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Monitoring of calcium stearate formation by thermogravimetry

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Abstract Naphthenates are produced when naphthenic acids present in crude oil are mixed with brine. They deposit at oil/water interface and are insoluble in either of the phases causing a large problem to the oil industry. Generally, naphthenates precipitate jointly with others compounds such as sulfates and carbonates. This fact makes difficult their characterization. In this study, calcium stearate formation from stearic acid was investigated, under different conditions, as a previous model to understanding of calcium naphthenate precipitation. Medium reactions distinct were studied and the results indicated that the ethanol medium was the most efficient for the formation of solids because in this only case, the stearic acid was completely converted into stearate. Monitoring of the conversion was performed by thermogravimetry in spite of this technique not be typical in salts characterization. Nevertheless, the thermogravimetric analysis showed that is possible to identify differences between an organic acid, a salt of this acid and an inorganic salt, in the same sample. Infrared spectra was used in order to confirm the results obtained by thermogravimetry. However, this technique showed less efficiency and sensibility.

Keywords Thermogravimetry · Calcium stearate · Naphthenates · Naphthenic acid · Monitoring

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Introduction

Naphthenic acids (NA) are natural constituents of crude oil and comprise a complex mixture of carboxylic acids [1, 2]. They present surfactant properties such as long chain aliphatic acids [3–5] and may combine with calcium present in brines in order to form deposits of calcium named calcium naphthenate. These precipitates accumulate themselves in heat exchangers and separators give rise to operational problems to the oil industry [2, 6–8]. It is generally accepted that reactions occur between NA in the oil phase and calcium ions in the water phase [9, 10] due to emulsifying properties of NA. However, the mechanism of calcium naphthenate formation is still limited.

Due to different structures of the NA, the physicochemical behavior is different for each type of acid present in crude oil [2] and, the characterization of these materials is so important for identification of individual compounds [1, 3]. Characterization of NA structures is complex not only because diversity of structures but also because typical analytical tools are not efficient for this. They have been associated and combined for a complete characterization [11]. Different techniques are applied to characterize the NA and naphthenates, among them FTIR [12], SEM and EDX [6], GC-MS [13].

The thermogravimetry (TG) has been usually employed to study the petroleum and petroleum products characterization [14]. However, the literature does not present references for using thermal analysis in naphthenate characterization. Nevertheless, literature has showed that thermal analysis is a great technique to characterize organic and inorganic compounds. Therefore, the different techniques complement themselves in the correct identification of the same compound.

In this work, laboratory investigations were performed using stearic acid in order to investigate the calcium stearate formation. Stearic acid (C_{18}) was choose because it is a fatty acid that has emulsifier characteristics and acts as amphiphilic compound meaning that it is soluble in organic solvent and water [6, 7, 15]. It can react with calcium and produce calcium stearate. In accordance with the soap industry, the naphthenate deposits may be produced from a long chain of aliphatic carboxylic acids [6]. For this reason, the stearic acid may be a good model to study the calcium-acid-compound formation.

It is known that solvents affect the dielectric constant of the medium, the interionic attraction and the solute–solvent interaction. In order to understand the effect of solvation in the salts' formation, different solvents were used: ethanol (miscible solvent with aqueous medium), dichloromethane (immiscible and denser than water), and heptol (50:50 heptane/toluene, immiscible and less dense than water). TG, FTIR and SEM analysis were applied in order to monitor the calcium stearate formation, the purity and yielding. Therefore, more importance was given to TG due to scientific data gap about its use in naphthenates characterization.

Experimental

Samples preparation

The naphthenic acid employed in this study was a stearic acid and it was purchased from Merck. Three different solvents were chosen for preparation of stearic acid solutions: ethanol (EtOH, Tedia Brazil), a miscible solvent with aqueous medium; dichloromethane (CH_2Cl_2, Tedia Brazil), immiscible and denser than water and heptol (50:50 heptane/toluene, Tedia Brazil), immiscible and less dense than water. Two experiments were performed with stearic acid: first one, at room temperature employing EtOH and CH_2Cl_2 as solvent. And, second one, at 75 °C for 1 h using heptol and EtOH. The stearic acid (1.536 g) was dissolved in 100 mL of such solvents reported. An aqueous calcium hydroxide solution (0.040 g in 100 mL of water) was mixed with stearic acid solutions prepared and stirred for a short time. The precipitate obtained was filtered and dried at 60 °C for 6 h. The solids produced were analyzed by FTIR, TG and SEM.

Thermogravimetry analysis

TG experiments were performed on a Netzsch STA-Luxx 409 PC apparatus under identical conditions. The measurements were conducted in alumina crucible using at about 10 mg of sample and a heating rate of 20 °C min^{-1}. Each sample was heated from room temperature to 700 °C under dynamic atmosphere (nitrogen, 50 cm^3 min^{-1}) and from 700 to 1000 °C at the same heating rate, under dynamic air atmosphere (50 cm^3 min^{-1}).

Fourier transform infrared spectroscopy

The Fourier transform infrared spectroscopy was used to identify the chemical components presents in the sample. FTIR spectra was recorded in a spectral range of 4000–400 cm^{-1} (Nexus 470 Thermo Nicolet) and the samples were prepared as standard KBr pellets (about 1.0% mass/mass).

Scanning electron microscopy and spectroscopy dispersive energy

The morphological evaluation of the solid was performed by scanning electron microscopy (SEM, JEOL JSM 5800 LV). The quality images were optimized by recover of precipitate. The average homogeneity of solid was analyzed by spectroscopy dispersive energy (EDS, NORAN 688A).

Results and discussion

Calcium stearate precipitates were obtained from all the organic solvents, but the characteristics these solids, for instance, composition and morphology, were distinct for each one. In the experiment with EtOH medium at room temperature, a rapid precipitation occurred and after 24 h, the content increased and it was localized on the bottom. In the other cases, the solid precipitated slowly.

The thermal behavior of the commercial sample of stearic acid and of the solids obtained using different solvents were evaluated by TG. Figure 1 shows a thermogravimetric curve of stearic acid and precipitates obtained at room temperature. As can be seen, the TG curve of stearic acid shows that it is thermally stable up to 269 °C

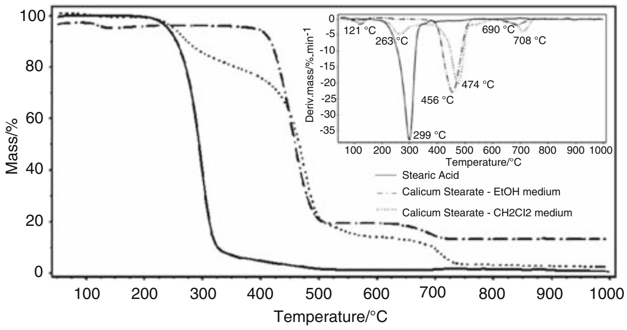

Fig. 1 TG curve of the stearic acid and precipitates obtained at room temperature. *Inset* corresponding DTG curves

(onset). TG curves of the calcium stearates produced at room temperature show a displacement of this value toward to higher temperatures confirming a salt formation; the onset is at about 420 °C and peak maximum is at 455 °C. Usually, salts derivative of the carboxylic acids present higher thermal stability and therefore, its decomposition occurs at high temperatures. According to Kasselouri et al. [16, 17] and Singh [18], the calcium carboxylate decomposes around 400 °C, that is, the result obtained in this work is in agreement with the literature. Furthermore, Gönen et al. [19] mentioned that a pure zinc stearate starts its degradation above 200 °C and finishes until 550 °C. The thermal decomposition products of zinc stearate are $ZnCO_3$ and ZnO likewise the products obtained by calcium stearate decomposition in this work. Table 1 presents thermogravimetric data of main stages for all solids produced.

The thermogravimetric analysis of the precipitate obtained from ethanol presented a little mass loss (2.13%) due to dehydration and solvent release. Actually, Singh [18] describes that peaks below 200 °C can be due to removal of hydrates. Considering that the solutions were prepared with organic solvent, probably the loss at about 120 °C corresponds to removal of solvates molecules. The second mass loss (76%) begins at 423 °C and it is due to calcium stearate decomposition. Calcium carbonate is obtained as sub-product of this reaction and it decomposes himself to calcium oxide and carbon dioxide at 653 °C with 6.30% of mass loss. The precipitate was considered 100% of calcium stearate because the mass loss related to solvent volatilization was very low and analyzing TG curve, there was one decomposition corresponding to only one specie present. A complete conversion happened because hydrogen bonding promotes the solubilization of acid and, consequently, the precipitation of salt. Besides that, only one phase is formed after mixture of reagents to stearate production. This fact allows a better contact between all reagents employed.

In dichloromethane medium, it is observed a precipitate with high content of stearic acid identified by mass loss at 265 °C in TG curve. The following mass loss (475 °C) is attributed to calcium stearate decomposition and the last one, at 709 °C is due to calcium carbonate decomposition. The low polarity of this solvent decreases the acid dissociation and yield of salt precipitation. Besides that, in dichloromethane medium, two phases were formed after the mixture of reagents becoming more difficult the contact between them decreasing the efficiency of stearic acid into stearate conversion.

Considering the investigation performed at 75 °C (Fig. 2), the TG analysis shows that in heptol medium, that is, an apolar solvent, the stearic acid is not converted totally to stearate. It is possible to verify three main mass loss regions in the 50–800 °C temperature range. The first

Table 1 Thermogravimetric data of solids produced

Sample	Steps	Onset temp./°C	Maximum temp. decomp./°C	Mass loss/%	Residue/%
Stearic acid	I	269	299	98.9	1.10
$CaSt_2$*	I	108	122	2.13	13.0
EtOH medium[a]	II	–	–	–	
	III	423	455	75.6	
	IV	653	688	6.30	
$CaSt_2$	I	86	106	1.41	2.19
CH_2Cl_2 medium	II	235	265	19.1	
	III	445	475	66.3	
	IV	656	709	11.0	
$CaSt_2$	I	83	114	10.1	1.13
EtOH medium[b]	II	254	289	8.87	
	III	420	445	72.3	
	IV	630	672	9.10	
$CaSt_2$	I	91	117	1.20	7.47
heptol medium	II	266	302	17.6	
	III	446	470	66.3	
	IV	673	709	7.43	

*$CaSt_2$, calcium stearate. Nomenclature used by Gönem et al. [19]

[a] Calcium stearate obtained at room temperature

[b] Calcium stearate obtained at 75 °C for 1 h

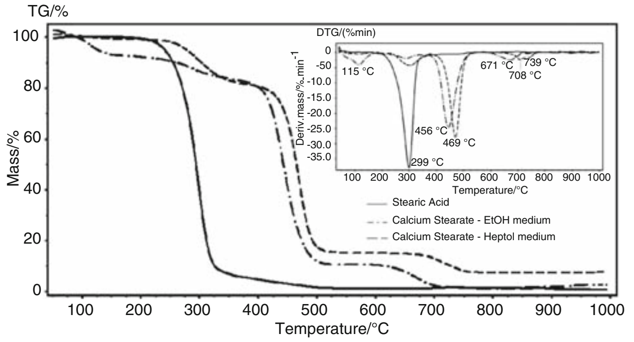

Fig. 2 TG curve of the precipitates obtained at 75 °C for 1 h. *Inset* corresponding DTG curves

mass loss observed in the TG curve is due to decomposition of stearic acid not reacted (18%) and the second (66%) is related to calcium stearate decomposition. The third one begins at 673 °C and corresponds to carbon dioxide release produced by calcium stearate decomposition. The calcium carboxylate decomposes around 400 °C and produces calcium carbonate and this leads to the formation of calcium oxide at about 700 °C.

Still in the experiment at 75 °C, considering ethanol medium (polar solvent), TG results shows that the precipitate obtained is lightly contaminated by stearic acid and it presents solvate molecules, that is, the reaction is not complete. However, the contamination with stearic acid is so low that it is not almost detected in TG curve. It can be seen that there is a mass loss at 90 °C indicating a solvent release and the mass loss at about 300 °C is due to stearic acid that did not react. The other losses indicate the same results reported above, i.e. calcium stearate (470 °C) and calcium carbonate contamination (709 °C).

Fourier transformed infrared (FTIR) spectroscopy was employed to monitor the formation and purity of precipitates. Figure 3 exhibits a comparison of spectra to stearic acid and calcium stearate obtained in ethanol and dichloromethane medium. A typical spectrum of carboxylic acid can be seen in Fig. 3a. Bands at about 1,700 and 935 cm^{-1} are assigned to the stretching vibration of the carbonyl group and bending vibration of the hydrogen bond, respectively. Spectra showed in Fig. 3b corresponds to precipitate obtained in ethanol solution. The band at about 1,700 cm^{-1} is absent as well as 935 cm^{-1} band, indicating that the precipitate is not carboxylic acid. On the other side, two bands can be observed at about 1,580 and 1,545 cm^{-1}. They are assigned to the asymmetric and symmetric stretching vibration of the carboxylate ion confirming stearate precipitation [20, 21]. In accordance with FTIR library, the precipitate obtained is a calcium stearate. For the Fig. 3c (dichloromethane solution), the bands at about 1,580 and 1,545 cm^{-1} appear, but weak bands at 1,700 and 935 cm^{-1} are still observed, indicating that the conversion of stearic acid is not completed. The precipitate formed is a mixture of calcium stearate and stearic acid as suggested by TG analysis.

The FTIR spectrum for calcium stearate obtained in heptol medium at 75 °C (Fig. 4) exhibits bands at 1,580 and 1,541 cm^{-1} assigned to carboxylate ion (stearate) and bands at 1,707 and 929 cm^{-1} characteristic of carboxylic acid. These results indicate that the heptol solution has not provided a complete conversion of stearic acid into stearate, in accordance to TG analysis. In the case of calcium stearate obtained in ethanol medium at 75 °C, the FTIR spectrum shows bands corresponding to carboxylate. The bands assigned to carboxylic acid do not appear in spectra, suggesting a pure precipitate. However, the TG analysis

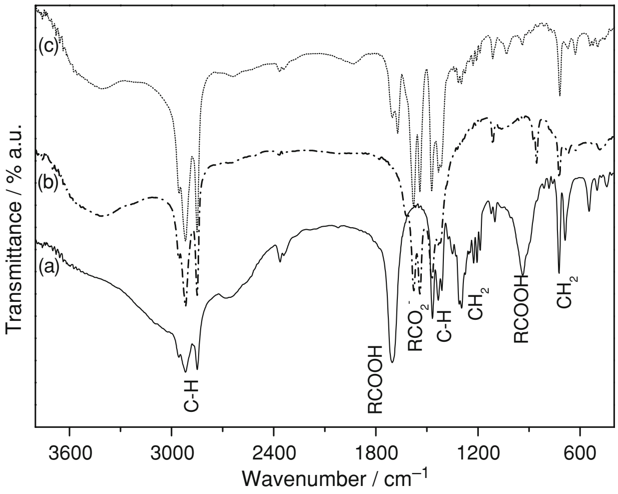

Fig. 3 Comparison of FTIR spectra between two solvents at room temperature. a Stearic acid. b Calcium stearate—EtOH medium. c Calcium stearate—CH_2Cl_2 medium

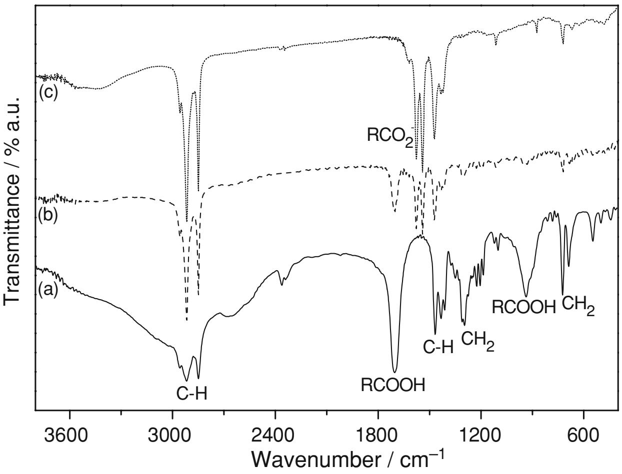

Fig. 4 Comparison of FTIR spectra between two solvents at 75 °C for 1 h. a Stearic acid. b Calcium stearate—heptol medium. c Calcium stearate—EtOH medium

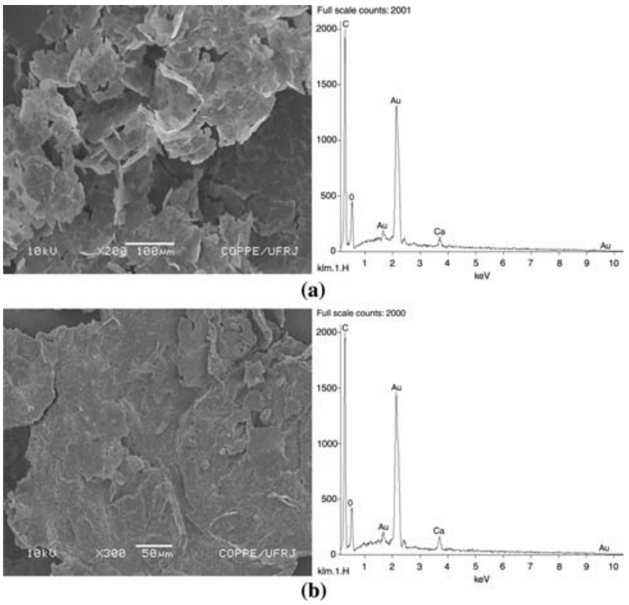

Fig. 5 SEM micrographs (magnification ×300) of the calcium stearate produced at room temperature: (**a**) EtOH and (**b**) CH_2Cl_2 medium

showed a little contamination by stearic acid. Probably, this contamination is so low that it is not detected in FTIR spectrum.

The morphology of solids produced at room temperature was studied by scanning electron microscopic and the micrographs are given in Fig. 5. When a polar solvent was used, that is, in ethanol medium, calcium stearate exhibits a flaky morphology (Fig. 5a). The EDX analysis indicates that the precipitate is homogeneous with similar distribution of Ca, C and O in the whole sample, as can be seen through elements intensity. This result is in good accordance with that reported by Dyer et al. [6]. For an apolar solvent (CH_2Cl_2 medium), the precipitate has a sheet-like morphology (Fig. 5b). The EDX analysis also indicates a homogeneous distribution of Ca, C and O in the whole sample.

Conclusions

This study on the formation of calcium stearate has showed that the choice of an adequate solvent system is an important parameter to investigate calcium stearate formation. The use of an organic solvent with polarity and miscibility with water distinct has indicated that influences both in the shape and in the composition of the solid produced. Calcium stearate precipitates were obtained from three different organic solvents. However, the ethanol medium was the most efficient for the formation of solids. Only in this case, the stearic acid was completely converted into stearate. The increasing of temperature did not provide so great results. The employment of calcium hydroxide as calcium source has afforded changes in reaction medium of pH and calcium concentration at the same time. TG and FTIR analysis has together allowed confirm the composition of solids produced and differentiate an organic acid of an organic salt and this of an inorganic salt. However, TG has showed more efficiency and sensible to naphthenate studies because it recognized naphthenate formation under conditions that FTIR did not achieve. Therefore, these laboratory investigations have showed that calcium stearate formation from stearic acid could be monitoring by TG and they have corresponded to a good model system for naphthenate production.

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