Thermochimica Acta, 155 (1989) 241–246
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

DETERMINATION AND STUDY OF THERMAL STABILITIES OF SURFACE-ACTIVE COMPOUNDS OCCURRING NATURALLY IN IRAQI CRUDE OILS

DHOAIB AL-SAMMERRAI and HAZIM AL-NAJJAR

Petroleum Research Centre, P.O. Box 10039, Jadiriyah, Baghdad (Iraq)

(Received 3 April 1989)

ABSTRACT

Surface-active compounds occurring naturally in Iraqi crude oils obtained from various fields have been determined quantitatively using a chromatographic technique, and their concentrations correlated with characteristic properties of the crude oils, such as API gravity, sulphur content and heavy metals content. The thermal behaviours and stabilities of these compounds under various atmospheres were also studied using thermoanalytical techniques such as differential scanning calorimetry and thermogravimetry. The results obtained, which were compared with those of a known surface active compound, indicate that the surface-active compounds occurring naturally in the Iraqi crude oils studied are mainly of the carboxylate type.

INTRODUCTION

Surface-active agents such as petroleum sulphonates, carboxylates, quaternary ammonium salts and polymeric compounds have been suggested as potential additives to enhance oil recovery [1,2]. These usually function by reducing the interfacial tension between the crude oil and the slug of surfactant-bearing injected water [3].

Effective oil recovery with the aid of these agents is no longer a question of feasibility but rather a question of economics. The development of a successful field application of surfactant flooding requires a knowledge of the estimated amounts of naturally occurring surface active compounds already present in a particular crude oil, and also information about their thermal stabilities.

Various analytical, spectroscopic and chromatographical methods for the quantitative determination and identification of these naturally occurring compounds in crude oils have been described [4,5]. However, no information is available about their thermal stabilities, although the literature contains work related to the thermal behaviours and stabilities of many well known surface-active compounds [6,7].

0040-6031/89/$03.50

The objectives of the present work were as follows.

(a) To determine the total amounts of surface-active compounds occurring naturally in a number of Iraqi crude oils obtained from different locations and to correlate the concentrations of these naturally occurring surface-active compounds with some of the characteristic properties of the crude oils, e.g. API gravity, sulphur content and heavy metals content.

(b) To study the thermal behaviour patterns and stabilities of these compounds using various thermoanalytical techniques, including DSC and TG techniques.

EXPERIMENTAL

Apparatus

A chromatographic column of 100 cm length and 2.5 cm internal diameter, fitted with a TFE-fluorocarbon stopcock of 2 mm bore, was used for the adsorption procedure.

The thermoanalytical measurements were carried out in a Heraeus TA 500 thermal analyser.

Materials

Ethyl alcohol (90%) and chloroform (AnalaR grade) were obtained from M&B Ltd. Silica gel of 200 mesh was obtained from Merck. Fresh crude oil samples from various locations were obtained from local refineries. The API gravities, sulphur contents and metals contents of the five crude oils are presented in Table 1.

TABLE 1

Some characteristic properties of the crude oils studied

Type of crude	API gravity	Sulphur content (wt.%)	Metals content (ppm)	S.A. compounds content [a] (wt.%)
A	38	1.7	31	0.00625
B	36	1.75	68	0.0575
C	33	3.4	75	0.0675
D	28	3.7	192	0.0750
E	15	7.5	300	0.2000

[a] S.A., surface-active.

Procedures

Determination of surface active compounds

The column was filled with 100 cc of chloroform and 15 g of the silica gel was then poured into the chloroform. The column had to be kept free of air bubbles in order to avoid channelling. The flow of the chloroform was started, and maintained until the liquid level was within 1 cm of the surface of the gel. The crude oil sample (2 g, weighed to the nearest 0.001 g) was then dissolved in 20 cc of chloroform with stirring, and the solution poured into the column. The stopcock was opened and the flow rate adjusted to between one and four drops per second.

The oil was then eluted into a receiving beaker with about 250 cc of chloroform, with care being taken that the level of the solvent was always about 1 cm above the surface of the silica gel. This was followed by elution of the surface-active compounds into a different beaker with about 300 cc of ethyl alcohol.

The surface-active compounds were determined quantitatively by evaporating off the ethanol over a water bath, and heating the beaker in an oven for 30 min under vacuum at 100 ° C. The drying was repeated until a constant weight was obtained. A blank determination was also carried out.

Thermoanalysis

In the DSC measurements, surface-active compounds weighing 5–10 mg were heated at a rate of 10 ° C min^{-1} in an aluminium crucible under a static air or nitrogen atmosphere. The reference cell was filled with pure dried aluminium oxide powder.

The DSC apparatus was standardized using pure tin prior to the start of the determinations. TG and DTG measurements were performed simultaneously by heating a sample weighing 5 mg in a platinum crucible at 20 ° C min^{-1} in a nitrogen atmosphere flowing at a rate of 1 l h^{-1}. All measurements were performed in duplicate.

RESULTS AND DISCUSSION

The surface-active compounds contents (in weight percent) determined for the five crude oils according to the procedure described above are also given in Table 1.

It can be seen that the API gravity values of the crude oils decrease with increasing surface-active compounds content.

A correlation was also observed between total sulphur content and surface-active compounds content. As can be seen from Table 1, the heaviest crude (Crude E) had the highest sulphur and surface-active compounds

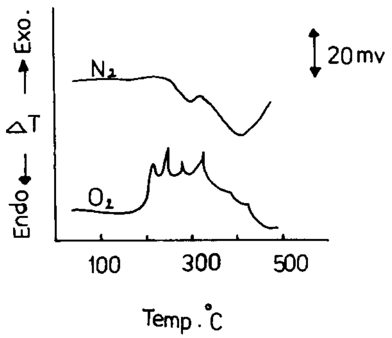

Fig. 1. Typical DSC traces of naturally occurring surface-active compounds.

contents, while the lightest crude (Crude A) had the lowest sulphur and surface-active compounds contents.

A significant correlation was also observed between metals content and surface-active compounds content. As can be seen from Table 1, crudes with high metals contents had a high percentage of surface-active compounds, and conversely, crudes with low metals contents had a low percentage of surface-active compounds e.g. Crude E was found to have metals and surface-active compounds contents of 300 and 0.2%, respectively, while Crude A, which was the lightest crude studied, had metals and surface-active compounds contents of 31 and 0.006%, respectively.

Typical DSC curves of the naturally occurring surface-active compounds, obtained between room temperature and 500 ° C in nitrogen and oxygen atmospheres, are displayed in Fig. 1. The main feature recorded in the inert atmosphere of nitrogen gas was a gradual endothermic offset commencing at about 250 ° C, which corresponds to the degradative volatilization of these compounds. The values of the onset temperature of volatilization recorded from the DSC traces correlated well with those recorded from the corresponding TG and DTG traces, as shown in Table 2. The DSC traces recorded in oxygen atmosphere (Fig. 1) exhibited a complex exothermic onset commencing at about 200 ° C which is related to a complicated process of oxidative degradation of these surface-active compounds.

Representative TG and DTG traces for the naturally occurring surface active compounds, recorded between room temperature and 600 ° C in nitrogen gas, are displayed in Fig. 2. The DTG trace indicates that the weight loss process was of a complex nature.

Table 2 also shows percentage weight losses at 100 ° C intervals recorded from the TG curves in nitrogen. The residue in weight percent remaining at the end of the temperature programme was about 42%, and this was composed mainly of alkali and alkaline earth oxides and carbonates.

The DSC and TG curves of a well known surface-active compound (sodium alkanoate) are shown in Figs. 3 and 4, respectively.

TABLE 2

DSC and TG data on surface-active compounds studied in nitrogen atmosphere

Surface-active compound	Onset temp. of volatilization (°C)		wt. % lost at 100 °C intervals (TG)					
	DSC	TG	0–100	100–200	200–300	300–400	400–500	500–600
A	244	240	0	0	15.5	15.0	20	5.0
B	250	245	0	0	15.0	15.5	18	5.0
C	252	246	0	0	15.0	16.0	18	4.0
D	260	256	0	0	12.8	14.0	25	5.4
E	266	262	0	0	11.5	14.5	25	6.0
Sodium alkanoate	260	250	0	0	14.5	14.0	30	0

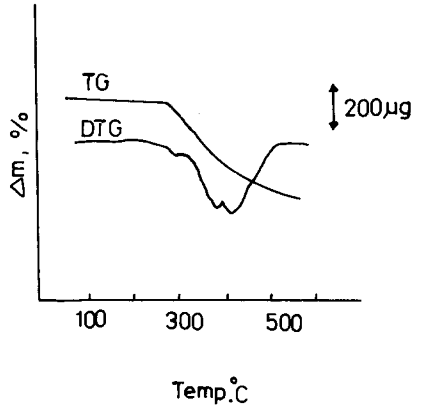

Fig. 2. Typical TG and DTG curves of naturally occurring surface-active compounds in nitrogen gas.

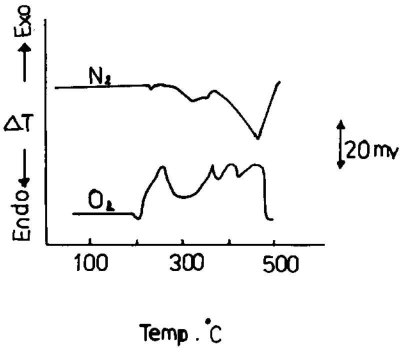

Fig. 3. DSC curves of a known surface-active compound.

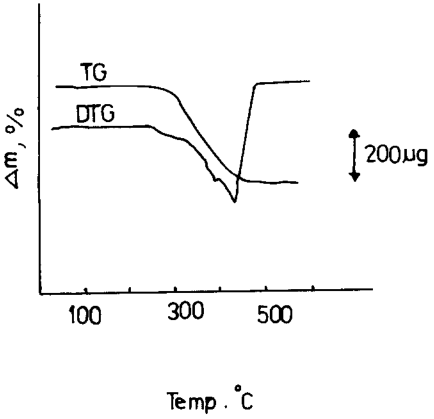

Fig. 4. TG and DTG traces of a known surface-active compound in nitrogen gas.

It is clear from Figs. 1–3 and Table 2 that there is a close resemblance between the features and behaviour of the naturally occurring and the known surface-active compounds, indicating that the surface-active compounds occurring naturally in the Iraqi crude oils studied are mainly of the carboxylate type.

REFERENCES

1 M.M. Schumacher, Enhanced Recovery of Residual and Heavy Oils, Noyes Data Corporation, U.S.A., 2nd edn., 1980.
2 D.O. Shah and R.S. Schechter, Improved Oil Recovery by Surfactant and Polymer Flooding, Academic Press, New York, 1977.
3 M. Latil, Enhanced Oil Recovery, IFP Publications, Paris, 1980.
4 ASTM Standard Methods, Philadelphia, 1982: D 2548, D 855 and D 1216.
5 K.R. Voss, C.E. Bricker, M.J. Michnik and G.P. Willhite, Soc. Petrol. Eng. J., December (1981) 771.
6 D. Al-Sammerrai and F. Abdul-Razaak, Thermochim. Acta, 77 (1984) 185.
7 T. Meisel, I. Lanyi and P. Frangosini, J. Therm. Anal., 17 (1979) 529.