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CARBOXYMETHYLATION OF PEAT BY MONOCHLOROACETIC ACID

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Efficient use of peat is one of the critical problems of the peat industry. Extensive chemical processing of the whole peat biomass to produce from it various humic preparations is the optimal method [1].

Carboxymethylation of cellulose and wood is a promising method for manufacturing surfactants that can be used to regulate the rheological properties of suspensions [2]. Much has been published on carboxymethylation of wood [2–7]. Thus, carboxymethylation products are widely used in industry. The process itself is thoroughly studied [5].

Markin et al. [3] first studied the reaction of lignocarbohydrates (wood of various origins) with monochloroacetic acid (MCAA) in propan-2-ol at 50–150°C. All studied lignocarbohydrates of various compositions reacted with MCAA in propan-2-ol to form partially water-soluble (42–64%) products containing up to 12.0% carboxymethyls [3]. The effect of preliminary base treatment of birch wood on its carboxymethylation in propan-2-ol was studied [6]. The content of carboxymethyls depended on the time and temperature of the preliminary base treatment.

Peat and wood have similar chemical compositions and the same biological nature. Peat, in contrast with wood, contains in addition to cellulose lignin, hemicellulose, and humic compounds, which react readily with bases and contain a significant number of acidic OH groups, which are most reactive in basic medium. Several studies have addressed the alkylation of peat [8–10]. Peat has been alkylated using alcohols in acidic medium in order to extract bitumens and waxes [10]. However, carboxymethylation of peat in various media has not been reported. Therefore, our goal was to study carboxymethylation of peat by monochloroacetic acid in propan-2-ol in the presence of NaOH in order to develop a method for preparing water-soluble polymeric surfactants.

The chemical composition of starting transition valley peat was determined. The moisture and ash contents were 8.0 and 9.7%, respectively. Starting peat contained 16.63% bitumen; 32.89, humic acids; 9.92, readily hydrolyzed polysaccharides; 9.38, cellulose; and 21.5, lignin. The content of total OH groups was determined as 13.6% (0.08 mol OH/g peat). The amount of MCAA used in the syntheses was 3.5 g (0.25 mol/mol peat OH).

The reaction with NaOH, in contrast with carboxymethylation of wood, was carried out under more mild conditions at 50–100°C because humic acids are thermally labile at temperatures up to 100°C [1]. The maximum solubility of the peat carboxymethylation products was achieved upon treatment with NaOH at 100°C for 3 h and carboxymethylation for 3 h at 50°C.

The effect of the duration of preliminary base treatment of the peat at 50°C on the properties of its carboxymethylation in propan-2-ol was studied. Table 1 presents the results.

The carboxymethylation product with the maximum solubility in water and aqueous base and the highest carboxymethyl content was produced after treatment of peat with aqueous base solution for 6 h at 50°C (carboxymethylation at 50°C for 3 h) (Table 1).

The effect of the temperature of preliminary base treatment for 3 h on the properties of its carboxymethylation products in propan-2-ol was studied. Table 1 gives the results.

Carboxymethylation of peat at various temperatures showed that the content of carboxymethyls in the products increased smoothly as the base-treatment temperature increased from 50 to 100°C. Products with the maximum solubility in water and aqueous base solution (2%) were produced at preliminary base-treatment temperature 100°C.

The relative viscosity of aqueous solutions of the peat carboxymethylation products varied in the range 0.91–1.16 (Table 1). The content of carboxymethyls depended on the time and temperature of preliminary base treatment.

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TABLE 1. Properties of Carboxymethylated Peat* Derivatives

Example	t, h	T, °C	Content of carboxymethyl groups, %	Solubility in H_2O, %	Solubility in NaOH (2%), %	η_{rel}, aqueous solution
1	1		13.2	42.7	44.6	0.91
2	2		13.4	53.3	56.1	1.01
3	3	50	14.8	56.7	66.0	1.03
4	4		16.0	61.1	72.1	1.10
5	5		16.6	83.1	81.5	1.14
6	6		21.2	88.0	90.5	1.16
7		60	16.6	61.7	68.9	1.04
8		70	17.7	67.2	76.2	1.05
9		80	18.5	73.4	80.8	1.06
10		90	19.6	78.3	84.7	1.08
11		100	20.5	80.1	87.2	1.10

*Peat mass, 3.0 g; base treatment temperature, 50°C; carboxymethylation time, 3 h; carboxymethylation temperature, 50°C; base treatment time, 3 h.

Thus, products with given properties, i.e., directed synthesis of carboxymethyl esters, could be synthesized by varying the conditions of peat base treatment before carboxymethylation.

The chemical composition of starting peat was determined using handbook methods [11, 12]; moisture, gravimetrically after drying in a drying cabinet at 100 ± 5°C; ash content, by combustion in a muffle furnace at 600°C; bitumen, by extraction with alcohol:benzene (1:2); lignin, by the Komarov H_2SO_4 method; humic acids, by extraction with basic sodium pyrophosphate; polysaccharides, calculated by difference. Hydroxyls were determined by the acetylation method [12]. The content of total OH groups in starting peat was 13.6%.

Carboxymethylation of peat was performed as follows. A weighed portion of air-dried peat sample (3.0 g) was placed into a three-necked round-bottomed flask equipped with a stirrer and reflux condenser, treated with stirring with isopropanol (60 mL), stirred, gradually treated with aqueous NaOH (20 mL, 30%), stirred at 50°C for 1–6 h, gradually treated with MCAA (3.5 g, 0.25 mol/mol peat OH), and held at 50–100°C for 1–6 h. When the reaction was finished, the product was filtered off, washed with EtOH (96%), acidified by AcOH (90%) to pH 5, washed until neutral and a test for chloride ion using $AgNO_3$ solution was negative, and dried at 60°C in a drying cabinet to constant mass.

Carboxymethylated peat derivatives were analyzed for carboxymethyl content and solubility in water and aqueous base (P, %). The relative viscosities (η_{rel}) of their aqueous and basic solutions were determined according to the standard for CMC [13].

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