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Synthesis and Physicochemical Study of Tetraaquatritetraphthalatodiiron(III)

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Abstract—An iron(III) complex of terephthalic acid of the general formula $Fe_2[C_6H_4(COO)_2]_3(H_2O)_4$.was synthesized. The composition and structure of the complex were studied by X-ray phase analysis and IR spectroscopy. The thermal stability of the complex was studied in the range 20–900°C. It was shown that doping with a $Fe_2[C_6H_4(COO)_2]_3(H_2O)_4$ reagent improves the rheological properties of heavy oil.

Keywords: coordination compounds, terephthalic acid, structure, thermal stability, heavy oil, rheological properties

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Phthalates and terephthalates of various metals have found wide application in industry. For example, zinc terephthalate is used as vulcanization activator in rubber production and calcium terephthalate, as lubricator for prevention of rubber sticking to engineering fibers [1]; tin terephthalate is used as capacitive dielectric [2]; ruthenium terephthalate exhibits semiconductor properties [3, 4]. Due to their layered structure [5–7], metal phthalates and terephthalates are widely used as molecular sieves and adsorbents, in particular, copper(II) terephthalate is used as adsorbent for N_2, Ar, and Xe [8].

In the present work we synthesized an iron(III) terephthalate complex and studied its physicochemical properties. The composition and structure of the complex were confirmed by elemental analysis, IR spectroscopy, X-ray phase analysis (XPA), and differential thermal analysis (DTA).

According to the XPA data, the synthesized iron(III) terephalate complex consists of a single phase and has a high symmetry (unit cell parameters 18.40, 9.95, and 9.75 Å).

The elemental analysis of the complex corresponds to tetraaquatriterephthalatodiiron(II) $Fe_2[C_6H_4(COO)_2]_3\cdot(H_2O)_4$.

The complex is formed in three stages. At the first stage $FeSO_4$ reacts with water forms a hexaaqua complex.

$$FeSO_4 + 6H_2O = [Fe(OH_2)_6]^{2+}SO_4^{2-}.$$

At the second stage $[Fe(OH_2)_6]^{2+}$ is readily oxidized to $[Fe(OH_2)_6]^{3+}$ via a loss of one π_d electron.

$$\sigma_d^{\text{antib}} \uparrow\uparrow \; \sigma_d^{\text{antib}} \uparrow\uparrow,$$

$$\pi_d \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \; \pi_d \uparrow\downarrow \uparrow\downarrow \uparrow,$$

$$[Fe(OH_2)_6]^{2+} \; [Fe(OH_2)_6]^{3+}.$$

The standard potential of the system $Fe^{3+} + \bar{e} = Fe^{2+}$ is 0.76 V, and, therefore, the Fe^{2+} ion can be oxidized in an acid medium even with molecular oxygen.

$$2Fe^{2+} + 1/2O_2 + 2H^+ = 2Fe^{3+} + H_2O, E = 0.46 \text{ V}.$$

At the third stage the terephthalate anion destroys the Fe^{3+} hexaaqua complex to form the complex $Fe_2[C_6H_4(COO)_2]_3\cdot(H_2O)_4$.

The IR spectrum of $Fe_2[C_6H_4(COO)_2]_3\cdot(H_2O)_4$ shows well-defined bands of asymmetric and symmetric vibrations of the carboxylate groups at 1610–1377, 1593–1412, and 1528–1463 cm^{-1} (Fig. 1) [9, 10]. The large differences between ν_{as} and ν_s of 233, 181, and 65 cm^{-1}, respectively, suggest monodentate and bidentate bonding of the metal ions with the tere-

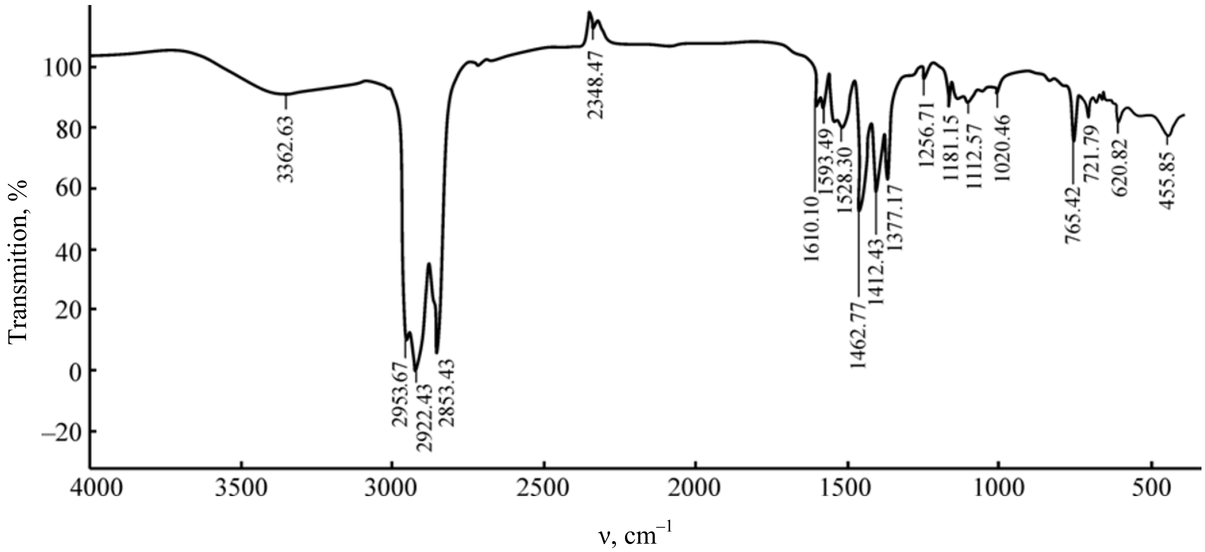

Fig. 1. IR spectrum of $Fe_2[C_6H_4(COO)_2]_3(H_2O)_4$.

phthalate carboxyls [10]. The broad band at 3100–3700 cm^{-1} (with a maximum at 3363 cm^{-1}) belongs to water molecules.

We suggest that the $Fe_2[C_6H_4(COO)_2]_3{\cdot}(H_2O)_4$ complex has a chain polymer structure in which one of the terephthalate anions forms a bridge between the central atoms, binding with them in a bidentate manner ($\Delta\nu_a - \nu_s = 1528 - 1463 = 65$ cm^{-1}), and the other two anions bind with the metal in a monodentate fashion ($\Delta = 233$ and 181 cm^{-1}). The coordinated water molecules readily form intramolecular hydrogen bonds with the carbonyl oxygen.

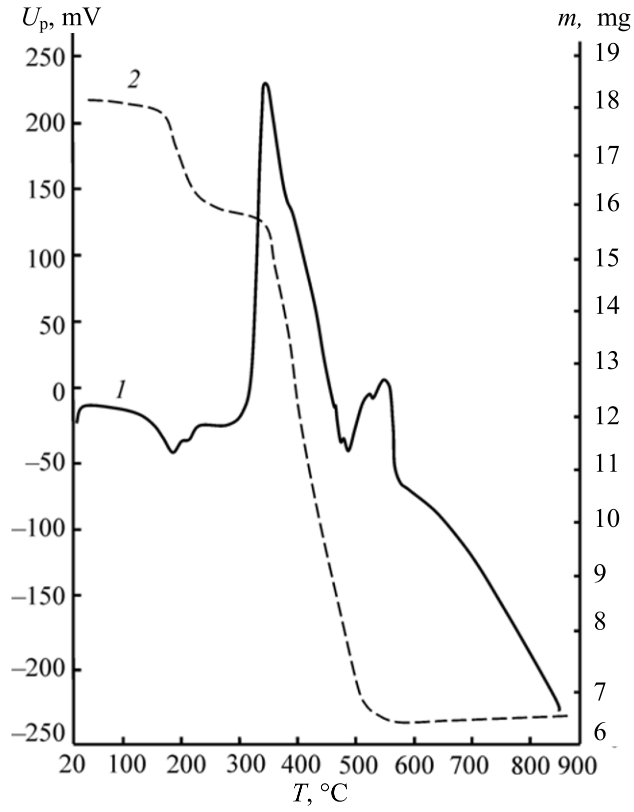

Fig. 2. Thermoanalytical curves of $Fe_2[C_6H_4(COO)_2]_3(H_2O)_4$: (*1*) DTA and (*2*) TG.

According to the thermoanalytical data (Fig. 2), the decomposition of the $Fe_2[C_6H_4(COO)_2]_3{\cdot}(H_2O)_4$ complex occurs via consecutive elimination of four water molecules in the temperature range 150–250°C and is accompanied by a small but well-defined endothermic peak with two maxima at 196 and 225°C. The high water elimination temperature (150°C) suggests that water molecules are bound with each other and terephthalate carboxyl oxygens by strong hydrogen bonds and are not coordinated to the central ion. Thus, of the four water molecules two are coordination and the other two are crystallization. The experimental and calculated weight losses due to elimination of water molecules are 11.1 and 10.93%, respectively.

The decomposition of the anhydrous complex occurs in the temperature range 300–510°C and is accompanied by a well-defined exothermic peak with maxima at 372 and 420°C. Then up to 900°C decomposition and burning off the organic residue take place. The experimental and calculated weight losses are 53.67 and 53.44%, respectively. The DTA curve shows one more exothermic peak (maxima at 500 and 510°C) in the range 480–544°C; the weight loss of 0.3 mg (3.6% of the total weight) could not be

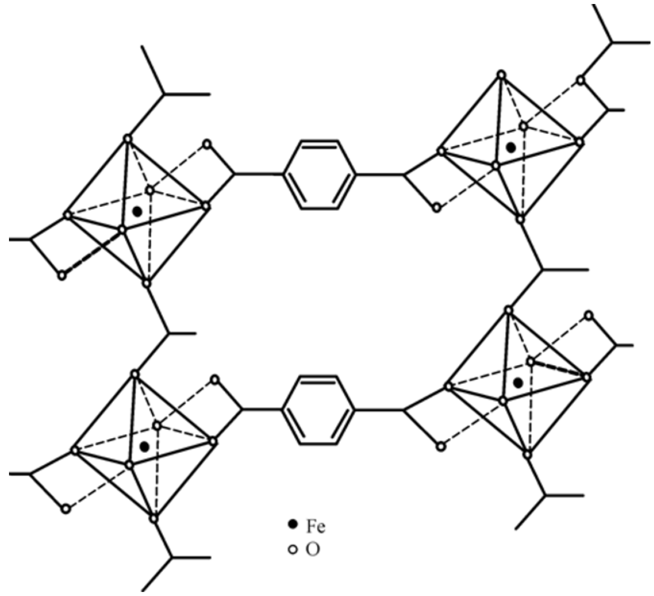

Fig. 3. Suggested structure of $Fe_2[C_6H_4(COO)_2]_3(H_2O)_4$.

assigned with any specific process. The final thermolysis product is Fe_2O_3.

Thus, the physicochemical study established that the synthesized compound has the formula $\{Fe_2[C_6H_4(COO)_2]_3(H_2O)_4\}_n$. The suggested polymeric layered structure of the complex is shown in Fig. 3. As mentioned above, the water molecules in the crystal occupy different positions: two of them are coordinated to metal, and the other two reside between layers.

It was shown that doping heavy oil with the BAF-2 reagent on the basis of tetraaquatritertephalatodiiron(III) decreases the oil viscosity from 9 to 2.1 sSt and improves its rheological properties (see table).

Effect of the BAF-2 reagent of the characteristics of heavy oil[a]

Parameter	Without BAF-2	With BAF-2 (160 mL)
Oil content, %	60.0	80
Specific weight, kg/m^3	878.0	889.0
Water content, %	8.0	3.0
Viscosity, St	9.0	2.1
Tar, %	36.0	0.0
Mechanic mixtures, %	32.0	17.00

[a] Sample volume 300 mL.

EXPERIMENTAL

X-ray phase analysis was performed on a Commander Sample ID (Coupled Two Theta Theta) diffractometer with a copper cathode. The IR spectra were measured on a Thermo Scientific Nicolet 1810 spectrometer in the range 400–4000 cm^{-1} for suspensions in mineral oil at room temperature.

Thermal analysis was performed on a Netzsch STA 449 F3 Jupiter instrument. Elemental analysis was performed on a Carlo Erba CHNS/O EA1108 analyzer. The metal content was calculated from the weight loss curve.

Tetraaquatritetraphthalatodiiron(III). Terephthalic acid of chemical grade, 0.498 g, was dissolved with heating in 50 mL of distilled water, and 0.50 g of $NaHCO_3$ was added. Powdered $FeSO_4 \cdot 7H_2O$ of pure grade, 0.556 g, was added to the resulting hot solution. The solution acquired a pale green color which gradually turned into light brown. The precipitate was filtered off, washed with several portions of distilled water, and dried first in air and then in an oven at 50° C. Yield 80%, light brown crystalline powder. Found, %: C 43.012; H 2.988; Fe 16.605. $C_{24}H_{14}Fe_2O_{16}$. Calculated, %: C 42.985; H 2.900; Fe 16.716.

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