Electrokinetic properties of silica-titania mixed oxide particles dispersed in aqueous solution of C.I. Direct Yellow 142 dye – effects of surfactant and electrolyte presence

Stanisław Chibowski 1, Małgorzata Wiśniewska 1, Monika Wawrzkiewicz 2, Zbigniew Hubicki 2, Olena Goncharuk 3

1 Department of Radiochemistry and Environmental Chemistry, Institute of Chemical Sciences, Faculty of Chemistry, Maria Curie-Sklodowska University in Lublin, Maria Curie-Sklodowska Sq. 3, 20-031 Lublin, Poland;
2 Department of Inorganic Chemistry, Institute of Chemical Sciences, Faculty of Chemistry, Maria Curie-Sklodowska University in Lublin, Maria Curie-Sklodowska Sq. 3, 20-031 Lublin, Poland;
3 Department of Amorphous and Structurally Ordered Oxides, O. O. Chuiko Institute of Surface Chemistry, National Academy of Science of Ukraine, 17 General Naumov Str., 03164 Kiev, Ukraine.

Corresponding author: stanislaw.chibowski@poczta.umcs.lublin.pl (Stanisław Chibowski)

Abstract: The mixed SiO2-TiO2 oxide obtained by the pyrogenic method with the silica:titanium percentage ratio equal to 20:80 (ST80) was used in the experiments. The influence of azo dye C.I. Direct Yellow 142 (DY) adsorption at the mixed oxide-solution interface on the electrokinetic properties of solid particles was studied. To determine solid surface charge density and zeta potential of examined suspensions the potentiometric titration and Doppler laser electrophoresis techniques were applied. The changes in structure of electrical double layer formed on the mixed oxide surface in the dye presence were specified as a function of DY concentration, inorganic salt addition and surfactant introduction. The effects of surfactant type and its concentration were determined. Three surfactants of different ionic character (anionic SDS, cationic CTAB and nonionic Triton X-100) were used in measurements. The obtained electrokinetic characteristics of ST80 mixed oxide dispersed in aqueous solutions with various adsorbate compositions is essential for such suspensions stability.

Keywords: silica-titania composite, mixed oxide, zeta potential, solid surface charge density, dye adsorption, surfactant effect

1. Introduction

A composite material is made from at least two constituent compounds with considerably different physical or chemical properties. This material is characterized by different properties in comparison to the individual components, which remain separated from each other in the final structure by the interface layer (Elhajjar et al., 2017). Thus, it is a material obtained in an artificial way, at least biphasic and heterogeneous. The composite may include various materials, e.g. metal, metal oxide, carbon, ceramics, glass, polymers, etc. (Camargo et al., 2009). Due to the appropriate combination of individual components, the final material with the required properties and parameters, that would not be possible to achieve for individual components, is obtained.

Among the composites four main classes can be distinguished: structural composites, laminates, micro/nano composites and structural alloys (Murr, 2015). The first one are continuous structures of individual components - layers of rods or regular three-dimensional structures, e.g. resembling a honeycomb. Laminates consist of fibers embedded in binders. Depending on how the fibers are ordered, three composite types occur - fibers arranged in one direction, composite mats - fibers arranged in two perpendicular directions or disordered ones. In the case of micro/nano composites, the regular structure of two or more components is already organized at the supramolecular level. In turn,
structural alloys have a very regular microstructure and are a kind of alloys (metal/metal, metal/nonmetal, polymer/polymer, polymer/metal and polymer/nonmetal alloys).

Composites are widely used in various fields of human activity as construction materials in many technical fields, including architecture - e.g. concrete, reinforced concrete (Berdos et al., 2020), in aeronautics and astronautics - e.g. elements of airplanes, rockets, artificial satellites (Rathod et al., 2017), in the wheel and rail transport - e.g. springs and car bumpers (Ishikawa et al., 2018), in the production of machine parts, sport equipment and products - e.g. boats, skis, poles, javelins (Tong, 2019), in stomatology and medicine - implants, tissue regeneration systems (Park et al., 2017) as well as in environmental protection - removal of hazardous substances from gas and liquid phases (Wiśniewska et al., 2016a; Bazan-Woźniak et al., 2017; Ciesielczyk et al., 2017; Wawrzkiewicz et al., 2017a).

Mixed oxides are a wide group of composites due to their unique properties, such as high specific surface area and high concentration of active surface centers. There are terminal =M-O(H)-M= groups (Gun’ko et al., 2010), which are hydrophilic and possess different acid-base properties. This ensures the catalytic activity of such composites in different catalytic processes (Gun’ko et al., 2012) and their high adsorption efficiency towards various adsorbates such as polymers, metal ions and dyes (Wiśniewska et al., 2015a; Wawrzkiewicz et al., 2017b). An example of mixed oxide is silica-titania (ST) oxide. Due to presence of =Si-O(H)-Ti= and =Ti-O(H)-Ti= groups on its surface with significantly stronger Brønsted and Lewis acid sites than the terminal OH ones, this composite shows better sorption properties in comparison to individual oxides (Gun’ko et al., 2017).

In the present paper the electrokinetic characteristics of silica-titania mixed oxide dispersed in aqueous solution was provided. The parameters describing the structure of electrical double layer (edl) such as solid surface charge density and zeta potential of solid particles were determined. It should be noted that this structure of surface layer influences the solid suspension stability, which is very important for the solid phase separation from the solution after the adsorption process (Wiśniewska et al., 2015b). The effects of C.I. Direct Yellow 142 dye presence and their concentration were examined. Moreover, the impact of various surfactants with different ionic character and type of supporting electrolyte on the electrokinetic parameters of mixed oxide-dye interface was specified. Such systems containing two adsorbates (dye+surfactant and dye+salt) are more similar in composition to real industrial wastewater from e.g. textile factories and tanneries. Thus, the obtained results can be helpful in elaboration of effective procedures of these impurities removal from wastewaters using mixed oxide sorbents.

2. Materials and methods

2.1. Adsorbent and adsorbates characteristics

Mixed silica-titania oxide (pilot plant at the Institute of Surface Chemistry, Kalush, Ukraine) with the SiO2: TiO2 percentage ratio 20:80 (designed as ST80) were used as the adsorbent. The solid was characterized by the following textual parameters: the Brunauer-Emmett-Teller (BET) specific surface area 22 m2/g, the micropore area 6.7 m2/g, the average pore diameter 11 nm (mesopores), the total pore volume 0.0609 cm3/g, the micropore volume 0.0029 cm3/g. They were determined using low-temperature nitrogen adsorption-desorption isotherms method (ASAP 2405 porosimeter, Micrometritics). Mixed SiO2-TiO2 oxide was obtained applying the pyrogenic synthesis method by co-burning silicon and titanium tetrachlorides in a hydrogen-oxygen flame at a temperature of 1100-1400 °C. The titania phase in ST80 consists of a blend of anatase and rutile with C_anatase/C_rutile ratio (expressed as wt%) equalled 0.84. Surface content of titanium inmixed oxide determined by Auger electron spectra is 81.4% (Gorbik et al., 2007).

The diazo acid dye, namely C.I. Direct Yellow 142 (DY), widely applied in the textile industry during dyeing and printing operations, was used as an adsorbate. It was purchased from Sigma-Aldrich, Germany. Its molecular formula is C32H2S3N16Na2O2S2 and molecular weight is 794.73 g/mol. The surface active agents such as anionic sodium dodecyl sulphate (SDS), cationic hexadecyltrimethylammonium bromide (CTAB) and nonionic 2-[4-(2,4,4-trimethylpentan-2-yl)phenoxy]ethanol (Triton X-100) of laboratory grade were also used (Sigma-Aldrich, Germany). Additionally, the influence of salt addition (Na2SO4, Na2CO3 delivered by POCh, Poland) was
examined. All experiments were performed at 25°C using the following concentrations: dye - 10, 20 and 30 mg/dm³, surfactant - 0.1 i 0.5 g/dm³ and salt - 10 g/dm³.

2.2. Methods

Potentiometric titrations were performed in order to the determination of pH_{pzc} value of the examined system (pzc – point of zero charge) and solid surface charge density changes as a function of solution pH (examined pH range was 3-10). The prepared aqueous suspension containing 0.3 g of the solid in 50 cm³ of appropriate solution was introduced to the thermostated Teflon vessel (thermostat RE 204, Lauda). Next, it was titrated with NaOH of concentration 0.1 mol/dm³ using automatic microburette Dosimat 765 (Metrohm). The pH changes after the addition of each portion of base were monitored using pHmeter PHM 240 (Radiometer) as well as glass and calomel electrodes (Backman Instruments). The specialized “titr_v3” computer program developed by Janusz (1994) was applied to the calculation of the solid surface charge density \( \sigma_0 \) (\( \mu \text{C/cm}^2 \)). It was based on the following equation:

\[
\sigma_0 = \frac{\Delta V \cdot \varepsilon_0}{m s}
\]

where \( \varepsilon_0 \) is the base (NaOH) concentration (mol/dm³), \( F \) is the Faraday constant (C/mol), \( m \) is the solid mass in the suspension (g), \( S \) is the specific surface area of the solid (m²/g), \( \Delta V \) is the difference in the volume of base which must be added to bring the pH of suspension and reference solution (water) to the specified value (dm³).

Electrophoretic mobility \( U_e \) (cm²/Vs) measurements were made using a zetameter Zetasizer Nano ZS (Malvern Instruments) equipped with a universal dip cell. These experiments enable determination of pH_{iep} value of the examined system (iep – isoelectric point) and the zeta potential of the solid. The suspensions were prepared by the addition of 0.03 g of the mixed oxide to 100 cm³ of the appropriate solution. After 3-minute sonification (XL 2020 sonificator, Labcaire System Limited) the obtained suspension was divided into 8 parts. In each of them the appropriate solution pH value was adjusted, namely: 3, 4, 5, 6, 7, 8, 9 and 10 (with the accuracy of 0.1).

The electrophoretic mobility of solid particles was measured using Doppler laser electrophoresis technique. The zeta potential \( \zeta \) (mV) was calculated with the special computer program coupled with zetameter using the Henry equation (Hunter 1988):

\[
U_e = \frac{2 \pi \varepsilon_0 \varepsilon \eta}{3 \eta} f(\kappa \alpha)
\]

where \( \varepsilon \) is the dielectric constant, \( \varepsilon_0 \) is the electric permeability of vacuum (F/m), \( \eta \) is the viscosity of liquid medium (Pa·s), \( f(\kappa \alpha) \) is the Henry function.

The single zeta potential value represents the average of 5 repetitions and the measuring error did not exceed 5%.

3. Results and discussion

3.1. Effects of dye presence and its concentration

The previous studies indicated that \( \equiv \text{TiOTi} \) and \( \equiv \text{SiOSi} \) groups, as well as in a smaller number of \( \equiv \text{TiOSi} \) ones, are present on the surface of the mixed oxide (Gun’ko et al., 2007). These groups interact with water molecules, which causes surface hydroxylation manifesting in the formation of -OH groups (Janusz, 1994). The latter are amphoteric in nature and undergo the below reactions (on the example of the \( \equiv \text{TiOTi} \) group):

\[
\equiv \text{TiOTi} - \text{OH} + \text{H}^+ \leftrightarrow \equiv \text{TiOTi} - \text{OH}_2^+
\]

\[
\equiv \text{TiOTi} - \text{OH} \leftrightarrow \equiv \text{TiOTi} - \text{O}^- + \text{H}^+
\]

The total charge accumulated on the solid surface depends on the number of these two types of charged surface groups. As can be seen in Fig. 1(a) the point of zero charge (pzc) of ST80 mixed oxide is at pH 7 (the concentrations of negatively and positively charged surface groups are the same). In turn, the isoelectric point (iep) of the solid, at which the total charge accumulated in the slipping plane area is zero, occurs at pH about 3.2 (Fig. 1(b)). Such a large difference in the location of pzc and iep points can be caused by the presence of certain impurities on the mixed oxide surface, as well as the
overlapping of the diffusion parts of electrical double layers formed on opposite pore walls present in the adsorbent structure (Skwarek, 2014).

![Fig. 1. pH dependence of: (a) surface charge density, (b) zeta potential of ST80 mixed oxide without ad with adsorbed DY with different concentrations](image)

The addition of C.I. Direct Yellow 142 to ST80 aqueous suspension causes a significant increase in surface charge density and the shift of the pH_{pzc} point towards more basic pH values (Fig. 1(a)). This dye has sulfate groups with negative charge at both ends of its molecule. Their adsorption results in the formation of positively charged active groups on the solid surface, according to the reaction:

$$\equiv \text{TiOTi} - \text{OH} + \text{DY}^- + \text{H}^+ \leftrightarrow \equiv \text{TiOTi} - \text{OH}^- \text{DY}^-$$

The higher the DY concentration, the greater number of dye molecules undergo binding to the surface groups of the mixed oxide, which results in more visible increase in the $\sigma_0$ and pH_{pzc} values in comparison to the system without dye. The pH_{pzc} of ST80+DY system (with the highest examined dye concentration) reaches value about 8.6.

The presence of the DY adsorbed layers also affects the zeta potential ($\zeta$) of the ST80 particles dispersed in the aqueous solution - the electrokinetic potential of mixed oxide-dye system in the whole examined pH range is lower than that obtained for solid suspension in the absence of organic adsorbate (Fig. 1(b)). The lowering effect is greater, when the dye concentration is higher. Such behavior of the examined suspensions is probably the result of the slipping plane shift from the surface of the colloidal particle due to the adsorption of relatively large dye molecules (M’Pandou and Siffert, 1987), as well as the presence of negatively charged functional groups of adsorbed DY molecules in the slipping plane area (Wiśniewska et al., 2015c, 2016b).

3.2. Effects of salt presence and its type

The addition of inorganic salt completely changes the surface and electrokinetic characteristics of the ST80-DY interface (Fig. 2). The selected salts (Na_2SO_4 and Na_2CO_3) exist in ionic form in aqueous solutions, and thus their cations and anions (Ct⁺ and An⁻) affect the solid surface charge density, through the following reactions with mixed oxide surface groups:

$$\equiv \text{TiOTi} - \text{OH} + \text{An}^- + \text{H}^+ \leftrightarrow \equiv \text{TiOTi} - \text{OH}^- \text{An}^-$$

$$\equiv \text{TiOTi} - \text{OH} + \text{Ct}^+ \leftrightarrow \equiv \text{TiOTi} - \text{O}^- \text{Ct}^+ + \text{H}^+$$

The presence of inorganic salt ions in the system results in significant reduction of the surface charge density, at pH> 5 - for Na_2CO_3 and at pH>6 - for Na_2SO_4 (Fig. 2(a)). It is caused by the presence of salt anions in the by-surface layer of the solution. These ions can freely locate between adsorbed dye molecules due to their small size compared to the size of DY molecules. On the other hand, a clear increase in the electrokinetic potential value of the ST80+DY system in the presence of salts can be observed (Fig. 2(b)). Sodium cations are probably responsible for this phenomenon. They are located in the slipping plane area, neutralizing the negative charge accumulated in the solution layer directly adjacent to the solid surface.
Fig. 2. pH dependence of: (a) surface charge density, (b) zeta potential of ST80 mixed oxide with adsorbed DY (20 mg/dm³) without and with different types of inorganic salt (10 g/dm³)

3.3. Effects of surfactant presence, its type and concentration

The presence of surfactant causes changes in both the solid surface charge density (Fig. 3 (a)) and the zeta potential value of ST80 particles covered with the mixed dye+surfactant layers (Fig. 3 (b)). The addition of Triton X-100 has the smallest impact on the surface charge density of ST80, probably due to its nonionic character. On the other hand, the introduction of anionic SDS causes a slight increase in σ₀ value, which can indicate the competition of surfactant and dye molecules (of the same ionic character) for mixed oxide surface area (Wiśniewska and Nowicki, 2020). The greatest changes in the surface characteristics of ST80 were caused by the presence of cationic CTAB. In this case, a significant reduction in the surface charge density of the solid covered with the mixed DY+CTAB adsorption layer was obtained. These two adsorbates endowed with an opposite electrical charge form complexes in solution. These complexes can adsorb onto the solid surface, changing significantly the charge distribution both close to the solid surface and in the diffusion part of edl. The obtained results also suggest that adsorption of single cationic surfactant molecules is also possible. The evidence of such behaviour is the decrease of the mixed oxide surface charge density, which is associated with the creation of an additional number of negatively charged adsorption sites.

Fig. 3. pH dependence of: (a) surface charge density, (b) zeta potential of ST80 mixed oxide with adsorbed DY (20 mg/dm³) without and with different types of surfactants (0.1 g/dm³)

The largest changes in the electrokinetic potential value of the ST80+DY system, was also caused by the presence of CTAB (Fig. 3(b)). The increase in zeta potential is the result of the specific structure of the mixed adsorption layer, which is composed not only of dye-surfactant complexes, but also of single CTAB molecules. This structure ensures a large accumulation of positive charges in the slipping plane area, which is manifested by a significant increase of the electrokinetic potential. The addition of Triton X-100 and SDS causes only minimal changes in the zeta potential values of the ST80+DY system. In the
case of SDS, this confirms that its molecules adsorb preferentially in comparison to dye molecules and interact with the solid surface with hydrophilic heads. In turn, the hydrophobic tails are directed towards the solution without affecting the zeta potential of the mixed oxide particles.

For each surfactant used in the research, the effect of its concentration on the charge of both the surface and diffusion layers within edl was determined (Figs 4-6).

![Fig. 4](image1.png)

*Fig. 4. pH dependence of: (a) surface charge density, (b) zeta potential of ST80 mixed oxide with adsorbed DY (20 mg/dm³) without and in the presence of SDS with different concentrations*

![Fig. 5](image2.png)

*Fig. 5. pH dependence of: (a) surface charge density, (b) zeta potential of ST80 mixed oxide with adsorbed DY (20 mg/dm³) without and in the presence of CTAB with different concentrations*

![Fig. 6](image3.png)

*Fig. 6. pH dependence of: (a) surface charge density, (b) zeta potential of ST80 mixed oxide with adsorbed DY (20 mg/dm³) without and in the presence of Triton X-100 with different concentrations*
In the case of anionic SDS, the rise in its concentration causes noticeable decrease in both the η and ζ values (Fig. 4). This indicates an increase in the packing of the adsorption layer in which the surfactant molecules are located in both the surface and diffusion areas of electrical double layer.

Opposite behaviour (in relation to suspension in the presence of SDS) is shown by ST80+DY systems containing higher concentration of CTAB. In this case, there is an increase in both the surface charge density and the zeta potential values compared to an analogous system containing lower concentration of CTAB (Fig. 5). As in the case of SDS, the mixed adsorption layer probably contains a greater number of positive surfactant molecules (both in the form of complexes and single molecules), which is reflected in the increase of the values of parameters characterizing electrical double layer formed at the solid-liquid interface.

The increase in the concentration of Triton X-100 has a small effect on both the surface charge and the charge of the diffusion layer of ST80 particles in the presence of the dye (Fig. 6). This is primarily due to the nonionic nature of this surfactant. The observed slight differences can be caused only by minimal changes in the position of the slipping plane. This effect can occur as a result of the adsorption of dye-surfactant complexes or single DY and Triton X-100 molecules.

4. Conclusions

The presence of adsorption layers of C.I. Direct Yellow 142 anionic dye on the surface of silica-titania mixed oxide surface causes the increase of the solid surface charge density in the whole range of examined pH and the pH_{pzc} point shift (from about pH 7 obtained for the system without dye) towards more basic pH values (to pH about 8.6 for system containing DY with the highest concentration). The addition of DY causes a clear decrease in the electrokinetic potential of ST80 particles, throughout the whole pH range it assumes negative value. The change in charge distribution resulting from the location of inorganic salt ions in different parts of electrical double layer is the main reason of the observed changes in the electrokinetic characteristics of ST80+DY systems. The structure of the mixed layer formed as a result of the addition of surfactant, depends on the ionic nature of the surfactant and its concentration. The smallest effect on the surface charge density and zeta potential of the examined systems is caused by the nonionic Triton X-100 molecules. Changes in the surface and electrokinetic properties of dye-containing suspensions observed as a result of introduction of the anionic SDS to the system, result mainly from its competitive adsorption with dye molecules, whereas in the case of cationic CTAB addition - from the formation of DY-CTAB complexes.

References


