THERMAL PROPERTIES AND CRYSTALLIZATION BEHAVIOUR OF SOLID N-PARAFFIN COMPONENTS DERIVED FROM MUKTA CRUDE OIL

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Abstract. *The solid n-paraffins component derived from Mukta crude oil, and its narrow fractions were analysed for penetration, phase transition temperature behaviour and for associated energies. Crystallization of these n-paraffins in different solvent systems viz. toluene, cyclohexane, n-heptane and methyl ethyl ketone was also studied. The interdependence of thermal and crystallization properties in relation to the composition of solid paraffins was determined.*

Key words: *paraffins, crude oil, urea adductables, DSC, GC*

Introduction

Mukta crude oil available from Bombay offshore region (India) is quite rich in waxes (wax content ~9 wt.%) and is associated with high pour point (27 °C). The waxes present in it largely consist of n-paraffins. In our earlier communication [1] we have reported the separation, fractionation and structural characterization of total normal paraffins (TNP) present in this crude oil. Effect of composition of n-paraffins on their thermal properties and crystalization behaviour in different solvent systems have been reported in the present paper.

Experimental

The total n-paraffin component (TNP) separated from Mukta crude oil by urea adduction and its narrow fractions (M_1 to M_5) were taken; their physical properties and carbon number distribution are given in Table 1. Details of their separation and characterization have already been reported [1]. Needle penetration measurements on TNP and its fractions were made on Sur Berlin PNR-10 penetometer following ASTM D-1321 procedure. The penetration was measured at different temperatures ranging from 10° to 55 °C at interval of 5 °C and their penetration behaviour is shown in Figure 1. The thermal characteristics were temperature of melting/crystallization and their associated energies were measured using a Perkin-Elmer DSC calorimeter. The temperature and output scales were caliberated with indium cyclohexane and power calibration with aluminium oxide. The condition of the measurements were starting isotherm 230K, final isotherm 400K, rate of heating 10K/min and rate of cooling -10K/min. About 5 mg sample was taken and heating/cooling rate were 10K/min and -10 °C/ min. respectively. The melting and crystallization peaks were characterized by the temperature of their maximum. Enthalpies of melting and crystallization were obtained by integration of areas below the corresponding peaks. The thermal parameters and crystallization behaviour of these solid paraffins in different solvents are given in Tables 2 and 3 respectively. These were calculated from thermograms presented in Figures 2 and 3.

Results and Discussion

Needle penetration-temperature behaviour: In all samples needle penetration increases significantly with increasing temperature irrespective of the boiling range/ melting point and other physical properties of the solid

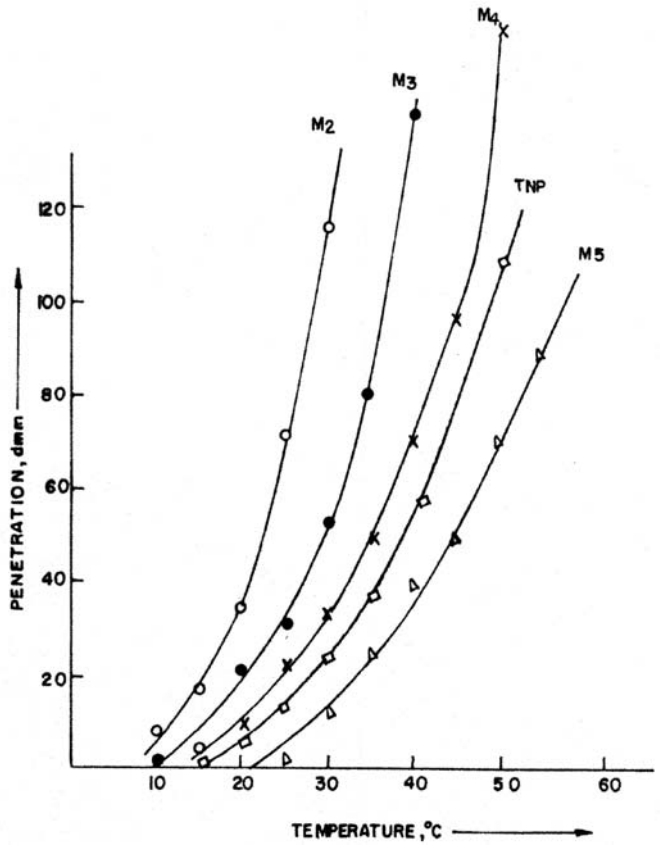

Figure 1. Penetration temperature behaviour of TNP and its fractions

Table 1. Characterization of total n-parrafin component (TNP) and its fractions

n-Paraffin Components	Yield wt. %	Melting temp. °C ++	Density at 15 °C	Molecular* weight	Viscosity cSt, 70 °C	Average carbon No.	Carbon Number Range %			
							C_{15}-C_{20}	C_{20}-C_{26}	C_{26}-C_{32}	$>C_{32}$
TNP (270-546 °C)	100	52.6	0.8396	404	8.15	25.03	17.7	42.2	34.4	5.7
M1 (270-300 °C)	6.41	Liquid	0.7870	233	2.15	–	–	–	–	–
M2 (300-350 °C)	10.73	36	0.7934	273	2.68	20.52	52.2	46.3	1.5	0
M3 (350-400 °C)	22.92	38.7	0.8028	349	3.80	22.18	28.8	63.6	7.6	0
M4 (400-450 °C)	28.46	41.3	0.8121	408	5.72	26.54	1.3	48.7	48.9	1.2
M5 (450 °C+)	31.48	65.8	0.9135	527	16.43	30.60	0	4.5	73.6	21.9

* Calculated from Maxwell graphical correlation
++ As obtained by DSC

Table 2. Thermal characteristics of total n-parrafin component (TNP) and its fractions

n-Paraffin Components	Phase Transition (Melting), °K			Crystallization Temperature, °K				Enthalpy	
	Tm_1	Tm_2	Tm_3	Tc_1	Tc_2	Tc_3	Tc_4	Melting ΔHm Jg/K	Crystallization ΔHc Jg/K
TNP(270-546 °C)	291.7	318.7	325.6	–	–	318.0	–	157.2	-154.8
M2 (300-350 °C)	276.2	293.8	309.0	270.7	–	301.1	–	152.9	-144.6
M3 (350-400 °C)	286.0	–	311.7	281.3	289.9	308.1	–	234.5	-226.2
M4 (400-450 °C)	289.0	296.4	314.3	283.9	293.7	309.8	314.4	162.7	-160.6
M5 (450 °C+)	295.5	328	338.8	295.0	319.6	319.6	329.0	162.7	-160.6

Table 3. Crystallization behaviour of total n-paraffin component (TNP) and its fraction in solvents

n-Paraffin Components	Crystallization Temperature (Tc,oK) in Different Solvents							
	MEK			n-Heptane		Cyclohexane		Toluene
	Tc_1	Tc_2	Tc_3	Tc_1	Tc_2	Tc_1	Tc_2	Tc_1
TNP (270-546 °C)	313.5	320.5	–	291	–	285.1	265.1	~291
M2 (300-350 °C)	294.7	303.6	–	266	304.7	264.2	258.9	266.4
M3 (350-400 °C)	308.3	315.5	325.1	299	311.8	273.7	262.3	277.6
M4 (400-450 °C)	315.7	325.1	–	301	324.8	284.5	268.9	289.6
M5 (450+ °C)	320.9	322.3	–	300.6	–	293.3	269.3	296.9

paraffin components (Table 1). This relationship is parabolic in nature (Figure 1) and at a particular temperature, fraction 'M5' observed the lowest penetration followed by TNP and 'M2' fraction observed the maximum. Penetrations for 'M3' & 'M4' fractions lie in between. The melting point of the fractions varies from 27.9 to 67.5 °C while the melting point for TNP is 59 °C. The melting point data indicates that the penetration pattern correlate well with the melting point.

Phase Transition Parameters: From DSC thermograms it is observed that the first solid-solid transition is highest in fraction 'M5' which have highest boiling range 450 °C+ (melting point 67.5 °C) and it decreases with decreasing carbon number and melting points of the fractions (Figure 2 and Table 2). This transition is normally interpreted as an orthorhombic-orthorhombic transition [2]. In TNP and its fractions 'M2' to 'M5' the chain length disorder varies significantly from carbon number C20.52 to C30.60 and yield % also varies from 11 to 31 % (Table 1). The distribution of n-paraffins (Table-1) indicated that the concentration of lower alkanes diminishes with increasing boiling range of the fractions as expected. This results in the significant variation in chain length disorder as being observed in the present study.

It is further observed that as the temperature is increased all the fractions and TNP show another solid-solid transition. Similar multiple solid-solid transition was observed in pure $nC_{23}H_{48}$ alkane. This transition is again orthorhombic-orthorhombic transition but with different space group [2,3].

Before the melting temperature is reached, TNP and its fractions all shows yet another solid-solid phase transition but these merged with solid-liquid transition and this transition has been identified as orthorhombic-hexagonal

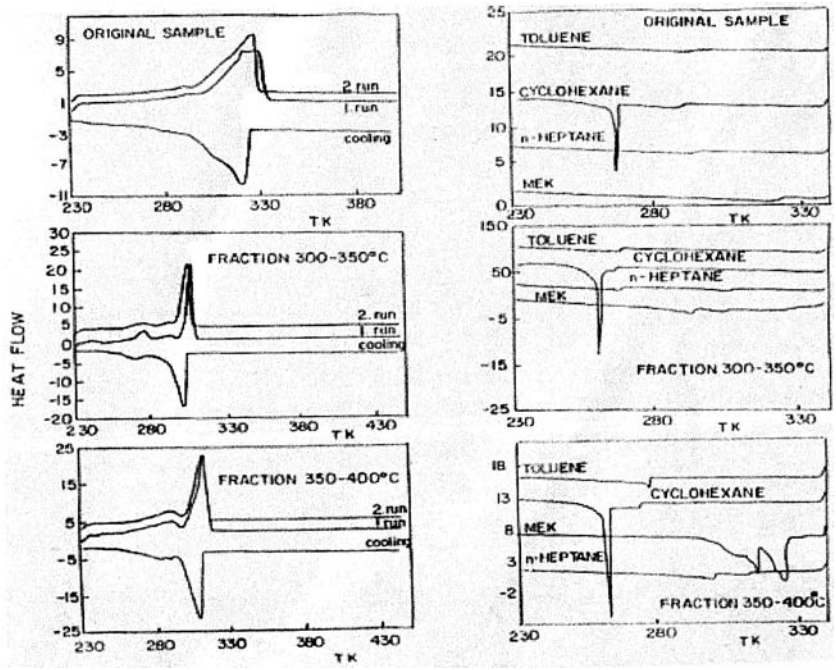

Figure 2. DSC Thermogram of TNP and its M_2 & M_3 fractions

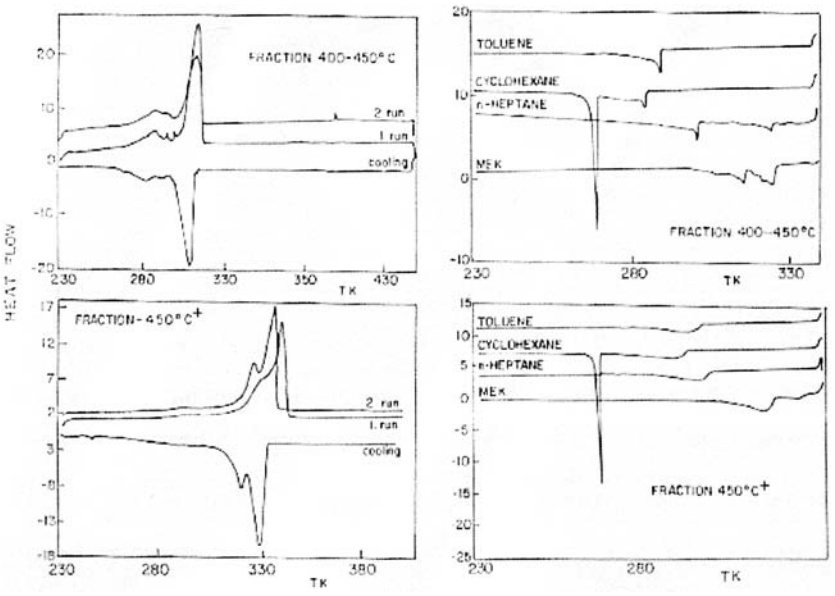

Figure 3. DSC Thermogram of TNP and its M_4 and M_5 fractions

transition [4]. This transition appears just a few degree below the melting point of the respective n-paraffins and would decide the limiting temperature upto which the hardness of the paraffins is preserved [5,6]. The width of the peak corresponding to this transition also is the indication of the polydispersity of n-paraffins in the sample. In the present study the peak corresponding to this transition is wider compared to its narrow boiling range fractions (Figure 2).

The enthalpy of melting (ΔHm) and enthalpy of crystalliztion (ΔHc) increases with increasing melting point/ average carbon number of the fractions. The enthalpy of crystallization data (Table 3) for these paraffins are also lower to their corresponding (ΔHm) values.

Crystallization of n-Paraffins: Crystallization of n-paraffins from their solutions in different solvent systems as given in Table 3 indicated that:

- The crytallization temperature is highest in methyl ethyl ketone followed by n-heptane and toluene, the lowest being in cyclohexane and this trend is independent of the boiling range/average carbon number of the adductables.
- In all solvents the crystallization temperature increases with increasing boiling range/melting point of the fractions.
- There are two to three crystallization temperatures of TNP and its fractions in all solvents except toluene.
- Maximum value of crystallization temperature observed in respect of the n-alkanes under investigation. This indicated that irrespective of the nature of the solvents the values are lower with their maximum Tm or Tc values.
- The crystallization exotherm at 260–270 °K in cyclohexane solution is due to crystallization of cyclohexane.

From cyclohexane to methyl ethyl ketone the difference in crystallization temperature for TNP is of the order of 35°C and this order increases with increasing boiling range of the fractions. Solvent matrix thus shows a great influence on the crystallization behaviour of these n-paraffins.

Role of Transition Characteristics on Needle Penetration: It has been observed that the needle penetration greatly depends upon the transition temperature and as soon as this temperature is approached the penetration increases rather rapidly (Figure 1). At a temperature quite close to the solid-liquid transition temperature, the n-paraffins become soft. The sharpness of penetration temperature curve at the transition temperature has been found to depend on the carbon number distribution in the paraffins. In TNP and its fractions the existance of multiple solid-solid transition indicates that all the low transitions are orthorhombic and these differ only in their space group. The needle penetration is dependent to the transition temperature and as well on the average carbon number/ molecular weight.

Conclusion

Phase transition in solid n-paraffins greatly controls the hardness behaviour of n-paraffins and is dependent on the carbon number distribution. The n-paraffins becomes soft at temperature close to the phase transition temperature. Further the crystallization behaviour of the solid n-paraffin components is greatly influenced by the nature of the solvent present in the system.

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