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Separation of TiO_2 particles from water and water/methanol mixtures by cationic dextran derivatives

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ABSTRACT

Cationic polysaccharides with N-alkyl-N,N-dimethyl-N-(2-hydroxypropyl)ammonium chloride pendent groups attached to a dextran backbone were used to flocculate titanium dioxide (TiO_2) particles suspended in water as well in water/methanol mixtures (90:10 and 50:50 v/v %). The investigations were performed with respect to the polycation dose, the suspension medium composition and the length of alkyl substituent at the quaternary nitrogen (alkyl = ethyl, octyl, dodecyl). The supernatant residual turbidity values were much lower for TiO_2 particles dispersed in solvent mixtures than in water. This finding was explained by the solvent mixtures effect on the charges of both the particle surface and polyelectrolyte chains. The alkyl substituent length did not affect in a dramatic way the separation of TiO_2 particles. The supernatant zeta potential dependence on the polycation dose when water/methanol mixtures were used as dispersion medium indicated a charge patch mechanism for the flocculation of TiO_2 particles, which was supported by particle aggregates size measurements.

1. Introduction

Dispersions of fine particles in both aqueous and nonaqueous media play an important role in a wide variety of industrial and environmental processes. When immersed in an aqueous media, some particles acquire charges (negative or positive) at their surface due to the dissociation of the surface groups (Gregory, 2006). The electrostatic repulsive forces between the particles carrying the same charge are the main source for stabilization of the suspension. On the other hand, particles in any suspension experience attractive van der Waals forces, effective only at short distances, which can promote reversible or irreversible aggregation. The competition between these forces dictates the suspension state, stable or separated. Some industries like paints and pigments, cosmetics, pharmaceuticals, ceramics require a good stability of the suspensions, while other ones including paper, waste water treatment, minerals necessitate separation of the dispersed particles. The interactions between the charges on the surface of dispersed particles (inorganic and organic) and low molecular weight salts as well as macromolecular compounds have been widely studied as they can improve either the stabilization or separation processes of the aqueous colloidal dispersions (Constantin et al., 2013; Dragan, Ghimici, Cristea, & Airinei, 1999; Gaudreault, Di Cesare, Weitz, & van de Ven, 2009; Ghimici & Brunchi, 2013; Mishra, Tripathy, Srivastava, Pandey, & Behari, 2009; Pina, Nakache, Feret, & Depraetere, 1999; Sanghi, Bhattacharya, & Singh, 2007; Singh, Sharma, Tripathy, & Sanghi, 2009). Several factors control and govern the polymer induced separation (coagulation/flocculation) -dispersion processes. Thus, there is a large number of studies where characteristics involving the polymers (the charge density, the molar mass, the hydrophobicity, the type of functional groups and their arrangement in the polymer chain), the suspended particles (size, shape, morphology and charge) and the dispersion medium (pH, ionic strength, dielectric constant, temperature) have been related with the flocculation efficiency (Bolto & Gregory, 2007; Chen, Liu, & Wang, 2007; Divakaran & Sivasankara Pillai, 2004; Ghimici & Constantin, 2011; Ghimici, Constantin, & Fundueanu, 2010; Liimatainen et al., 2011; Lin et al., 2012; Prado, Matulewicz, Bonelli, & Cukierman, 2011; Schwarz et al., 2007; Singh, Pal, Rana, & Ghora, 2013; Yang et al., 2012).

Most of the flocculation studies were performed on particles suspended in water. But, as mentioned earlier, dispersions of particles in various solvents are also used in many industrial activities such as ceramics, cosmetics, paints, printer ink, magnetic material, electronic parts. Hence, the suspended particles will be present in the industrial wastewaters containing organic solvents which have to be treated for their removal. In spite of it, little attention has been paid to the separation of particles from nonaqueous as well as mixtures of aqueous/nonaqueous solvents (Hsu & Chang, 2000; Lee, Uhm, Rhee, & Lee, 2010; Odriozola, Schmitt, Callejas-Fernandez, & Hidalgo-Alvarez, 2007). In the above mentioned investigations, the particles destabilization processes have been carried out mainly

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Table 1
Characteristics of the polycation samples.

Sample	Cl_i (mequiv./g)	X (mol% quaternary amino group)	ξ (20 °C water)[a]	η (mL g^{-1})[b]
D40-Et30	1.59	30	0.42	813
D40-Oct30	1.27	30	0.42	689
D40-Dod30	1.32	30	0.42	170

[a] ξ, the charge density parameter calculated according to Manning (1969):

$$\xi = \frac{e^2}{\varepsilon kTb} \quad (1)$$

e, the elemental charge; ε, the dielectric constant of the solvent; k, the Boltzmann constant; T, the temperature in °K and b, the average spacing between two vicinal ionized groups on the polyion based on a repeating unit length of 0.515 nm for the D-glycopyranose unit (Pass & Hales, 1981).
[b] $[\eta]$ values were obtained by fitting the Rao equation (Rao, 1993) to the viscosity data (η_{sp}/c versus c) of the cationic polyelectrolytes in salt free aqueous solutions.

in the presence of low molar mass salts. In this context, the goal of the current work is to investigate the separation of titanium dioxide (TiO_2) particles suspended in water as well in water/methanol mixtures (90:10 and 50:50 v/v %) by some hydrophilic and amphiphilic cationic polysaccharides based on dextran. As far as we know from the literature search such a study has not been undertaken previously. Our previously published results indicated these polymers as promising flocculants in aqueous clay suspensions (Ghimici, Morariu, & Nichifor, 2009; Ghimici & Nichifor, 2010, 2012). The use of polysaccharide derivatives is gaining importance in the solid–liquid separation processes as they combine the advantages of both synthetic (low polymer dose) and natural (biodegradability and low toxicity) polymers (Chen et al., 2007). The presence of dextran, and hence biodegradable linkages, in these samples could confer it self-degradation characteristics which will diminish the "secondary pollution" of the environment. This makes possible the using of these samples in the real waste waters treatment. TiO_2 has been chosen as model dispersion particles as it is frequently used in industries such as paints, cosmetics and papers.

The flocculation efficiency, followed by turbidity and zeta potential measurements, was investigated and discussed with regard to changes in the polycation dose, suspension medium composition, and the length of the alkyl substituent at the quaternary nitrogen (alkyl = ethyl, octyl, dodecyl). Particle aggregates size measurements, Z-Average (d, nm), at the optimum polycation dose were also performed by DLS measurements.

2. Experimental

2.1. Materials

Cationic polysaccharides with pendent quaternary ammonium groups were synthesized by chemical modification of dextran sample with a molar mass M_w = 40 kg mol^{-1} (Sicomed S.A., Bucharest), as previously described by Nichifor, Stanciu, & Simionescu (2010). Briefly, the polysaccharide (1 g) was dissolved in deionized water (10 mL) and an equimolar mixture of epichlorohydrin and N,N-dimethyl-N-alkylamines (2–4 mol reagents/glucopyranosidic dextran unit) (from Aldrich) was added, and the resulting solution was stirred for 6 h at 70 °C. The polymer was recovered by precipitation with acetone, and purified by repeated precipitation and sequential dialysis against 0.1 N HCl and water. Dialysis tubing with a cut-off of 12,000 Da from Sigma was used for this purpose. The dialyzed solution was freeze dried (24 h at −57 °C and 0.04 mbar) and a white powder was obtained. The modification process proceeded in a homogeneous medium and no micellization of the reagents took place. These reaction conditions allowed an even (statistical) distribution of the charged groups along the polysaccharide chains. Chemical structure, shown in Fig. 1, was proved by ^{1}H NMR and elemental analysis.

The polymer code is D40-R30, where D means dextran, 40 is dextran molar mass in kg mol^{-1}, R is the alkyl substituent at the amino group, and 30 = DS ± 2 mol/% (DS is expressed as moles of amino groups per 100 glucopyranosidic units; DS = 100x/(x + y), where x and y are the molar fraction of substituted and unsubstituted glucosidic units, respectively). The content in amino groups (DS) was determined from the nitrogen content (elemental analysis, by means of a CHNS 2400 II Perkin Elmer analyzer) and the chloride ion content was measured potentiometrically by titration with 0.02 N $AgNO_3$ aqueous solution. Table 1 lists several properties of the cationic polymers.

TiO_2 particles, crystalline form anatase, as determined by X-ray analysis (Bruker D8 ADVANCE, Germany) was supplied by Sigma–Aldrich. The hydrodynamic size of the particles, Z-Average (d, nm), determined by DLS measurements, was 401.7 nm in water, 377 nm in 90:10 and 504 nm in 50:50 water/methanol mixtures. The isoelectric point (IEP), i.e., the pH at which zeta potential vanishes to zero, was found at about 2.56. IEP was determined by measuring the electrokinetic potential of the TiO_2 suspension (water as dispersion medium) as a function of pH by means of Zetasizer Nano-ZS, ZEN-3500 model (Malvern Instruments, Malvern, England) using an MPT-2 automated titrator. pH was adjusted by adding 0.1 N HCl.

Methanol (99.8%), analytical grade product, was supplied by Chemical Company, Romania.

2.2. Methods

The aqueous polymer solutions, stabilized at room temperature for 1 day before use, were prepared with distilled water; the concentration of the polymer solutions (c_i) was 1 g L^{-1}. The TiO_2 model dispersions were prepared with distilled water as well as with water/methanol mixtures (90:10 and 50:50 v/v %). The concentration of the TiO_2 model dispersions was 0.05 g L^{-1}, the initial pH 6.2 and zeta potential ζ_{water} = −38.1 mV, $\zeta_{water/methanol\ 90:10}$ = −31 mV, $\zeta_{water/methanol\ 50:50}$ = −18 mV. In order to fully disperse the TiO_2 powder the dispersions were sonicated for 15 min using an ultrasonicator (SONICS VCX 750). The flocculation experiments were conducted at room temperature. Fifty ml of the TiO_2 suspension were placed into 100 ml glass beakers. Different volumes of

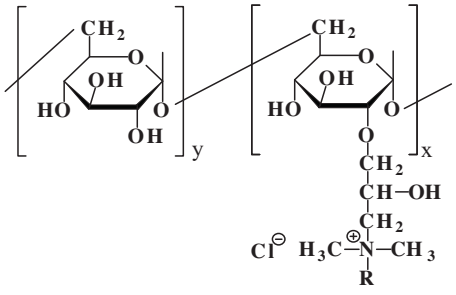

Fig. 1. General chemical structure of polycations based on dextran. R = ethyl, octyl, dodecyl.

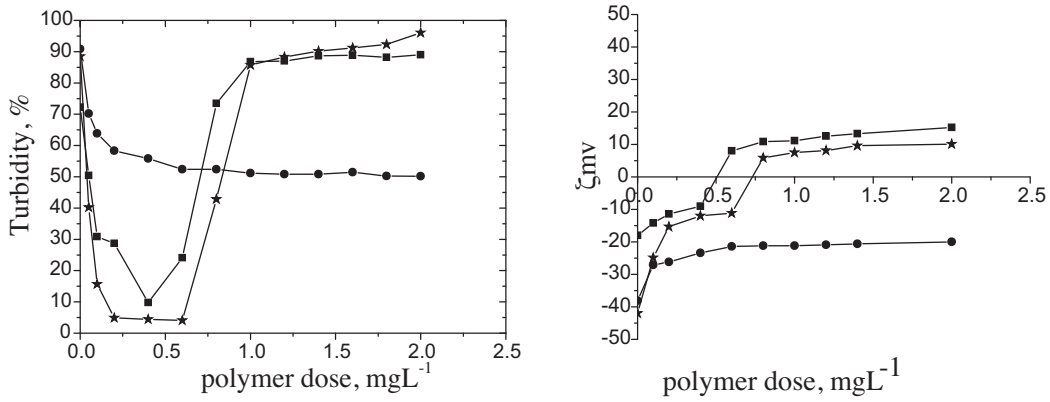

Fig. 2. The residual turbidity (%) (a) and zeta potential (ζ) (b) dependence on the polymer dose for D40-Et30 in: (circle) water; (star) water/methanol mixture 90:10; (square) water/methanol mixture 50:50.

polymer solutions (5–100 μL) were added at 500 rpm and stirring was continued with the same speed for about 3 min and then decreased to about 100 rpm for 15 min. After 1200 min the sample of supernatant (10 ml) was drawn out using a pipette from a depth of 0.5 cm below the surface and the turbidity was measured with a spectrophotometer SPECORD 1300 Analytik Jena at $\lambda = 400$ nm. Blank experiments were performed in the absence of polymer to evaluate "natural" sedimentation of the suspensions under the selected experimental conditions (pH, concentration of suspended mater, dispersion medium). The residual turbidity (%) was expressed as percent of the initial turbidity of the TiO_2 suspensions, at time zero, in the absence of polymer. All experiments were performed in triplicate and the mean turbidity values were calculated. Standard deviation determined for the experiments was ±4%. After 1200 min settling time, the residual turbidities for the blank experiments were about 93% for TiO_2 dispersed in water, 88.47% and 72.23% for TiO_2 dispersed in water/methanol mixtures 90:10 and 50:50, respectively.

The zeta potential of supernatant was measured after 1200 min of settling time with a Zetasizer Nano-ZS, ZEN-3500 model (Malvern Instruments, Malvern, England).

In the following, the polymer dose refers to the polymer concentration in its mixture with the TiO_2 suspension.

3. Results and discussion

Figs. 2–4 show changes in the residual turbidity and zeta potential values of the TiO_2 suspensions, prepared in water as well in water/methanol mixtures (90:10 and 50:50 v/v %), as a function of the polymer dose, namely, D40-Et30 (Fig. 2), D40-Oct30 (Fig. 3), D40-Dod30 (Fig. 4). Comparing the residual turbidity–polymer dose graphs, two main trends became clear: (i) the residual turbidity values changed with addition of different doses of polymers, irrespective of the particles dispersion medium composition; (ii) for the same polymer dose, the supernatant residual turbidity values were much lower when TiO_2 particles were dispersed in solvent mixtures than in water (Figs. 2a, 3a and 4a). Some explanations could be given for these results.

3.1. Suspensions of TiO_2 particles in water

It is well known that several forces are responsible for the polymer–particle interactions, namely electrostatic and/or hydrophobic attractions, hydrogen bonding, ion binding (Bolto & Gregory, 2007). The partners involved in the systems studied herein are represented, on the one hand, by cationic polysaccharides, hydrophilic (D40-Et30) as well as amphiphilic (D40-Oct30 and D40-Dod30) with low molar mass (40 kDa) and a medium charge content (30%) and, on the other hand, by the TiO_2 particles. As regard the latter one, there are different types of surface groups on titanium dioxide particles (—$TiOH_2$, —TiOH, —TiO^-), their concentrations depending on the pH of the suspension (Riley, 2005). Thus, at pH higher than that corresponding to the isoelectric point, the concentrations of —TiOH and titanium dioxide positively charged groups (—Ti—OH + $H^+ \rightarrow$ —$TiOH_2^+$) decrease and that of the oxide negatively charged ones (—Ti—OH + OH— $\rightarrow$ —TiO^- + H_2O) increase.

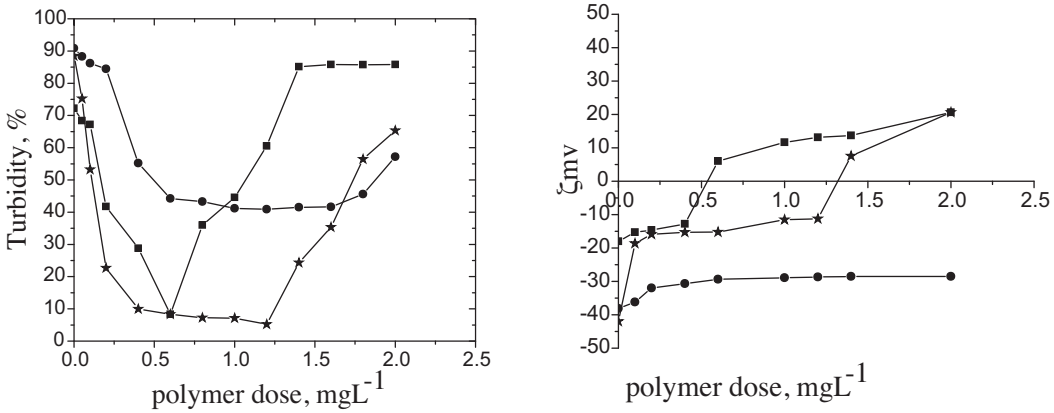

Fig. 3. The residual turbidity (%) (a) and zeta potential (ζ) (b) dependence on the polymer dose for D40-Oct30 in: (circle) water; (star) water/methanol mixture 90:10; (square) water/methanol mixture 50:50.

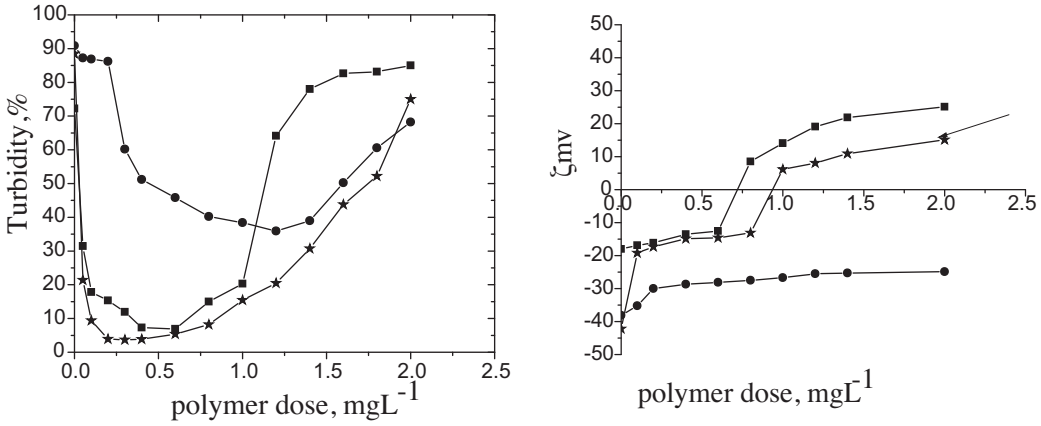

Fig. 4. The residual turbidity (%) (a) and zeta potential (ζ) (b) dependence on the polymer dose for D40-Dod30 in: (circle) water; (star) water/methanol mixture 90:10; (square) water/methanol mixture 50:50.

In water, the pH value corresponding to the isoelectric point of the TiO_2 particles under investigation is 2.56 (see Section 2). As the natural pH of the TiO_2 suspension is 6.2, the $-TiO^-$ groups prevails on the particle surface ($\zeta_{water} = -38.1$ mV). Based on the above mentioned characteristics of polymers and suspended particles, one may assume that the electrostatic attraction between the positively charged polymer and negative sites of the particle surface should have the main contribution to the reduction of the supernatant residual turbidity. However, the flocculation performance of these cationic polysaccharides is quite low when water was used as dispersion medium for the TiO_2 particles (the minimum residual turbidity values were located around 50% for D40-Et30, 41% for D40-Oct30 and 36% for D40-Dod30). This finding could be ascribed both to the hindered attractive electrostatic interactions and absence of the nonelectrostatic affinity polycation – TiO_2 particles. In order to get more information and find some explanations regarding this behavior we performed zeta potential measurements (Figs. 2b, 3b and 4b). For all of the three samples investigated a small increase of the initially negative value of ζ potential (−38.1 mV) with polycation dose was noticed: up to −20 mV for D40-Et30, −28.5 mV for D40-Oct30 and −24.9 mV for D40-Dod30. The negative values of the zeta potential over the entire range of the polymer doses used in this study show that a part of the surface charges are not compensated by these polycations; this confirms that electrostatic attraction forces between the negative charges on the particle surface and the positive charges on the polymer chain are diminished, probably by the steric and/or electrostatic repulsion forces between the adsorbed chains on different particles and/or the adsorbed chains and free chains in solution. In a review paper, Claesson et al. mentioned that undercompensation of the surface charge was also noticed in case of adsorption of cationic polyelectroytes with low and medium charge density on highly negatively charged mica surfaces (Claesson, Poptpshev, Blomberg, & Dedinaite, 2005). The authors explained that in absence of strong non-electrostatic interactions with substrate, the uncharged portion on the polyelectrolyte chain between two charged segments is extending into solution in the form of loops and tails; the steric repulsions between adsorbed chains with such conformations prevent full charge compensation by the adsorbing polyelectrolyte. In the present study the possible nonelectrostatic affinity of polymers to substrate were checked by investigating the effect of unmodified dextran sample on the separation of TiO_2 particles suspended in water and water methanol mixtures. The TiO_2 suspension was very stable over the entire range of dextran doses, irrespective of the dispersion medium composition, that means there are no other attraction forces than electrostatic ones between TiO_2 particles and polymer backbone (Fig. 5). Based on this result and on the Claesson mention, one may assume that in our experiments also the (electro)steric repulsion forces between already adsorbed polyelectrolyte chains could be the main cause for the low electrostatic attraction interactions and hence, low separation efficiency of titanium dioxide particles by the D40-R30 samples. In addition, the $TiOH_2^+$ groups present on the particles surface, even in lower amount than TiO^- groups, could have a contribution in the repulsion of the positively charged polysaccharide segments.

The slight increase in separation efficacy for amphiphilic dextran derivatives (R = octyl and dodecyl) (lower values of the minimum residual turbidity than in case of the hydrophilic polysaccharide) could be the result of their ability to form intermolecular hydrophobic associations. As TiO_2 particles are of hydrophilic nature, the hydrophobic attractions are more probably to happen between the hydrophobic units belonging to the already adsorbed chains and free chains in solution. Pina et al. (1999) investigated the interactions between the hydrolysed styrene maleic anhydride copolymer (hSMA) and titanium dioxide and found that in the adsorption process are involved electrostatic and nonelectrostatic interactions between the substrate and the copolymer as well as hydrophobic associations between the preadsorbed copolymers and the free hSMA copolymers in solution via their phenyl groups; the last ones led to the hSMA adsorbed amount increase at higher salt concentration.

A plateau of the residual turbidity of aqueous suspensions was recorded for all of the polymers, but its width decreased as the length of the alkyl chain increased. It lasts over the whole

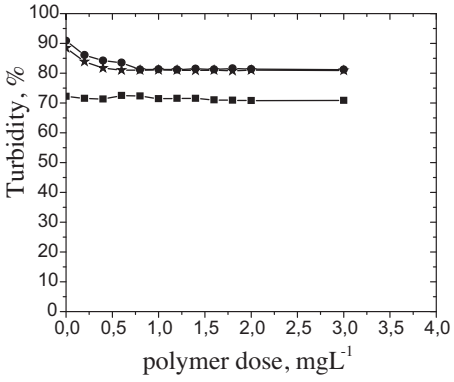

Fig. 5. The residual turbidity dependence (%) on the polymer dose for dextran in: (circle) water; (star) water/methanol mixture 90:10; (square) water/methanol mixture 50:50.

polymer dose range studied in the presence of D40-Et30 (Fig. 2a) but in the case of amphiphilic polymers it was followed by a certain increase of the residual turbidity (at polymer dose of 1.4 mg L^{-1} for D40-Dod30 and 1.8 mg L^{-1} for D40-Oct30) indicating the start of redispersion. Probably, at higher polymer doses, the intermolecular hydrophobic associations between the alkyl side groups belonging to the already adsorbed chains and free chains in solution cause a supplementary adsorption of the polymer chains at the solid/liquid interface and thereby their steric repulsions and increase of the residual turbidity. The amount adsorbed is enough for starting redispersion, but not sufficient for supplementary TiO_2 particles neutralization (the process is not accompanied by a decrease in zeta potential values, see Figs. 3b and 4b).

3.2. Suspensions of TiO_2 particles in water/methanol mixtures

Figs. 2a, 3a and 4a also present the effect of D40-R30 on the separation of TiO_2 particles dispersed in water/methanol mixtures 90:10 and 50:50. A pronounced removal efficiency of titanium dioxide particles (over 90%) has been recorded at low polymer doses, irrespective of the polycation sample and water/methanol mixtures composition. Worthy of note is that the minimum residual turbidity values (up to 10%) have been obtained over polycation doses ranging from 0.2 mg L^{-1} to 0.6 mg L^{-1} for D40-Et30, 0.4 mg L^{-1} to 1.2 mg L^{-1} for D40-Oct30 and 0.1 mg L^{-1} to 0.8 mg L^{-1} for D40-Dod30 when water/methanol mixture 90:10 was used as the dispersion medium. After the end of the flocculation window (in case of solvent mixture 90:10) or at higher polymer doses than those corresponding to the minimum residual turbidity values (in case of solvent mixture 50:50) a steep increase of the residual turbidity occurred, hence the restabilization of the suspension as an outcome of the electrostatic and/or steric chain repulsions.

The explanation for the high degree of separation of the TiO_2 particles by D40-R30 when mixed solvent systems were used as dispersion medium could stem in the solvent mixtures effect on both the charges on the particle surface and polyelectrolyte chains. Less polar dispersion media of water/methanol mixtures enable less particle surface groups to dissociate ($\zeta_{90/10} = -31$ mV and $\zeta_{50/50} = -18$ mV) and consequently, the electrostatic repulsive interactions between the TiO_2 particles decrease. The lower values of zeta potential in solvent mixtures than in water confirm the rule that electrokinetic potential decreases as the volume fraction of alcohol increases (Hesleitner, Kallay, & Matijević, 1991). The reduction of the absolute ζ values at high volume fraction of alcohol (higher than 20%) was also found in case of salty dispersions of hematite particles (Hesleitner et al., 1991), latex microspheres (Odriozola et al., 2007), and TiO_2 (Kosmulski & Matijević, 1992). Some contradictory data has been reported for dispersions containing low volume fractions of alcohol in water (up to 10%). Thus, an increase of the absolute ζ values (a maximum) was noticed by Seeberg and Berg (1997) in case of polystyrene latex dispersion in 1-propanol/water mixture; the authors explained the appearance of this maximum in terms of changes of the dielectric constant of the media close to the particle' surfaces. Odriozola et al. (2007) reported zeta potential data for latex microspheres immersed in salty (KBr of different concentrations) water–alcohol media and found absolute maxima of ζ for water/ethanol and water/1-propanol mixtures; for methanol, no maximum of the absolute ζ value was observed. Also, Kosmulski and Matijević (1992) found that at 1×10^{-3} M KCl the replacement of water with methanol (10 and 30%) did not affect ζ of TiO_2 dispersions, except for the region of pH > 9, where some decrease was observed for 30% methanol. The results of our study showed no maximum of the ζ values when TiO_2 particles were dispersed in 10% methanol/water mixture.

As regards the polyelectrolyte, we have to mention that even the polyelectrolyte solutions which were added to the suspension have been prepared in distilled water, the interactions between polycations with TiO_2 particles take place in water/methanol mixtures. This is supported by similar residual turbidity values obtained when both the polymer solution and TiO_2 dispersion were prepared in solvent mixture with the same composition.

These solvents influence both the polyelectrolyte ionic groups dissociation and polymer chain conformation. However, the reduction of the dissociation is less significant for strong basic polyelectrolytes than for TiO_2 particles. The different behavior determines an increase of the charge ratio between polymer and particles and enhances the polymer adsorption on particle surface. As concern the chain conformation, we assume that in case of the hydrophilic sample (D40-Et30) the macroion chains become more coiled than in water, where they have some extension as $\xi = 0.42$ (see Table 1) and according to the Manning counterion condensation model, the counterion condensation is not expected ($\xi < \xi_{cr} = 1$) (Manning, 1969). The polyion chain size decrease in medium with lower dielectric constant than water is also caused by the weakening of the ionizable groups dissociation along the polyion backbone and hence, the lowering of the intra/intermolecular repulsive interactions between the charged groups. Our assumption is sustained by the viscosity results obtained in case of another hydrophilic cationic dextran derivative with higher charged content, D40-Et94 (Ghimici, Nichifor, & Wolf, 2009). One has also to mention that any polymer chain will initially adsorb from solution with a conformation that is close to what it has in solution and then relax toward the solid surface (Bremmel, Jameson, & Bigg, 1998). If we assume that, in water–methanol mixtures, the cationic polysaccharide chains adsorb on the TiO_2 particle surface with a more coiled (compact) conformation than in water, then they will form patches with higher local charge density inducing higher surface charge heterogeneity, which is known to enhance the flocculation efficiency (Bouyer, Robben, Yu, & Borkovec, 2001). Such a behavior would explain the better flocculation efficacy of the polyelectrolyte in water/methanol mixtures.

Related to the amphiphilic polyelectrolytes, it is well known that in aqueous solutions they tend to form associates when the polymer concentration increases beyond a critical concentration, called critical aggregation concentration. Previous fluorescence and microcalorimetric studies performed on these polymers revealed the occurrence of intra- and intermolecular hydrophobic associations at polymer concentrations of about 3 g L^{-1} for D40-Oct30 and 0.01 g L^{-1} for D40-Dod30 (Bai, Nichifor, Lopes, & Bastos, 2005; Nichifor, Lopes, Bastos, & Lopes, 2004). In water/methanol solvent mixtures, on the one hand, the intra- and intermolecular hydrophobic associations are disrupted and hence the coil dimensions should increase; on the other hand, the less number of dissociated groups should lead to a more compact macromolecular coil compared with that in water, as in the case of the hydrophilic sample. The viscosity measurements performed on solutions of D40-Dod30 in water, methanol and mixtures of water/methanol revealed that the mixtures of water/methanol were better solvents for this polymer than the solvents alone (Ghimici & Nichifor, 2009). Among the mixed solvents, the water/methanol mixture 50:50 gives the higher viscosity, perhaps because of the best balance between the good solvent for the polysaccharide backbone (water) and amphiphilic side chains (methanol) ($[\eta]_{H_2O} = 170$ ml $g^{-1} < [\eta]_{90/10\text{water/methanol}} = 203$ ml $g^{-1} < [\eta]_{50/50\text{water/methanol}} = 513$ ml g^{-1}). Looking at the $[\eta]$ values one could observe that the impact of the water/methanol solvent mixture on the chain conformation of D40-Dod30 is opposite to that on the hydrophilic sample, that is, the coil expansion. The polymer chains unfolding results in increasing accessibility of the polymer charges, and hence of their electrostatic attraction to the surface charges. The higher hydrodynamic dimensions of the macroions in water/methanol mixtures 90:10 and 50:50 lead to large polymer patches on the particle surface which,

according to Bouyer et al. (2001), increase the flocculation efficiency. This also could determine the larger optimum concentration range noticed in case of the amphiphilic samples than that of the hydrophilic one (D40-Oct30 in water/methanol 90:10 and D40-Dod30 both in water/methanol 90:10 and 50:50). However, the more rapid increase of the residual turbidity after the minimum was reached, in case of mixed solvent 50/50 as dispersion medium, could be ascribed to the low number of charges on the TiO_2 particles surface ($\zeta = -18$ mV) which imply that at overdose a great number of the polyion charges remain uncompensated leading to quick restabilization due to the repulsion electrostatic forces.

The zeta potential of the supernatant dependence on the polycation dose when water/methanol mixtures were used as dispersion medium gave information about the flocculation mechanism involved in the flocculation process (Figs. 2b, 3b and 4b). The shape of the curves is similar for all of the samples investigated both in 90:10 and 50:50 particles dispersion medium. The zeta potential values increased gradually with polymer dose until the end of the flocculation window in water/methanol 90:10 (0.6 mg L^{-1} for D40-Et30, 1.2 mg L^{-1} for D40-Oct30, 0.8 mg L^{-1} for D40-Dod30) and the dose corresponding to the minimum residual turbidity in water/methanol 50:50 (0.4 mg L^{-1} for D40-Et30, 0.6 mg L^{-1} for D40-Oct30, 0.6 mg L^{-1} for D40-Dod30). Further increase of polymer dose led to a steep increase in ζ and charge reversal which explained the increase of the residual turbidity and consequently, the restabilization of the suspension. In all cases ζ reached the charge neutralization point for a polycation dose which was higher than those corresponding to the end of the flocculation window: around 0.75 mg L^{-1} for D40-Et30, 1.33 mg L^{-1} for D40-Oct30, 0.94 mg L^{-1} for D40-Dod30 in the former dispersion medium and around 0.50 mg L^{-1} for D40-Et30, 0.55 mg L^{-1} for D40-Oct30, 0.70 mg L^{-1} for D40-Dod30 in the latter one; this finding pleads for the charge patch flocculation mechanism for TiO_2 particle separation. In this case aggregation occurs as a result of attraction between oppositely charged regions on partially covered particles. Further, one observes that the charge neutralization point shifts to lower polymer doses with decreasing the dielectric constant of the dispersion medium. As mentioned earlier, with decreasing the dispersion medium polarity less number of negative charges on the particle surface resulted and consequently, lower amount of polyelectrolyte was needed to neutralize the particle charges. The phenomenon that the higher the concentration of organic solvent the easier for charge reversal to occur was also observed by Hsu and Chang (2000) for TiO_2 particles (anatase) dispersed in a water/methanol mixture and $CaCl_2$ and $AlCl_3$ used as electrolytes.

Going back to the flocculation mechanism, we performed the next experiment in order to clarify it. The already flocculated TiO_2 particles from suspensions prepared in water/methanol 90:10 with D40-Et30 and D40-Dod30 (polymer dose 0.4 mg L^{-1}, residual turbidity around 4%) were stirred again for 60 min at 500 rpm. After a settling time of 15 min, the supernatant residual turbidity values were 3% and 4.5% for D40-Et30 and D40-Dod30, respectively. According to Yan et al., flocs which are initially formed via charge neutralization and then broken up by shearing can easily re-form upon removing the shearing forces, while polymer – bridged particles stay apart once broken up, since polymer tails and loops bridging across two or more particles are physically disrupted by the shearing forces (Yan, Glover, Jameson, & Biggs, 2004). Based on this finding, the result of the above experiment supports that the charge patch is the main separation mechanism of the TiO_2 particles by the investigated cationic polysaccharides. Nevertheless, a small contribution of bridging mechanism due to the interparticle hydrophobic associations cannot be excluded during separation of the TiO_2 particles by the amphiphilic cationic dextran derivatives.

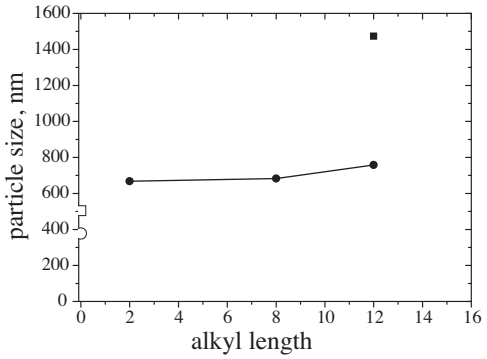

Fig. 6. Particle aggregate size at optimum polymer dose as a function of the length of the alkyl substituent R, in 90:10 water/methanol mixture (solid circle): 0.4 mg L^{-1} for D40-Et30; 1 mg L^{-1} for D40-Oct30; 0.4 mg L^{-1} for D40-Dod30; and in 50:50 water/methanol mixture (solid square): 0.4 mg L^{-1} for D40-Dod30. TiO_2 particle size in 90:10 (empty circle) and in 50:50 water/methanol mixtures (empty square) without polymer.

We have also undertaken measurements of particle aggregates size, Z-Average (d, nm) at polycation doses located in the flocculation window as well as of the initial TiO_2 particles suspension by DLS measurements (water/methanol 90:10 and 50:50) (Fig. 6). The small increase in particle size sustains also our assumption that the patch mechanism plays the predominant role in the separation process of the TiO_2 particles.

4. Conclusion

The separation of TiO_2 particles suspended in solvents with different polarities, water and water/methanol mixtures (90:10 and 50:50 v/v %), by cationic polysaccharides based on dextran, hydrophilic (D40-Et30) as well as amphiphilic (D40-Oct30 and D40-Dod30) was investigated. The main findings of this work can be outlined as follows:

- The residual turbidity values changed with addition of different doses of polymers, irrespective of the particles dispersion medium composition.
- The flocculation performance of all investigated dextran derivatives was quite low when water was used as dispersion medium for the TiO_2 particles; this might be caused by the (electro)steric repulsion forces between already adsorbed polyelectrolyte chains which prevent the polyelectrolyte/particles electrostatic attractions.
- The separation efficiency significantly increased (over 90%) when titanium dioxide particles were dispersed in mixed solvent systems; less polar dispersion media led to the decrease of the number of dissociated groups on the particle surface as well as on the polyelectrolyte chains, and affected polymer conformation.
- Changes in the alkyl substituent length did not lead to a noticeably improvement of the separation efficiency for TiO_2 particles.
- The charge neutralization point shifted to lower polymer doses with decreasing the dispersion medium polarity.
- The turbidity and zeta potential results pointed to the patch flocculation mechanism.

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