



Influence of the solid type on the adsorption mechanism of nonionic polymers in the metal oxide/water solution system—temperature effect



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ARTICLE INFO

Article history:

Received 18 April 2013

Received in revised form 14 June 2013

Accepted 15 June 2013

Available online 24 June 2013

Keywords:

Adsorbent pore size

Structure of polymer film

Polyethylene glycol

Polyvinyl alcohol

Polymer adsorption

Macromolecule conformation

ABSTRACT

The main purpose of the study was to determine the effect of adsorbent type (surface characteristics and pore size) on nonionic polymers adsorption mechanism on the solid surface in the temperature range 15–40 °C. Polyethylene glycol (PEG) and polyvinyl alcohol (PVA) were used in the experiments as adsorbates. The following metal oxides were applied: aluminum (III) oxide, silicon (IV) oxide, zirconium (IV) oxide and controlled porosity glass (CPG). Polymer adsorption mechanism and structure of its adsorption layer at the metal oxide–aqueous solution interface were proposed based on the data obtained from the techniques: spectrophotometry, viscometry, microelectrophoresis and potentiometric titration. They allowed the determination of the amount of adsorbed polymer, the linear dimensions of polymer chains in the solution, the thickness of the polymer adsorption layer, the free energy of polymer adsorption and the surface charge density of the adsorbent in the absence and presence of PEG and PVA. It was indicated that the polymer adsorption on the metal oxide surface increases with the rise of temperature. It is caused by conformational changes of adsorbing macromolecules expressed in the increase of linear dimension of polymer chain. Such specific conformation of the macromolecular compound influences the structure of its adsorption layer. Both PEG (containing only hydroxyl groups) and PVA (containing 2% of acetate groups besides hydroxyl ones) show the smallest adsorption on the silica surface. In the case of the other examined oxides, polymers demonstrate different behavior. PEG adsorption is the greatest on the CPG surface, whereas PVA is the highest on the zirconia surface. It can be caused by various pore sizes of the applied metal oxides whose adsorbing PEG and PVA chains are able to penetrate or not (depending on a macromolecule diameter).

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1. Introduction

The specific conformation of polymeric chains adsorbed on the surface of colloidal particle is essential for stability of such a system [1–4]. The adsorption process of various substances (low molecular and macromolecular) [5,6] is essential for many practical applications. Thus, the basic research concerning the adsorption of polymeric substances at the solid–liquid interface is very important due to wide usage of such systems in many fields of human activity. The most important of them are as follows: production of cosmetics, pharmaceuticals, paint, paper, food processing, drinking water purification, wastewater treatment and oil recovery [7–11].

The arrangement of polymeric macromolecules in the adsorption layer is a result of type and strength of interactions between the solid active sites and the polymer segments. Two opposite effects are responsible for the processes occurring in the solid–polymer solution system. The first one is the attraction between the polymer segments and the solid surface groups, which is the driving force of adsorption. On the other hand, the entropy effect opposes adsorption.

As a result, these two competitive effects determine the conformation of polymer chains in the adsorption layer.

The adsorption process in the solid–solution systems depends on many parameters related to nature of solid surface, polymer type and solution conditions. The most important factors influencing the adsorption process of macromolecules on the metal oxide surface are the following: polymer characteristics—its molecular weight, concentration, polydispersity and possibility of ionization of polymer functional groups; solid properties—surface charge density (pH_{pzc} —point of zero charge), zeta potential (pH_{iep} —isoelectric point), its purity, size of adsorbent particles and their porosity; solution conditions—pH, ionic strength and temperature.

One can influence on the interaction between the polymer segments and the solvent molecules (changing the macromolecule conformation) by temperature increase [1]. In most cases, the temperature rise improves the solvent quality: the polymer segment–solvent molecule interactions are more favorable than those of the segment–segment and solvent–solvent ones. As a consequence, the development of polymer coils and the increase of macromolecule linear dimensions in the solution occur. Undoubtedly, this stretched conformation of the polymeric chains in the solution affects the mechanism of their adsorption on the solid surface. Therefore, the effective control of suspension stability

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can be accomplished by the appropriate temperature adjustment, without changing any other parameters in the colloidal system. Although temperature is a very important factor for stability of solid suspension in the polymer presence, the world literature reports are scarce concerning this problem [12].

Thus, the main purpose of the present study is the determination of temperature impact in the range 15–40 °C on the conformation of polyethylene glycol (PEG) and polyvinyl alcohol (PVA) in the metal oxide water suspension.

The applied adsorbents (ZrO₂, Al₂O₃, SiO₂ and controlled porosity glass [CPG]) have well-defined physicochemical properties, i.e. the specific surface area, pore size and solubility. Besides, they are the subject of model research, and their properties are very well documented in the literature [13,14]. On the other hand, the chosen polymers are widely used in many industrial branches as effective stabilizers and flocculants of technological systems. For this reason, their certain quantities may be found in the industrial wastewaters. Additionally, technological operations are often carried out at different temperatures. Thus, the presented results may contribute to the development of effective methods of water purification from polymeric impurities by the use of mineral adsorbents.

The studies concerning each of the adsorbent separately have already been published [15–18]. In this paper, they are just collected. This allowed the comparison of the adsorption behavior of applied polymers on the surface of various solids as a function of temperature.

2. Experimental

In the experiments, four metal oxides – aluminum (III) oxide (Merck); alumina, silicon (IV) oxide (Merck); silica, zirconium (IV) oxide (Aldrich); zirconia and controlled porosity glass (CPG) – were applied. CPG was prepared using Vycor glass according to the procedure described elsewhere [19,20]. This solid has the following percentage composition: SiO₂ 55%, B₂O₃ 35% and Na₂O 10%. All adsorbents were washed before experiments to achieve the supernatant conductivity of less than 2 μS/cm. The physicochemical characteristics of the applied solids is given in Table 1. Their specific surface areas and mean pore diameters were determined by the BET method using the Accelerated Surface Area and Porosimetry apparatus (Micromeritics Instruments), whereas the average grain sizes were obtained from the dynamic light scattering technique using Zetasizer 3000 (Malvern Instruments). The values of pH_{pzc} (pzc – point of zero charge) were obtained from potentiometric titrations. Three types of active groups are present on the adsorbent surface: neutral –Me–OH, positive –Me–OH₂⁺ and negative –Me–O[–] (Me – metal atom). At pH_{pzc}, the numbers of negatively and positively charged groups equal one another. As a result, the solid surface is electrically neutral.

The samples of polyethylene glycol–PEG (Fluka), with the weight average molecular weight (M_w) equaled 2000, and polyvinyl alcohol –PVA (Fluka), with M_w 22,000, were used in the study. Both polymers are classified as nonionic ones.

PEG functional groups do not undergo dissociation. The molecular formula of PEG is as follows: HO–CH₂–(CH₂–O–CH₂)_n–CH₂–OH. As can be seen, its macromolecules contain the hydroxyl groups at the end of their chains and oxygen atoms belonging to the ether groups.

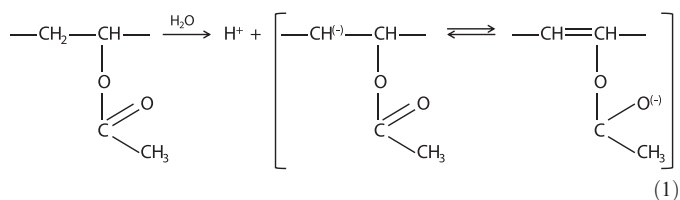
Thus, the hydrogen bridges are responsible for PEG adsorption on the metal oxides surface. The possible ways of hydrogen bridges formation in the adsorbent–PEG system are presented in Fig. 1. The

Table 1
Characteristics of adsorbents.

Adsorbent	Specific surface area (BET) [m ² /g]	Mean pore diameter [nm]	Pore volume [cm ³ /g]	Mean grain diameter [nm]	pH _{pzc} at 25 °C
ZrO ₂	4.9	6.7	0.009	226	7.0
Al ₂ O ₃	155	6.1	0.257	470	8.0
CPG	58.4	72.4	1.059	304	7.0
SiO ₂	326	13.6	1.132	350	<3.0

electrostatic interactions practically have no impact on the PEG adsorption.

Polyvinyl alcohol used in the experiments was characterized by the degree of hydrolysis 97.5%. It means that its macromolecules contain besides hydroxyl groups (–OH) some acetate ones (–CO(COCH₃)). These groups are created in the production process of PVA as a result of incomplete hydrolysis of polyvinyl acetate. Thus, its macromolecules contain 2.5% acetate groups. The C–H bonds in α position in relation to the acetate groups possess acidic properties. The proton from –CH₂– segment, adjacent to the segment containing acetate groups, undergoes dissociation. The formed electric charge is concentrated on carbonyl oxygen of the acetate group. In this way, the acetate groups in the PVA macromolecules gain negative charge according to the reaction:



Thus, PVA macromolecules bond with the adsorbent surface not only through hydrogen bridges but also due to the electrostatic attraction between negatively charged polymer chains and positively charged solid surface (at pH < pH_{pzc}).

Adsorption, viscosity, zeta potential and solid surface charge density measurements were carried out in the temperature range 15–40 °C. NaCl (1 × 10^{–2} mol/dm³) was used as the supporting electrolyte.

The adsorption measurements were made by the static method in the polymer concentration range 10–200 ppm at pH 6. The appropriately chosen weight of the solid sample (0.025 g–ZrO₂, 0.04 g–Al₂O₃, 0.06 g – CPG and 0.03 g–SiO₂) was added into the Erlenmeyer flask containing 10 cm³ of polymer solutions of known concentration. Then the solution pH was adjusted. Such prepared suspension was shaken in a water bath for 24 h, and its pH was monitored. Then the sediment was centrifuged and 5 cm³ of supernatant was taken for analysis. The amount of the adsorbed polymer was obtained from the difference between the polymer concentration in the solution before and after the adsorption process. For this purpose, the reactions of polyethylene glycol with tannic acid (causing polymer solution turbidity) [21] and polyvinyl alcohol with H₃BO₃ and I₂ solutions (coloring polymer solution green) [22] were used. Absorbencies of the prepared solutions were measured with the UV-VIS Specord M42 spectrophotometer (Carl Zeiss Jena) at 600 nm (for PEG) and 682 nm (for PVA). All obtained results were the mean values of five independent measurements (the measurement error in all cases did not exceed 5%).

The thickness of the polymer adsorption layer (δ) was determined from the viscosity measurements [23] using a CVO 50 rheometer (Bohlin Instruments).

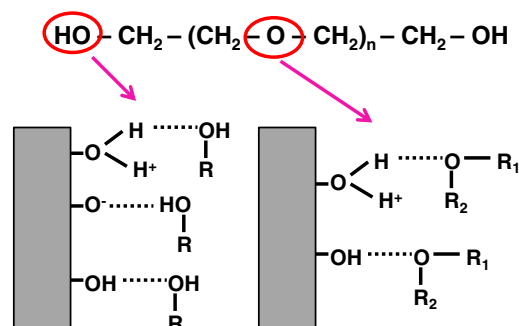


Fig. 1. Possible ways of hydrogen bridges formation in adsorbent PEG system.

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