

Studies of the mechanism of polyethylene oxide (PEO)
adsorption on the surface of Al₂O₃ in the presence of sodium
dodecylsulfate (SDS)

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An influence of polyethylene oxide (PEO) with sodium dodecylsulfate (SDS) interaction on the adsorption behavior of the polymer at Al₂O₃/solution interface was examined. Observed increase of the PEO adsorption in the presence of SDS resulted from a polymer-surfactant complex formation. The presence of the surfactant influences also on the structure of the adsorbed polymer layers. This effect was proved by viscometry measurements that allow calculate thickness of the adsorbed layer of the polymer on the surface of Al₂O₃ in the presence and the absence of SDS.

1. INTRODUCTION

Study of the adsorption mechanisms of polymers on solids is of the great meaning for understanding many processes running in the environment and industry. As examples may be pharmaceuticals, food, cosmetics or paper industry where polymers are applied as emulsifiers and stabilizers of colloid systems. Information, concerning behavior of such systems demands numerous fundamental investigations since precise and compact description of the adsorption mechanism of macromolecular substances, theoretical and experimental, is still not satisfactory [1,2]. Important knowledge of the interactions between the surface of the solid and macromolecule may be obtained from adsorption, electrochemical and calorimetric measurements carried on in well-chosen conditions. Performing these experiments one must in mind that usually a molecular weight of the polymers is not defined precisely so

some complicated techniques must be used to obtain its narrow molecular fraction. For this reason the adsorption of macromolecules runs in a different manner than the particles of small molecular weights. In adsorbed polymer particles one can distinguish three types of structures formed by polymer chain segments namely trains, loops and tails. Adsorbing macromolecule may characterize many conformations in bulk of the solution and at the solid-solution interface. Depending on such parameters as: type of the solvent, molecular weight and structure of the polymer as well as free adsorption energy of a separate segment, the macromolecule may form various number and length of trains, loops and tails. Thus, structural changes of a macromolecule are inseparable elements of its adsorption process. Introduction of a surfactant to a polymer solution-solid system may markedly influence the adsorption properties of the polymer. This problem is very interesting also from practical point of view because of increasing application of both, polymers and surfactant, in mineral processing [3-8]. Unfortunately literature data concerning such systems are scarce. In this paper an influence of SDS on adsorption behavior of polyethylene oxide on Al_2O_3 was investigated. Alumina was chosen because it's high durability, minute solutions, and well-defined oxide-solution interface. It allows perform measurements in broad pH range and is often used in many industrial processes. The polyethylene oxide is widely used as stabilizer or flocculant whereas SDS is one of the essential components of surface-active substances applied at the industry.

2. EXPERIMENTAL

As a nonionic polymer, polyethylene oxide (PEO) of molecular weights 100,000 and 300,000 delivered by „Aldrich” was used in experiments.

Sodium dodecylsulphate (SDS) $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ was applied as a surfactant.

Alumina, Al_2O_3 produced by “Merck” was used as a solid. Specific surface of Al_2O_3 determined by BET method was $62.4 \text{ m}^2/\text{g}$.

All sorption measurements were performed in NaCl solution of the concentration of $1 \times 10^{-3} \text{ M}$ in 25°C .

Adsorption of polyethylene oxide on the surface of Al_2O_3 without and with previously adsorbed SDS was determined turbidimetrically with application of the reaction of PEO with tannic acid [9]. Depending on the concentration of PEO the reaction gave solutions of various degree of turbidity that was measured after one hour at a wavelength of 600 nm using computerized SPEKORD M42 spectrophotometer with M500 program. Adsorbed amount of the polymer was equal the difference between its concentration in the solution before and after the adsorption process.

Thickness of adsorption layers of PEG was determined by measurement of suspension viscosity without and with adsorbed polymer. A series of the

alumina oxide suspensions of various solid volume fraction (ϕ) was shaken during 24 h then, their viscosity (η) and viscosity of parent solutions (η_0) were measured. Thus (η/η_0) dependence as a function of (ϕ) was obtained. In the same way the viscosity measurements were done for suspension with the polymer adsorbed. A thickness of the adsorbed layer was determined from comparison of ϕ values on Al_2O_3 in the presence and absence of the polymer layer [10].

An increase of the particle radius of the solid after adsorption of the polymer was equal to the thickness of the adsorbed polymer layer. As a consequence it gave higher volume fraction ϕ of dispersed solid phase, that is related with suspension viscosity by Einstein equation [11].

$$\eta/\eta_0 = 1 + k\phi$$

where: η -suspension viscosity, η_0 -viscosity of liquid phase (parent solution), k - Einstein coefficient that depends on shape and size of the dispersed solid.

In the same manner the thickness of the polymer adsorption layer with added SDS was measured. All thickness measurements of the adsorbed polymer layer were taken for volume fraction of Al_2O_3 (Φ_0) equal 0.0126.

A viscosity of solutions and suspensions was measured using CVO 50 rotation rheometer produced by Bohlin Instruments.

Mutual polymer-surfactant interactions were determined from surface tension changes of water solutions containing constant amount of the polymer (1×10^{-3} g/ml) and various concentrations of the surfactant. (SDS). Surface tension of PEO-SDS system was measured with thermostatic stalagmometer using "free drop" method in 25 °C [12,13].

3. RESULTS AND DISCUSSION

To analyze influence of SDS on the adsorption properties of PEO at oxide-solution interface one must earlier examine mutual interactions of the polymer-surfactant system in their water solution.

Surface tension of water solution of the surfactant in the presence of the polymer may demonstrate much lower value in comparison to that of water solution of the pure surfactant. Observed differences depends not only on the types of the polymer and surfactant but also their concentrations. Usually measurements of mutual polymer-surfactant interactions in water solutions are performed at the constant concentration of the polymer and various concentrations of the surfactant. This concentration of the surfactant, where surface tension of polymer-surfactant mixed solution starts to differ markedly from that of pure surfactant solution is called first point of transition. Such point proves polymer-surfactant complex formation [4, 6, 14].

Results of surface tension (γ) measurements of pure solutions of SDS and PEO as well as PEO-SDS in 0.1 M solution of NaCl are presented on Figures 1 to 3.

Critical micelle concentration (cmc), determined for SDS from obtained dependencies, was $1.4 \cdot 10^{-3}$ M (Figure 1). Measurements of the surface tension of the polymer solutions proved the lack of surface activity of PEO in the whole-examined concentration range.

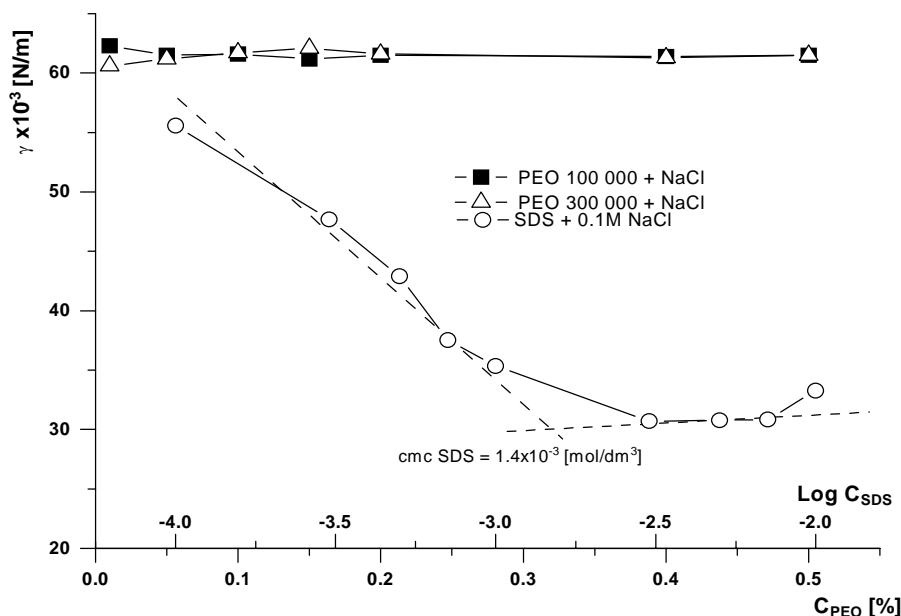


Fig. 1. Surface tension of SDS and PEO of various molecular weight as a function of their concentration in 0.1M NaCl solution

Figures 2 and 3 illustrate the changes of the surface tensions (γ) of SDS and SDS-PEO system for PEO of molecular weight 100,000 and 300,000 as a function of the surfactant concentration. In comparison to pure solutions of SDS a marked lowering of surface tension was observed for mixed solutions PEO-SDS, for both molecular weights of PEO. Such behavior suggests the formation of polymer-surfactant complexes in the system. As can be seen from mentioned figures, PEO-SDS complex formation starts at SDS concentrations lower than 1×10^{-4} M, irrespective of molecular weight and the concentration of the polymer. Such results prove strong mutual interactions between sodium dodecylsulfate and polyethylene oxide. Additional evidence for PEO-SDS complexes formation is the fact that plateau in the presence of the polymer starts at lower concentration of SDS than for pure surfactant.

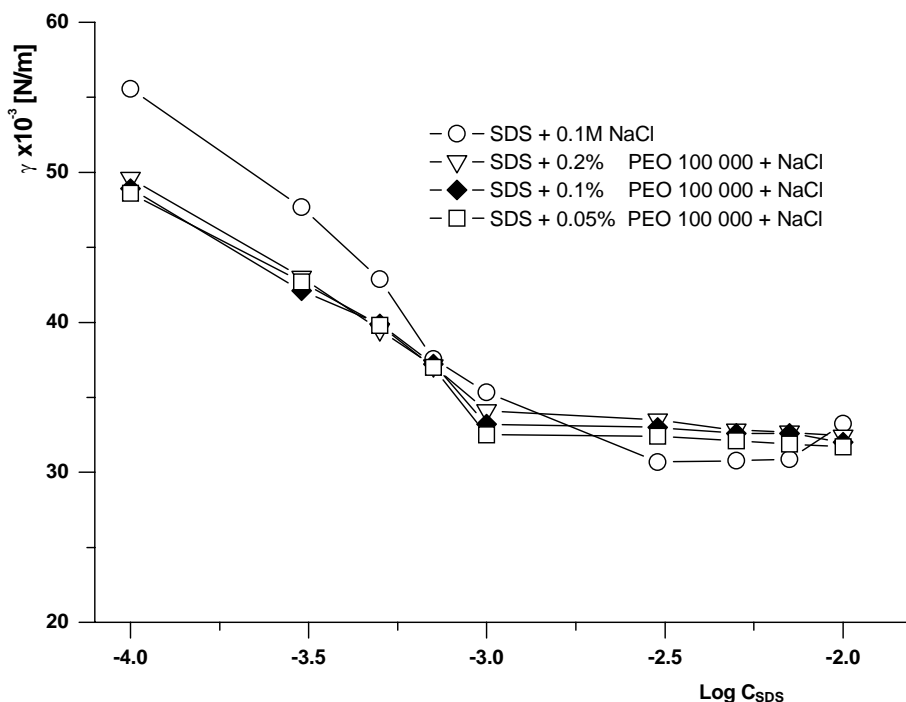


Fig. 2. Surface tension of SDS-PEO system as a function of SDS concentration ($C_{\text{NaCl}} = 0.1\text{M}$).

Considering PEO-SDS interactions in a solution, the adsorption measurements of the polymer from its pure solutions and mixed PEO- SDS solutions on Al_2O_3 surface were performed. Obtained results allowed estimate the adsorption activity of polymer-surfactant complexes existing in the solution.

Figure 4 presents adsorption isotherms obtained for pure solutions of PEO of molecular weights 100,000 and 300,000 whereas Figure 6 demonstrates an influence of the surfactant on the PEO adsorption on the surface of Al_2O_3 .

As can be seen from Figure 4 adsorptive saturation of Al_2O_3 surface was not achieved in studied concentration range of the system. Such plot of the isotherms may be caused by higher than one polydispersity index (W_p), of applied polymers. Where W_p is defined as the ratio weight average of $W_p = M_w/M_n$ molecular weight M_w to number average molecular weight M_n . Gradual increase of the adsorbed amount of the polymer does not arise from the increase of the polymer concentration but rather from the increase of the absolute number of long polymer chains. Magnitude of the adsorption depends on absolute number of big particles which adsorbing preferentially remove smaller ones from the surface [15-17].

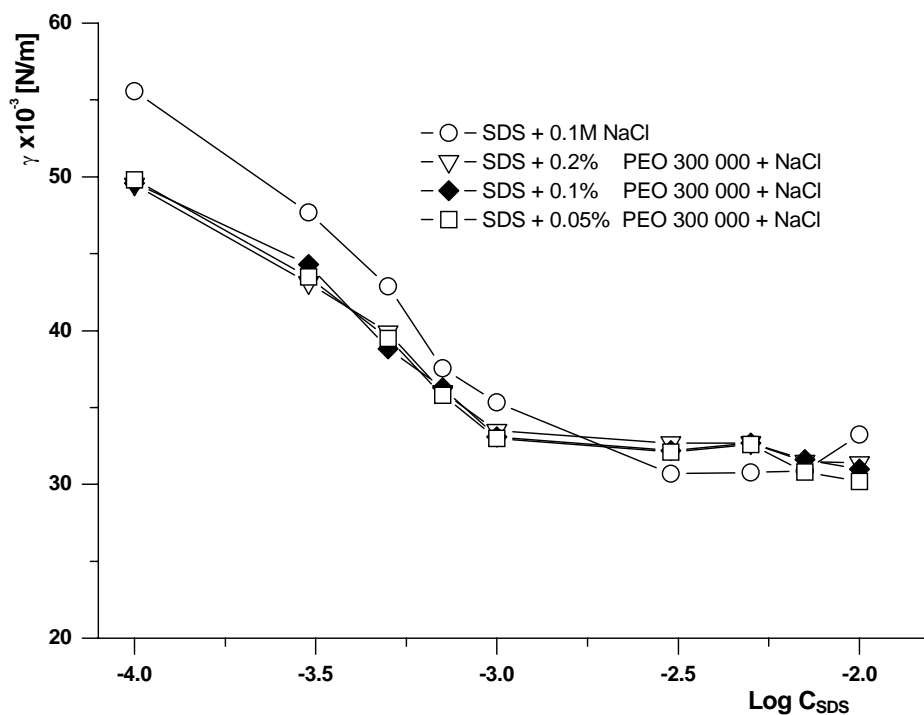


Fig. 3. Surface tension of SDS-PEO system as a function of SDS concentration ($C_{\text{NaCl}} = 0.1\text{M}$)

From a comparison of the dependencies presented on Figure 4 one can see that an increase of molecular weight of PEO gives distinct increase of the polymer adsorption. This increase is produced by higher affinity of big macromolecules, having more functional groups, than smaller ones to the surface of the solid, as well as appearance of various structures during adsorption of such chains at the solid-solution interface. That is because bonding of the macromolecule with the surface of the solid runs by small number of all existing segments presented in the macromolecule. According to this number of segments of the polymer chain, that interacts with the surface of the solid may be the same for different molecular weights, while total adsorbed amount of the polymer will be greater for its higher molecular weight [18-20]. In such case, number of segments of polymer chain, being at the interface as loops and tails will be simply higher. An influence of the molecular weight on the adsorbed amount of the polymer is presented on Figure 5.

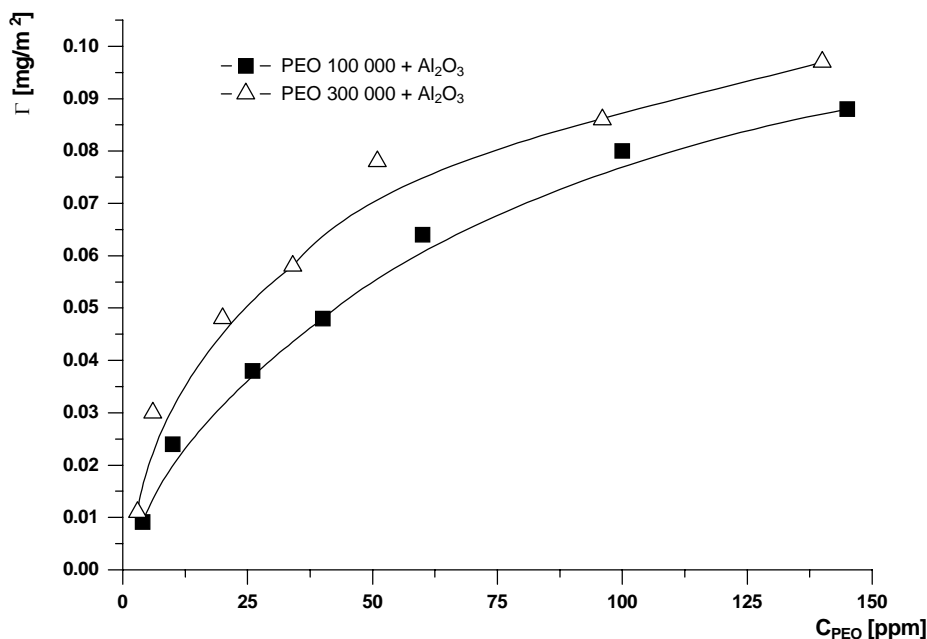


Fig. 4. Adsorption isotherm of PEO of various molecular weights on the surface of Al_2O_3 as a function of the equilibrium concentration of the polymer in the NaCl solution ($C_{NaCl} = 10^{-3} M/dm^3$).

The result is that the conformation of the chain with high number of loops and tails should give thicker adsorption layer, so does the increase of the polymer molecular weight. Results presented in Table 1. confirm such hypothesis. Obtained data reveal an increase of thickness of the adsorbed layer of the polymer with increasing of its molecular weight.

Figure 6 illustrates the influence of the surfactant on magnitude of the polymer adsorption in studied systems. As can be seen the adsorption of polyethylene oxide on the surface of Al_2O_3 increases in the presence of SDS.

This effect is probably connected with the formation of polymer-surfactant complexes. At the interface, the concentration of polymer and surfactant increases in comparison to bulk of the solution. In such place the conditions for PEO-SDS interactions are more favorable and formed complexes follow distinct increase of the polymer adsorption. Another important factor, influencing mutual polymer-surfactant interactions may be caused by changes of the macromolecule conformation in this area. Macromolecules at the solid surface vicinity may increase their linear dimensions (polymer coils may spread due to interaction of the oxide surface) that increases possibility of their interactions with surfactants.

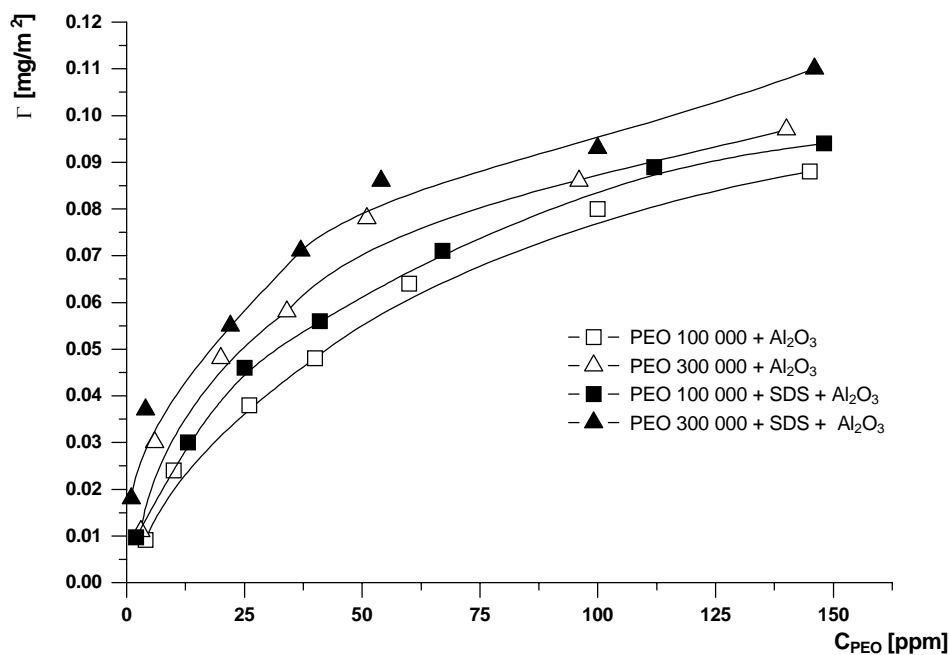


Fig. 6. Adsorption isotherm of PEO of various molecular weights on the surface of Al_2O_3 with and without SDS ($C_{SDS} = 10^{-3} M/dm^3$) as a function of the equilibrium concentration of the polymer in the NaCl solution ($C_{NaCl} = 10^{-3} M/dm^3$)

(A)

(B)

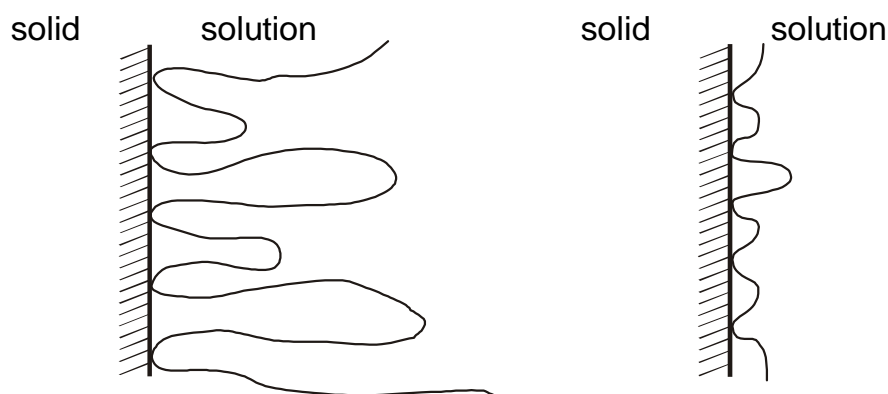


Fig. 5. Schematic presentation of the influence of the polymer chain length (molecular weight) on amount of adsorbed polymer: (A) big molecular weight – conformation with numerous loops and tails – high adsorption, (B) small molecular weight – flat conformation with dominating train structures – small adsorption

Tab. 1. Thickness of the adsorption layer of the polyethylene glycol on the surface of Al_2O_3 from the pure solutions of the polymer and mixed PEO-SDS ones

M_{cz} PEO	C_{PEO} [ppm]	δ [nm]	Γ [mg/m^2]	δ [nm] PEO-SDS	Γ [mg/m^2] PEO-SDS
100 000	100	11.1	0.08	12	0.089
300 000	100	12.6	0.086	13.5	0.093

Supplementary to adsorption measurements, that may confirm surfactant-polymer interactions in the discussed system, may be measurements of the thickness (δ) of adsorbed polymer layer without and with presence of the surfactant. Respective data are listed in Table 1.

Introduction of the surfactant to Al_2O_3 – PEO system results in the increase of the thickness of the polymer adsorption layer that may originate from the increase of PEO adsorption. It should be assumed that such increase of δ is probably caused chiefly by formation of PEO-SDS complexes at the interface. Occurring PEO-SDS interactions change structure of the macromolecules at the oxide interface as well as in the bulk of the solution. The macromolecules increase their linear dimensions that follow increase of its adsorption affinity and increase a thickness of the polymer layer.

4. CONCLUSIONS

Results of adsorption and viscometry measurements allowed formulate following conclusions:

- SDS presence markedly influenced amount of adsorbed PEO on the surface of Al_2O_3 . The increase of the polymer adsorption is connected with formation of polymer-surfactant complexes in water solution of PEO and SDS. The same complexes are formed also on the surface of Al_2O_3 .
- Polymer –surfactant interactions lead to the change of the structure of macromolecule in the solution and at the interface alike.
- Presence of the surfactant results in a certain increase of the thickness of the adsorbed polymer layers on the surface of Al_2O_3 .
- Molecular weight of the polymer, its concentration and size of the coil are main parameters influencing mutual PEO-SDS interactions.

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CURRICULA VITAE



Professor Stanisław Chibowski was born on 27th of September 1946. After graduation he studied chemistry at Maria Curie-Skłodowska University in Lublin. In 1971 obtained M. Sc. title and was employed in Agrophysics Institute of Polish Academy of Science in Lublin. Four months later in February 1972 started to work as technical assistant in freshly organized Department of Radiochemistry and Application of Radioisotopes at Faculty of Mathematics-Physics and Chemistry of Maria Curie-Skłodowska University under professor Jerzy Szczyca. In 1974 was promoted to scientific assistant post. In 1980 presented thesis entitled "Radiochemical Examinations of Polymer and Surfactant Macromolecules at the Surface of Calcium Carbonate". Studies on adsorption of macromolecules in fine dispersed solid – polymer solution systems resulted in many papers and habilitation "Studies on Adsorption Mechanism of Some Polymer Macromolecules at Solid-Water Solution Interface / Surface Conformations" presented in November 1990. In 1995 was appointed to an assistant professor post on Faculty of Chemistry, Maria Curie-Skłodowska University. In May 2002 was nominated associated professor. Scientific activity of professor comprises: adsorption mechanism and surface conformations of polymer substances at solid-polymer solution interface, structure of the electric double layer in the presence of polymers, stability of water

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suspensions in the presence of macromolecules, studies of natural isotopes migration in the environment (soils, water, alluvial and bottom sediments, plants) influence of soil minerals on the adsorption and accumulation of radionuclides and heavy metals in surface layer of soils and bottom sediments of surface waters and transfer of radioactive elements from soil to plants. Professor's scientific output consists of 125 papers. Many of them were published in famous journals with high impact factor from Philadelphia List. In the years 1991-2001 his papers were cited nearly 80 times. Professor was conferring three doctoral theses. He obtained several grants from Polish Scientific Studies Committee (KBN) and grant from International Atom Energy Agency (IAEA-Vienna). Since 1999 is head of Department of Radiochemistry and Colloid Chemistry, Faculty of Chemistry at Maria Curie-Skłodowska University, Vice-dean of the Faculty in the years 1996-2002. For term 2002-2005 elected Prorektor of Maria Curie-Skłodowska University. Professor Stanisław Chibowski is a member of Editorial board of "Physicochemical Problems of Mineral Processing" Commission of Nuclear Chemistry, Polish National Atom Agency and Editorial Board of periodical Polish-Ukrainian conferences "Theoretical and Experimental Studies of Interfacial Phenomena and Their Technological Applications". Professor Chibowski is a member of Polish Chemical Society and Lublin Scientific Society.



Dr Małgorzata Paszkiewicz was born in Zwierzyniec in 1965. In 1983 she was graduated from secondary school in Biłgoraj. In the same year she began studies on Faculty of Chemistry at Maria Curie-Skłodowska University in Lublin. She completed her studies in 1988 presenting final work entitled "*Adsorption of binary solutions of some non-electrolytes on porous aluminum oxides*" written under prof. Jarosław Ościk supervision. In 1988 started to work as a trainee in Central Laboratory of Maria Curie-Skłodowska University and in November the same year was engaged in Department of Radiochemistry and Colloid Chemistry, Faculty of Chemistry where she is working as senior specialist. In March 1998 she presented thesis on "*Studies on the influence of functional groups of macromolecules on their conformation at solid-water solution interface*" prepared under prof. Stanisław Chibowski supervision. Małgorzata Paszkiewicz is co-author of nine papers. All of them comprise problems of interactions in the systems of non-soluble metal oxides-polymer solution and behavior of these systems in the presence of surfactants. Results of her work were presented at several scientific conferences in Poland and abroad. At present Małgorzata Paszkiewicz continues studies on the aforementioned system with application of potentiometric titrations, microcalorimetric, spectrophotometric and visosimetric measurements.