

Abrasive Processing Steel in Aqueous Binary Compositions Polyelectrolyte-oligomer

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ABSTRACT: The results of investigation of the dispersing, rheological and surface-active properties of aqueous solutions of polyelectrolyte (PE) - sodium salt of carboxymethyl cellulose (Na-CMC), polyethylene glycol oligomers (PEGs) and their aqueous binary compositions (ABC) of Na-CMC-PEG are presented. A synergism of the dispersing action of the above components in binary solutions during abrasive treatment of steel has been revealed and its manifestation increases, when amine-containing PEG oligomers are added to the polyelectrolyte solution. The values of the dispersing action, surface tension and dynamic viscosity of aqueous binary compositions are established to be symbatically changed with the concentration of oligomers, which could be explained by the formation of polyelectrolyte-oligomeric complexes.

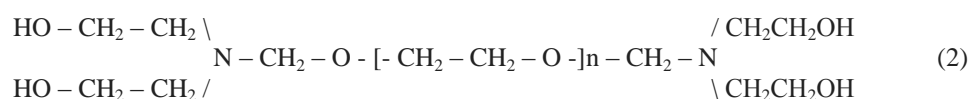
KEYWORDS: dispersion medium, abrasive treatment, oligomer, polyelectrolyte, intermolecular complex, synergism.

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I. INTRODUCTION

The limited reserves of raw materials in the world, especially oil, gas and coal, put the accent on the application of naturally renewable materials, seafood and wood processing's waste in order to solve an urgent technological problems [1]. It is known that solutions of polymers and oligomers, including those of natural origin, for example, Na-CMC solutions, are widely used as base ingredients for the production of coolant for the mechanical treatment of metals, hydraulic fluids, and quenching media [2]. However, in some cases there is a need to expand the range of physical and mechanical properties, especially rheological, surface-active and tribological of that objects. The resolution of this task seems quite possible, while involving a small additives of oligomers, like neat PEG400 (polyethylene glycol, Mw 400) or its amino-containing analogues: mono-anchor PEG (PEG400-1) and bi-anchor PEG (PEG400-2) [3] for modifying a polymer solutions. These oligomeric compounds have the following structure:



where $n = 9$.

So, the purpose of this work was to study the dispersing, surface-active, and rheological properties of aqueous solutions of Na-CMC, PEG400, its amino-containing analogs - PEG400-1, PEG400-2, and aqueous binary compositions (ABC) of Na-CMC-PEG, Na-CMC-PEG400-1, PEG400-2, correspondingly.

II. MATERIALS AND RESEARCH METHODS

The dispersing properties of aqueous solutions of PE (Na-CMC), PEG, and ABC PE-PEGs were characterized by the gravimetric method during abrasive dispersion of disks made of steel 45 on a friction machine [4] at a load of 0.1 mPa and a linear velocity of 0.12 m / s. Grey cast iron was utilized as lapping, silicon carbide (KZM28) was the abrasive. The dispersing effect of the components (c) of the dispersion medium was determined by the increase in removal ΔQ^C , i.e. by the difference between the amount of steel removal in solution (Q^S) and in water (Q^W): $\Delta Q^C = Q^S - Q^W$ [5]. A visual inspection of the samples shows that after the experiments the surface of the discs becomes dull, light gray in color, and the absence of scratches and burns on it indicates the normal course of the micro-cutting process.

The rheological properties of the solutions and compositions were investigated by rotational viscometry on a "Reotest-2" instrument with digital indication of the results at a shear rate of $Dr = 1312s^{-1}$ and a temperature of 25°C. The surface tension of Na-CMC solutions, oligomers, and ABC Na-CMC-PEGs solutions was determined using the modified Wilhelmi method (platinum plate) [6].

III. RESEARCH RESULTS AND DISCUSSION

3.1. DISPERSING PROPERTIES

Fig. 1 displays the concentration dependences of the dispersing properties of aqueous solutions of Na-CMC, oligomers PEG400, PEG400-1, PEG400-2, ABC Na-CMC-PEG400. The concentration of Na-CMC in ABC is 1% wt. and was selected taking into account the rheological parameters of the concentrate, the composition of which was determined according to the results of a study of the dispersing properties of ABC.

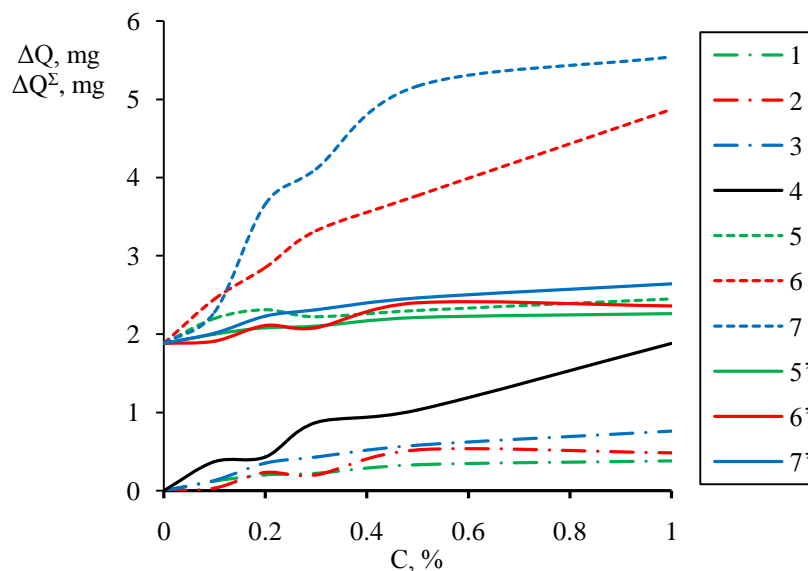


Fig. 1. Dependence of the gain of removal ΔQ St.45 on the concentration of aqueous solutions of PEG400 (1), PEG400-1 (2), PEG400-2 (3), Na-CMC (4), on the concentration of PEG in ABC Na-CMC PEG400 (5), Na-CMC-PEG400-1 (6), Na-CMC-PEG400-2 (7) and calculated $\Delta Q^{\Sigma C}$ values: for aqueous solutions of PEG400 (5'), PEG400-1 (6'), PEG400-2 (7') and Na-CMC ($C = 1.0\%$ wt.)

When comparing the obtained results on the increment in ΔQ values for aqueous solutions of Na-CMC, oligomers and ABC Na-CMC-oligomer (Fig. 1, curves 1-7, 5'-7'), it is seen that at the corresponding PEG concentrations, ΔQ values of ABC (ΔQ^{ABC}) are not the additive sum $\Sigma \Delta Q = \Delta Q^{PE} + \Delta Q^{OS}$ of the increase in metal removal in the oligomeric (ΔQ^{PE}) and aqueous solution of Na CMC (ΔQ^{OS}) (Fig. 1, curves 5', 6', 7'), which implies the mutual influence of the components on the dispersive properties of ABC. It is intrinsic for ABC based on PEG, and especially for amino-containing oligomers PEG400-1 and PEG400-2, a noticeable mutual reinforcement is observed ($\Delta Q^{ABC} > \Delta Q^{\Sigma C}$), i.e., the synergism of the dispersing effect in almost the entire range of oligomer concentrations occurs. The value of synergism (S,%) can be estimated by the difference between the values of ΔQ^{ABC} , obtained experimentally, and the calculated values of $\Delta Q^{\Sigma C}$, according the ratio:

$$S = [\Delta Q^{ABC} - (\Delta Q^{OS} + \Delta Q^{PE})] \cdot 100\% / (\Delta Q^{OS} + \Delta Q^{PE}) \quad [5].$$

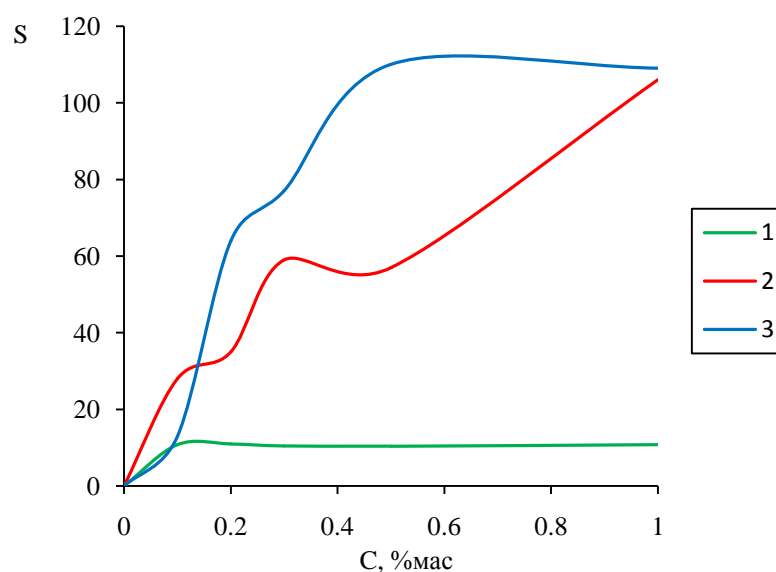


Fig. 2. The dependence of the synergy S on the concentration of oligomers PEG400 (1), PEG400-1 (2), PEG400-2 (3) in ABC Na-CMC-oligomer.

According to the calculations (the results are shown in Fig. 2), the S values for ABC based on the neat PEG400 in the concentration range of 0.1-1.0% wt. slightly depend on the oligomer content and do not exceed 11.0% (Fig. 2, curve 1). At the same time, the S values for ABC Na-CMC-PEG400-1 in this concentration range vary from 28.0% to 106.0%, and for ABC Na-CMC-PEG400-2 from 13.0% to 109.0% (Fig. 2, curves 2 and 3), which could be due to the presence of terminal amino-containing groups in the modified oligomers.

3.2. SURFACE ACTIVE PROPERTIES

It is noted [7], that the maximum dispersing effect of technological compositions, including coolants, is realized with an optimal combination of wetting and penetrating properties, which are defined by surface tension and viscosity. The results of measurements of the surface tension γ_g of aqueous solutions of Na-CMC, oligomers and ABC Na-CMC-PEGs depending on the concentration of components are presented in Fig. 3.

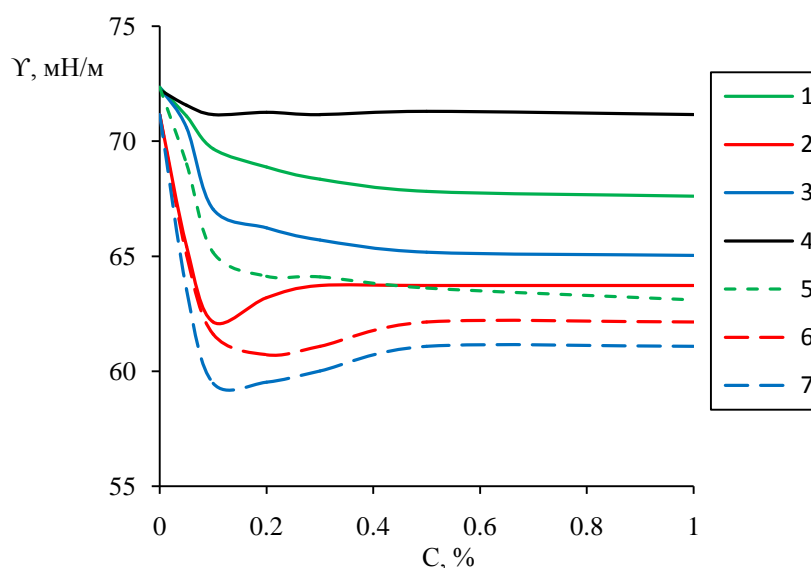


Fig. 3. The dependence of the surface tension γ of aqueous solutions of PEG400 (1), PEG400-1 (2), PEG400-2 (3), Na-CMC (4), ABC Na-CMC-PEG400 (5), Na-CMC-PEG400 -1 (6), Na-CMC-PEG400-2 (7) from the concentration of oligomers (1-3), Na-CMC (4) and oligomers in the ABC: Na-CMC-PEG400 (5); Na-CMC-PEG400-1 (6); Na-CMC-PEG400-2 (7).

A comparative analysis of the surface tension isotherms depicted in Fig. 3 shows that in the range of concentrations corresponding to the critical micelle formation concentration (CMC), the effect of the polyelectrolyte and oligomers on the decrease in γ value is not additive. Taking this into account, the sharp decline in γ^{ABC} values observed in Fig. 3, with uprise of the oligomer content could be attributed to the formation of intermolecular complexes (IMC) [10] of Na-CMC and PEG, which have a fairly clear ability to micelle formation. A quantitative assessment of the isotherms shows that the surface tension of binary solutions differs markedly: the maximum decrease in γ values of CMC (γ^{CMC}) is seen for ABC Na-CMC-PEG400-2 ($\gamma^{CMC} = 59.4$ mN / m, curve 7), for ABC Na-CMC-PEG400-1 $\gamma^{CMC} = 61.1$ mN / m (curve 6), and for ABC Na-CMC-PEG400 $\gamma^{CMC} = 62.4$ mN / m (curve 5), therefore, the stereochemistry of IMC and the shape of their micelles have certain differences. It should be emphasized that the most active, estimating by the γ^{CMC} values, IMC are formed in the ABC Na-CMC-PEG400-2, while γ values of PEG400-2 oligomer significantly differs (Fig. 3, curve 3) from those for the pure PEG400 (Fig. 3, curve 1), but, in turn, noticeably inferior compared to the PEG400-1 (Fig. 3, curve 2).

Thus, the surface-active properties of binary solutions of the polyelectrolyte-oligomer are determined not only by the γ values of the individual components, but also by the stereochemistry of the IMC and their subsequent micelle formation. As a result of those factors, the synergy of the surface-active and dispersing properties of the ABC components is realized.

3.3. RHEOLOGICAL PROPERTIES

The formation of IMC was assigned when previously studying the rheological properties of binary solutions of sodium polyacrylate (Na-PA)-non-ionic surfactants [8], PEG-nonionic surfactants [8, 9], polyacrylamide (PAA)-oligomeric surfactants [5] and the appropriate results ascertained a synergistic nonmonotonic changes in the viscosity, owing to the enhancing of surfactants' concentration. So, researches were conducted to monitor dependence of the dynamic viscosity of ABC Na-CMC-PEGs from the concentration of oligomers (the results are shown in Fig. 4).

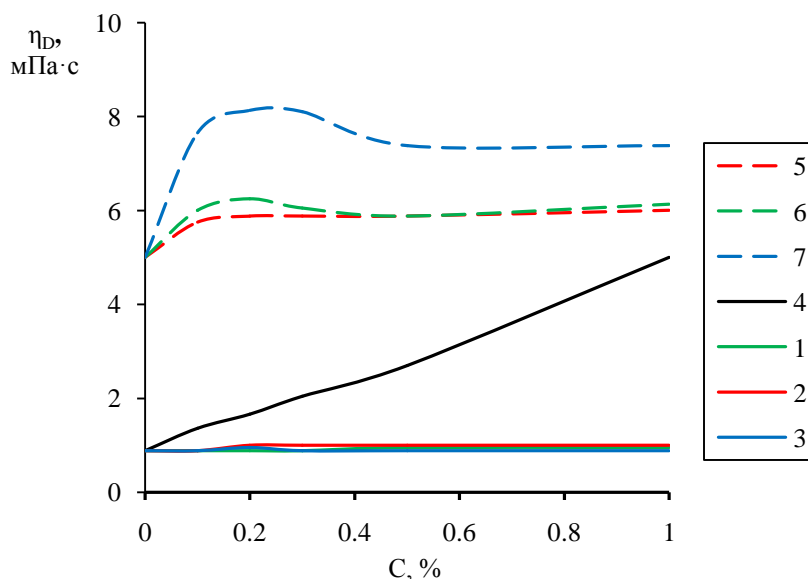


Fig. 4. The dependence of the dynamic viscosity η_D of aqueous solutions of PEG400 (1), PEG400-1 (2), PEG400-2 (3), Na-CMC (4), ABC: Na-CMC-PEG400 (5), Na-CMC- PEG400-1 (6), Na-CMC-PEG400-2 (7) from the concentration of oligomers (1-3, 5-7) and PE (4).

The interaction of oligomers with Na-CMC, as can be seen from Fig. 4, manifests itself in a significant growth in the dynamic viscosity of binary solutions in the concentration range of oligomers of 0.1-0.2% wt., and the presence of a maximum on the curves, indicating the existence of an optimal concentration (C_{OPT}) for PEG400-1 and PEG400-2 oligomers involved in the formation of IMC and subsequent micelle shaping. It is typical that the value of C_{OPT} practically coincides with the CMC of ABC Na-CMC-PEG400-1 and ABC Na-CMC-PEG400-2 (Fig. 3, curves 6 and 7), which allows us to propose a reasonable version for the manifestation of the synergism of surface active properties and the dispersing action of the binary solutions' components. The possibility of the formation of IMC between the Na-CMC polyanions and the amino-groups of oligomers was set up in [11], while the polyelectrolyte-oligomeric complex is stabilized by hydrogen bonds of the carbonyl and

OH-groups of Na-CMC with the carbonyl and amino groups of the oligomers. In binary solutions of Na-CMC-PEG400, the formation of IMC is apparently took place through hydrogen bonds only, involving the hydrogen atom of the terminal hydroxyl groups of the oligomer and ether oxygen of the glycopyranose unit in the Na-CMC. In this case, it can be assumed that after IMC being formed, micelles are emerged along the chain of Na-CMC polyanion, which causes the synergism of the surface-active and dispersing properties of ABC components. The feasibility of adsorption of surfactant molecules on macromolecules, e.g., Na-PA polyelectrolyte followed by subsequent initiation of micelle formation, leading to subsiding in CMC value and elevation in N (aggregation number) was described in [12].

IV. CONCLUSION

The concentration dependences of the surface-active, rheological and dispersing properties of aqueous solutions of polyelectrolyte, oligomers and binary solutions of Na-CMC-PEG are investigated. A synergy of the dispersing action of the ABC components was found and this magnitude is varied significantly for the initial PEG400 and its amino-containing mono-anchor and bianchor analogues (PEG400-1 and PEG400-2). The symbatism regarding the changes in the dispersing effect and surface tension of ABC from the concentration of oligomers was proved, which is accounted for by the formation of IMC of Na-CMC-PEG – modified PEGs. The formation of polyelectrolyte-oligomer complexes is affirmed by the presence of maxima on the concentration dependence of the dynamic viscosity of the ABC, while changes of η_D values correlate with ones for the dispersing action and surface tension of the corresponding binary solutions.

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