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Studies of temperature influence on adsorption behaviour of nonionic polymers at the zirconia–solution interface

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Abstract The temperature influence (15–35 °C) on the adsorption mechanism and conformation of nonionic polymers (polyethylene glycol (PEG), polyethylene oxide (PEO) and polyvinyl alcohol (PVA)) on the zirconium dioxide surface was examined. The applied techniques (spectrophotometry, viscosimetry, potentiometric titration and microelectrophoresis) allowed characterization of the changes in structure and thickness of polymer adsorption layers with the increasing temperature. The rise of temperature favours more stretched conformation of polymer chains on the ZrO_2 surface, which results in higher adsorption and thicker adsorption layer. Moreover, these conformational changes of adsorbed macromolecules affect the electric (solid surface charge density) and electrokinetic (zeta potential) properties of the zirconia–polymer interface. The obtained data indicate that the polyvinyl alcohol adsorption has a greater influence on zirconia properties in comparison to that of PEG and PEO. It is due to the presence of acetate groups in the PVA macromolecules (degree of hydrolysis 97.5%), which undergo dissociation.

Keywords Polyethylene glycol · Polyethylene oxide · Polyvinyl alcohol · Zirconia · Macromolecule conformation · Suspension stability

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Introduction

Colloidal suspensions play a very important role in everyday human lives, due to their common presence in biological, ecological, industrial and agricultural systems. Colloidal dispersions exist in blood in the human organism, in production processes of plastics, paints, cosmetics, pharmaceuticals, in water purification and separation of hazardous solids from chemical waste as well as reduction of plough-lands erosion and agricultural dispersion to efficient food production.

Such a dispersion may be stable for thermodynamic or kinetic reasons. Its destabilization resulting in solid particles aggregation can be achieved in two ways: by coagulation or flocculation process. The term coagulation is applied for the systems, in which the formed sediment is composed of closely packed particles, whereas flocculation is reserved for a looser form of aggregates. The coagulation precedes after the addition of a simple electrolyte of appropriate concentration, contrary to flocculation, which requires the addition of a suitable polymer. On one hand in the case of coagulation, the attractive van der Waals forces between the core particles are responsible for holding the aggregates together. On the other hand, in flocculation the close proximity of the solid particles is desired by the polymeric substance, attached to the colloidal particles or the unadsorbed one in the dispersion medium.

Similarly to destabilization of colloidal suspension, its stabilization can be acquired through electrostatic and polymeric interactions. Properly chosen simple electrolyte is responsible for the electrostatic stabilization. Its ionic strength should be sufficiently large to induce electrostatic repulsion between the solid particles. The thicknesses of their double layers have to exceed the range of the van der Waals attractions.

There are two different mechanisms of colloidal dispersion stabilization in the presence of a polymer: steric and depletion stabilizations. Steric stabilization is caused by the macromolecules attached to the particle surfaces, whereas the unadsorbed polymer chains remaining in the solution are responsible for depletion stabilization. It is possible to obtain the combinations of electrostatic and steric interactions (electrosteric stabilization) and also of depletion stabilization with both steric or electrosteric stabilization.

The stabilization and flocculation processes of colloidal suspension in the presence of a polymer have wide technological and biological applications because they offer several important advantages in comparison to electrostatic stabilization. They are: relative insensitivity to the presence of electrolytes, equal efficiency in both aqueous and non-aqueous dispersion media, the same effectiveness at both high and low solid contents and reversibility of flocculation.

The stabilization–flocculation properties of such systems depend on conformation of polymer chains attached to the solid surface and in the bulk solution. Many parameters associated with polymer and solid characteristics as well as solution conditions influence the macromolecule conformation. Of all these factors, only temperature effect on adsorption behaviour of polymer is not extensively discussed in the world literature [1–3]. Nevertheless, my previous investigations [4–6] indicated that temperature rise causes noticeable changes in the linear dimension of macromolecules and solid surface characteristics. Thus, the temperature conditions are very important for the colloidal system stability in the presence of polymer [7] and stabilization or destabilization effect may be achieved by proper choice of temperature range.

Thus, the aim of the present study is determination of the temperature influence on the adsorption layer structure of three nonionic polymers: polyethylene glycol (PEG), polyethylene oxide (PEO) and polyvinyl alcohol (PVA) on the zirconium dioxide surface. The stabilization properties of such systems are conditioned by this structure.

Experimental

The samples of zirconium dioxide—ZrO_2 (Aldrich) were used in the experiments. In order to eliminate inorganic contaminations, zirconia was washed with NaOH solution (1×10^{-1} mol dm^{-3}) and then with doubly distilled water. The supernatant conductivity after the washing process did not exceed 2 µS cm^{-1}. ZrO_2 was characterized by the BET surface area equal to 4.9 m^2 g^{-1}, mean pore diameter—6.7 nm, both obtained from low-temperature nitrogen adsorption–desorption method using the automatic adsorption analyzer ASAP 2405, (Micromeritics Instruments). The mean grain size was 452 nm measured with the Zetasizer 3000 laser zetameter (Malvern Instruments).

The samples of the following nonionic polymers were used in the study: polyethylene glycol PEG 2000 (Fluka), polyethylene oxide PEO 218000 (Fluka) and polyvinyl alcohols PVA 22000 as well as PVA 72000 (Fluka). Due to the fact that the PEG and PEO samples were characterized by the relatively low polydispersity index $D = 1.15$, but only the prepared PVA solutions were filtered through the cellulose membranes (Millipore). The filtration process was carried out to eliminate both inorganic contamination and lower and higher polymer fractions. The PVA 22000 solution was filtered through the membranes with NMWL (Nominal Molecular Weight Limit) equal to 10000 and 30000, whereas for the PVA 72000 they are 30000 and 100000. In the case of PVA 72000, its average molecular weight after the filtration process was determined using the viscosity method [8]. This molecular weight was equal to 38000.

Both PEG (PEO) and PVA are nonionic polymers. However, the PVA chains contain the acetate groups –CH_3COOH, which do not undergo hydrolysis in the production process of polyvinyl alcohol from polyvinyl acetate. The degree of PVA hydrolysis equals 97.5%, which means that 2.5% acetate groups do not undergo hydrolysis to hydroxyl ones. Thus, besides the hydroxyl groups –OH, the unhydrolysed acetate groups –CH_3COOH are present in the polyvinyl alcohol macromolecules. These groups dissociate with the increasing pH and PVA chains become negatively charged.

All measurements were carried out in the temperature range 15–35 °C and the NaCl solution (1×10^{-2} mol dm^{-3}) was used as the supporting electrolyte.

The adsorption measurements at pH 6 were taken with the static method in the polymer concentration range 10–200 ppm and with 0.8 g of ZrO_2. The pH of polymer solutions was set by the use of a pH-meter ϕ360 (Beckman) and with the HCl and NaOH solutions. The prepared suspensions were shaken in water bath (OLS 2000, Grant) for 24 h and meanwhile, the pH of solutions was checked. Then, the suspensions were centrifuged and 5 mL of the clear polymer solutions were collected for further analysis. The amount of the polymer adsorbed was determined from the difference between the PAA concentration in the solution before and after the adsorption process. The PVA concentration before and after its adsorption was determined based on the reaction of PVA with H_3BO_3 and I_2 solutions [9–11]. The obtained complex PVA–H_3BO_3–I_2 coloured the solution green. Its absorbance was colorimetrically measured at the wavelength 682 nm after 15 min from the start of the reaction with the UV–VIS Specord M42 spectrophotometer (Carl Zeiss Jena). The concentration of PEG (PEO) before and after the adsorption process was measured via the reaction of polymer with tannic acid [12]. All solutions were stored in the dark for 1 h and then their turbidity was measured at 600 nm.

The thickness of the polymer adsorption layers (δ) was determined from the viscosity measurements [13] using a CVO 50 rheometer (Bohlin Instruments). For this purpose, the following dependencies were used:

$$\delta = r\left[\left(\frac{\phi_{\mathrm{p}}}{\varphi_{\mathrm{o}}}\right)^{1/3} - 1\right] \qquad (1)$$

where r radius of the solid particle/nm, ϕ_{o} volume fraction of the solid without polymer, ϕ_{p} volume fraction of the solid with polymer:

$$\frac{\eta}{\eta_o} = 1 + k\varphi_o \qquad (2)$$

where η viscosity of the suspension/Pa s, η_{o} viscosity of the liquid phase/Pa s, k Einstein coefficient.

Based on Eq. 2, the calibration curves at 15, 25 and 35 °C were obtained. For this purpose, five suspensions of zirconia in the supporting electrolyte, corresponding to various volume fractions (ϕ_{o}) of the solid (0.5; 1; 1.5; 2 and 2.5 g of the solid were added to 40 mL NaCl solutions) were prepared. These suspensions were shaken for 24 h and their viscosities (η) and also viscosities of clear NaCl solution (η_{o}) were measured. It allows to obtain calibration curves as a dependence of η/η_{o} versus ϕ_{o}, which are depicted in Fig. 1.

The viscosity measurements in the presence of PVA were made in a similar way with the volume fraction of ZrO_2 equal to 6.545×10^{-3}.

The surface charge density of zirconia in the absence and presence of polymer was determined from the potentiometric titrations of 50 mL of polymer solution in the supporting electrolyte (or only the supporting electrolyte solution) and 4 g of ZrO_2. The suspensions prepared in such a way were put into the Teflon vessel. The final concentrations of polymer and supporting electrolyte were 100 ppm and $C_{\mathrm{NaCl}} = 1 \times 10^{-2}$ mol dm^{-3}. The initial pH of the solution (3–3.5) was adjusted by the use of HCl (1×10^{-1} mol dm^{-3}). For the potentiometric titrations, there were use of the following appliances: a burette Dosimat 665 (Methrom), thermostat RE204 (Lauda), a pH-meter 71pH meter (Beckman) connected with the computer and the printer. The solid surface charge density was calculated with the special program Miar_t whose author is W. Janusz.

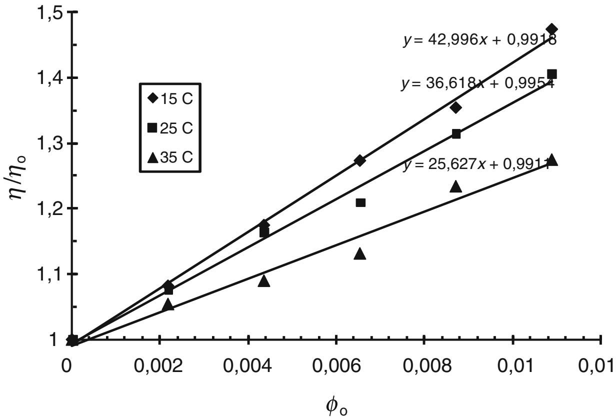

Fig. 1 The relative viscosities of ZrO_2 suspensions as a function of their volume fractions, $C_{\mathrm{NaCl}} = 1 \times 10^{-2}$ mol dm^{-3}

The zeta potentials of the ZrO_2 particles in the presence and absence of PAA were measured with the Zetasizer 3000 laser zetameter (Malvern Instruments). There was prepared a suspension containing 0.025 g of ZrO_2 in 250 mL of the supporting electrolyte or polymer solution ($C_{\mathrm{polymer}} = 100$ ppm, $C_{\mathrm{NaCl}} = 1 \times 10^{-2}$ mol dm^{-3}). This suspension was sonicated (ultrasonic processor XL, Misonix) and divided into five parts of volume 50 mL. Next, the appropriate pH value (ranging from 3–10) was adjusted in each sample. All the samples were thermostated at the time of their preparation.

Using the zeta potential data, the free energies of adsorption (ΔG°_{sp}) were calculated from the Pradip equation [14, 15]:

$$\Delta\mathrm{pH}_{\mathrm{iep}} = 1.0396 C_{\mathrm{O}} \exp\left(-\frac{\Delta G^{\mathrm{o}}_{\mathrm{sp}}}{RT}\right) \qquad (3)$$

where $\Delta\mathrm{pH}_{\mathrm{iep}}$ difference of $\mathrm{pH}_{\mathrm{iep}}$ of oxide without and with an adsorbed polymer, C_{o} concentration of a polymer, R gas constant, T absolute temperature.

Results and discussion

Figures 2 and 3 show the adsorption isotherms of PEG 2000 and PVA 22000 on the ZrO_2 surface at 25 °C for different pH values. The similar dependencies were obtained for PEO 218000 and PVA 38000.

As can be seen, the PEG (PEO) adsorption slightly depends on solution pH, whereas the PVA adsorbed amounts increase significantly with the increasing pH.

Both PEG and PVA are classified as nonionic polymers. However, the PVA chains contain the acetate groups –CH_3COOH, which do not undergo hydrolysis in the production process of polyvinyl alcohol from polyvinyl acetate. Both PVA 22000 and 38000 have the degree of hydrolysis equal to 97.5%, which means that 2.5% of the acetate groups remain unhydrolysed. Thus, besides –OH groups, the –CH_3COOH groups are present in the PVA chains. The acetate groups undergo dissociation with the rise of pH and the PVA macromolecules become negatively charged. Two types of PVA functional groups can

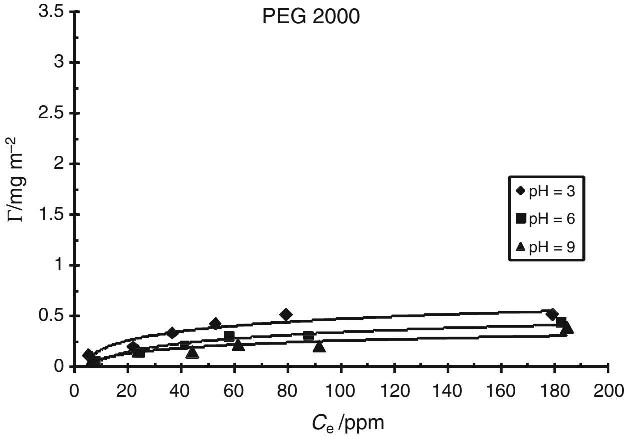

Fig. 2 Adsorption isotherms of PEG 2000 on the ZrO_2 surface for different pH values, $C_{NaCl} = 1 \times 10^{-2}$ mol dm^{-3}, 25 °C

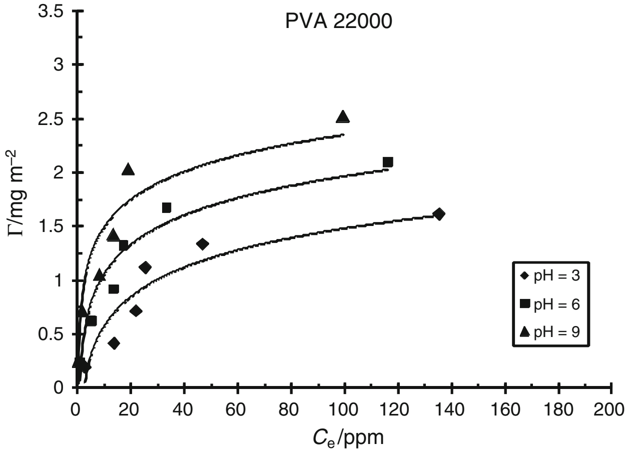

Fig. 3 Adsorption isotherms of PVA 22000 on the ZrO_2 surface for different pH values, $C_{NaCl} = 1 \times 10^{-2}$ mol dm^{-3}, 25 °C

interact with the solid active sites through the hydrogen bonds [16]. Additionally, the previous investigation indicated that the adsorption of acetate groups on the metal oxide surface is preferential [17].

On the other hand, pH influences also concentrations of the solid surface groups ($=ZrOH_2^+$, $=ZrO^-$ and $=ZrOH$). The pH_{pzc} of ZrO_2 changes from 6.5 to 7.0 in the 15–35 °C temperature range. Thus, at pH 3 the attractive interactions between the $=ZrOH_2^+$ surface groups and very few dissociated acetate groups $–CH_3COO^-$ start to appear. Besides, the conformation of weakly dissociated polymer macromolecules is more coiled. As a result, the PVA adsorption layer on the zirconia surface is flat. It causes the effect of blockade of the solid surface sites, which become inaccessible for other PVA macromolecules. As a consequence, lower polymer adsorption is obtained.

At $pH = pH_{pzc}$, the PVA macromolecules are practically fully dissociated, which results in coils developing and more stretched structure of adsorption layer. Such a conformation produces higher adsorption.

Strong electrostatic repulsion between the totally dissociated polyvinyl alcohol chains and the negatively charged ZrO_2 surface takes place at $pH > pH_{pzc}$. These repulsive interactions cause a very stretched conformation of the adsorbed macromolecules, which are densely packed in the adsorption layer. As a result, the highest adsorption level is achieved.

What is more, not only electrostatic forces but also hydrogen bridge interactions are responsible for PVA adsorption in the whole studied pH range. Hydrogen bonds play a large role especially at $pH > pH_{pzc}$, at which, regardless of strong repulsion between the polymer and the surface, the adsorption is the largest.

The calculated values of free energies (ΔG°_{sp}) of polymer adsorption (Table 1) proved that hydrogen bridges interactions are present in the studied systems. The obtained ΔG°_{sp} values range from -21.43 to -38.72 kJ mol^{-1}, which is in good agreement with literature data [18, 19].

The assumed adsorption mechanism confirms the comparative analysis of the adsorbed amounts of PVA and PEG (PEO) (Table 2). The adsorbed amounts of PVA are significantly higher than those of PEG. Thus, the adsorption affinity of PVA macromolecules for the zirconia surface is stronger than that for the PEG chains. In the case of PVA, both electrostatic and hydrogen bridge type interactions take place, whereas the PEG chains interact with the ZrO_2 surface only through hydrogen bonds. For this reason, the electrostatic interactions between the dissociated PVA

Table 1 Free energies of polymer adsorption on the ZrO_2 surface for different temperatures, $C_{NaCl} = 1 \times 10^{-2}$ mol dm^{-3}, $C_{polymer} =$ 100 ppm, pH = 6

System	T/°C	pH_{iep}	ΔpH_{iep}	C_o/mol dm^{-3}	ΔG°_{sp}/ kJ mol^{-1}
ZrO_2	15	7.15	–	–	–
ZrO_2–PEG 2000		6.75	0.4	5×10^{-5}	–21.43
ZrO_2–PEO 218000		6.5	0.65	4.6×10^{-7}	–33.82
ZrO_2–PVA 22000		6.1	1.05	4.5×10^{-6}	–29.51
ZrO_2–PVA 38000		5.6	1.55	2.6×10^{-6}	–31.76
ZrO_2	25	7.4	–	–	–
ZrO_2–PEG 2000		6.4	1.0	5×10^{-5}	–24.45
ZrO_2–PEO 218000		5.75	1.65	4.6×10^{-7}	–37.31
ZrO_2–PVA 22000		5.1	2.3	4.5×10^{-6}	–32.48
ZrO_2–PVA 38000		4.2	3.2	2.6×10^{-6}	–34.66
ZrO_2	35	7.85	–	–	–
ZrO_2–PEG 2000		6.65	1.2	5×10^{-5}	–25.73
ZrO_2–PEO 218000		6.1	1.75	4.6×10^{-7}	–38.71
ZrO_2–PVA 22000		4.6	3.25	4.5×10^{-6}	–34.45
ZrO_2–PVA 38000		3.55	4.3	2.6×10^{-6}	–36.58

chains and the solid surface have a great influence on its adsorption.

Figures 4, 5, 6 and 7 present the adsorption isotherms of PEG, PEO and PVA on the zirconium dioxide surface at 15, 25 and 35 °C (pH = 6). As can be seen the adsorption of polyethylene glycol and polyvinyl alcohol increases with the rising temperature. The analysis of the obtained isotherms is carried out in connection with the calculated values of free energies of the polymer adsorption ΔG°_{sp} (Table 1) and the determined thicknesses of polymer adsorption layers δ (Table 2). The increase of temperature causes more stretched conformation of the adsorbed polymer chains. It is due to the fact that the attractive interactions between the polymer segments and the solvent molecules are dominant.

At the lowest examined temperature (15 °C), the adsorbing polymer chains have a more coiled form. Such structure of the polymer adsorption layer composed of loosely tangled polymer coils does not consume many solid active sites, but their great number remains blocked. In other words, due to small straightening of macromolecules, their active groups are inaccessible to bonding with the solid surface, thus many of them are unadsorbed. On the other hand, the flatter conformation of the adsorbed chains causes blockade of solid active sites, on which other macromolecules cannot be adsorbed. This fact results in smaller values of free energies of polymer adsorption (Table 1) and thinner polymer adsorption layers (Table 2).

Temperature increase causes more stretched conformation of polymer chains, which is reflected in the increase of linear dimensions of adsorbing macromolecules [4]. Thus, at 35 °C the polymer adsorption layer at the interface consists mainly of tail and loop structures, which are oriented towards the bulk solution. Such developed conformation makes the adsorption of a larger number of polymer chains possible on the same unit of solid area. As a consequence, greater adsorption, higher values of free energies of adsorption and thicker adsorption layer are obtained.

Moreover, the increase of PVA adsorption layer thickness with the rise of temperature is more pronounced than

Table 2 Adsorbed amounts (Γ) and thicknesses of polymer adsorption layers (δ) on the ZrO_2 surface for different temperatures, $C_{NaCl} = 1 \times 10^{-2}$ mol dm^{-3}, $C_{polymer} = 100$ ppm, pH = 6

Polymer	15 °C		25 °C		35 °C	
	Γ/ mg m^{-2}	δ/ nm	Γ/ mg m^{-2}	δ/ nm	Γ/ mg m^{-2}	δ/ nm
PEG 2000	0.25	1.91	0.31	2.82	0.46	3.28
PEG 218000	0.40	3.88	0.72	5.08	0.94	6.62
PVA 22000	1.37	2.18	1.67	3.52	2.02	4.77
PVA 38000	1.62	4.36	1.86	6.34	2.13	8.64

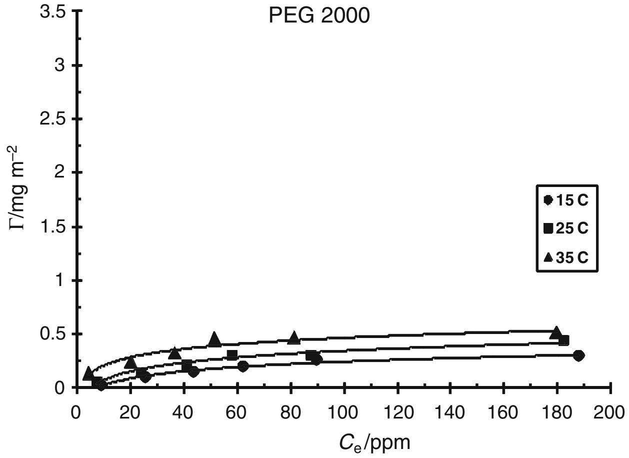

Fig. 4 Adsorption isotherms of PEG 2000 on the ZrO_2 surface for different temperatures, $C_{NaCl} = 1 \times 10^{-2}$ mol dm^{-3}, pH = 6

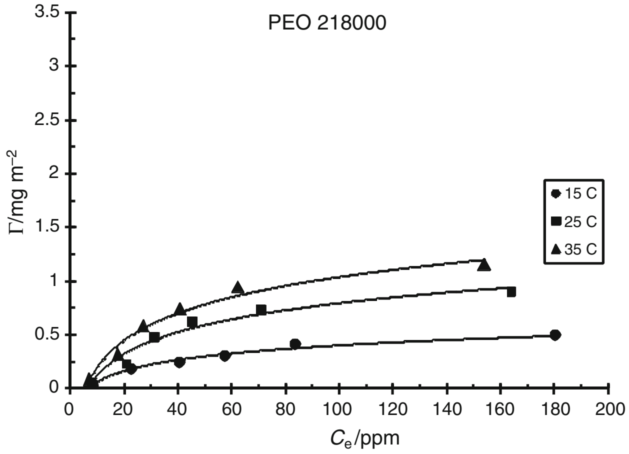

Fig. 5 Adsorption isotherms of PEO 218000 on the ZrO_2 surface for different temperatures, $C_{NaCl} = 1 \times 10^{-2}$ mol dm^{-3}, pH = 6

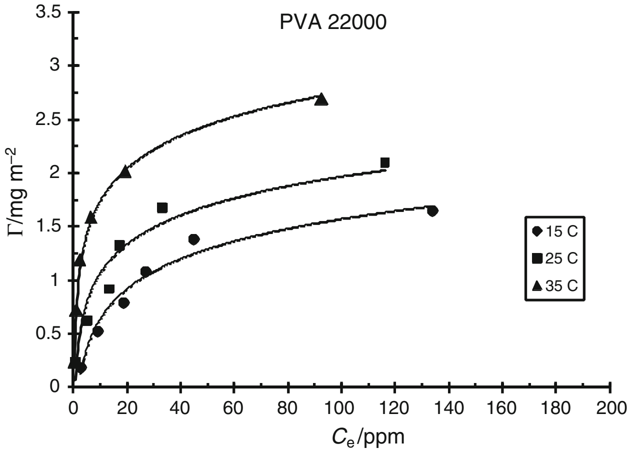

Fig. 6 Adsorption isotherms of PVA 22000 on the ZrO_2 surface for different temperatures, $C_{NaCl} = 1 \times 10^{-2}$ mol dm^{-3}, pH = 6

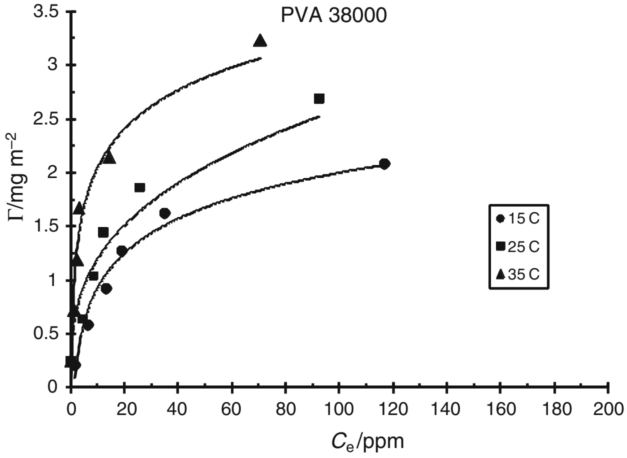

Fig. 7 Adsorption isotherms of PVA 38000 on the ZrO_2 surface for different temperatures, $C_{NaCl} = 1 \times 10^{-2}$ mol dm^{-3}, pH = 6

that of PEG (PEO). For example, in the case of PVA 22000, thickness of its adsorption layers increases 2.2 times in the 15°–35° temperature range, whereas for PEG (PEO) this increase is about 1.7 times. The rise of temperature favours more stretched structures of the adsorbed macromolecules, but for PVA this effect is intensified by the electrostatic repulsion between the negatively charged acetate groups belonging to the same and different polymer chains.

Very important parameters, which enable description of the PEG and PVA adsorption layer structures on the ZrO_2 surface are changes of the surface and diffuse layer charges in the presence of polymer. For this purpose, the potentiometric titrations and the zeta potential measurements of ZrO_2–NaCl, ZrO_2–NaCl PEG(PEO) and ZrO_2–NaCl–PVA systems were carried out in the temperature range 15–35 °C. The obtained data are presented in Figs. 8, 9, 10 and 11, 12, 13, respectively.

The analysis of potentiometric titration curves at 15 and 25 °C (Figs. 8, 9) suggests that the polymer adsorption does not influence the pH_{pzc} and causes minimal changes in the surface charge density. This behaviour is typical of nonionic polymers. The changes in the surface charge density of ZrO_2 in the presence of the polymer are noticeable at $pH > pH_{pzc}$. Such course of potentiometric titration curves indicates that polymer chains undergo bonding with the zirconia surface through the hydrogen bridges. Each way of specific interactions between the solid surface groups and the polymeric segments different from the above should lead to changes in potential creating ions concentration and more distinct ones in solid surface charge density will be observed.

Adsorption of the polymer at 35 °C causes the most noticeable changes in the ZrO_2 surface charge density.

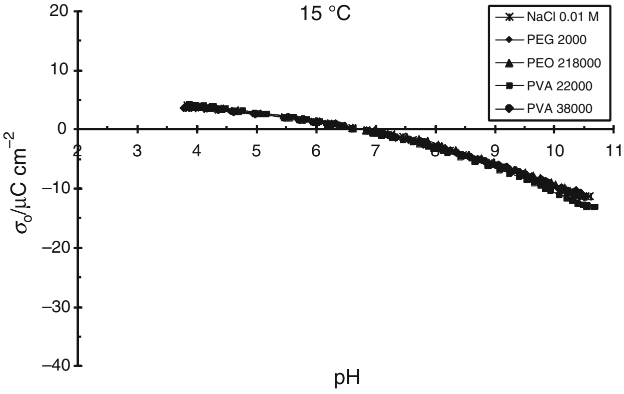

Fig. 8 Surface charge density of ZrO_2 in the presence and absence of polymer as a function of the solution pH at 15 °C, $C_{polymer} = 100$ ppm

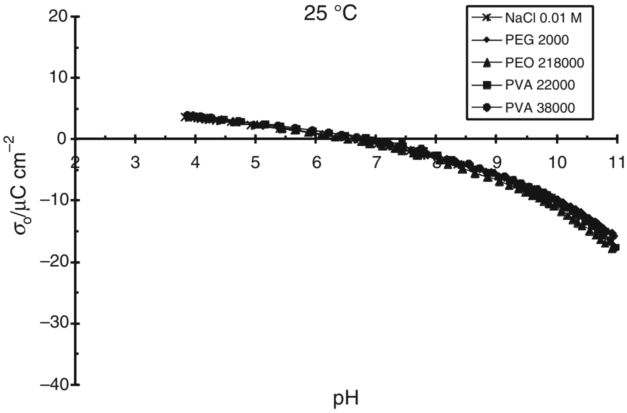

Fig. 9 Surface charge density of ZrO_2 in the presence and absence of polymer as a function of the solution pH at 25 °C, $C_{polymer} = 100$ ppm

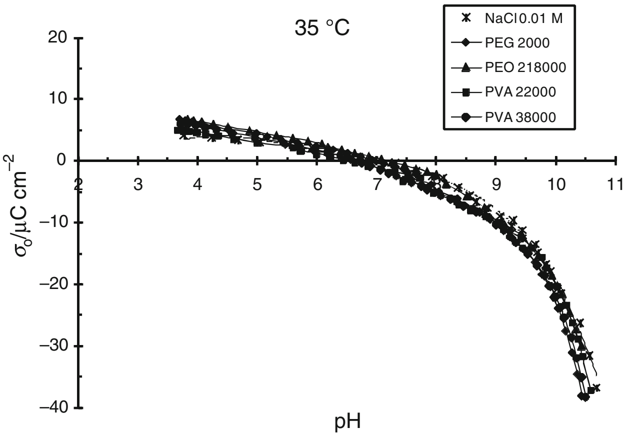

Fig. 10 Surface charge density of ZrO_2 in the presence and absence of polymer as a function of the solution pH at 35 °C, $C_{polymer} = 100$ ppm

In the pH range below pH_{pzc}, the polymer adsorption causes minimal increase of the zirconia surface charge density, whereas at $pH > pH_{pzc}$ it is small decrease. The

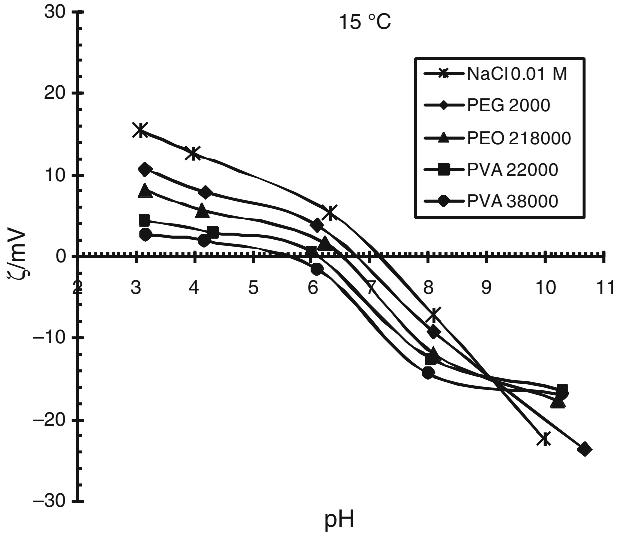

Fig. 11 Zeta potential of ZrO_2 particles in the presence and absence of polymer as a function of the solution pH at 15 °C, $C_{\text{polymer}} = 100$ ppm

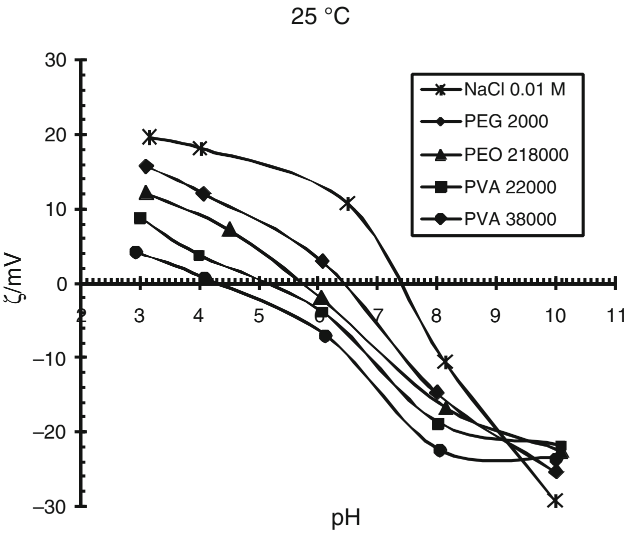

Fig. 12 Zeta potential of ZrO_2 particles in the presence and absence of polymer as a function of the solution pH at 25 °C, $C_{\text{polymer}} = 100$ ppm

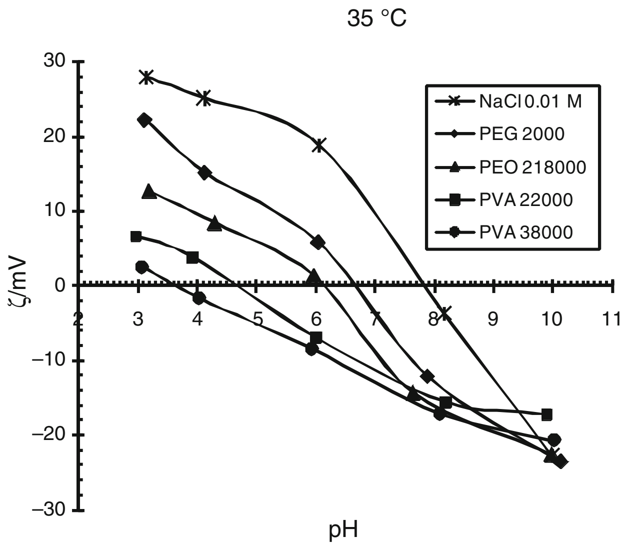

Fig. 13 Zeta potential of ZrO_2 particles in the presence and absence of polymer as a function of the solution pH at 35 °C, $C_{\text{polymer}} = 100$ ppm

most stretched conformation of the adsorbed macromolecules at the highest examined temperature can lead to changes in potential creating ions position in the surface layer, which has some influence on the increase of the solid surface charge density.

Additionally, in the case of PVA some contribution to the value of zirconia surface charge density in the presence of the polymer can have the acetate groups. At $\text{pH} < \text{pH}_{\text{pzc}}$, adsorption of PVA is not great and probably nearly all acetate groups undergo bonding with the zirconia surface, causing the increase of the solid surface charge density. Adsorption of polyvinyl alcohol with the dissociated functional groups can be treated as adsorption of polyanion, which is associated with creation of the positively charged sites on the solid surface. On the other hand, at $\text{pH} > \text{pH}_{\text{pzc}}$ PVA adsorption level and packing of polymer adsorption layer increases. As a result, not all acetate groups of the adsorbed macromolecules can be bounded with the adsorbent surface. Some of them are present in the surface layer with the tail and loop structures of the adsorbed polymer chains, which leads to lowering of the ZrO_2 surface charge.

Figures 10, 11 and 13 present the results of zeta potential measurements for ZrO_2 particles in the presence and absence of PEG (PEO) and PVA at 15, 25 and 35 °C. Their analysis indicates, that in the pH range 3–9 the zeta potential of zirconia particles in the presence of the polymer is lower than that without polymer. This effect is greater in the case of higher molecular weight of the polymer. The changes of zeta potential can be due to the three effects: (a) the shift of slipping plane due to polymer adsorption, (b) the blockade of solid active sites by the previously adsorbed polymer chains and supporting electrolyte ions and (c) the presence of the dissociable functional groups in macromolecules [13]. These three mechanisms have a different contribution to zeta potential lowering. This depends on a polymer type, its molecular weight and temperature conditions.

The effect of blockade of the solid active sites by the adsorbed macromolecules and electrolyte ions is more probable for lower temperature and low polymer molecular weight. In such cases, the conformation of the adsorbed polymer chains are rather flat, which inhibits the access of other polymer chains and electrolyte ions to the solid active sites. As a result, the composition of the charges in the slipping plane changes, influencing the zeta potential of the system.

On the other hand, the effect of the slipping plane shift becomes dominant for higher temperature and high polymer molecular weight. The conformation of the adsorbed macromolecules is more stretched perpendicularly to the solid surface due to a great polymer segment contribution to the loop and tail structures. It leads to pronounced shift of the slipping plane and reduction of the zeta potential.

Additionally, in the case of polyvinyl alcohol the presence of the dissociated acetate groups in the adsorbed chains is also responsible for decrease of the zeta potential of zirconia particles. One should note that this reduction of the zeta potential is associated with the presence of negatively charged polymer groups in the diffuse layer, which remain unadsorbed and exist in the tail and loop structures.

Moreover, with the decreasing temperature, the decrease in the zeta potential of the zirconia particles with the adsorbed polymer is more significant. The greater shift of pH_{iep} points of the solid with the polymer, in comparison to that without the polymer is obtained (Table 1). It is a result of the stretched conformation of the adsorbed macromolecules (thick adsorption layer, Table 2) leading to considerable shift of slipping plane and the most noticeable reduction of the zeta potential of ZrO_2 particles at 35 °C.

For all examined temperatures, adsorption of the polymer causes the increase of zeta potential of the solid in the pH range 9–10. Such behaviour of the system can be explained by displacement of potential creating ions perpendicularly to the surface. As a consequence, concentration of these ions in the diffuse layer rises causing the zeta potential increase.

Conclusions

The temperature increase in the range 15–35 °C influences the thickness and structure of the polymer adsorption layer on the ZrO_2 surface. The obtained results indicate that the polyvinyl alcohol (PVA) adsorption causes greater changes in zirconia surface properties than that of polyethylene glycol (PEG) and polyethylene oxide (PEO). It is associated with the presence in the PVA chains of unhydrolysed acetate groups, which undergo dissociation. Thus, not only hydrogen bridges interactions (as in the case of PEG and PEO) but also electrostatic forces are responsible for their adsorption on the solid surface.

The conformation changes of the adsorbed polymer with the rising temperature from the more coiled structure (at 15 °C) to the developed one (at 35 °C) result in the increase of the adsorbed amounts, thicknesses of polymer adsorption layer and free energies of adsorption.

Adsorption of the polymer at 35 °C causes the most noticeable changes in the ZrO_2 surface charge density and its zeta potential. The main reason for such behaviour is more stretched structure of the adsorbed polymer layers at higher temperature.

Additionally, the electrokinetic properties of the investigated systems in the presence of the polymer are the sum of three effects: the blockade of the solid active sites by the adsorbed polymer chains and electrolyte ions, the shift of slipping plane caused by the adsorption of polymer chains and the presence of functional groups undergoing dissociation. The contribution of these mechanisms to the changes of electrokinetic behaviour of such systems depends on the polymer type, its molecular weight and temperature conditions.

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