Journal of Thermal Analysis and Calorimetry, Vol. 56 (1999) 959-965

DSC AND RHEOMETRY INVESTIGATIONS OF CRUDE OILS

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Abstract

Thermal characteristics and rheological behaviour of eight crude oils covered a wide range of fluid composition and properties were studied by differential scanning calorimeter (DSC) and viscometry. Wax appearance temperatures (WAT) of crude oils were determined by DSC and viscometry. Good agreement is obtained between the results. The dynamic viscosity in the Newtonian temperature range of the crude oils (above 30°C) generally obeyed a simple first-order Arrhenius type of temperature dependence. Activation energies of flow in the non-Newtonian range are not uniquely defined.

Keywords: crude oil, differential scanning calorimeter, rheology, viscometer

Introduction

Crude oils are generally very complex chemical systems containing from hundreds to thousands of individual components in the range from simple low molecular mass *n*-alkanes to high molecular mass waxes and asphaltenes. Two types of wax are commonly encountered in crude oils, i.e., *macrocrystalline* waxes composed of mainly straight-chain paraffin's (*n*-alkanes) with varying chain length (about C_{20} to C_{50}) and *microcrystalline* waxes also containing a high proportion of isoparaffins and naphthenes (cyclic alkanes) with somewhat higher carbon numbers (C_{30} to C_{60}). These two types of wax have different properties regarding crystal growth and morphology [1]. When a wax containing crude oil is cooled below its wax appearance temperature (WAT), wax constituents tend to separate from the liquid phase of crude oil and starts to crystallise which causes several problems during production, storage and transportation. The crystallisation behaviour of crude oils is mainly dependent on the wax composition and distribution. This type of crude oils is low viscosity and Newtonian fluids at high temperatures, but during cooling owing to the precipitation of waxes they show non-Newtonian behaviour. Miller and Dawson [2] used DSC as a means of characterising waxes. They proposed that the alternative method of analysis give only a limited amount of information when applied to hydrocarbon wax. On the other hand DSC offers a scheme by which various hydrocarbon waxes may be fingerprinted. Giavarini and Pochetti [3] studied the some petroleum prod-

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

ucts as petroleum waxes, microcrytalline waxes, lube oils, fuel oils and bitumen's by DSC. They have proposed that the DSC is a useful technique to study the effects of additives and to determine the glass transitions of the samples studied. Hansen *et al.* [4] used DSC to study wax precipitation from a series of North Sea crude oils by measuring glass transition, wax precipitation and dissolution temperatures. The crude oils ranged from light paraffin condensates to heavy waxy crude oils. Purohit *et al.* [5] determined the changes in the rheological properties of vacuum distillate of Bombay crude oil. Waxes have been separated from this broad fraction and the dewaxed fractions have a much lower pour point and wider Newtonian flow range compared to the whole fractions. Zheming and Guozhong [6] found that the rheological properties of waxy crude oils are not only relative to their compositions, also dependent on the thermal history, shear action and time effect subjected in piping them. El-Gamal *et al.* [7] used polymers as flow improver in waxy crude oils. The majority of the prepared additives showed good performance in improving the flow properties of the crude oils studied. Kök *et al.* [8] studied the thermal characteristics of crude oils and their treatment with additives by DSC and thermomicroscopy. Different additives were found as more effective for different type of crude oils depending on the wax content. Crude oils showed a reduced pour point after treatment with additives.

Experimental

Eight crude oils covered a range of fluid composition and properties were used during the experiments. API gravity and paraffin content of the crude oils studied are given in Table 1. For DSC (Mettler TA 2000) experiments about 20–25 mg of samples were transferred into an aluminium crucible, which was sealed and weighted. Samples were heated at +80°C for one hour in close containers and shaken thoroughly to have a complete dissolution of waxes before the experiments. Experiments were performed in the temperature range of + 80 to –20°C at 2°C min^{-1} cooling rate. Calibration for temperature and heat flow determinations was carried out using the

Table 1 Properties of crude oils

Crude Oil	API gravity	Paraffin cont./wt%
Crude Oil-1	36.5	7.5
Crude Oil-2	38.0	8.8
Crude Oil-3	26.6	10.5
Crude Oil-4	37.5	12.4
Crude Oil-5	36.3	12.9
Crude Oil-6	40.0	16.9
Crude Oil-7	38.3	17.6
Crude Oil-8	35.7	18.5

Table 2 Apparent viscosity (c_p) of the viscosity standards

T(°C)	S-60		S-200		S-600	
	original	measured	original	measured	original	measured
20	138.2	134.8	574.5	560.9	2267.0	2241.1
25	101.8	99.8	399.0	389.4	1462.0	1439.2
38	51.15	49.9	174.3	170.1	540.1	526.9
40	45.92	44.8	153.0	149.7	462.7	451.9

melting point and heat of melting of high-purity compounds. The rheological behaviour of the samples were characterisd with a Rheomat 30 viscometer was equipped with a cooling bath, a temperature programmer, a rheoscan and a plotter. Experiments were performed in the temperature range of +80 to −20°C at 0.5°C min^{-1} cooling rate at three different shear rates 30, 110, 205 s^{-1}. In order to test the accuracy of the viscometer, apparent viscosity of several viscosity standards were measured at four different temperatures before the experiments. Table 2 represents the original and measured apparent viscosity values of the standards.

Results and discussion

The majority of crude oils contains waxes which can precipitate during cold weather and cause a lot of problems as deposition in pipelines and production equipments well known in petroleum industry. Transportation of waxy crude oils creates technical and economic problems, the magnitude of which depends on several parameters such as pour point, transportation method and the ambient temperature. Therefore, crystallisation temperature, commonly called wax appearance temperature (WAT) at which visible crystallisation occurs is an important parameter. WAT is determined by the intersection of the baseline and extrapolation of the peak (Fig. 1) in DSC experiments (Table 3). Waxy and high pour point crude oils are low viscosity and Newtonian fluids at high temperatures but exhibit non-Newtonian behaviour owing to the precipitation of waxes as crude oil is cooled. In this part of the research, eight crude oils were characterised rheologically with emphasis on properties related to the content of wax. The kinematic viscosity of the crude oils in the Newtonian region was measured using glass capillary viscometer tubes between +70 and +40°C. With rotational viscometers the fluids, the viscosity to be measured, is located between two rigid boundary surfaces, which are symmetrical from the point of view of rotation and arranged co-axially, one of which rotates at a chronologically constant angular velocity. To this effect a moment of torque must act on each boundary surface. Both moments of torque have the same amounts, but in opposite direction. From the connection between the moment of torque and angular velocity, the viscosity is determined. Temperature *vs.* apparent viscosity graphs of crude oil-7 at three different shear rates is given in Fig. 2. In all crude oils studied apparent viscosity of

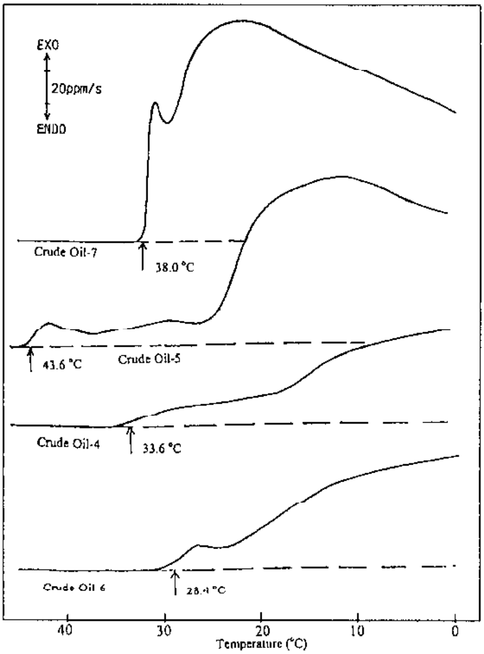

Fig. 1 DSC curves of different crude oils (WAT determinations)

the crude oils are increased as the temperature is decreased and higher apparent viscosity is obtained at lower shear rates. As a result of these experiments, it was observed that crude oil-3 has the highest viscosity values whereas crude oils-2 and 6 has the lowest viscosity in the temperature interval studied. In order to see the reproducibility, experiments for three crude oils were repeated at 100 s^{-1} under the same

Table 3 Wax appearance temperatures of crude oils (°C)

Crude Oil	DSC results	Viscometry results
Crude Oil-1	24.6	32
Crude Oil-2	23.4	17
Crude Oil-3	38.2	34
Crude Oil-4	33.6	28
Crude Oil-5	43.6	33
Crude Oil-6	28.4	30
Crude Oil-7	38.0	27
Crude Oil-8	36.2	30

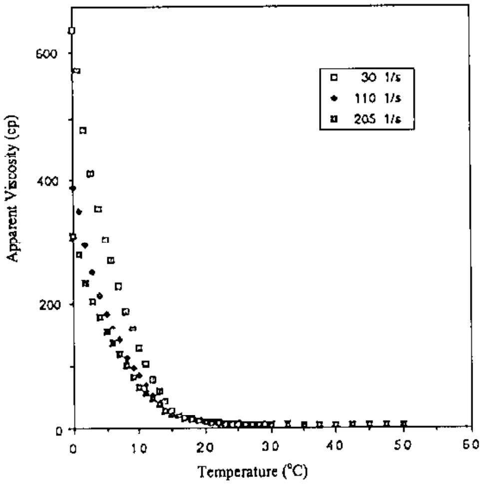

Fig. 2 Apparent viscosity *vs.* temperature curve of crude oil 7

experimental conditions mentioned above. Approximate apparent viscosity values are obtained in reproducibility experiments.

Kinematic viscosity of the crude oils was measured at 5°C intervals in the Newtonian temperature (+80 to +40°C). The Newtonian viscosity is essentially determined by the hydrocarbon group type (alkanes, cycloalkanes, aromatics, resins and asphaltenes) and the carbon number distribution. The temperature dependence in the Newtonian range is expressed by Guzman-Andrade type equation [9].

$$\mu = Ae^{E_a/RT} \tag{1}$$

where, μ is the Newtonian dynamic viscosity, E_a is viewed as the activation energy of viscous flow, A is the constant largely dependent on the entropy of activation of flow, R is the universal gas constant and T is the absolute temperature. By linearizing the Eq. 1 the following form is obtained.

$$E = 2.303R[\mathrm{d}(\log\mu)/\mathrm{d}(1/T)] \tag{2}$$

Equation 2 represents that the slope of logμ *vs.* $1/T$ is equal to $E/2.303R$. Table 4 represents the activation energies of crude oils those varied between 15.8 and 24.5 kJ mol^{-1}. These values are in very good agreement with the activation energy values of the same type crude oils [4, 10]. In non-Newtonian flow regime, μ has to be replaced by apparent viscosity, η. In the plot of apparent viscosity *vs.* temperature (Fig. 3), WAT is determined where the experimental curve deviates from the extrapolated Arrhenius curve. The WAT of the crude oil samples is given in Table 3. The flow behaviour of crude oils is considerably modified by the crystallisation of paraffins corresponding respectively to the variation of the apparent viscosity. Below

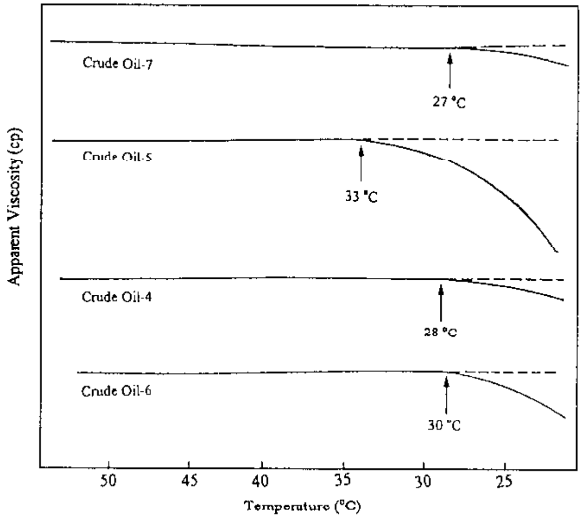

Fig. 3 Apparent viscosity *vs.* temperature curve of different crude oils (WAT determinations)

Table 4 Activation energies and Arrhenius const. of the crude oils

Crude Oil	E/kJ mol^{-1}	A/1 min^{-1}	Corr. coeff.
Crude Oil-1	18.5	$3.32\cdot10^{-03}$	0.997
Crude Oil-2	19.9	$1.47\cdot10^{-03}$	0.999
Crude Oil-3	24.5	$6.38\cdot10^{-04}$	0.998
Crude Oil-4	17.7	$4.62\cdot10^{-03}$	0.999
Crude Oil-5	21.6	$2.75\cdot10^{-03}$	0.998
Crude Oil-6	15.8	$7.62\cdot10^{-03}$	0.998
Crude Oil-7	18.1	$2.01\cdot10^{-03}$	0.999
Crude Oil-8	21.1	$4.02\cdot10^{-03}$	0.997

WAT flow becomes non-Newtonian and reaches close to Bingham and Casson plastic model.

Conclusions

Thermal characteristics and rheological behaviour of eight crude oils covered a wide range of fluid composition and properties were studied by DSC and viscometry. In DSC experiments, WAT is determined manually by intersection of the baseline and extrapolation of the peak. In general WAT of crude oils with viscometry is determined where the experimental and predicted Newtonian curves separate. A good agreement is obtained between the results.

Activation energies of crude oils in the Newtonian temperature range (usually above 30–35°C) calculated by fitting viscosity data to a simple Arrhenius type exponential equation. The calculated activation energies of Newtonian viscous flow rate were in most around 20 kJ mol^{-1}. Activation energies of flow in the non-Newtonain temperature range are not uniquely defined.

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