance of particle) and dR_f (the thermal resistance of base fluid) and since all infinitesimal layers are in parallel the reverse value of the thermal resistance of the column of length $2L$ can be found:

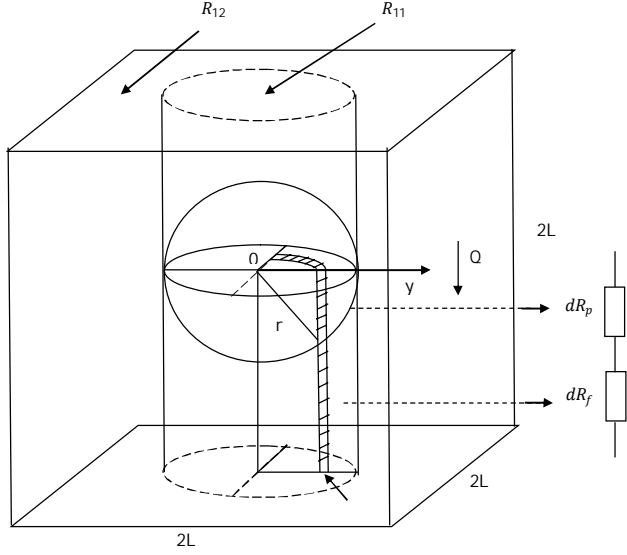


Fig. 4. The network consisting of infinitesimal layers of thickness dy .

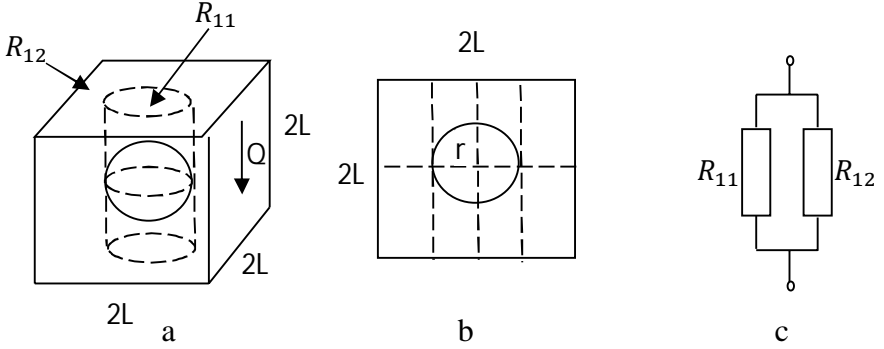


Fig. 5. A unit cell (a), fragmentation of the unit cell by adiabatic planes (b), and connection of thermal resistances of the cell parts (c).

$$\begin{aligned}
 \frac{1}{R_{11}} &= 4 \int_0^r \frac{1}{2dR_p + 2dR_f} = \\
 &= 4 \int_0^r \frac{1}{\frac{2(L - \sqrt{r^2 - y^2})}{k_f \frac{\pi}{2} y dy} + \frac{2\sqrt{r^2 - y^2}}{k_n \frac{\pi}{2} y dy}} = \int_0^r \frac{\pi k_f y dy}{L - \beta \sqrt{r^2 - y^2}} \quad (14)
 \end{aligned}$$

where, $\beta = 1 - k_f/k_n$ and r is the radius of the particle.

Introducing the aggregation coefficient, $\alpha = N_c/(N_n + N_c)$ and $1 - \alpha = N_n/(N_n + N_c)$, $r_c = nr_n$ and $h = [6/\pi(1 - \alpha + \alpha n^3)]^{1/3}$ the effective coefficient of thermal conductivity of nanofluids, taking into account the aggregation, will be determined as:

$$\frac{k_{ef}}{k_f} = \frac{(1 - \alpha)}{2} \left\{ \left[2 - \frac{\pi}{2} h^2 \varphi^{\frac{2}{3}} \right] - \frac{\pi}{\beta} \left[\frac{1}{\beta} \ln \left(1 - \beta h \varphi^{\frac{1}{3}} \right) + h \varphi^{\frac{1}{3}} \right] \right\} + \frac{\alpha}{2} \left\{ \left[2 - \frac{\pi}{2} n^2 h^2 \varphi^{\frac{2}{3}} \right] - \frac{\pi}{\beta} \left[\frac{1}{\beta} \ln \left(1 - \beta n h \varphi^{\frac{1}{3}} \right) + n h \varphi^{\frac{1}{3}} \right] \right\}. \quad (15)$$

When the aggregation of nanoparticles is absent $\alpha = 0$ and $h = (6/\pi)^{1/3}$ the formula (15) is transformed into the form:

$$\frac{k_{ef}}{k_f} = \frac{1}{2} \left\{ \left[2 - \left(\frac{9\pi}{2} \right)^{\frac{1}{3}} \varphi^{\frac{2}{3}} \right] - \frac{\pi}{\beta} \left[\frac{1}{\beta} \ln \left(1 - \left(\frac{6}{\pi} \right)^{\frac{1}{3}} \beta \varphi^{\frac{1}{3}} \right) + \left(\frac{6}{\pi} \right)^{\frac{1}{3}} \varphi^{\frac{1}{3}} \right] \right\}. \quad (16)$$

Taking into account the presence of a liquid nanolayer around a nanoparticle leads to an increase in the effective volume concentration of nanoparticles by $(1 + \delta)^3$ times:

$$\varphi_{ef} = n_n \frac{4}{3} \pi (r_n + \lambda)^3 = n_n \frac{4}{3} \pi r_n^3 (1 + \delta)^3 = (1 + \delta)^3 \varphi \quad (17)$$

Yu and Choi (2003) using the effective medium theory for non-aggregating nanoparticles and taking into account the interfacial interaction between nanoparticles and fluid obtained the following expression for the «equivalent thermal conductivity coefficient of a nanoparticle»⁷:

$$k_{ne} = \frac{[2(1 - \gamma) + (1 + \delta)^3(1 + 2\gamma)]\gamma}{(\gamma - 1) + (1 + \delta)^3(1 + 2\gamma)} k_n, \quad (18)$$

where, $\gamma = k_{layer}/k_f$ – is the ratio of the thermal conductivity of the nanolayer to the thermal conductivity of the fluid.

Substituting k_n to k_{ne} and φ to φ_{ef} in Equations (15) and (16) we can also take into account the effect of interfacial nanolayer on the thermal conductivity of nanofluids.

Thus by considering both the aggregation of nanoparticles and the

⁷Yu W., Choi S.U.S. The role of interfacial layers in the enhanced thermal conductivity of nanofluids: a renovated Maxwell model // J. Nanopar Res., 2003, №5, p.167-171

presence of a nanolayer around nanoparticles for thermal conductivity enhancement of nanofluids we obtain:

$$\frac{k_{ef}}{k_f} = \frac{(1 - \alpha)}{2} \left\{ \left[2 - \frac{\pi}{2} h^2 \varphi_{ef}^{\frac{2}{3}} \right] - \frac{\pi}{\beta'} \left[\frac{1}{\beta'} \ln \left(1 - \beta' h \varphi_{ef}^{\frac{1}{3}} \right) + h \varphi_{ef}^{\frac{1}{3}} \right] \right\} + \frac{\alpha}{2} \left\{ \left[2 - \frac{\pi}{2} n^2 h^2 \varphi_{ef}^{\frac{2}{3}} \right] - \frac{\pi}{\beta'} \left[\frac{1}{\beta'} \ln \left(1 - \beta' n h \varphi_{ef}^{\frac{1}{3}} \right) + n h \varphi_{ef}^{\frac{1}{3}} \right] \right\}. \quad (19)$$

Consideration only the presence of a nanolayer without the aggregation of nanoparticles, yields:

$$\frac{k_{ef}}{k_f} = \frac{1}{2} \left\{ \left[2 - \left(\frac{9\pi}{2} \right)^{\frac{1}{3}} \varphi_{ef}^{\frac{2}{3}} \right] - \frac{\pi}{\beta'} \left[\frac{1}{\beta'} \ln \left(1 - \left(\frac{6}{\pi} \right)^{\frac{1}{3}} \beta' \varphi_{ef}^{\frac{1}{3}} \right) + \left(\frac{6}{\pi} \right)^{\frac{1}{3}} \varphi_{ef}^{\frac{1}{3}} \right] \right\}, \quad (20)$$

where $\beta' = 1 - k_f/k_{ne}$.

Graph 2 compares the predicted thermal conductivity enhancement determined by present model with the experimental data for nanofluids (a) «CuO + Water»^{8,9} [12], (b) «Al₂O₃ + Water»^{9,10}, (c) «CuO + Ethylene glycol»⁹ and (d) «Al₂O₃ + Ethylene glycol»⁹. The effect of an aggregation of nanoparticles and the presence of an ordered nanolayer around nanoparticles on the thermal conductivity of the nanofluids are presented by curves 1 (Equation (16)), 2 (Equation (15)), 3 (Equation (20)) and 4 (Equation (19)).

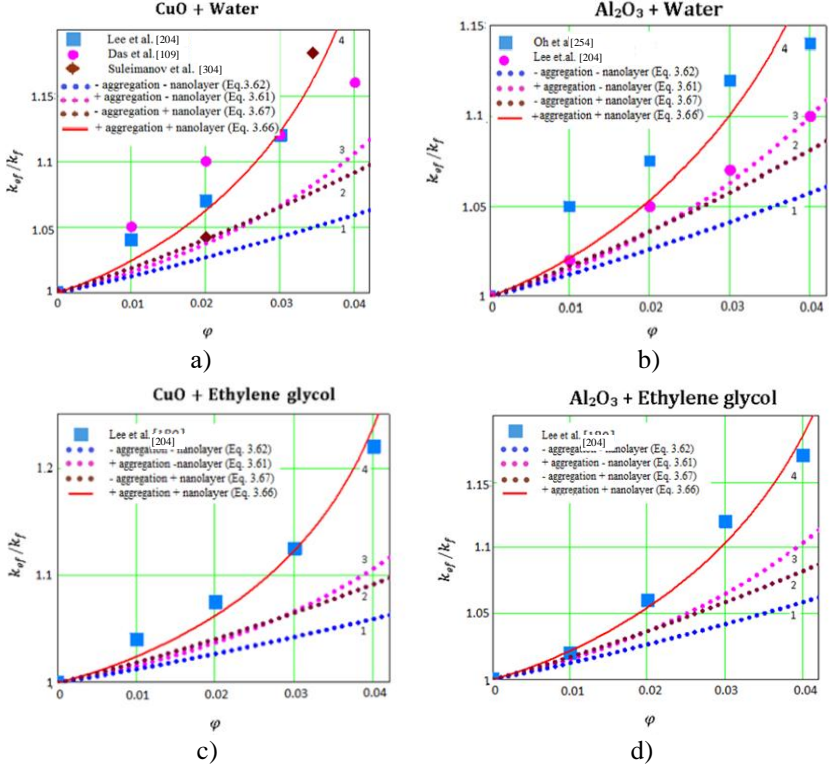
The values of nanolayer thickness were estimated through the formula (7): $A_{CuO} = 28.4 \cdot 10^{-20} J$, $A_{Al_2O_3} = 15 \cdot 10^{-20} J$, $A_{water} = 3.8 \cdot 10^{-20} J$, $A_{EG} = 5.7 \cdot 10^{-20} J$, $\sigma_{water} = 72 mN/m$, $\sigma_{EG} = 48 mN/m$ and using the Berthelot composition rule $A_{AB} \approx \sqrt{A_A A_B}$ with $D = 0.165 nm$ at $t = 25^\circ C$. The graphs were constructed on Mathcad 15 using the following parameters: the radius of the nanoparticle $r_n = 10 nm$, the thickness of the nanolayer according to the formula (7) $\lambda \approx 1 \div 1.3 nm$, the thermal conductivity of the nanolayer $k_{layer} = 2k_f$

⁸Das S.K. Temperature dependence of thermal conductivity enhancement for nanofluids / S.K. Das, N. Putra, P. Thiesen et al. // J. Heat Transfer, 2003, 125, p.567-574.

⁹Lee S. Measuring thermal conductivity of fluids containing oxide nanoparticles, / Lee S., Choi S.U.S., Li S. et al. // J. Heat Transfer, 1999, 121, p.280-289.

¹⁰Oh D. Thermal Conductivity Measurement and Sedimentation Detection of Aluminum Oxide Nanofluids by Using the 3x Method. / D. Oh, A. Jain, J. K. Eaton et al. // Int. J. Heat Fluid Flow, 2008, 29, p.1456-1461.

($\gamma = 2$), the aggregation coefficient $\alpha = 0.1$, the radius of the cluster formed from the nanoparticles $r_c = 3r_n$, the thermal conductivity coefficient for: water $k_f = 0.6 \text{ W}/(\text{m} \cdot \text{K})$, ethylene glycol $k_f = 0.254 \text{ W}/(\text{m} \cdot \text{K})$, copper oxide (CuO) $k_n = 400 \text{ W}/(\text{m} \cdot \text{K})$, alumina (Al_2O_3) $k_n = 30 \text{ W}/(\text{m} \cdot \text{K})$.



Graph 2. Model predictions compared with the experimental data. (a) CuO + Water, (b) Al_2O_3 + Water, (c) CuO + Ethylene glycol and (d) Al_2O_3 + Ethylene glycol. ($r_n = 10 \text{ nm}$, $\lambda = 1 \text{ nm}$, $k_{layer} = 2k_f$ ($\gamma = 2$), $\alpha = 0.1$, $r_c = 3r_n$).

As can be seen from Graph 2(a)-(d), in the absence of a nanolayer around nanoparticles and the absence of aggregation of nanoparticles, in our model we obtain understated values of the thermal conductivity enhancement of nanofluids (curve 1). Considering only aggregation or only the presence of a nanolayer around nanoparticles improves the situation, but still the value of the ratio k_{ef}/k_f is lower in comparison

with the experimental data (curve 3 and 2, correspondingly). By taking into account both the aggregation of nanoparticles and the presence of a nanolayer around nanoparticles, a good correlation with the experimental data is achieved (curve 4), because as mentioned above the molecular structure of the liquid layering is significantly more ordered than that of the bulk liquid, what leads to a higher thermal conductivity compared to the liquid and on the other side the contribution of the cluster formed by the aggregation of nanoparticles on the thermal conductivity of the column is higher compared to the nanoparticle in the absence of their sedimentation.

The following regularity appears: at low concentrations ($\varphi < 0.03$), the aggregation of nanoparticles and the presence of a nanolayer have the same effect on the thermal conductivity of nanofluids, but with an increase in the volume fraction of nanoparticles in the base liquid, starting with $\varphi = 0.03$, the contribution of aggregation to the enhancement of thermal conductivity (curve 2) becomes larger as compared to the effect of the nanolayer (curve 3). This is understandable, since with the increase in the concentration of nanoparticles in the fluid, the aggregation of nanoparticles occurs with a higher probability. The disadvantage of the proposed model is not taking into account the sedimentation of big clusters of nanoparticles, (and also the assumption of monodispersity of clusters) that at high concentrations of nanoparticles leads to unrealistically high values of the thermal conductivity enhancement in comparison with the experimental data. In this model we also assumed that the thermal conductivity of clusters is the same as thermal conductivity of nanoparticles. But the effect of these disadvantages on the thermal conductivity at low concentrations of nanoparticles is negligible.

Modeling of anisotropic thermal conductivity of nanofluids with magnetic nanoparticles. Despite many studies on the thermal properties of ferrofluids, where the formation of chain clusters of magnetic nanoparticles under an external magnetic field is considered to be the main cause of anisotropic thermal conductivity of ferrofluids, this mechanism has not yet been proven theoretically. To explain the effect of magnetic field on the thermal conductivity enhancement of ferrofluids we performed theoretical calculations by taking into account the aggregation structure of magnetic nanoparticles under external magnetic field and the obtained results are compared with the

available experimental data [1].

First, the thermal conductivity of ferrofluids was determined in the absence of an external magnetic field for the static case, when spherical nanoparticles can be considered to be immobile, assuming that the magnetic nanoparticles are not aggregated and evenly distributed in the fluid. We used the technique applied to create the model of effective thermal conductivity of nanofluids [3] and obtained the formula for thermal conductivity of ferrofluids:

in the case of non-aggregated nanoparticles,

$$k_{na} = -\frac{\pi k_f}{2\beta^2} \ln \left(1 - 2\beta \sqrt[3]{\frac{3\varphi}{4\pi}} - \frac{k_f}{\beta} \sqrt[3]{\frac{3\pi^2\varphi}{4}} + \left[1 - \sqrt[3]{\frac{9\pi\varphi^2}{16}} \right] k_f \right), \quad (21)$$

in the case of aggregated nanoparticles,

$$k_a = -\frac{2k_f}{\beta^2} (\ln(1 - \beta) + \beta), \quad (22)$$

where, $\beta = 1 - k_f/k_p$, φ is the volume concentration of nanoparticles, k_p and k_f are the thermal conductivity of the particle and the base fluid, respectively.

Under a homogeneous magnetic field, part of magnetic nanoparticles forms chainlike clusters along the magnetic field direction and with increasing magnetic field strength this process is enhanced. In this case the total volume of a ferrofluid can be represented as a sum of two parts: the volume with aggregated magnetic nanoparticles (chainlike clusters) V_a and the volume with non-aggregated uniformly dispersed nanoparticles V_{na} .

The thermal conductivity of ferrofluids in the case when a magnetic field is parallel to the temperature gradient (k_{\parallel}) can be found as (In this case the thermal resistance of a ferrofluid can be represented as the resistance of two parallel-connected elements (see fig. 6a)):

$$k_{\parallel} = k_a \varphi_a + (1 - \varphi_a) k_{na}. \quad (23)$$

When the magnetic field is perpendicular to the temperature gradient the thermal conductivity of ferrofluids (k_{\perp}) can be represented as for the sequences indicated in fig. 6b elements:

$$k_{\perp} = \left(\frac{\varphi_a}{k_a} + \frac{1 - \varphi_a}{k_{na}} \right)^{-1}. \quad (24)$$

where,

$$\varphi_a = \frac{V_a}{V_a + V_{na}} = \frac{1}{1 + \frac{\pi}{6} \left(\frac{1}{\alpha} - 1 \right) \frac{1}{\varphi}}$$

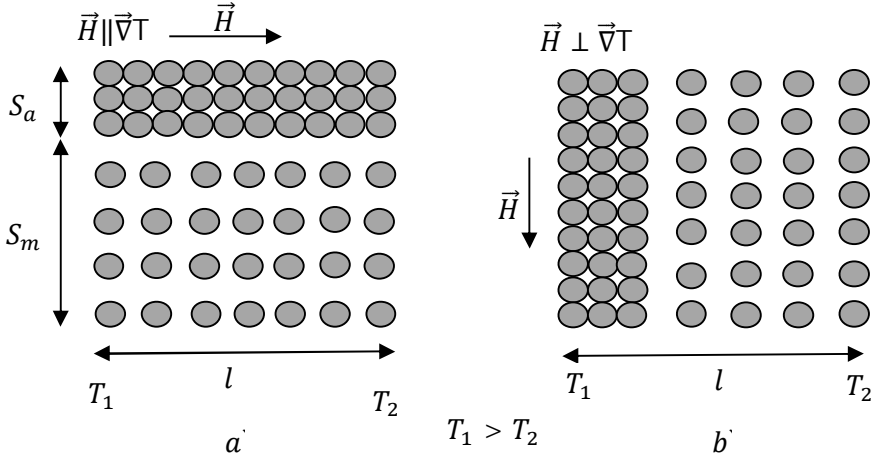


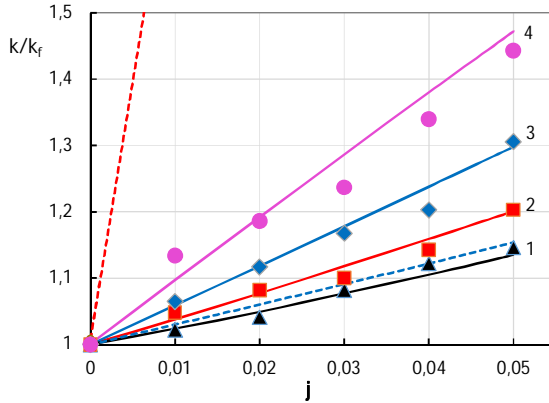
Fig. 6. Schematic cross-section of a ferrofluid structure consisting of chainlike clusters and non-aggregated uniformly dispersed nanoparticles: (a) the magnetic field is parallel to the temperature gradient, (b) the magnetic field is perpendicular to the temperature gradient.

Graphs 3 and 4 compare the predicted thermal conductivity enhancement determined by present model via the formulas (23 and (24)) with the experimental data for «Fe – water»¹¹ ferrofluid and for «Fe₃O₄ – kerosene»¹² ferrofluid, respectively.

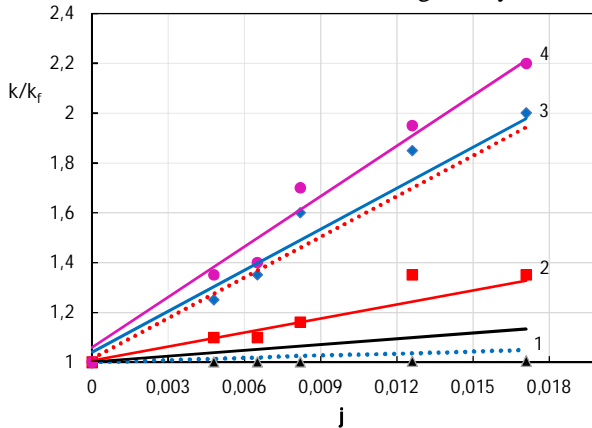
In the absence of a magnetic field the thermal conductivity enhancement of ferrofluids (triangles) does not differ from that for nanofluids with nonmagnetic solid particles. In the presence of a magnetic field perpendicular to the temperature gradient we get almost the same results for thermal conductivity enhancement of ferrofluids (curve 1). In a magnetic field parallel to the temperature gradient (curves 2, 3, 4) the

¹¹Li Q., Xuan Y., Wang J. Experimental Investigations on Transport Properties of Magnetic Fluids // Exp. Therm. Fluid Sci., 2005, 30, p.109-116.

¹²Philip J., Shima P. D., Raj B. Enhancement of Thermal Conductivity in Magnetite Based Nanofluid Due to Chainlike Structures // Appl. Phys. Lett. 2007, 91, p.2003108.



Graph 3. Model predictions compared with the experimental data for «Fe – water» ferrofluid. The solid line 1 ($\alpha = 0.400$) corresponds to the thermal conductivity enhancement in a magnetic field perpendicular to the temperature gradient and solid lines 2 ($\alpha = 0.167$), 3 (0.267), 4 (0.400) correspond to the thermal conductivity enhancement in a magnetic field parallel to the temperature gradient. Symbols represent experimental data in a magnetic field with intensity ($H = 0G$ triangles), (100G squares), (160G diamonds), (240G circles). The upper HS limit is delineated by the red dotted line while the lower HS bound is given by blue dotted line.



Graph 4. Model predictions compared with the experimental data for magnetite « Fe_3O_4 – kerosene» ferrofluid. The solid line 1 ($\alpha = 0.80$) corresponds to the thermal conductivity enhancement in a magnetic field perpendicular to the temperature gradient. Solid lines 2 ($\alpha = 0.62$), 3 (0.85), 4 (0.88) correspond to the thermal conductivity enhancement in a magnetic field parallel to the temperature gradient. Symbols represent experimental data in the magnetic field with intensity ($H = 0G$ triangles), (125G squares), (200G diamonds), (300G circles). The upper HS bound is delineated by the red dotted line while the lower HS bound is given by blue dotted line.

thermal conductivity enhancement of ferrofluids is higher than in the perpendicular direction (curve 1) and with an increase of the magnetic field strength, the thermal conductivity enhancement increases.

These results show that with increasing magnetic field strength, a greater number of nanoparticles aggregate by forming a chainlike structure, whose contribution to the thermal conductivity of ferrofluids is higher than structures with non-aggregated nanoparticles.

Due to the high susceptibility a relatively weak magnetic field (~600 G) will cause a strong magnetization (90% of the saturation magnetization) in ferrofluids. As can be seen, the Langevin parameter is responsible for the formation of the chainlike structure of magnetic nanoparticles along the magnetic field, and therefore the aggregation degree should also be proportional to the Langevin parameter, in other words, the magnetic field strength $\alpha \sim L \sim H$. As can be seen from Graphs 3 and 4 the proposed model predicts a good agreement with the experimental data.

In an external magnetic field, when the energy of the magnetic dipole interaction becomes sufficiently strong compared to the thermal energy ($L > 1$), the magnetic moments of the nanoparticles begin to orient in the direction of the magnetic field, forming chains along this direction, the length of which increases with increasing magnetic field strength. These chains create a more efficient bridge to transfer heat along the direction of the chain. According to our model, the total volume of ferrofluid consists of two parts: the volume with aggregated magnetic nanoparticles (chainlike clusters) and the volume with non-aggregated uniformly dispersed nanoparticles. With an increase in the external magnetic field, the degree of aggregation - the fraction of the volume with aggregated magnetic nanoparticles increases. Thus, the contribution of chainlike clusters to the thermal conductivity of a ferrofluid depends on the magnetic field strength and the direction of these chains relative to the temperature gradient; when the direction of the chain is parallel to the temperature gradient, we observe a higher increase in thermal conductivity and almost no change in thermal conductivity when the direction of the chain is perpendicular to the temperature gradient.

Thermophysical properties of nano- and microfluids with particles of metal string complexes $[\text{Ni}_5(\mu_5\text{-pppmda})_4\text{Cl}_2]$ and $[\text{Ni}_3(\mu_3\text{-ppza})_4\text{Cl}_2]$. We investigated in detail the stability and thermophysical properties of micro- and nanofluids containing monocrystalline micro-

particles of metal-string complexes of pentanickel (Ni5) and trinickel (Ni3) and polycrystalline nanoparticles of Cu and Al [2, 5, 8]. From SEM images of Ni5 and Ni3 microfluids, it is seen that a stable colloidal dispersion is retained 6 hours after preparation (fig. 7).

In our opinion there are three reasons for the better stabilization of the Ni3 and Ni5 metal-string complexes microparticles in the base fluid: a) The hydrogen bonds are formed between the MSC particles through their organic fragments and water molecules, b) The densities of Ni3 ($\rho_m = 1.644 \text{ q/sm}^3$) and Ni5 ($\rho_m = 1.668 \text{ q/sm}^3$) complexes microparticles are much smaller compared to Cu nanoparticles ($\rho_{Cu} = 5 \text{ q/sm}^3$), though greater than the base fluid ($\rho_{bf} = 1,07 \text{ q/sm}^3$), 3) The SEM micrographs (fig. 7) clearly show the formation of microparticles assemblies whose dimensions are determined by the equilibrium between of gravity and buoyancy.

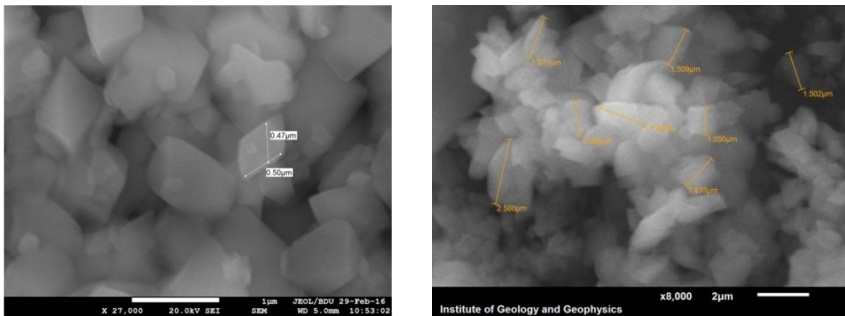
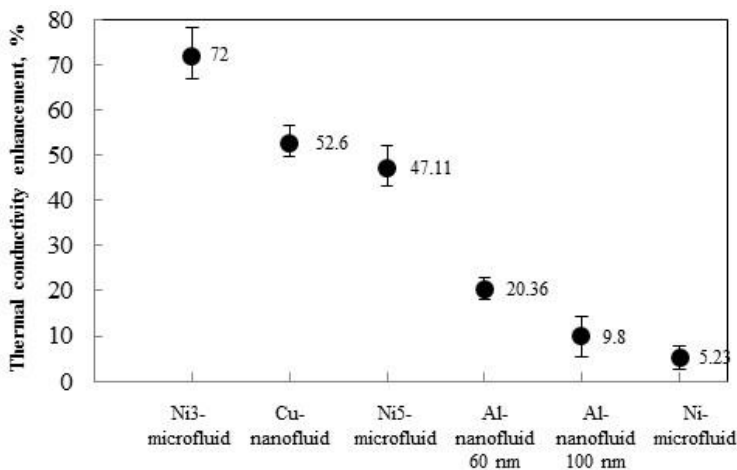


Fig. 7. SEM images of (a) microparticles of monocrystalline metal string complex $[\text{Ni}_5(\mu_5\text{-pppmda})_4\text{Cl}_2]$ (after 6 h of preparation) and (b) microparticles of monocrystalline metal string complex $[\text{Ni}_3(\mu_3\text{-ppza})_4\text{Cl}_2]$ (1%) in base fluid (30% glycerol+70% water).

At large interparticle separation (compared to atoms), such as the 0.2-0.5 μm observed in our measurements, stable «secondary minimum» associations between colloidal particles can form with high degrees of order and with thixotropic colloidal structure (fig. 7).

The thermal conductivity enhancement of nanofluids was studied up to the volume fraction of 5%, because further increasing of the concentration of nanoparticles leads to instability and sedimentation. The results obtained are shown in Graph 5.



Graph 5. The thermal conductivity enhancement for various nano- and microfluids with a volume fraction of particles of $\varphi = 5\%$.

Comparison shows that the best results were achieved using microparticles of monocrystalline MSCs $[\text{Ni}_3(\mu_3\text{-ppza})_4\text{Cl}_2]$ as well as $[\text{Ni}_5(\mu_5\text{-pppmda})_4\text{Cl}_2]$, and copper nanoparticles. Compared to the base fluid, the thermal conductivity coefficient increased by 72% for «Ni3–water–glycerol», 53% for «Cu–water–glycerol», and 47% for «Ni5- water–glycerol». The results were lower for Al nanofluid and Ni microfluids: roughly 20% for 60 nm Al nanofluid, 10% for 90-110 nm Al nanofluid, and only around 5% for Ni microfluid. The results can be explained within the framework of the proposed model of thermal-conductivity enhancement in nanofluids (microfluids). To compare the role of the monocrystalline structure of microparticles of metal-string complexes Ni3 and Ni5 in the thermal conductivity of microfluids, we used polycrystalline Ni microparticles of the same size.

Achieving a high increase in thermal conductivity when using metal-string complexes Ni3 and Ni5 microparticles, in our opinion, is associated, firstly, with the high stability of these particles in the base fluid, which is achieved due to the formation of hydrogen bonds between metal-string complexes particles through its organic fragments and water molecules, in secondly, with mono crystallinity of particles of metal string complexes. The absence of such bonds between microparticles of ordinary metals and their oxides and liquid molecules leads to their rapid settling in the liquid, due to which an increase in thermal

conductivity when metal (or their oxides) microparticles are added to the liquid is not observed.

Increased numbers of scattering centers in the polycrystalline metal (i.e. grain boundaries between monocrystalline units) raise the contribution of residual thermal resistance to the total thermal resistance. The scattering of the conduction electrons in grain boundaries leads to decreasing in the thermal conductivity of the polycrystalline metal in comparison with the monocrystalline one. In the case of polycrystalline Ni microparticles, the increase in thermal conductivity was only 5.23%, and the system is unstable due to the rapid sedimentation of particles (Graph 5). As can be seen from SEM microphotographs (fig. 7), the MSC particles $[\text{Ni}_3(\mu_3\text{-ppza})_4\text{Cl}_2]$ and $[\text{Ni}_5(\mu_5\text{-pppmda})_4\text{Cl}_2]$ are monocrystalline: the particles have the correct geometric shape, due to the monocrystalline nature of the MSC particles, the residual thermal resistance in them is insignificant, which favors their high thermal conductivity.

Since the practical application of nanofluids is always associated with their flow, we also studied the rheological properties of Cu nanofluids and Ni₃ and Ni₅ microfluids. The results once again confirm our assumptions about the high stability of metal string complex microparticles in the base liquid due to the formation of a colloidal structure. The base fluid is Newtonian, but the addition of nanoparticles changes its rheological behavior to pseudoplastic. The rheology of the studied nanofluids is well described by the power law of Ostwald-De Weil.

The mechanism for increasing the viscosity of a nanofluid compared to the base fluid is complex. Some researchers believe that dispersed systems such as suspensions of nano-, microparticles in liquid in rheological models should be considered as two-phase systems in which the «free» dispersion medium (that part of it that is not enclosed inside particle aggregates and is not attached in any way particles) actually determines their viscosity. Adding solid particles to a liquid increases their viscosity due to the following factors: particles move as solids at a constant speed and disrupt the fluid's velocity profile. The velocity gradient in the local region of the fluid between the particles becomes higher compared to a pure fluid. Increased fluid stress between particles causes higher stress for the same overall velocity gradient, and this manifests itself as higher viscosity. And there is also additional vertical momentum transfer due to solid particles, which is similar to molecular momentum transfer, which

also increases the viscosity of the suspension.

Some authors argue that the addition of nanoparticles to a liquid, leads to a «structuring» of the liquid, i.e. the presence of a nanoparticle in a liquid increases the average radius of interaction between liquid molecules by means of nanoparticles. Nanofluids turn out to be more ordered than the base liquid, and with increasing particle concentration, the degree of ordering of the carrier liquid increases. The characteristic linear scale of the short-range order of molecules near the nanoparticle turns out to be approximately twice as large as in the base liquid. An increase in the degree of fluid ordering leads to an increase in its effective viscosity. Nanoparticles at low strain rates, in addition to performing translational motion, still have time to rotate, which makes a significant contribution to the viscosity of the nanofluid.

Our studies have shown that the viscosity of nanofluids decreases with increasing particle size. This is explained by the fact that with a decrease in the size of nanoparticles, their specific surface grows in inverse proportion to the radius of the particles, and with an increase in the specific surface, the internal friction against the movement of liquid by the nanoparticles increases. The behavior of viscosity in the case of formation of aggregates is determined by the thixotropic colloidal structure. In such systems, an increase in shear rate destroys the colloidal structure, resulting in a decrease in viscosity.

The study of the surface tension of nano- and microfluids showed that in all cases the surface tension of the nanofluid decreases compared to the base liquid. This is more evident in the case of the Ni5 microfluid. The addition of 5% copper nanoparticles reduces the surface tension of the liquid by 15.6%, and the addition of the same amount of Ni5 microparticles to the same liquid results in a decrease of 37.5%. A strong decrease in surface tension indicates that Ni3 and Ni5 MSC microparticles were better distributed over the entire volume and surface of the liquid, due to which the wetting of the dispersion with nano- and microparticles is lower compared to the wetting of the base liquid and the hydrodynamic resistance to the flow of this suspension will be lower.

Aggregative stability of quartz suspensions. We studied in detail the influence of zeta potential on the fluidization of quartz suspensions and the possibility of its chemical control [6, 9]. In our studies, to determine the zeta potential, we used the streaming potential method

and the Helmholtz-Smoluchowski equation. The process of fluidization of untreated and chemically treated quartz sand with water at an average pressure of 0.01 MPa was studied.

Fluid filtration has a significant impact on the sanding process as sand production begins at a certain critical pressure drop. Obviously, reducing the viscosity or improving the throughput of the porous medium significantly reduces the chance of sand production.

The filtration coefficients of the liquid before and after the treatment of the porous medium were determined on the basis of Darcy's law.

The main component of the chemical reagent used is the reaction product of amines and phosphoric esters – triethanolammonium phosphate. To process quartz sand, 0.25-4.0 ml of the aggregation mixture and 20 ml of electrolyte were added to 30 g of sand, a 2% potassium chloride solution was used as the electrolyte, after which the whole mass was mixed.

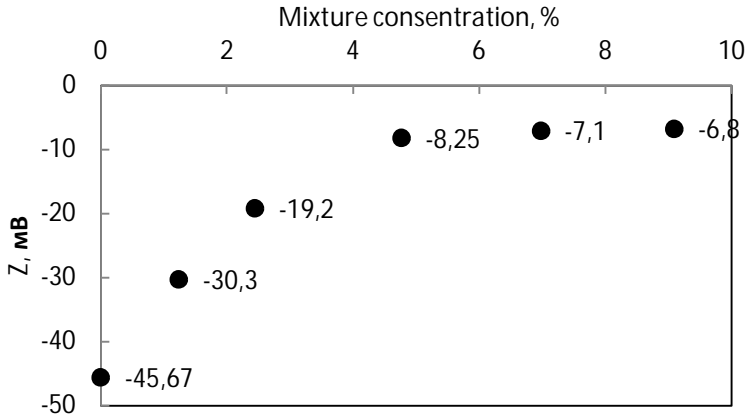
The surface of the oxide crystals SiO_2 is partially hydrated. H_2SiO_3 is formed and can be ionized $\text{H}_2\text{SiO}_3 \leftrightarrow \text{H}^+ + \text{HSiO}_3^-$. The HSiO_3^- ions, which are «related» to SiO_2 , selectively adsorb on the surface of SiO_2 , giving it a negative charge (potential-determining ions), and the H^+ ions go into the solution as counter ions.

When treating sand by the aggregating system, the triethanol ammonium phosphate is positively charged and joins the dense layer of counterions, which results in a thickness reduction in the diffuse portion of the electrical double layer around the sand and hence a decrease in the zeta potential (Graph 6).

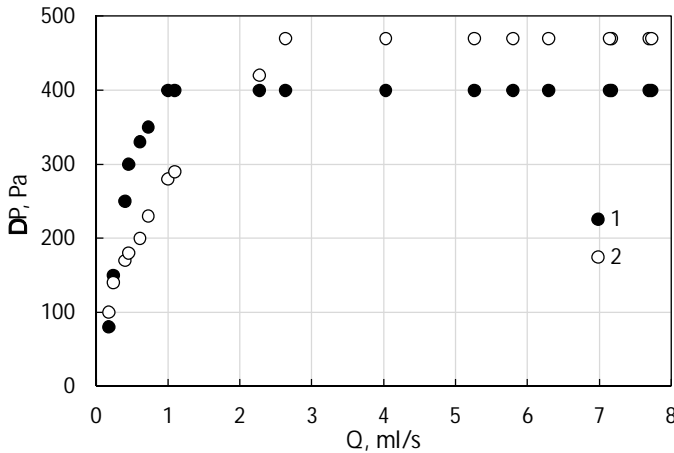
In the Graph 7 the fluidization characteristics ($\Delta P-Q$) were presented.

As can be seen from Graph 7, the velocity of fluidization onset for treated sand is 2.632 times higher than that for non-treated sand, and the transition from the filtration state to the fluidization state for treated sand is smoother (the slope of the curve in the filtration zone for treated sand is 2.815 times less than that for untreated sand): Fluidization occurs at higher fluid velocity for treated sand. This indicates that the monodispersity of the sand was lost due to treatment and the sand became polydisperse as a result of grain aggregation, which leads to an increase in the carryover velocity of particles.

The graph also shows that, before fluidization at the same pressure



Graph 6. Dependence of sand zeta potential on the triethanol ammonium phosphate concentration.



Graph 7. Fluidization curves of untreated (1) and treated (2).

differential, the filtered fluid volume is much higher for treated sand (2.632 times higher at the transition point from the filtration zone into the fluidization zone) compared to that for untreated sand. This shows that the treatment increases the sand resistance to fluidization by fluid: The fluid can also be filtered through treated sand at high velocities, leaving the sand motionless.

The fourth chapter presents the results of a study of the interaction

and structural features in dilute aqueous solutions of polyethylene glycols of various fractions.

Interaction of macromolecules with solvent molecules in a polyethylene glycol-water system. We studied the conformation and size of macromolecules in an aqueous solution of polyethylene glycols by our new refractometric method [14, 15, 17, 19, 23-26, 29]. Due to the fact that, at optical frequencies, dipoles and ions do not follow changes in the direction of the electric field of the light wave, the main contribution to the polarization of the medium is made by electrons oscillating under the influence of this field, and in this case the Lorentz-Lorentz equation is applicable for a homogeneous medium. For dilute aqueous solutions of polymers, taking into account the contributions of all components present in the solution to the polarization of the medium, this law after certain transformations takes the form:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{n_w^2 - 1}{n_w^2 + 2} + \frac{c}{3} \left(\frac{M_w}{M_p} - \frac{\rho N_A}{M_p} \alpha_w \right) k, \quad (25)$$

where, n and n_w – the refractive index of the solution and water, respectively, M_w, M_p – is the molar mass of water and polymer, respectively, ρ is the density of the solution, N_A is the Avogadro constant, k – is the interaction parameter that determines the number of water molecules associated with one macromolecule (the number of hydration of the macromolecule), α_w – polarizability of free water molecules unbounded to polymer macromolecules.

Having plotted the concentration dependence of the ratio $\frac{n^2-1}{n^2+2}$ of the refractive index of the diluted aqueous polymer solution in the coordinates $(n^2 - 1)/(n^2 + 2)$ - c , determining k by the slope of this dependence and by formula (25), we can analyze the nature of the interaction of polymer macromolecules with water molecules. Also, using the Lorentz-Lorentz law

$$\frac{n^2 - 1}{n^2 + 2} = \frac{n_w^2 - 1}{n_w^2 + 2} + \frac{c\rho N_A}{3M_p} \alpha_p, \quad (26)$$

we determine the polarizability of the unhydrated macromolecule while maintaining the conformation in a dilute aqueous solution of polyethylene glycol with different molecular weights, and assuming the polarizability of the macromolecule to be approximately equal to

its volume $\alpha_p \approx V_{macro} = 4\pi \left(\sqrt{\langle R_i^2 \rangle} \right)^3 / 3$, we estimated the inertial radius of the macromolecule $\sqrt{\langle R_i^2 \rangle} = \sqrt[3]{3\alpha_p / (4\pi)}$, as well as the root mean square distance between the ends of the macromolecular chain: $R_{cp.KB.} = \sqrt{\langle R^2 \rangle} = \sqrt{6\langle R_i^2 \rangle}$.

Calculations show that for all polyethylene glycols studied, the mean-square distance between the ends of the macromolecular chain decreases with increasing polymer concentration in the solution (that is, the macromolecular «coils» coagulate), and saturation is achieved starting from a certain concentration. This result can be explained by the fact that between the «coils» there is a strong interaction, and they penetrate into each other. The initial concentration of stabilization of the size of macromolecules with an increase in the molecular weight of the polymer shifts toward lower concentrations. This can be explained by the fact that, at the same concentration, long-chain macromolecules occupy a larger volume than short-chain macromolecules, and therefore the interaction of long-chain macromolecules begins with a lower concentration with an increase in the molecular weight of polyethylene glycol. Some parameters related to the concentration of stabilization of the sizes of macromolecules (c_{st}) are given in Table 1.

Table 1. Parameters of macromolecules at a concentration of stabilization (c_{st})

M	600	1000	1500	3000	6000	20000
n	13.63636364	22.72727273	34.09091	68.18182	136.3636364	454.5455
L, m	0.000000006	0.00000001	1.5E-08	3E-08	0.00000006	2E-07
C_{cr}, %	2	1	0.8	0.7	0.5	0.2
α, m³	2.17E-28	3.32E-28	5.5E-28	1.1E-27	2.5E-27	1E-26
R_n, m	3.8103E-10	4.38992E-10	5.19E-10	6.54E-10	8.59868E-10	1.36E-09
R_{cp.KB}, m	9.33329E-10	1.07531E-09	1.27E-09	1.6E-09	2.10624E-09	3.34E-09
b, m	1.45184E-10	1.15628E-10	1.08E-10	8.56E-11	7.39373E-11	5.58E-11
N	41.32695543	86.48387294	139.0318	350.5	811.4981775	3581.567
b/d	0.665980242	0.530405937	0.494904	0.392624	0.339162016	0.256154

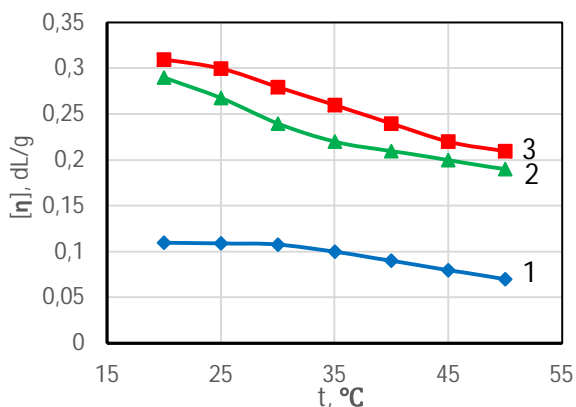
Effect of sodium hydroxide on the interactions of polyethylene glycol macromolecules with water molecules. We have tried in this work to find out the nature of macromolecules interactions with an aqueous medium on the basis of rheological properties of dilute water

solutions of polyethylene glycols with different molecular mass (1000, 3000, 6000, 8000 and 20000) in the temperature range 293-313°K, in the presence of sodium hydroxide (0.1 mol/l) in solutions [4, 7]. The concentration dependencies of reduced viscosities (η_{red}) were constructed and the intrinsic viscosities ($[\eta]$) and Huggins constants (K_h) for these solutions were found from the graphs according to the Flory-Huggins equation. The mean-square distance between the ends of the macromolecular chain $\langle h \rangle$ for different PEGs were approximately evaluated using the Flory-Huggins formula. The parameters (K and α) of the Mark-Kuhn-Houwink equation ($[\eta] = KM^\alpha$) were found from the dependence $lg[\eta]$ vs. lgM . The activation energies of viscous flow were determined using Arrhenius equation: $\eta = \eta_0 \exp(\Delta E/RT)$, where R is the universal gas constant and T is the temperature.

As seen from figure 8 the intrinsic viscosities rise with an increase in molecular mass of PEG and decreases with an increase in temperature. It is well known that the intrinsic viscosity determines the behavior of isolated macromolecules and it is a measure of the energy loss due to a friction of isolated macromolecules in solvent during their rotation and translational movement. The sizes of macromolecular coils increase with an increase in molecular mass of PEG that leads to the increase of intrinsic viscosity. Flow of coils becomes easy with an increase in temperature owing to weakening of an interaction between segments of the macromolecular chain. As can be seen from the figure, the intrinsic viscosity increases when we add sodium hydroxide (0.1 mol / l) to aqueous solutions of PEG. This fact can be explain by the bound of Na^+ ions to the macromolecular chains that causes the repulsion of chains segments and the increasing of macromolecular coils sizes.

The Huggins constants for the system « $H_2O + PEG20000$ » approximately equal to 0.25-0.26 at room temperatures, what means PEG 20000 good solves in water at these temperatures, but with an increase in temperature beginning with the temperature 35°C the Huggins constants become greater than 0.5, that indicates the solubility of PEG in water becomes weakly. The adding of NaOH to the water solution of PEG leads to the weakening of solubility of PEG at any temperatures, including the room temperatures also. Probably it is caused by decreasing of free water molecules number in solution, owing the hydration of Na^+ and OH^- ions with free water molecules proportionally to

their concentration in solutions. Using the parameters of the Mark-Kuhn-Houwink equation it was established that an adding of NaOH to the aqueous solutions of PEG leads to the «neutral» interactions between the segments of macromolecular coils and water molecules, thereby the macromolecular coils in the presence of NaOH accept the unperturbed state as in θ solutions. The presence of NaOH in water solutions of PEG leads to an increase of activation energies of viscous flow that occurs because the sizes of macromolecular coils increase with adding of sodium hydroxide and thereby the displacement of macromolecular coils becomes difficult.



Graph 8. Graphs of the temperature dependence of intrinsic viscosities of the systems (1) “(0.1mol/l NaOH+H₂O) + PEG 3000”, (2) “H₂O + PEG 20000” и (3) “(0.1моль/л NaOH+H₂O) + PEG 20000”.

Effect of potassium hydroxide on the formation of macromolecular tangles in aqueous solutions of polyethylene glycols. We studied the effect of potassium hydroxide on the size of macromolecular coils in aqueous solutions of polyethylene glycol 20000 by the refractometric method, determined the «conformational» polarizability, the mean-square distance between the ends of the macromolecular chain using the Lorentz-Lorentz equation [10, 11].

For all solutions of polyethylene glycol, the mean-square distance between the ends of the macromolecular chain decreases with increasing

concentration of the polymer in the solution (i.e. the macromolecular «coils» coagulate) and stabilize starting from a certain concentration (Graph 9). This result can be explained by the fact that between the «coils» there is a strong interaction, and they penetrate into each other. The presence of KOH in an aqueous solution of polyethylene glycol leads to an increase in the size of macromolecular coils. The initial concentration of stabilization of the size of macromolecules with an increase in the concentration of potassium hydroxide shifts toward higher concentrations. This behavior can be explained by the fact that hydrated potassium ions are attached to the macromolecule, as a result of which the units of the macromolecules seem to repel each other and the penetration of the macromolecular coils into each other is hindered. In addition, hydrated potassium ions and hydroxide ions penetrating into the coils prevent the approach and coagulation of macromolecules. With an increase in the concentration of KOH in the polymer solution, this interaction intensifies.

Structural features of dilute aqueous solutions of polyethylene glycols. The mixtures of PEG (1-5%) with molecular mass of 3000 and 20,000 in an aqueous solution of NaOH (0.1 mol/l) was prepared, the dynamic viscosity and conductivity of which were measured in the temperature range 293-353 K.

The dielectric permittivity was measured by the bridge method on a specially assembled setup. The cell was a capacitor with gold-plated electrodes filled with the test solution. The setup made it possible to measure the electrical capacity and conductivity of the sample at electric field frequencies of 20÷200000 Hz.

The concentration and temperature dependences of the relaxation times of aqueous solutions of polyethylene glycols with different molecular weights of the polymer were studied.

For each solution, Cole-Cole diagrams (graphs of the dependence of the imaginary part of the permittivity on its real part) were constructed, from which the relaxation time of the structures existing in the solutions was found. The relaxation times were used to estimate the sizes (~10 nm) of water-polymer complexes using the Debye formula. We note that the dispersion observed at the considered frequencies, in our opinion, is α -dispersion and is associated with the movement of charges in the electric double layer of the water-polymer complex

under the action of an electric field. To observe this dispersion, a small amount of NaOH (0.1 mol/L) was specially introduced into the studied solutions.

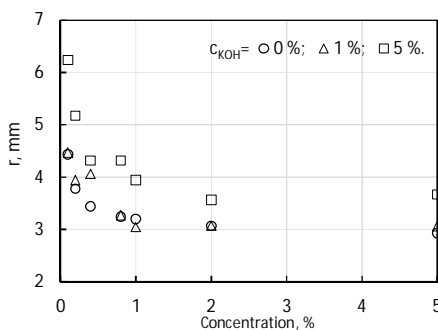
It was found that for both PEG fractions (3000 and 20000) the relaxation time of the structures existing in the solution increases with increasing PEG concentration in the solution, but decreases with increasing temperature. The relaxation time of the relaxers existing in solutions also increases with an increase in the molecular weight of polyethylene glycol.

These results can be explained in terms of the α polarization of supramolecular structures, i.e., hydrated macromolecular coils that exist in the considered dilute aqueous solutions of polyethylene glycols. With an increase in the polymer concentration in the solution, macromolecular coils begin to interact with each other and penetrate each other. As a result, water-polymer complexes are formed - relaxers, consisting of two, three, etc. macromolecular coils that penetrate each other. This is also confirmed by the refractometry data (formulas (25) and (26)), the relaxer sizes (~ 10 nm), estimated by the Debye formula at two, three, etc. times larger than the size of macromolecular coils determined by the refractometric method. With an increase in the molecular weight of the polymer in solution, more and more water molecules are bound by hydrogen bonds with macromolecules, increasing the size of hydrated macromolecular coils. As the temperature rises, these hydrogen bonds are destroyed, which leads to a decrease in the size of the relaxers.

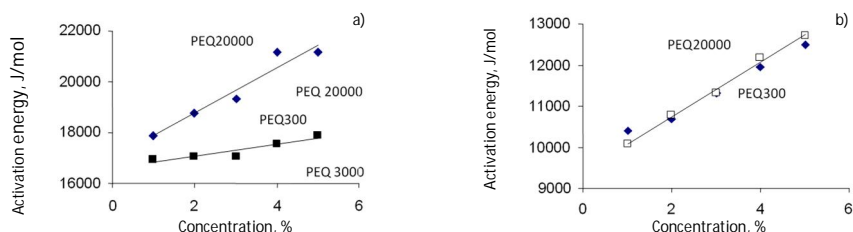
The results obtained by the method of low-frequency dielectric spectroscopy are also confirmed by the rheological method

The temperature dependences of the viscosity and electrical conductivity of prepared PEG solutions were constructed and the Gibbs activation energies of the viscous flow and electrical conductivity were determined from the plots (Graph 10).

As can be seen from the figure, with an increase in the concentration of PEG, both Gibbs energies (the activation energy of the motion of neutral molecules $\Delta G(\eta)$ and charged particles $\Delta G(\sigma)$) increase. An increase in the molecular mass of PEG leads to an increase in the activation energy of the Gibbs of the viscous flow (Graph 10a), while the activation energy of the motion of charged particles does not depend on



Graph 9. Graphs of the dependence of the mean-square distance between the ends of the macromolecular chain on the polymer concentration in aqueous solution of polyethylene glycol 20000 in the presence of potassium hydroxide. $C_{\text{KOH}} = 0\%$ (\circ), 1% (\square), 5% (\triangle).



Graph 10. Dependences of the Gibbs activation energies of viscous flow (a) and electrical conductivity (b) on polymer concentration in dilute aqueous solutions of PEG.

the molecular weight of the PEG and is the same for PEG 3000 and PEG 20000 (Graph 10b). These results can be explained as follows. PEG macromolecules in water are hydrated: free water molecules form hydrogen bonds with oxygen ions in the PEG macromolecular chain. The number of water molecules forming hydrogen bonds increases with increasing both the concentration and molecular mass of the polymer. Hydrated Na^+ and OH^- ions in an aqueous solution, which are responsible for the electrical conductivity of solutions, also bind their hydration shells to macromolecular chains through hydrogen bonds. In connection with the foregoing, the movement of both neutral units (water molecules and macromolecules) and charged ions is impeded with an increase in the concentration of PEG in the solution. The independence of the activation energy of the movement of charged particles from the molecular mass of PEG in solution indicates that hydrated Na^+ and OH^- ions form hydrogen bonds with terminal oxygen ions in the

macromolecular chain, the number of which does not depend on the molecular mass of the polymer, but depends on their concentration.

The fifth chapter presents the results of refractometric determination of ion hydration numbers in dilute aqueous solutions of electrolytes.

Refractometric determination of ion hydration numbers in dilute aqueous solutions of electrolytes.

The electrolyte dissolved in water dissociates into ions due to strong interaction with water molecules. Under the action of the electric field of the ions, the water molecules are reoriented and create hydration shells around the ions, the structure of which differs from the structure in bulk water. Hydration of ions significantly affects the behavior of electrolyte solutions, especially transport properties. It has been found that in dilute solutions, some ions enhance («create structure»), while others decrease («destruction of structure») the structure of water. Both the effects of the ionic structure of water and the effects of direct hydration play an important role in biological processes. Thus, the two-state model of water, due both to the hydration of ions in aqueous electrolyte solutions and to the effects of temperature and pressure in the absence of ions, successfully explains the denaturation of proteins. On the other hand, the passage of sodium and potassium ions through membrane channels is associated with the relative ease of hydration and dehydration of these ions. Electrolytes are also used to stabilize colloidal suspensions to increase the zeta potential of the latter. In this case, the hydration of ions, when the dispersed phase is water, strongly affects the zeta potential of such suspensions.

Hydration numbers, hydration radii and lifetime of water molecules in hydration shells can be determined by various methods based on various properties of electrolyte solutions: spectroscopy (NMR, visible, ultraviolet, infrared - Raman, etc.), diffraction (X-ray, neutron, electron), X-ray absorption, transport (transfer number, ionic conductivity, mobility, viscosity, diffusion, etc.), thermodynamics (enthalpy and entropy, activity, density, compressibility, solubility, vapor pressure, boiling and melting points, etc. etc.), computer simulation (molecular dynamics and Monte Carlo) and other methods (isotope dilution, permittivity, refractive indices, etc.). The values of the hydration

number of a given ion, obtained by different methods, generally differ greatly and rarely agree with each other. In many cases, discrepancies arise from difficulties in interpreting the results or in separating the results according to the constituent ions of the electrolyte. Therefore, the search for new approaches to determining the hydration numbers of ions remains relevant in the light of studying the interaction of ions with an aqueous medium, their influence on the structure of water, and hence on biological processes. The influence of one or another ion on the structural properties of aqueous solutions of water-soluble polymers, in particular, polyethylene glycols, strongly depends on the hydration of the considered ion.

Refraction of solutions carries information on the structure of the solution and on the dissolution of the substance in this solvent. In the work, the hydration numbers of ions in dilute aqueous solutions of some electrolytes were determined by the refractometric method [13, 16, 18, 20-22].

Due to the fact that at optical frequencies, dipoles and ions do not follow changes in the direction of the electric field of the light wave, the main contribution to the polarization of the medium is made by electrons, and in this case, for aqueous solutions of electrolytes (K_iA_j) the Lorentz-Lorentz equation can be applied:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{N_{H_2O}\alpha_{H_2O}}{3} + \frac{N_{K^{+j}}\alpha_{K^{+j}}^*}{3} + \frac{N_{A^{-i}}\alpha_{A^{-i}}^*}{3} + \frac{N_{K_iA_j}\alpha_{K_iA_j}}{3}, \quad (27)$$

where, n the refractive index of the solution, α_{H_2O} , $\alpha_{K^{+j}}^*$, $\alpha_{A^{-i}}^*$, $\alpha_{K_iA_j}$ polarizability of water molecules, hydrated cations K^{+j} of valency $+j$ and anions A^{-i} of valency $-i$, neutral molecules K_iA_j ($K_iA_j \rightarrow iK^{+j} + jA^{-i}$), respectively, N_{H_2O} , $N_{K^{+j}}$, $N_{A^{-i}}$, $N_{K_iA_j}$ the number of free water molecules, cations K^{+j} and anions A^{-i} , neutral molecules K_iA_j in a unit volume solution, respectively. The terms on the right-hand side of equation (27) express the contributions to the total polarization of the solution made by free water molecules not involved in hydration, K^{+j} , A^{-i} ions, and undissociated, neutral K_iA_j molecules, respectively. Taking advantage of the fact that the polarizability of the

hydrated ion can be taken proportional to the cube of the radius of this ion, and the volume of the hydrated ion can be represented as the sum of the volume of the anhydrate ion and the volume of the hydrated shell, the Lorentz-Lorentz equation can be represented as:

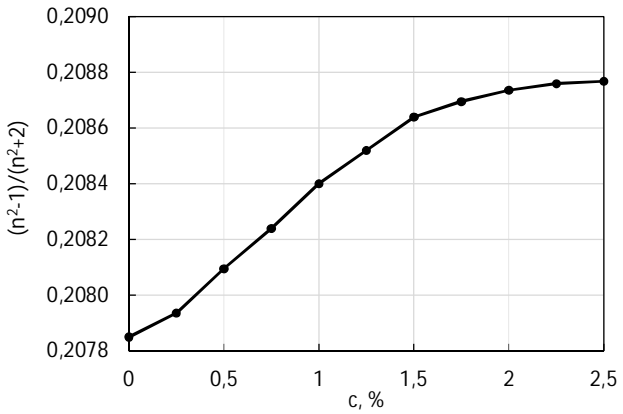
$$\frac{n^2 - 1}{n^2 + 2} = \frac{n_{H_2O}^2 - 1}{n_{H_2O}^2 + 2} + \frac{c\rho N_0 \alpha_{H_2O}}{3M_{K_iA_j}} \left[i \left(\frac{r_{K^{+j}}}{r_{H_2O}} \right)^3 + j \left(\frac{r_{A^{-i}}}{r_{H_2O}} \right)^3 + h_{K^{+j}} + h_{A^{-i}} \right] \quad (28)$$

where, ρ is the density of the solution, N_0 is the Avogadro constant, $M_{K_iA_j}$ is the molar mass K_iA_j , r_{ion} and r_{H_2O} are the radii of a hydrated ion of this type (cation K^{+j} or anion A^{-i}) and water molecules, h_{ion} is the number of hydration of the ion (cation K^{+j} or anion A^{-i}).

Using equation (28), from the plot of the relationship $(n^2 - 1)/(n^2 + 2)$ of the concentration of the electrolyte, the angular coefficient of the graph allows us to determine the sum of the hydration numbers of the cation K^{+j} and the anion A^{-i} in solution at different electrolyte concentrations K_iA_j :

$$h_{K^{+j}} + h_{A^{-i}} = \frac{3M_{K_iA_j} \operatorname{tg} \varphi}{\rho N_0 \alpha_{H_2O}} - i \left(\frac{r_{K^{+j}}}{r_{H_2O}} \right)^3 - j \left(\frac{r_{A^{-i}}}{r_{H_2O}} \right)^3. \quad (29)$$

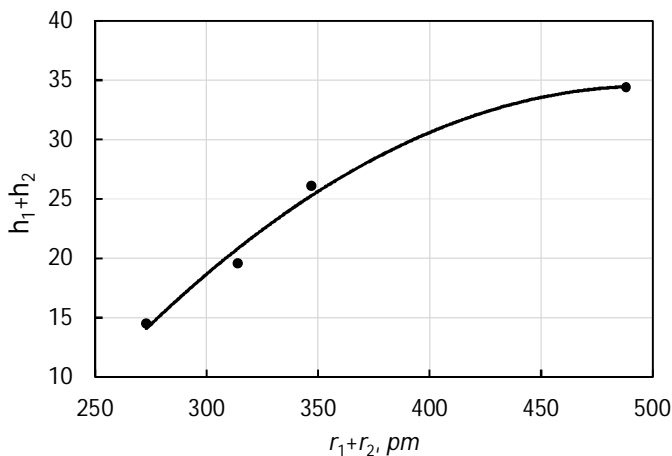
We applied this model to determine the number of ion hydration in dilute aqueous solutions of magnesium sulfate $MgSO_4$ (Graph 11) and potassium salts KOH , KCl , KI , KIO_3 (Graph 12).



Graph 11. The concentration dependence of the ratio $(n^2 - 1)/(n^2 + 2)$ for an aqueous solution of magnesium sulfate

Considering the values of parameters included in the formula (29) taken from the literature, by the angular coefficient of the graph presented in Graph 11, the sum of the hydration numbers of ions Mg^{2+} and SO_4^{2-} in an aqueous solution of magnesium sulfate was determined for the following concentrations: $h_{Mg^{2+}} + h_{SO_4^{2-}} \approx 21.71$ for concentrations $c < 1.5\%$, $tg\varphi = 0.0559$ and $h_{Mg^{2+}} + h_{SO_4^{2-}} \approx 7.46$ for concentrations $1.5\% < c < 2\%$, $tg\varphi = 0.0224$. A comparison of the sum of the hydration numbers of ions Mg^{2+} and SO_4^{2-} and those taken from the literature with those obtained in our work at concentrations $c < 1.5\%$, $tg\varphi = 0.0559$ shows satisfactory agreement: $h_{Mg^{2+}} + h_{SO_4^{2-}} = 16 + 6 = 22$.

Graph 12 shows a plot of the sum of the hydration numbers of potassium ion and OH^- , Cl^- , I^- and IO_3^- anions versus the sum of the radii of the potassium ion and corresponding anions.



Graph 12. Dependence of the sum of hydration numbers of potassium ion and OH^- , Cl^- , I^- and IO_3^- anions on the sum of the radii of potassium ion and corresponding anions.

It can be seen that with increasing anion radii, the sum of ion hydration numbers increases. If the hydration number of potassium ions is assumed to be the same in all cases, then the increase in the sum can be explained by an increase in the surface area of anions with an increase in their radii. Despite the identical charges of all the anions, the

steric factor plays the main role in this case: with increasing radii of the anions new positions arise for placing water molecules on the surface of the anion and the hydration numbers of anions grow in the following sequence: OH^- , Cl^- , I^- and IO_3^- . A satisfactory correlation is observed between our and the literature data.

CONCLUSIONS

1. The thickness of the ordered liquid nanolayer around the nanoparticle in nanofluids was determined by calculating the Van der Waals attraction energy between the solid nanoparticle and the liquid nanolayer. It was revealed that the thickness of the nanolayer does not depend on the radius of the nanoparticle and is determined mainly by the specific interaction between this liquid and the solid nanoparticle through the Hamaker constant, surface tension, and the contact angle in the case when the radius of the nanoparticle is much greater than the thickness of the nanolayer. It was found that the stronger the wetting, the greater the thickness of the ordered liquid nanolayer. The average speed of Brownian motion of nanoparticles in nanofluids is estimated. It has been proven that the heat transfer frequency between liquid molecules is two orders of magnitude higher than the heat transfer frequency between nanoparticles and, therefore, the corresponding contribution of the Brownian motion of nanoparticles to the thermal conductivity of nanofluids can be neglected.

2. A new model of the effective thermal conductivity of nanofluids has been created taking into account the aggregation of nanoparticles and the presence of an ordered liquid nanolayer around the nanoparticle. The predictions of the proposed model are in good agreement with the experimental thermal conductivity data for nanofluids CuO + Water, Al_2O_3 + Water, CuO + Ethylene Glycol, and Al_2O_3 + Ethylene Glycol. It was found that at low nanoparticle concentrations, both aggregation and the presence of a nanolayer make almost identical contributions to the thermal conductivity of nanofluids, but with an increase in the volume fraction of nanoparticles in the base fluid, starting from a concentration of $\varphi = 0.03$, the contribution of aggregation

becomes larger compared to the contribution of the nanolayer.

3. On the basis of experimental data, as well as a mathematical model that takes into account the aggregation of nanoparticles, it was found that the thermal conductivity enhancement of nanofluid at low concentrations of nanoparticles is directly proportional to their volume fraction, thermal conductivity, and inversely proportional to the radius of a nanoparticle.

4. A new model of thermal conductivity of ferrofluids based on the aggregation structure of magnetic nanoparticles under the influence of an external magnetic field has been created. Under external magnetic field, when the interaction energy of this field with a magnetic dipole of a nanoparticle becomes greater than thermal energy, magnetic dipoles begin to line up along the magnetic field, forming chains along this direction, the length of which increases with increasing magnetic field strength. These chains form effective bridges for heat transfer along them. According to the proposed model, the total volume of ferrofluid consists of two parts: a volume with aggregated magnetic nanoparticles (chain clusters) and a volume with non-aggregated, uniformly dispersed nanoparticles. The degree of aggregation of magnetic nanoparticles increases in proportion to the strength of the external magnetic field. The contribution of chain clusters of nanoparticles to the thermal conductivity of ferrofluids depends both on the intensity and on the direction of the magnetic field relative to the temperature gradient: when the direction of the magnetic field parallel to the temperature gradient there is a high increase in thermal conductivity, and when the direction of the magnetic field is perpendicular to the temperature gradient, the magnetic field does not change the thermal conductivity of ferrofluids.

5. For the first time, it was found that microfluids containing microparticles of metal-string complexes dispersed in a liquid have a high thermal conductivity comparable to that of nanofluids. It was experimentally found that the thermal conductivity enhancement at 5% volume fraction of nanoparticles for the Ni₃-water-glycerol system is about 72%, for the Cu-water-glycerin system 53%, and for the Ni₅-

water-glycerin system 47 % compared with the base fluid.

6. It was shown that Ni₃ and Ni₅ microfluids have higher stability than other nanofluids studied, due to the formation of hydrogen bonds of metal-string particle complexes with water molecules, their low density and the appearance colloidal structure. Due to their colloidal structure, microfluids Ni₃ and Ni₅ have thixotropic rheology. A high increase in the thermal conductivity of microfluids is also associated with the monocrystallinity of the used metal-string complexes microparticles. The growth of scattering centers in a polycrystalline metal, i.e., the grain boundaries between monocrystalline units, increases the contribution of residual thermal resistance to the total thermal resistance. The scattering of conduction electrons at the grain boundary leads to a decrease in the thermal conductivity of a polycrystalline metal in comparison with a monocrystalline one. The proposed model of thermal conductivity of nanofluids predicts that a very high increase in thermal conductivity (about 10 times) can be achieved if the metal-string microparticles of the Ni₃ and Ni₅ complexes are replaced by nanoscale ones.

7. It was shown that the reason for the violation of the aggregate stability of a quartz suspension by chemical exposure, when using a reagent developed on the basis of triethanolamine and orthophosphate acid is a decrease in the zeta potential due to the adherence of positively charged triethanolammonium phosphate to a dense layer of counterions in the double electric layer of sand particles. It was revealed that the chemical treatment of a quartz suspension contributes to a significant increase in both the initial fluidization rate and the liquid filtration coefficient. A correction to the Richardson-Zacke equation is proposed, taking into account the aggregation of quartz particles. A model is proposed to explain the filtration properties of treated sand, taking into account the effect of aggregation on the porosity of the medium.

8. Using the Lorentz-Lorenz equation, a number of characteristics of macromolecules in aqueous solutions of polyethylene glycols with different molecular mass (600, 1000, 1500, 3000, 6000, 20,000) are

determined: the mean-square distance between the ends of the macromolecular chain, the segment length and the number of Kuhn segments. It was found that the values of the mean-square distance between the ends of the macromolecular chain are approximately two orders of magnitude smaller than the contour length of the chain, i.e. the macromolecular chain is in the form of a coil. It was revealed that the presence of potassium hydroxide in aqueous solutions of polyethylene glycols complicates the coagulation of macromolecular coils. The initial concentration of coil size stabilization shifts toward higher polymer concentrations with increasing concentration of potassium hydroxide in solution.

9. The intrinsic viscosities, Huggins constants, the parameters of the Mark-Kuhn-Houwink equation, the mean-square distance between the ends of the macromolecular chain and the overlap concentration and activation energy of the viscous flow depending on the temperature and molecular mass of the polymer in the temperature range 293-313K in dilute aqueous solutions of polyethylene glycols of various fractions (1000, 3000, 6000, 8000 and 20,000) were determined by the viscosimetry method. By the values of the exponent of the Mark-Kun-Houwink equation it was found that the PEG macromolecular chains in water take the form of macromolecular coils. It was found that the sizes of macromolecular coils for all the studied solutions increase with increasing molecular mass of PEG and decrease with increasing temperature.

10. It was found that when 0.1 mol/l of sodium hydroxide is added to dilute aqueous solutions of polyethylene glycols, Na^+ ions form bonds with oxygen ions in the macromolecular chain, as a result of which the chain segments, repelled from each other, contribute to the expansion of the coils. It was found that the addition of 0.1 mol/l of NaOH also leads to a neutral interaction of segments of the macromolecular chain with water molecules, i.e. macromolecular coils in dilute PEG aqueous solutions accept an unperturbed conformation, as in theta solvents. The presence of NaOH in aqueous PEG solutions also leads to an increase in the activation energy of the viscous flow, since due to the increase in the size of macromolecular coils their movement

in solutions is hampered. A new approach is proposed for estimating the interaction energy between a macromolecule and solvent molecules per unit volume fraction of the polymer.

11. It was shown that with increasing polymer concentration in the solution, the macromolecular coils interacting with each other begin to penetrate each other. With an increase in the molecular mass of the polymer in solution, more and more water molecules are bound by hydrogen bonds to macromolecules, increasing the size of hydrated macromolecular coils. With increasing temperature, these hydrogen bonds are destroyed, which leads to a decrease in the size of macromolecular coils. It is shown that the dispersion observed at low frequencies of the electric field in aqueous solutions of polyethylene glycols is a α -dispersion and is associated with the movement of charges under an external electric field in the double electric layer of the water-polymer complex. It was found that for dilute aqueous PEG solutions, the relaxation time of structures, existing in the solution increases with increasing both the concentration and molecular mass of the polymer, but decreases with increasing temperature.

12. A new refractometric method is proposed for determining the ion hydration numbers in electrolytes using the Lorentz – Lorenz equation. The hydration numbers of ions in dilute aqueous solutions of magnesium sulfate $MgSO_4$, as well as potassium salts KOH , KCl , KI , KIO_3 estimated by this method are in good agreement with published data determined by other methods.

Author's publications on the subject of the doctor thesis:

1. Abbasov, H.F. Modeling of anisotropic thermal conductivity of ferrofluids // Journal of Dispersion Science and Technology, – 2020, 41 (7), – p.1030-1036.

<https://doi.org/10.1080/01932691.2019.1614040>

2. Suleimanov, B.A., Ismayilov, R.H., Abbasov, H.F. Thermal conductivity of nano- and microfluids with $[Ni_5(\mu_5\text{-pppmda})_4Cl_2]$ metal string complex particles // First Eurasian Conference on Nano-

technology «Nanotech Eurasia – 2019», Baku, Khazar University, Azerbaijan, – 3 – 4 October, – 2019, – p.44.

3. Abbasov, H.F. Determination of nanolayer thickness and effective thermal conductivity of nanofluids // Journal of Dispersion Science and Technology, – 2019, 40 (4), – p. 594-603.
<http://dx.doi.org/10.1080/01932691.2018.1475241>
4. Abbasov, H.F., Masimov, E.A. Interaction of polyethylene glycol macromolecules with water molecules in the presence of sodium hydroxide // XIII International Scientific Conference «Problems of solvation and complexation in solutions», Suzdal, Russia, – 1 – 6 July, 2018, – pp.228-229.
5. Suleimanov, B.A. Thermal-conductivity enhancement of microfluids with $Ni_3(\mu_3\text{-ppza})_4Cl_2$ metal string complex particles / B.A. Suleimanov, H.F. Abbasov, F.F. Valiyev [et al.] // J. Heat Transfer, – 2018, 141 (1), – p. 012404-1-012404-5,
<http://dx.doi.org/10.1115/1.4041554> .
6. Исмаилов, Ф.С., Сулейманов, Б.А., Исмаилов, Р.Г., Матиев, К.И., Аббасов, Х.Ф., Ибаев, З.Д. Химический состав для агрегации песка в нефтяных скважинах // Евразийский патент No 025958, 2017.
7. Abbasov, H.F. Effect of sodium hydroxide on the interactions of polyethylene glycol macromolecules with water molecules // Journal of Polymer Research, – 2017, 24 (8), – p.115-1-115-5.
<http://dx.doi.org/10.1007/s10965-017-1275-7>
8. Suleimanov, B.A. Thermophysical properties of nano- and microfluids with $[Ni_5(\mu_5\text{-pppmda})_4Cl_2]$ metal string complex particles / B.A. Suleimanov, H.F. Abbasov, R.H. Ismayilov [et al.] // Colloids and Surfaces A: Physicochemical and Engineering Aspects, – 2017, 513 (5), – p. 41-50.
<http://dx.doi.org/10.1016/j.colsurfa.2016.11.026>
9. Suleimanov, B.A., Abbasov, H.F. Chemical control of quartz suspensions aggregative stability // Journal of Dispersion Science and

Technology, – 2017, 38 (8), – p.1103-1109.

<http://dx.doi.org/10.1080/01932691.2016.1224189>

10. Аббасов, Х.Ф., Масимов, Э.А. О влиянии гидроксида калия на формирование макромолекулярных клубков в водных растворах полиэтиленгликоля 20000 // VI Всероссийская научная конференция (с международным участием) «Физикохимия процессов переработки полимеров», – Иваново, Россия: – 03 – 07 Октября, – 2016, – с.36.
11. Масимов, Э.А., Аббасов, Х.Ф. Влияние гидроксида калия на формирование макромолекулярных клубков в водных растворах полиэтиленгликоля 20000 // J. of Qafqaz University, – 2016, 4 (1), – p.44-48.
12. Suleimanov, B.A., Abbasov, H.F. Effect of Copper Nanoparticle Aggregation on the Thermal Conductivity of Nanofluids // ISSN 0036-0244, Russian Journal of Physical Chemistry A, – 2016, 90 (2), – pp. 420-428.
<http://dx.doi.org/10.1134/S0036024416020308>
13. Масимов, Э.А., Аббасов, Х.Ф. О рефрактометрическом определении чисел гидратации ионов в разбавленных водных растворах электролитов // Международный журнал прикладных и фундаментальных исследований, – 2015, № 3, – с.181-185.
14. Abbasov, H.F. Conformational Characteristics of Polyethylene Glycol Macromolecules in Aqueous Solutions According to Refractometry Data // ISSN 0036-0244, Russian Journal of Physical Chemistry A, – 2014, 88 (6), – p. 942-945.
<http://dx.doi.org/10.1134/S0036024414060028>
15. Масимов, Э.А., Аббасов, Х.Ф. О конформации макромолекул в водных растворах полиэтиленгликолей // V Всероссийская научная конференция (с международным участием) «Физикохимия процессов переработки полимеров», – Иваново, Россия: – 16 – 19 Сентября, – 2013, – с.29.
16. Masimov, E.A., Abbasov, H.F. Hydration Numbers of Ions in

Aqueous Solutions of KOH, KCl, KI, and KIO₃ According to Refractometric Data // ISSN 0036-0244, Russian Journal of Physical Chemistry A, – 2013, 87 (8), – pp. 1430-1432.

<http://dx.doi.org/10.1134/S0036024413080153>

17. Məsimov, E.Ə., Abbasov, H.F., İbrahimov, N.Ə., Sultanova, X.B. Polietilenqlikolun sulu məhlullarında makromolekulların xarakterik parametrlərinin refraktometrik təyini // «Fizikanın müasir problemləri» VI Respublika konfransı, – Bakı, BDU-nun Fizika İnstitutu: – 14 – 15 dekabr, – 2012, – s. 188-192.
18. Masimov, E.A., Abbasov, H.F. Refractometry Determination of the Hydration Number of Ions in Diluted Aqueous Solutions of Magnesium Sulfate // ISSN 0036-0244, Russian Journal of Physical Chemistry A, – 2012, 86 (3), – pp. 399-401.
<http://dx.doi.org/10.1134/S003602441203020X>
19. Масимов, Э.А., Аббасов, Х.Ф. Рефрактометрическое определение характеристических параметров макромолекул в водных растворах полиэтиленгликоля // IV Съезд Биофизиков, – Нижний Новгород, Россия: – 20 – 26 Августа, – 2012, – с. 153.
20. Масимов, Э.А., Аббасов, Х.Ф. Рефрактометрическое определение числа гидратации ионов в водных растворах некоторых солей калия // VII Международная научная конференция «Кинетика и механизм кристаллизации. Кристаллизация и материалы нового поколения», – Иваново, Россия: – 25 – 28 Сентября, – 2012, – с.72-73.
21. Məsimov, E.Ə., Abbasov, H.F. Aqar gelinin kalium hidrosidin duru sulu məhlulunda ionların hidratlaşmasına təsiri /Azerbaijan Journal of Physics, «Fizika», – 2011, Vol. XVII, № 2, Series: Az. – p. 26-29.
22. Масимов, Э.А., Аббасов, Х.Ф. О Рефрактометрическом определении числа гидратации ионов в разбавленных водных растворах сульфата магния // XI Международная конференция «Проблемы сольватации и комплексообразования в растворах», – Иваново, Россия: – 10 – 14 Октября, – 2011, – с. 118.

23. Abbasov, H.F. On interaction of macromolecules with the molecules of solvent in the system polyethylene glycol-water // Azerbaijan Journal of Physics, «Fizika», –2010. Vol. XVI, №3-4, Series: En, – p. 92-93
24. Масимов, Э.А., Аббасов, Х.Ф. О конформационной поляризуемости макромолекул в разбавленных водных растворах полиэтиленгликолей // VI Международная научная конференция «Кинетика и механизм кристаллизации. Самоорганизация при фазообразовании», – Иваново, Россия: – 21 – 24 Сентября, – 2010, – с.253.
25. Məsimov, E.Ə., Abbasov, H.F., İbrahimov, N.Ə. Polietilenqlikol makromolekullarının konformasiya polyarizasiyasının bəzi aspektləri // – Bakı: J of Qafqaz University, 2010. 1 (29), – p.27-29.
26. Məsimov, E.Ə., Abbasov, H.F., Hübətov, Ş.Ə. Aqar gelinin spektral xassələrinə polietilenqlikolun və kalium hidroksidin təsiri // «Fizikanın müasir problemləri» IV Respublika konfransı, – Bakı, BDU-nun Fizika Problemləri İnstitutu: – 24 – 25 dekabr, – s. 109-111.
27. Masimov, E.A., Abbasov, H.F. About structural changes in diluted aqueous solutions of polyethyleneglycols // XVII International conference on chemical thermodynamics in Russia, – Kazan, Russia: – 29 June – 3 July, – 2009, – p. 187.
28. Məsimov, E.Ə., Abbasov, H.F., Həsənov, H.Ş. Polietilenqlikolun duru sulu məhlullarının struktur xüsusiyyətləri // –Bakı: J. of Qafqaz University, – 2008. 21, – p.73-76.
29. Масимов, Э.А., Аббасов, Х.Ф. Некоторые Рефракционные свойства разбавленных водных растворов полиэтиленгликолей // II Республиканская конференция, – Баку, БГУ: – 28 – 29 ноября, – 2008, – с. 113.
30. Масимов, Э.А., Аббасов, Х.Ф. Структурные изменения разбавленных водных растворов полиэтиленгликоля // XV Всероссийская конференция «Структура и динамика молекулярных систем», – Яльчик: – 30 июня – 4 июля, – 2008, – с.3.

- 31.** Məsimov, E.Ə., Abbasov H.F. Polietilenqlikolun sulu məhlullarının struktur xüsusiyyətlərinin alçaqtezlikli dielektometriya üsulu ilə tədqiqi // – Bakı: AMEA-nın «Xəbərlər» jurnalı, – 2008. №3, – s.79-92.
- 32.** Məsimov, E.Ə., Abbasov, H.F. Sulu məhlulların struktur xüsusiyyətlərinin alçaqtezlikli dielektrik spektroskopiya metodu ilə öyrənilməsi // – Bakı: Bakı Universitetinin xəbərləri, Fizika-riyaziyyat elmləri seriyası, – 2007, №2, – s.109-127.

The defense will be held on **23 December 2022** at **15⁰⁰** at the meeting of the Dissertation council BED 2.19 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at Baku State University

Address: AZ 1148, Baku, Z. Khalilov str. 23, Main campus, Baku State University

Dissertation is accessible at the Baku State University's Library.

Electronic versions of dissertation and its abstract are available on the official website of the Baku State University.

Abstract was sent to the required addresses on **22 November 2022**.

Signed for print: **18.11.2022**
Paper format: **A5 (60' 90 1/16)**
Volume: **78 936**
Number of hard copies: **20**