INVESTIGATION OF CARBOXYMETHYL CELLULOSE ADSORPTION ON A MODEL CHARGED INTERFACE

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ABSTRACT
This report concerns electro-optical study of colloid-polyelectrolyte complexes of sodium carboxymethyl cellulose (NaCMC) and gamma-aluminium oxide ($\gamma$-Al$_2$O$_3$) at pH 6.0 and fixed ionic strength. A frequency plateau shrink and a shift towards lower frequencies were observed after NaCMC adsorption especially near the point of zero charge. The electro-optical effect dependence on electric field strength shows that the coated particles reach full orientation at lower values of the applied electric field than particles with the highest charge density, previously investigated. Electrophoretic measurements, used as an additional analysis of the changes in the suspensions, showed particles’ charge overcompensation above $1 \times 10^{-3}$ g/L NaCMC and a saturation of electrophoretic mobility at the highest investigated concentrations of the polymer.

Keywords: adsorption, colloid, electro-optics, interface, polyelectrolytes

Introduction
The adsorption of polyelectrolytes (PE) on colloid particles has attracted the attention of many researchers due to their various practical applications – stabilization of suspensions in biological, medical and chemical industrial processes, gene therapy (4), fabrication of nanomaterials (2), modification of surfaces for changes of their adhesion properties, etc.

$\gamma$-Al$_2$O$_3$ is a detailed investigated amphoteric oxide with well-defined surface covered by Al$_2$(OH)$_3$. It forms fractal-shaped anisometric aggregates of particles stuck together in the process of their industrial formation. The sticking is not dense so the aggregates are porous. Unlike the ideal anisometric shapes – rods, discs, rotational ellipsoids, etc., traditionally used in the electro-optic studies because of their shape simplicity, fractal structures are much more widespread in nature. That is why $\gamma$-Al$_2$O$_3$, being fractal and amphoteric, can be used as a model surface allowing investigation of adsorption behaviour of both positively and negatively charged PEs, biopolyelectrolytes and their derivatives on a much more realistic interface. The disadvantage of that interface is that the electro-optical parameters are difficult to be calculated because of its complexity. Despite this, successful exploration of such complex surfaces would be able to expand the practical applicability of electro-optics as a method.

This study carried out at pH 6.0, was made as a prolongation of a previous one made at pH 4.5 at which $\gamma$-Al$_2$O$_3$ particles possess maximal positive charge (3). At lower pH values its solutions begin to lose their colloid state and gradually turn into molecular solutions improper to be investigated by the electro-optical method – electric light scattering, applicable only for colloid systems studies. The point of zero charge (PZC) of the suspension is at pH 8.5 so the suspension is with middle by magnitude positive charge at pH 6.0. Above the PZC the oxide particles are negatively charged but this charge range is not in interest for the present investigation because the adsorbed NaCMC is negatively charged in aqueous solution due to dissociation of the sodium ions. This difference between the charges signs of the particles and the polymer is important for the adsorption process because it depends basically on the forces of electrostatic attraction between the charged macromolecules and the counter-charged solid-liquid interface.

Suitable particles concentration (0.5 g dm$^{-3}$) was preliminary defined to be within the linear part of the concentration dependence of the electro-optical effect (EOE) with big enough signal/noise ratio. The previously used particle concentration 0.1 g dm$^{-3}$ (3), was found to be unsuitable for the present investigation because the
suspensions flocculated after PE addition. Despite that, present results and these in Ref. (3) are comparable due to the fact that the data are expressed by the relative EOE – ΔI/I₀, not by the absolute one, ΔI.

Materials and methods

The γ-Al₂O₃ and the NaCMC are products of “Degussa”. According to the electron micrographs (1) the oxide aggregates size is about 300 nm and consist of about 20 nm single spherical particles. The mean specific surface of the suspension is about 200 m²/g. The NaCMC (“Blanose 12M31FD”) with molecular mass 250 kDa has 10³ monomers and its degree of substitution is 1.2.

Oxide particles were sonicated for 30 seconds to increase their adsorption surface (Ultrasound Disintegrator UD-11 automatic, frequency 22 ± 1.65 kHz). Adsorption was achieved by mixing equal volumes of aqueous solutions of PE and γ-Al₂O₃ with pH (6.0) and ionic strength (2.5·10⁻⁴ mol.dm⁻³), followed by stirring for 30 minutes with magnetic bar. The adsorption conditions were adjusted by the use of 0.2 M HCl, NaOH and NaCl. Suitable NaCMC concentrations (in the range 5·10⁻⁴ – 5·10⁻² g.dm⁻³) were determined by electrophoresis.

The electro-optical method – electric light scattering – is based on the orientation of charged anisometric colloid particles in electric field, detected by light scattering at observation angle 90°. The orientation degree depends on the electric field strength and determines the difference (ΔI = I₁O - I₀) in the scattered light intensity when the field is applied (I₁O) or absent (I₀) – absolute EOE, ΔI. The ratio ΔI/I₀ is called relative EOE. When the system is optically stable, the variation of the EOE reflects directly the changes in the particles’ electric polarizability (γ). The steady-state EOE (ΔI/I₀) allows investigation of the geometrical and the optical properties of the colloid particles. The optical, the geometrical and the electrical properties are linked and dependent on each other. This dependence is expressed by the following formula: ΔI/I₀ = G . (γ E² 15 k₈T), where G is an optical function, E is the applied electric field strength, k₈ – the Boltzman constant, T – the absolute temperature.

When the electric field is turned off, the particles disorientate because of the Brownian motion. This is an important parameter called relaxation or decay time (τ) which depends on particles size definable by certain formula so it can give a notion of suspensions polydispersity. Decay time values are linked with the rotational diffusion coefficient D_r as it follows: τ = 1/6D_r (5).

Results and Discussion

The electrophoretic mobility U_eph (Fig. 1) of the oxide particles after adsorption of NaCMC alters insignificantly at low PE concentrations because they are insufficient to cause considerable particles charge decrease. At 1·10⁻³ g.dm⁻³ NaCMC, the particles charge is completely neutralized, the suspensions flocculate and no mobility in electric field exists so this is the isoelectric point. At higher concentrations the oxide particles reverse their charge sign. Above 3·10⁻² g.dm⁻³ NaCMC the electrophoretic mobility (U_eph) is constant so adsorption amount of PE has reached its maximum. The electrophoretic measurements prove that NaCMC adsorption really happens.

The small insetted graphic on Fig. 1 represents the dependence of the electric polarizability (γ) of the particles on NaCMC concentration. The comparison between both graphics indicates analogous behaviour detected independently by the use of two methods – electro-optics and electrophoresis. Before overcharging, the two parameters (U_eph and γ) decrease, and above charge inversion – they increase. Of course, unlike electrophoretic mobility, electric polarizability cannot possess negative values. Comparison of alteration tendencies of the values modules is important in that case.

The amplitudes of the frequency and field strength dependencies of the EOE indicate EOE decrease below PZC and an increase above it. This is a widely observed behaviour.
in that kind of studies due to the changes in the electric polarizability of the particles caused by the PE adsorption. So it is not surprising.

The plateaus of the frequency dependencies (Fig. 2) begin at 400 Hz both for uncoated particles and all colloid-PE complexes at the pH and the ionic strength of the experiment. Its upper boundary, however, shifts. For the uncoated particles it is 10 kHz, for the complexes with 5·10\(^{-3}\) g.dm\(^{-3}\) NaCMC and below this concentration, it is 5 kHz. Above 5·10\(^{-3}\) g.dm\(^{-3}\) NaCMC the upper boundary of the frequency plateaus gradually shrinks to 3 kHz. The EOE decreases after the plateau frequencies. So does the relaxation frequency of the coated particles. This is easy to be seen in the insetted plot in Fig. 2 where the frequency dependences are normalised to unity for better visualization. The plateau of an aqueous γ-Al\(_2\)O\(_3\) suspension, containing no added indifferent electrolyte, is between 1 kHz and 10 kHz (3). So the lower boundary of all the studied colloid solutions is shifted towards the hertz frequency region. This result can be observed both for the coated particles and the uncoated ones. Therefore NaCMC adsorption is not the reason for this shift. It must be due to the added low molecular electrolyte because the suspensions are with changed ionic strength and pH by comparison with the pure aqueous suspension.

The shift in the upper boundary of the frequency plateau towards the lower frequencies, however, is observed just for the suspensions containing coated particles. So this result may be attributed to NaCMC adsorption.

Relaxation times detection at disorientation of the particles after switching off the applied electric field is the electro-optical way to detect the fact of adsorption (except the electrophoresis). The adsorbed PE amounts enlarge the particles dimensions, so they disorient slower and the decay times increase proportionally to PE concentrations at constant electric field intensity. In Fig. 3 the decay time changes with electric field strength are presented.

As it is seen, the low concentrations of NaCMC – 1·10\(^{-4}\) g.dm\(^{-3}\) and 5·10\(^{-4}\) g.dm\(^{-3}\), do not change significantly the relaxation times. The adsorbed amount of PE is too low and the colloid particles dimensions do not change considerably. The complexes with constant electrophoretic mobility display significant increase in the particles sizes in comparison with the ones at low PE concentrations. Surprisingly, the decay times’ differences of the suspensions containing low NaCMC concentrations do not correspond to the differences between their concentration values. Similar tendency is also observed in the case of the suspensions with the highest NaCMC concentrations. Their decay time values are close to one another whereas the concentration difference is half an order. Only at low field strength, when the biggest particles are orientated, a considerable difference can be noted in that case. Analogous results were also obtained previously (3).

This discrepancy in the case of the low NaCMC concentrations may be explained with the complex structure of the oxide aggregates. Being fractals, build by numerous individual particles stuck together, but not densely, they possess cavities big enough to allow the macromolecules chains to get inside and adsorb at the inner interface. So the particle dimensions do not change as much as they would if no cavities existed. Of course, the outer surface is much more accessible, so the macromolecules adsorption at it is most probable and further concentration increase, though, leads to increase in the particles dimensions. The complexes with constant electrophoretic mobility, practically do not sense concentration changes because the NaCMC film at their interface is maximally dense and the electrostatic repulsion between the macromolecules in the film do not allow adsorption of additional PE chains.

The EOE dependences on the electric field strength (Fig. 3, insetted) are measured at 1 kHz – a value from the plateaus of all the frequency dependences. The field strength dependences show that maximally overcharged particles manifest significantly lower EOE than the uncoated ones. This also may be attributed to γ-Al\(_2\)O\(_3\) structural characteristics. PE amounts adsorbed at the outer surface,
responsible for the increase in the electric polarizability and the EOE above the PZC, are not sufficient to reach the polarizability values of the bare interfaces.

Fig. 3. Dependence of the γ-Al$_2$O$_3$ particles relaxation times on field intensity at pH 6.0, ionic strength 2.5 · 10$^{-4}$ mol.dm$^{-3}$, NaCMC concentrations (g.dm$^{-3}$):

- ■, no NaCMC;
- ○, 1 · 10$^{-4}$; ■, 5 · 10$^{-4}$; △, 1 · 10$^{-2}$; ◄, 5 · 10$^{-2}$

Insetted: The γ-Al$_2$O$_3$ suspensions EOE on electric field intensity at the same experimental conditions

The first concentration above the PZC – 5 · 10$^{-3}$ g.dm$^{-3}$, possesses hardly measurable EOE. It appears at values of the electric field intensity at which the EOEs of the other suspensions saturate so the electric polarizability of these particles must be too close to zero to overlap the sensitivity of the electro-optical device. Surprisingly, such a result is not observed for the suspension containing 5 · 10$^{-4}$ g.dm$^{-3}$ NaCMC although both concentration values are equally distant from the PZC – half an order. The steady state EOE is better achievable at the present experimental conditions than at pH 4.5 (3) where at the maximal electric field intensities that our electro-optical device can generate, the EOE demonstrates just an approach to saturation. Apparently, this result is due to the fact that at the two pH values (4.5 and 6.0) the particles charge is different. Consequently, that inequality is a reason for adsorption of unequal PE amounts causing unequal electric polarizability of the colloid-PE complexes. Thus, at constant electric field strength the lower polarizability at pH 6.0 saturates, whereas the bigger one at pH 4.5 does not.

Conclusions

In summary the following conclusions can be derived:

The NaCMC adsorption causes a decrease in the relaxation frequency of the oxide particles.

The low molecular electrolyte present in the investigated colloid solutions is a reason for the overall shift of the frequency plateau towards the hertz region. It begins at 400 Hz instead at 1 kHz as in the case of aqueous oxide suspension.

Colloid-PE complexes at the present experimental conditions express an easily achievable steady-state EOE in comparison with the previous investigation (3).

The increase in the relaxation times expresses disproportional correlation with the concentration increase. This observation suggests that the chains of the macromolecules may penetrate into the cavities existing in the γ-Al$_2$O$_3$ colloid particle and adsorb at their inner surfaces.

Acknowledgment

The author is grateful to Assoc. Prof. A.M. Zhivkov and Dr. M. Buleva from the Rostislaw Kaischew Institute of Physical Chemistry, Bulgarian Academy of Sciences for the help and the stimulating discussions concerning the experimental work and the interpretation. He is also grateful to Anna Y. Gyurova for the wording of the article.

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