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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Purification of Fat-containing Wastewater with a Complex Based on Poly-*N,N,N,N*-Trimethyl[methacryloyloxyethyl]ammonium Methyl Sulfate and Sodium Dodecyl Sulfate

Yu. V. Shulevich, T. Kh. Nguen, A. V. Navrotskii, and I. A. Novakov

Volgograd State Technical University, Volgograd, Russia

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Abstract—Possibility of using complexes based on poly-*N,N,N,N*-trimethyl[methacryloyloxyethyl]ammonium methyl sulfate and sodium dodecyl sulfate for purification of fat-containing wastewater was examined.

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Food industry plants produce a large amount of waste with a high concentration of contaminants, which constitute a complex dispersed system containing emulsified proteins, carbohydrates, lipids, mineral salts, and suspended substances of organic origin.

Such a wastewater cannot be delivered to municipal treatment facilities because they disrupt the normal course of the biological purification process, which impairs the quality of wastewater discharged upon purification into water bodies. Therefore, the problem of recovery of fat and protein substances from wastewater formed at food industry plants has become particularly currently pressing.

Purification of wastewater from food industry plants is a labor-consuming task that consists in developing conditions and methods for destabilizing these systems [1].

A rather effective way to purify fat-containing wastewater (FCW) to remove both protein and fat contaminants is by flotation with preliminary coagulation of proteins with inorganic salts and synthetic flocculants, such as active silicic acid or polyacrylamide. Salts of iron and aluminum are commonly used as inorganic coagulants [2, 3]. This approach has the following disadvantages: low flotation activity of fats and the resulting increase in the optimal concentration of reagents [4]; presence of secondary contaminations in the form of chlorides and sulfates, which cannot be removed by biological purification methods from water being purified; and, occasionally, necessity for alkalization to provide hydrolysis of the coagulant. The last procedure is inappropriate because the pH of the medium is a strictly controlled parameter for wastewater to be discharged into sewage.

A possibly effective approach to FCW purification is to use of complexes of cationic polyelectrolytes with oppositely charged surfactants. Combining properties of cationic flocculants and the solubilizing capacity of surfactants, complexes of this kind (PESC) promote faster and more complete separation of dispersions containing emulsified fats [5].

The aim of our study was to examine the flocculating capacity of PESC for fat-containing wastewater.

EXPERIMENTAL

Poly-*N,N,N,N*-trimethyl[methacryloyloxyethyl]ammonium methyl sulfate was synthesized using the procedure described in [6]. The characteristic viscosity of a solution of the polyelectrolyte (PE) synthesized, measured in a 0.05 N solution of sodium chloride at 30°C, was 7.7 dl g^{-1}.

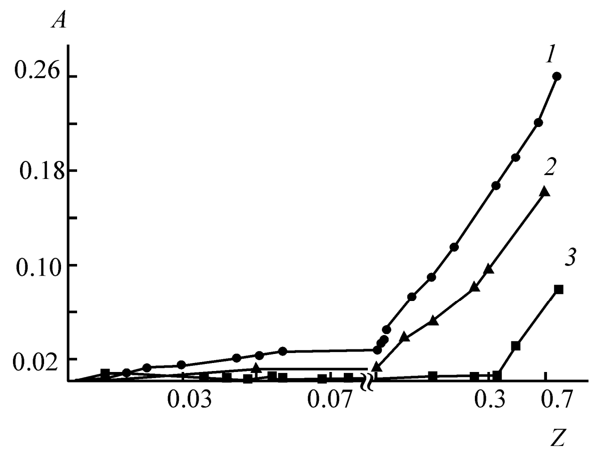

Fig. 1. Optical density A of PESC solutions vs. the composition Z of the PE-based complex. (*1*) Poly-1,2-dimethyl-5-vinylpyridinium methyl sulfate, (*2*) poly-[*N*-benzyl-*N,N*-dimethyl-*N*-methacryloyl)]ammonium chloride, and (*3*) poly-*N,N,N,N*-trimethyl[methacryloyloxyethyl]ammonium methyl sulfate.

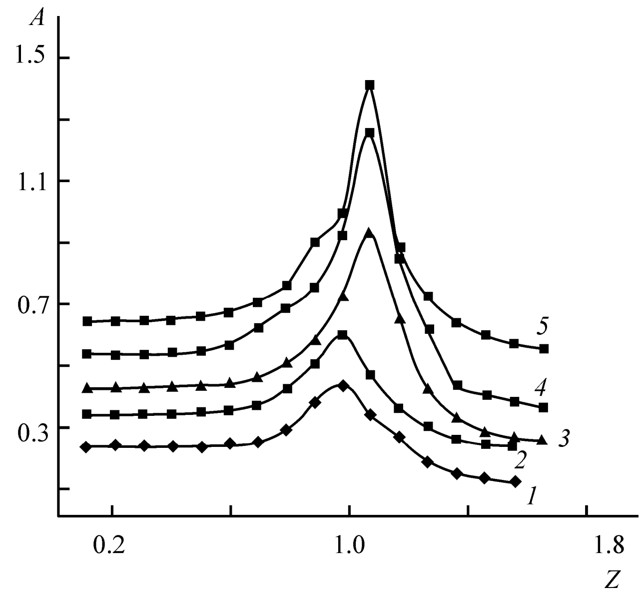

Fig. 2. Optical density A of wastewater with varied content of fat vs. the composition Z of the complex. PE concentration 0.1 mM. Content of fat in wastewater (mg l^{-1}): (*1*) 10, (*2*) 20, (*3*) 30, (*4*) 40, and (*5*) 50.

Sodium dodecyl sulfate (SDS) manufactured by Merck was used without additional purification.

The flocculating capacity of PESC was studied on wastewater formed at a food plant in Volgograd and taken from a collector to which wastewater is delivered from all technological lines without any preliminary purification.

The minimum PE concentration necessary for the complex to be formed in wastewater was estimated by turbidimetric titration. For this purpose, we added an SDS solution in portions to a wastewater sample under agitation. After adding each portion of SDS, the wastewater sample was agitated for 2 min and then its optical density was measured with a KFK-3 photoelectrocolorimeter.

To examine the effect of the keeping time, we added PE and SDS to a wastewater sample in amounts necessary for a complex of the limiting composition to be formed. Wastewater was kept for 1–3 h. Then, a second portion of SDS was added to wastewater to provide the working composition of the complex. Wastewater was agitated for 15 min and settled for 30 min, after which the optical density was measured with the KFK-3 photoelectrocolorimeter.

To perform a chemical analysis, we added PE and SDS to a wastewater sample, with SDS added in two portions with an interval of 3 h, after which the wastewater sample was agitated, settled, and filtered.

The contents of fats, suspended substances, and dry residue and the chemical oxygen demand (COD) were determined using the procedures described in [7–9].

Complexes of PE with oppositely charged surfactants are spontaneously formed on mixing aqueous solutions of the components through an electrostatic interaction of oppositely charged groups of PE and surfactants and hydrophobic interactions of aliphatic moieties of surfactant ions, which leads to their segregation and formation of a micellar phase in complex species [10]. The binding of surfactant ions with PE has a cooperative nature, i.e., almost the whole amount of surfactants added to the system is bound with PE beginning from a certain surfactant concentration in solution, named critical aggregation concentration (CAC). The CAC corresponds to a surfactant concentration at which intracomplex micelles start to be formed. As a rule, the CAC is lower than the critical micelle concentration (CMC) of surfactants in pure water by 1.5–2 orders of magnitude. As a result, soluble complexes are formed in the system, depending on the relative amounts of components in the system, up to the limiting composition of the complex, Z_{lim}.

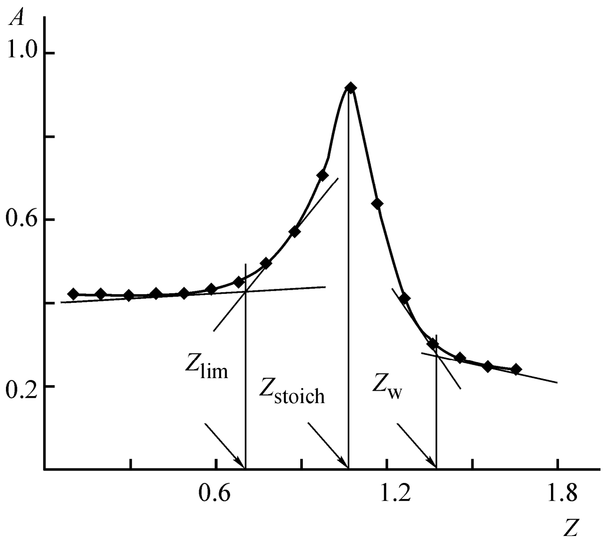

Fig. 3. Optical density A of wastewater vs. the composition Z of the complex. Content of fat in wastewater, 30 mg l^{-1}; PE concentration 0.1 mM.

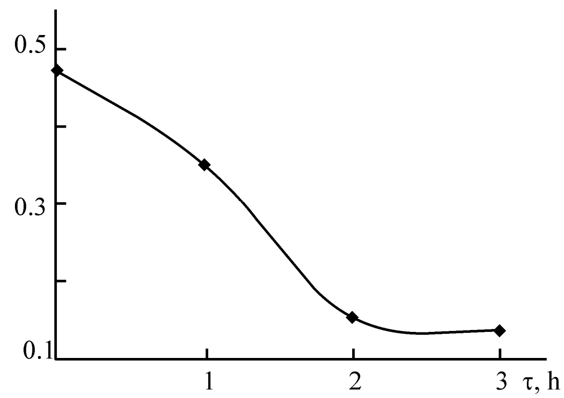

Fig. 4. Effect of the time interval τ between addition of surfactant portions corresponding to formation of complexes with the limiting and working compositions in the system on the optical density A of wastewater.

By the composition Z of the complex we understand the ratio between the molar concentrations of the surfactant and PE. The solubility of the complex species in solution is provided by free, unbound to surfactant ions, parts of the macromolecule. The limiting composition of soluble complexes corresponds to the maximum content of the surfactant in a complex species that retains its solubility. Further increase in the amount of the surfactant in the system to above Z_{lim} leads to phase separation in the system, with the result that a precipitate is formed from, as a rule, stoichiometric complex (Z = 1) insoluble in aqueous media, and the complex of limiting composition remains in solution. At Z = 1, the whole amount of the polymer is bound into an insoluble complex [11].

A characteristic feature of PESC is the presence of surfactant micelles bound to the polymer coil by ionic bonds and possessing a substantial solubilizing capacity for organic compounds of various classes, and just this circumstance enables their use in purification of fat-containing wastewater.

It was shown in [6] that the chemical nature of PEs strongly affects the fundamental aspects of complex formation. In particular, it was found for a number of cationic polyelectrolytes, poly-1,2-dimethyl-5-vinylpyridinium methyl sulfate, poly-[*N*-benzyl-*N,N*-dimethyl-*N*-methacryloyl)]ammonium chloride, and poly-*N,N,N,N*-trimethyl[methacryloyloxyethyl]ammonium methyl sulfate that, owing to the highest liophilizing capacity, the last PE is characterized by the largest value of the limiting composition (Fig. 1). The limiting composition is 0.5 for complexes of this PE with SDS, and 0.1–0.15 for the other two PEs.

Because the limiting composition corresponds to the maximum content of surfactant ions in a complex species that retains its solubility in water and the amount a solubilized substance (e.g., fat) is directly proportional to the amount of the surfactant, it is advisable to use the complex based on poly-*N,N,N,N*-trimethyl[methacryloyloxyethyl]ammonium methyl sulfate for flocculation of fat-containing wastewater.

The flocculating capacity of the complex was studied in a wide range of reagent concentrations at a varied content of fat in wastewater. Figure 2 shows how the optical density of wastewater with varied content of fat depends on the composition Z of the complex. These data demonstrate that that the process of complexation in wastewater is described by general laws of PESC formation. Up to a certain composition of the reaction mixture (limiting composition of the complex), the optical density of the system remains almost unchanged. An increase in Z above this value leads to a steep rise in the turbidity of the system because of the formation of insoluble complexes. At Z = 1, the optical density of the system reaches its maximum value, and further increase in Z causes a sharp decrease in the optical density because of the precipitation of the stoichiometric water-insoluble complex. It should be noted here that, at PE concentrations of 0.053–0.074 mM, no complexes are

Results of a chemical analysis of fat-containing wastewater

c_{PE}, mM	Concentration of fats, mg l^{-1}	COD	Suspended substances	Dry residue
	at a standard value of a parameter			
	25.0	354.0	215.0	541.6
0	75.0	1275.0	184.0	898.4
0.15	15.0	602.4	138.8	342.8
0.20	7.5	294.0	194.4	147.2
0.28	5.0	147.1	144.8	228.0

formed in wastewater. This may be due to the low molar concentration of PE in the system, which is insufficient for the complex to be formed.

At a fat concentration in wastewater of 10–30 mg l^{-1}, a PE concentration of 0.087 mM is necessary for the complex to be formed. An increase in the fat concentration to 50 mg l^{-1} results in that the necessary PE concentration grows. In this case, a PE concentration of 0.1 mM is required. Apparently, the PE concentration necessary for the complex to be formed in wastewater depends on the concentration of fat impurities. The reason is that nonpolar substances solubilized by surfactant micelles hinder micelle formation by raising the CAC [12].

In purification of wastewater, including that containing fat, it is necessary to reach the minimum turbidity (optical density). That is why we introduced the notion of the working composition of the complex, Z_w, which exceeds the value for the stoichiometric composition and provides the minimum optical density of wastewater upon treatment with reagents (Fig. 3). In all experiments, Z_w was 1.3–1.5.

Wastewater purification to remove fat impurities involves impurity solubilization by intracomplex micelles, and, therefore, it is advisable to perform the purification process in two stages. In the first stage, the polyelectrolyte and surfactant was added to wastewater in amounts necessary for a complex of the limiting composition to be formed, and in the second, the remaining amount of the surfactant was introduced to provide the composition Z_w necessary for a stoichiometric complex to be formed in the system and be completely removed from wastewater.

The data in Fig. 4 demonstrate that the lowest optical density of wastewater is obtained upon addition of surfactant portions to wastewater with an interval of 2–3 h.

To evaluate the efficiency of purification of fat-containing wastewater with PE-surfactant complexes, we made a chemical analysis of wastewater before and after its treatment with the complex in order to determine the content of fats and other no less important parameters characterizing the degree of wastewater purification.

The table lists chemical analysis data on wastewater purification.

It can be seen in the table that addition of PE in an amount of 0.15–0.28 mM makes it possible to reduce the content of fats in wastewater to below the permissible value. However, at a PE concentration of 0.15 mM, the COD exceeds the permissible value. The optimal, as regards the whole set of parameters, PE concentration is 0.28 mM.

CONCLUSIONS

(1) Polyelectrolyte–surfactant complexes can be used in purification of fat-containing wastewater.

(2) Because of having the largest value of the limiting composition ($Z = 0.5$) as a result of the high liophilizing capacity of the polymer chain, the complex based on poly-*N,N,N,N*-trimethyl[methacryloyloxyethyl]-ammonium methyl sulfate is the most effective reagent for wastewater purification. By using this complex, it is possible to reduce the content of fats in wastewater by 93%, COD by 59%, content of suspended substances by 67%, and that of the dry residue by 58%. These parameters conform to the regulations concerning the discharge of wastewater to the municipal sewage system.

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