The Study on the Reduction of the Viscosity of Transported Heavy Crude Oil by Fe(II) and Fe(III) Complexes with Phthalic Acid

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ABSTRACT: *The coordination compounds of Fe (II) and Fe(III) with phthalic acid were synthesized. The compounds were studied by X-Ray Diffraction (XRD), Differential Thermal Analysis (DTA), and IR spectroscopy. It has been established that, regardless of the oxidative number of iron, the synthesis products have the same chemical composition and chemical formula - $[Fe_2(o\text{-}C_6H_4(COO)_2)_3]$. It also found that the carboxyl groups of phthalate dianion have a monodentate and bridging function and the complex itself is a polymer-layered structure. Based on the obtained results, a schematic structure of the complex was proposed. Also were studied the thermal stability of the complex in the temperature range 20-660 ℃ and the supramolecular interaction of this substance with the rheological properties of heavy commercial oils. This significantly reduces the viscosity of heavy oil during transportation. Coordination polymer-based composites have been developed and tested. The use of composite solves several technological problems associated with the transport of high-viscosity oil.*

KEYWORDS: *Complex; Structure; Muradhanly; Reagent; Rheology; Coordination polymer; Nanomer.*

INTRODUCTION

The great interest in phthalates and terephthalates different metals in, which lately is the possibility of their becoming substitutes of natural elements and adsorbents, particularly zeolites and clays, which is directly

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connected with the porous-coated polymer structures of these compounds [1-3]. For example, due to the layered structure, phthalates and terephthalates are widely used as molecular sieves and adsorbents, in particular, copper terephthalate is used to absorb N_2, Ar, Xe [4]. Zinc terephthalate is used as an activator of vulcanization, in the production of rubber, calcium terephthalate, as a lubricant, to prevent the adhesion of rubber to processing fibers [5], tin terephthalate as a capacitive dielectric [6], and ruthenium terephthalate exhibits semiconductor properties [7,8] etc. The present work is devoted to the study of the complexes of the formation of phthalic acid with iron (II) and (III) and the physico-chemical study of the resulting complexes.

EXPERIMENTAL SECTION

X-ray phase analysis was performed on a Commander Sample İD (Coupled Two Theta/) device WL = 1.54060. IR spectrum of filmed on a Nicole 1810 spectrometer from Thermo Scientific, in the 400-4000 sm^{-1} region, the threshold was 69.041, and the sensitivity was 6S. The sample was prepared as a suspension in vaseline oil at room temperature.

Derivatogramms written by NETZSCH STA 449F3 STA449F3A-0836-M Derivatograph (FRG). (Range 20/10 (c/m)/650).

Elemental composition of the resulting compounds were determined by gas chromatography on the CHNSO "E" analyzer of the firm CARLO ERBA. The metal content calculated loss curve was from the mass by the amount of carbonate obtained after heating on derivatograph to 600 °C.

Synthesis of the compound

The starting materials were $FeSO_4{\cdot}7H_2O$, $FeCl_3{\cdot}6H_2O$, $NaHCO_3$, $C_6H_4(COOH)_2$ (phthalic acid) CP(GOST 3759-75). Phthalic acid in the amount of 1.66 g (0.01 mol) and 4.98 g (0.03 mol) dissolved in 50 and 100 ml of distilled water with addition of 1.68 g (0.02 mol) and 5.04 g (0.06 mol) of $NaHCO_3$, respectively. To the resulting hot solutions, 2.78 g and 5.41 g of $FeSO_4{\cdot}7H_2O$ and $FeCl_3{\cdot}6H_2O$ powders were slowly added. When $FeSO_4{\cdot}7H_2O$ is added to the solution, the solution first acquires a pale green color, which is characteristic of cationic aquo complexes of Fe (II) [9]. The pale green color gradually turns into a light brown color. In addition to a $FeCl_3{\cdot}6H_2O$ to the solution, a semicrystalline powder of light-brown color immediately precipitates. Thus, a light brown polycrystalline powder precipitates out of both solutions.

The filtered precipitates were washed several times with warm distilled water, dried first in air, and then in an oven at 50°C. The identification of new compounds carried out by various physicochemical methods, such as XRD, DTA, IR spectroscopy and chemical element analysis.

The discussion of the results

X-ray phase analysis

X-ray phase studies have shown that the products obtained are composed of one phase and they are not very high crystalline, but the diffraction pattern has clear intense maxima and they are distributed throughout the angles that the compounds have a high symmetry. In the diffractogram of both compounds, all the maxima are well indicated with maxima a = 11.256, c = 8.61, c = 10.56 A°. This is an indication that two and trivalent iron salts produce the same substance, the X-ray diffraction pattern of which is provided in Fig. 1.

Elemental analysis

Elemental composition of synthesized products is shown in Table 1.

According to the results of chemical element analysis of synthesized products, it concluded that the composition of the compounds obtained corresponds to the chemical formula of triflate (D). Thus, the results of the two studies are in good agreement with each other.

IR-spectroscopic study.

The IR spectrum of the complex compound is presented in Fig. 2. In the IR spectrum of the compound, absorption bands at 1610 and 1377 cm^{-1} and at 1568 and 1416 cm^{-1} are observed, which refer to stretching vibrations of carboxyl groups, in particular, to ν (c = 0) and ν (c-0), respectively. For a symmetrical group COO^1, these frequencies correspond to ν_a (COO-) and ν_s (COO-). For the first group of frequencies, the value of the difference $\Delta=[\nu_a(COO-) - \nu_s(COO-)]$ is 233 cm^{-1}.

This means that the carboxyl groups with the metal ion are bound monodentately. The second group of frequencies, this value is 152 cm^{-1}, which shows

Table 1: The results of the elemental analysis of synthesized products.

Compounds	Gross formula	Content (found/calculated), %		
		Fe	C	H
$Fe_2({}_OC_6H_4(COO)_2)_3$	$Fe_2C_{24}H_{12}O_{12}$	18,45/18,54	47,12/47,68	2,03/1,99
$Fe_2({}_O.C_6H_4(COO)_2)_3$	$Fe_2C_{24}H_{12}O_{12}$	18,57/18,54	47,21/47,68	2,04/1,99

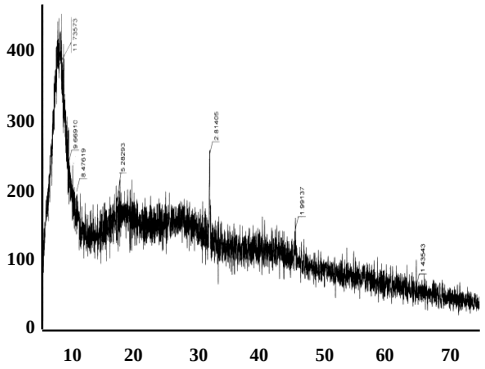


Fig. 1: X-ray of complex compounds.

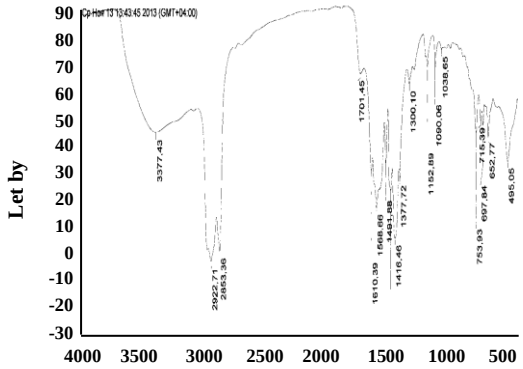


Fig. 2: IR spectrum of a complex compound.

the bridging of the carboxyl group to the metal [10]. Thus, it turns out that in the complex there are two types of binding of carboxyl groups: monodendentate and bridging.

On this basis it is possible to make such conclusion, that two acid anions of phthalic acid with a metal are bound monodentately, and the third anion forms a bridge between two metals.

In addition, three bands in the interval 890–720 cm^{-1} (deformation vibrations of COO-) and a strong band at 497 cm^{-1} π-(CO_2), which are not present in bridge complexes [11] are observed in the IR spectrum.

Thermogravimetric studies.

The complex compound triflatadodi Fe (III) is stable up to a temperature of 240 ^{0}C. Beginning at a temperature of 240 ^{0}C, the anhydrous complex compound decomposes first slowly to a temperature of 320 ^{0}C, and then at a high rate. The destruction of the complex compound is accompanied by an exothermic effect in the temperature range of 240–480 ^{0}C with a single maximum at 416 ^{0}C. At the same time, the mass loss is experimentally 52.4 %, (calculated 51.66 %). The residual mass is 48.1 %, which corresponds to the final thermolysis product $Fe_2(CO_3)_3$. The calculated mass of this product is 48.34%.

Thus, the results of thermogravimetric analysis show that the complexes are anhydrous. The results of elemental analysis also confirm this. However, in the IR spectrum and the thermogram of the studied complexes, water absorption bands also observed on the TG curve of mass loss without any effect. Then we can confidently say that the sample dried up not completely. The thermogram of the complex compound is shown in Fig. 3. The results of the conducted studies have shown that complexes obtained from two and trivalent iron have the same chemical formula. The yield of the product obtained from the double-gland iron is very low should be noted.

This fact can be explained by the fact that in addition to the solution of the sodium salt of the acid $FeSO_4 \cdot 7H_2O$, first obtained the hexaakva complexes:

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

The acquisition of a solution of a pale green color indicates the formation of a hexaqua complexes. Then, due to the loss of one πd-electron, the $[Fe(OH_2)_6]^{+2}$ ion is fairly easily oxidized to:

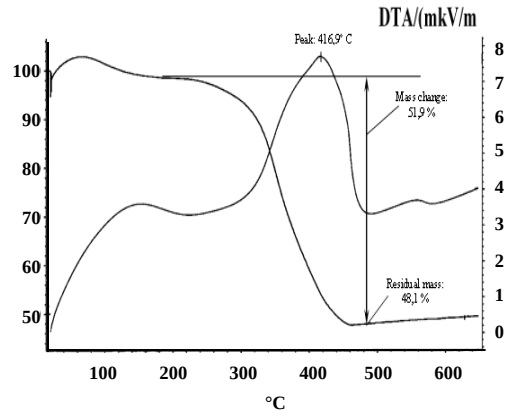
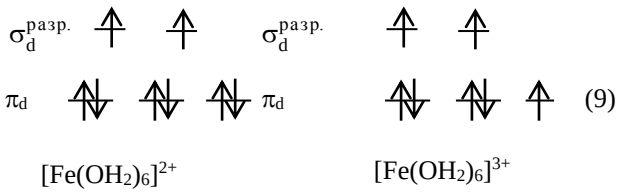


Fig. 3: Thermogravimetric diagram of complex compound.



(9)

Such a transition is explained by the fact that the standard potential of the

$Fe^{3+} + e^- = Fe^{2+}$ $[Fe(OH_2)_6]^{+2}$ system is approximately equal to 0.76V, therefore the Fe^{2+} ion is fairly easily oxidized in an acid medium even by molecular oxygen:

$$2Fe^{2+} + {}^1/_2O_2 + 2H^+ = 2Fe^{3+} + H_2O \qquad E° = 0.46V.$$

In the next step, the phthalic acid anion destroys the hexaquioxomplexes 3^+ and as a result the complexes - $Fe_2(o\text{-}C_6H_4(COO)_2)_3$ is formed and precipitated. Therefore, in the formation of a complexes with ferrous iron, the yield of the product decreases as in the case of result of the lack of an anion of phthalic acid, as in the case of the production of Fe (III) terephthalate [12].

Thus, in the complexes, the coordination number of iron is four, and the coordination polyhedron is a flat square, which is characteristic of the trivalent gland Fe(III). Based on the obtained results, the structure of the complexes can be schematically depict the following form (Fig. 4):

The supramolecular interaction of the obtained substance with the rheological properties of heavy oils was studied also [13, 14,15].

Novelty of the offered way is use as composition on the basis of solution of nanostructure coordination polymer, the consisting akva- complexes of Fe (III) with phthalic and p-phthalic acids, the general formula $\{Fe_2[C_6H_4(COO)_2]_3 \cdot 4H_2O\}$ n where n = 500 - 1000 and also in addition containing sulfanol.

DISCUSSION AND RESULTS

The observed effect is reached due to features of structure the complexes of polymers (the central atoms iron (III), and ligands of n-and about - phthalic acids are), in which framework the columns having the form of a hexagonal prism with a diameter about 2,5 n are formed. The contact of such materials having polymeric and layered frame 3D structure with heavy oil, leads to spontaneous formation not of valent supramolecular connections with the high-molecular hydrocarbonic and hetero containing oil components responsible for the increased viscosity of the hydrocarbonic environment.

Preparation of composition on the basis of polymer is as follows: at continuous hashing enter the measured quantity of a sulfanol after which dissolution, add polymer into the container with water, continuing to mix within 5 minutes. Process is carried out with an atmospheric pressure and room temperature.

The offered way is carried out as follows: enter the composition representing solution on the basis of nanostructural coordination polymer of the Fe (III) with phthalic and p-phthalic acids prepared by the known technique into oil (Muradkhanla's field, Azerbaijan, Table 2).

The water composition of polymer mixes up with oil at a ratio solution to raw materials as (1 ÷ 5) : 30. It is also necessary to pay attention that the place of input of reagent has to be located on a technological stream above that point in which it is necessary to provide reduction of viscosity.

Enter composition on the basis of polymer at a solution ratio to oil (1 ÷ 5): 30 into 300 ml (262,8 g) of oil. 0,1% are a part of composition on the basis of water solution of polymer (masses.) sulfanol, 0,5% (masses.) polymer, the rest – technical water. Comparative data on influence of a ratio of composition to oil on indicators of its kinematic viscosity are provided in Table 3. Apparently from the obtained data, the best results have been received at a composition ratio to oil as 4: 30. Proceeding from it, this ratio is accepted as optimum for further examples. At the same time the kinematic viscosity of oil decreases to value 44,71 of mm^2/sec.

Table 2: Physical and chemical characteristics of oil of the field of Muradkhanli.

Indicators	Value	Analysis method
Density, kg/m^3	876,7	GOST 3900
Kinematic viscosity, mm^2/sec.	83,32	GOST 33
Amount of pitches, %	18,32	chromatography
Amount of asphaltenes, %	4,86	GOST 11858
Amount of paraffin, %	6,21	GOST 11851
Vapur Pressure, kPa	23,4	GOST 1756
Pour point, ^{0}C	+9	GOST 20287
Mechanical mixes, %	0,0234	GOST 6370
Amount of salts, mg/l	47,3	GOST 21534
Amount of water, %	0,15	GOST 2477

Table 3: Tendency of change of viscosity of oil depending on a ratio to raw materials.

Solution ratio to raw materials	Kinematic viscosity of oil, mm^2/sec.
-	83,32
1 : 30	72,18
2 : 30	50,43
3 : 30	45,22
4 : 30	44,71
5: 30	51,42

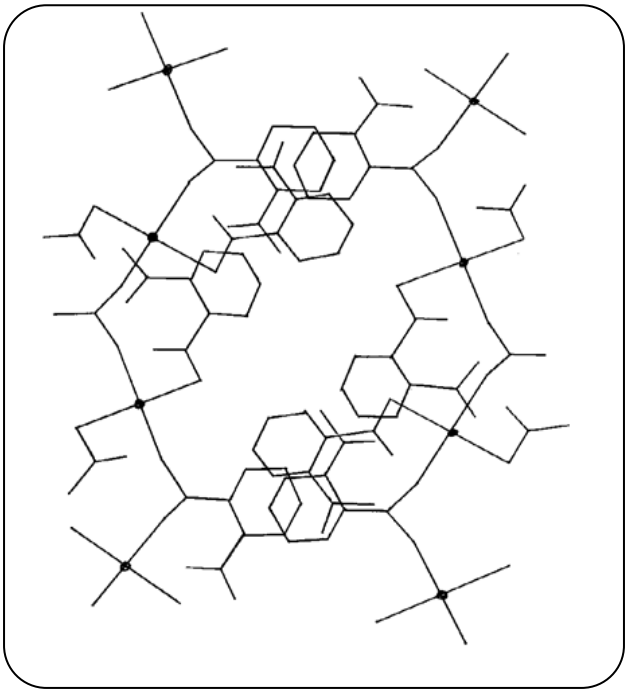


Fig. 4: The proposed schematic structure of the complex compound.

CONCLUSIONS

Apparently from the presented examples, the offered way favourably differs in efficiency to use the polymer of containing of compositions which receiving is based on application of the components made commercially, the polymers which don't have optical and geometrical isomers, and for achievement of considerable improvement of rheological properties of hydrocarbonic system (decrease in kinematic viscosity) there is enough use of insignificant amount of nanostructural coordination polymer that allows to improve not only conditions, but also profitability of transportation high-viscosity oil.

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