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COMPOSITION AND PROPERTIES OF SOLID ALKANES EXTRACTED FROM A WAXY PETROLEUM FLUIDS

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Abstract.

Assam crude oil long residue ($370^{o}C^{+}$) is highly waxy/aromatic in nature associated with high pour point ($51^{o}C$). The solid alkane components of this fraction extracted through urea adduction were analyzed for their composition by GC and for their thermodynamic parameters by DSC. These data have been correlated. The effect of concentration of urea adductables on the plastic viscosity and yield stress of non-adductables (denormalized oil) at different temperatures has been investigated.

Key words: *Crude oil, long residue, alkanes, thermal properties, urea adduction, flow behaviour*

Introduction

Assam crude oil is waxy in nature (wax content 11 %, pour point $30^{o}C$) and thus has poor flow behaviour at low temperature. The waxes are predominant in the fraction boiling over $370^{o}C$. n-Alkanes are main constituents of these waxes. It was of interest to characterize the n-alkanes present in this fraction ($370^{o}C^{+}$) of the crude for their composition and properties to understand the flow behaviour of crude oil. In the present communication the effect of solid alkanes on the low temperature rheological characteristics such as pour point, yield stress and viscosity temperature behaviour of long residue have been studied and discussed along with the phase transition and carbon number distribution of n-alkanes in the sample.

Experimental

Assam crude oil long residue $370\ ^{o}C^{+}$ having physico-chemical characteristics as given in Table 1was taken for these studies. The n-alkanes were separated from it through urea adduction [1]. The carbon number distribution of urea adductables (referred as n-alkanes was determined by gas chromatography.

The phase transition temperature viz. temperature of melting (T_m) and associated energy (ΔH_m) of the alkanes were determined [2]. The thermogram i.e. heat flow versus. temperature of the sample is given in Figure 1, which also show the thermodynamic parameter viz. temperature of melting and associated energy with change of phase. The non-adductable components referred to denormalized oil (DNO) in the present study were also analyzed for the physical properties are

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also given in Table 1.The low temperature rheological characteristics namely plastic viscosity and yield stress of the DNO was determined using Haake RV-12 rotational viscometer. These characteristics were measured in Newtonian as well as non-Newtonian region and were obtained at varying temperature from 70 to 30^{o}C. The effect of concentration of n-alkanes in the DNO from 2 to 18 wt % was also determined as shown in Table 2.

The saturate and aromatic components present in the residue 370^{o}C^{+} were separated by elution chromatography using silica-alumina adsorbents. These components were analyzed for viscosity temperature behaviour using AIMIL-EMILA rheometer and the variation of viscosity with temperature is shown in Table 3 [3].

Result and Discussion

The Assam crude long residue 370^{o}C^{+} has a pour point 51 ^{o}C and has 18 wt % n-alkanes. These n-alkanes have melting point 70^{o}C having carbon ranging from C_{20} to C_{37}. and are widely distributed. On removal of alkanes by urea adduction, the pour point of the residue has reduced to 30^{o}C from 51^{o}C. The thermogram of n-alkanes Figure 1, indicated that the first solid-solid transition occur at 49.16^{o}C [2]. On further heating, the second transition i.e. solid-liquid that is maximum and is observed at 59.53^{o}C. This change from first to second transition involves energy of 157.5 J/gm.

Aromatic components have considerably higher viscosity than the saturate components as well as from the parent sample at all temperatures ranging from 85 to 45 ^{o}C. A wide difference in the viscosities has been observed between long residue, its saturate and aromatic fraction at all temperature, Figure 2. The data on plastic viscosity and yield stress as presented in Table 2, indicated that:

- The plastic viscosity of residue (370^{o}C^{+}), denormalized oil and blends of n-alkanes in denormalized oil increases with decreasing temperature of measurements.
- The plastic viscosity of denormalized oil is higher than the long residue at all temperature.
- Increase in concentration of n-alkanes in denormalized oil decreases the plastic viscosity of the blend at temperature from 70 to 50^{o}C.
- The samples start showing yield stress around their pour points.
- The increase in n-alkane concentration from 2 to 18 wt % increases the pour point from 30 to 51^{o}C of the blends

Table 1. Physico-chemical characteristics of Assam long residue 370 ^{o}C^{+} and its denormalized oil (DNO)

Characteristics	Long residue 370^{o}C	DNO (urea non-adductables)
Pour Point, ^{o}C	51	30
Viscosity, cSt At 80 ^{o}C At 100 ^{o}C	 32.65 16.45	 118.7 47.6
Density, at 70 ^{o}C	0.9111	0.9488

Table 2. Effect of n-alkanes on plastic viscosity and yield stress of denormalized oil (DNO)

Properties	n-Alkanes, wt % concentrations									
	0 (DNO)	2	4	6	8	10	12	14	16	18
Pour point, ^{o}C	30	33	36	39	39	42	45	48	48	51
Plastic viscosity (mPa.S)										
At 70^{o}C	40	36	32	30	28	28	24	24	24	20
60^{o}C	73	68	64	60	56	50	44	42	42	36
50^{o}C	145	123	110	89	80	70	68	66	64	100
45^{o}C	205	181	142	129	120	115	150	250	275	350
40^{o}C	339	290	250	210	177	205	300	-	-	-
35^{o}C	508	-	-	-	-	-	-	-	-	-
30^{o}C	968	-	-	-	-	-	-	-	-	-
Yield stress, Pa										
At 60^{o}C	0	0	0	0	0	0	0	0	0	0
50^{o}C	0	0	0	0	0	0	0	0	0	30
45^{o}C	0	0	0	0	0	0	30	50	90	-
40^{o}C	0	0	0	0	5	10	90	-	-	-
35^{o}C	5	15	-	-	-	-	-	-	-	-
30^{o}C	50	75	-	-	-	-	-	-	-	-

Table 3. Viscosity-temperature behaviour of long residue and its saturate & aromatic components

Temperature, ^{o}C	Viscosity, cP		
	Long residue, 370^{o}C^{+}	Saturates	Aromatic
85	21	3	55
80	25	3.5	65
75	30	4	85
70	36	5	120
65	43	6	165
60	50	8	240
55	90	10	350
50	220	27	560
45	400	85	890

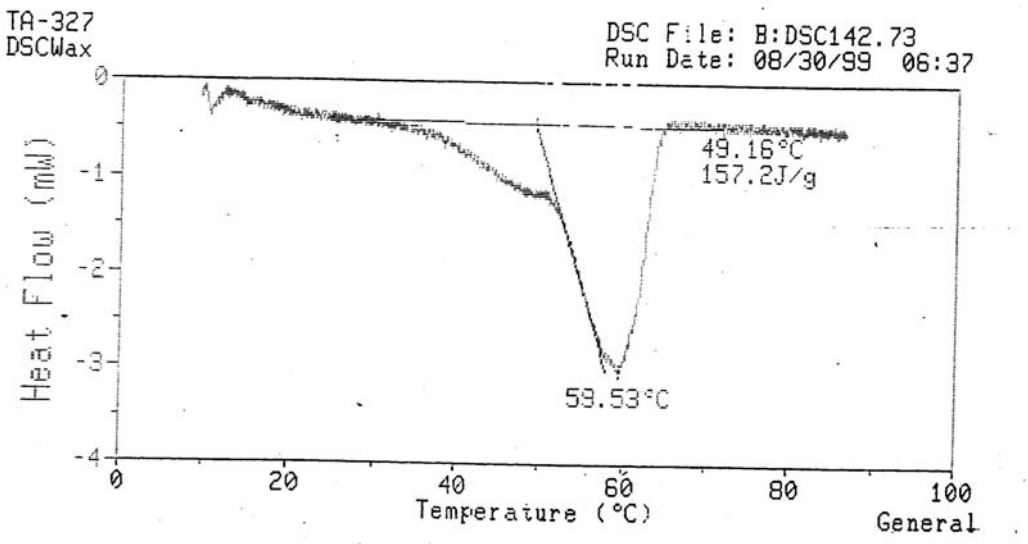

Fig. 1 : DSC thermogram of urea adductable derived from 370 ^{0}C $^{+}$ residue of Assam crude

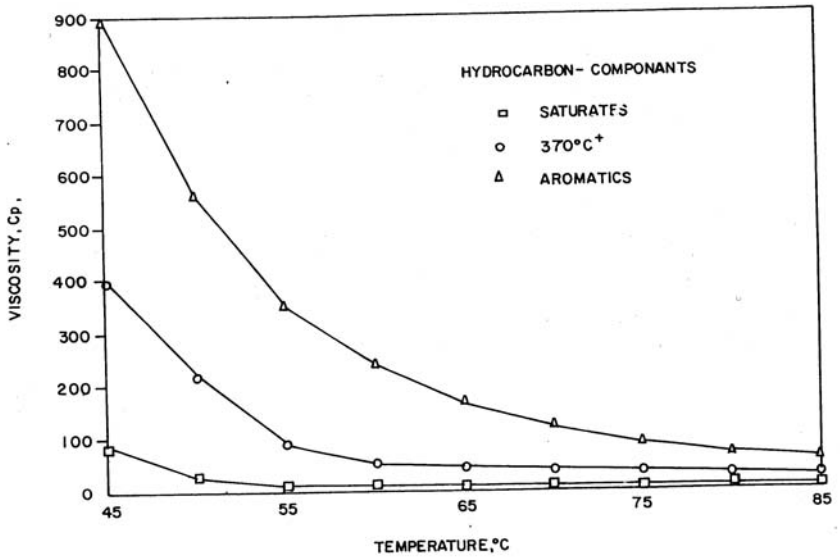

Fig 2: Viscosity-temperature behaviour of 370 $^{0}C^{+}$ long residue and its components

Conclusions

Removal of n-alkanes considerably lowers the pour point of the residue. These n-alkanes greatly control the low temperature flow properties of the waxy fluids.

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