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## Fractionation of wax from heavy petroleum fractions of different geological origins and their characterization by DSC and HTGC

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### ABSTRACT

Four north east indian crude oils having different geological origins namely DK (Eocene), SL (Barail), JN (Tipam) and KMC (Girujan) were collected from wells of different locations. The crude oils were distilled up to 300°C at atmospheric pressure. Waxes from the heavy fractions (300°C+) were separated by solvent extraction method using methyl isobutyl ketone (MIBK) as solvent at different temperatures (40-0°C). n-Alkanes and iso- and cyclo- alkanes were separated from the wax fractions by urea adduction method. The separated wax and iso- and cyclo- alkane fractions were then analyzed by high temperature gas chromatography (HTGC) for n-alkane carbon no. distribution and different non n-alkane compounds present in different wax fractions and differential scanning calorimetry (DSC) for solid-liquid transition temperatures. Clear differences were observed for the above parameters in the different fractions. On increasing the temperature of dewaxing there is an increase in average carbon number, peak carbon number and also the molecular weight of the separated wax. In all the crude oils maximum wax separation temperature was found to be 30°C. At 40°C negligible amount of wax was obtained. Major portion of the separated waxes have alkane carbon number from 17-25 followed by 26-35 alkane carbon number. DK, SL and JN contain significant amount of C30 and above hopanes whereas KMC contains very insignificant quantities of hopanes. The concentration of C18 isoprenoid, pristane and phytane are more in DK and JN than that of SL and KMC. The solid-liquid transition of waxes increases with increase of separation temperature of the wax. At 0°C both solid-solid as well as solid-liquid transition state of wax was observed. But at higher wax separation temperature only one transition i. e. solid-liquid state was observed.

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### KEYWORDS

RCO;  
HTGC;  
DSC;  
HPLC;  
Wax;  
Hopane.

### INTRODUCTION

Waxes from mineral sources have been known for

well over a century. Originally petroleum wax was regarded as unavoidable and unwelcome byproduct arising from the dewaxing of lubricating and gas oil<sup>[1]</sup>. At

present waxes are widely used in all types of food industry, drugs, medicaments, cosmetics and a lot of other applications in house and industry. The purity of waxes along with its excellent moisture, vapour and water resistance, relative chemical inertness and freedom from odour and tastes are the predominant factor for its widespread use. Wax is usually referred to a substance that is solid at ambient temperature and viscous liquid when it is subjected to slightly higher temperature. Petroleum waxes are generally produced from lubricating oil base stocks, residual distillates, tank bottoms and sucker rod waxes.

The petroleum waxes are a solid mass consisting of variety of hydrocarbons in the range of  $C_{22}$ - $C_{65}$  carbon numbers having varying degrees of plasticity, water repellency, slipperiness and gloss and melts on heating<sup>[2]</sup>. The chemical composition of wax is complex; all the products have relatively high molecular weight profiles, with the functionality ranging from products, which contain mainly normal alkanes to those, which are mixtures of hydrocarbons and reactive functional species. Based on the separation techniques petroleum waxes are classified into three categories, namely paraffin, intermediate and microcrystalline waxes. In general paraffin wax contains individual alkanes ranging from about 18 carbons to about 45. Intermediate waxes contain individual chain length up to 60 carbon atoms whereas microcrystalline waxes contain mixtures of n-, iso- and cyclo alkanes. The carbon number content per molecule can vary from mid thirties to well over eighty<sup>[2]</sup>.

The identification and characterization of waxes starts with the simple tests of solubility and melting point<sup>[3-4]</sup>. Fractionation of waxes on the basis of their melting point and separation of straight, branched and cyclo paraffins can provide the systematic analysis of waxes. During the study of the efficacy of paraffin inhibitor on crude oil, Del Carmen Garc a et al<sup>[5]</sup> separated the alkanes from  $>200^{\circ}\text{C}$  petroleum fraction by HPLC using n-heptane as solvent. The saturated fraction was further fractionated into n- and iso+cyclo paraffin by using molecular sieve ZSM-5 catalyst. Boukadi et al.<sup>[6]</sup> separated the wax from crude oil by adsorption of asphaltenes on alumina. The maltene fractions were separated into wax and non-wax fraction via acetone precipitation techniques. The fraction was then analyzed by high temperature GC Ben Warton et al.<sup>[7]</sup> analyzed

a series of crude oils of varying ages, source types and depositional environments for the branched alkanes by comparison of mass spectra and gas chromatographic reaction behaviour with authentic reference compounds. Most thermodynamic models consider wax to be comprised entirely of n-alkanes, but it is not correct. More than 50% of wax is a very complex mixture of branched and cyclic compounds comprising at least 7-8 homologous series of hydrocarbons in differing proportions<sup>[8]</sup>. Differential scanning calorimetry as well as Fourier transform infra red spectroscopy are used to identify waxes<sup>[9-11]</sup>. DSC allows melting point determination and thermal characterization of waxes<sup>[12]</sup>. Characterized the waxes by DSC and thermo microscopy technique. They observed that best correlation between pour point and DSC results obtained when  $>2\text{wt.}\%$  wax precipitated. DSC and X-ray diffraction methods are used by many researchers to evaluate the crystal structure of the wax<sup>[13,14]</sup>. Boukadi et al.<sup>[6]</sup> characterized the paraffin deposits in tank bottom by high temperature gas chromatography. The purpose of this study was to investigate the physical and chemical characteristics of waxy portions of crude oils of different geological origins to help researchers to formulate suitable pour point depressants to minimize wax deposition problems during winter seasons in crude oil transportation pipe lines as well as wells containing crude oils of high wax content. The analysis of the wax fractions are done by HTGC and DSC.

## MATERIALS AND METHODS

Four crude oils from different sources were selected on the basis of their origins of different geological time scale; DK from Eocene, SL from Barail, JN from Tipam and KMC from Girujan origin. After distilling the crude oils up to  $300^{\circ}\text{C}$  at atmospheric pressure, the residue i. e.  $300^{\circ}\text{C}+$  fractions were taken as feedstock.

### Fractionation of wax at different temperatures

Fractionation of wax at temperatures, such as  $40^{\circ}\text{C}$ ,  $30^{\circ}\text{C}$ ,  $20^{\circ}\text{C}$ ,  $10^{\circ}\text{C}$  and  $0^{\circ}\text{C}$  were achieved by using the following procedure: about 10g of  $300^{\circ}\text{C}+$  fraction was heated to  $50^{\circ}\text{C}$  to make it homogeneous liquid. About 100ml of methyl iso butyl ketone (MIBK) was then added to the liquid with constant stirring. The mixture

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was then allowed to cool at 40°C for 2 hours without any vibration. The separated wax was then filtered by applying vacuum through a water jacketed Grouch crucible also kept at 40°C containing Whatman 2 filter paper. The wax on the filter paper was washed several times with small volumes of MIBK kept at 40°C.

### Purification

The crude wax on the filter paper was transferred to a suitable container by dissolving it with hot n-heptane. Activated neutral alumina was then added slowly to the solution with constant stirring till the solution becomes colourless/pale yellow. The supernatant liquid was then filtered to a pre-weighed container. The alumina was washed several times with hot n-heptane and the washings were added to the pre-weighed container. The n-heptane from the solution was evaporated off on a hot plate to recover purified wax. This wax was named as fraction 1. The whole process was repeated at 30, 20, 10 and 0°C to get fractions 2, 3, 4 and 5.

### Compositional analysis of wax fractions

Wax fractions as separated above were analyzed for their n and iso+cyclo paraffin content. About 50mg of wax fraction was taken in a 25ml conical flask, 5ml of toluene-methanol mixture (3:1 v/v) was added to the flask with constant stirring until the saturates was completely dissolved. Then 2ml of saturated urea solution in methanol was added and the mixture was thoroughly mixed. The precipitated mixture of the adduct and the crystalline urea was allowed to stand overnight at 0°C. The content in the flask was then filtered through ordinary filter paper. The residue on the filter paper was washed several times with small volumes of methanol to remove adhering iso+cyclo alkanes. From the filtrate the excess methanol was removed by heating it on a water bath to make the toluene-methanol ratio of 3:1 v/v. 1ml of saturated urea was again added to it and the whole process was repeated. The residue on the filter paper was allowed to dry in air. It was then transferred to a separating funnel by dissolving with hot water. Pure n-alkanes from the solution in the funnel were then extracted with n-hexane. The beaker containing the filtrate was heated on a hot plate to remove toluene and methanol. After complete evaporation of toluene and methanol from the beaker pure iso+cyclo alkanes was

taken out of the beaker by dissolving with n-hexane. The weight of pure n-alkanes and iso+cyclo alkanes was taken after removing n-hexane from the respective beakers.

### HTGC analysis of wax fractions

Wax fractions separated as above were analyzed by a thermo ultra trace gas chromatograph equipped with a 30 m x 0.25mm DB1 HT fused silica capillary column. 2µl of 1% wax solution in n-hexane was injected to the GC. The GC was programmed as- constant injector temperature at 320°C with 20:1 split ratio, column temperature programmed from 80°C with 0min. hold time to 380°C with 10 min. hold time at 8°C/min. heating rate. Total time of analysis was 46.5min.

### HTGC analysis of iso + cyclo alkanes from RCO wax

The same method as applied for analysis of wax fractions was used.

### DSC analysis of wax fractions

The analysis was carried out by Mettler Toledo DSC 822<sup>e</sup> (Switzerland) instrument. About 5mg of wax sample was taken in an aluminium sample holder. The holder was then put in the heating chamber of the DSC system. The analytical method was: initial temperature was 25°C, initial hold time 0 min., final temperature 100°C; final hold time 0 min. heating rate 5°C/min., at a flow rate of 40ml/min. Total time of analysis was 15 mins.

## RESULTS AND DISCUSSION

The concentration of different wax fractions is tabulated in TABLE 1. KMC contains highest content of total wax (21.6%), JN and SL contain equal amount of total wax (12%). DK contains least of the four, having only 9.3%. The data in TABLE 1 indicates that KMC feedstock have a linear distribution of wax content, i. e. maximum wax content at 0°C fraction and minimum at

TABLE 1: Fractionation of wax at different temperatures

Sample	% Yield of wax					Total wax %
	Fractionation temperature					
	0°C	10°C	20°C	30°C	40°C	
DK	2.01	1.46	5.56	0.78	0.14	9.95
SL	3.44	1.34	3.23	2.23	0.66	10.90
JN	2.36	1.78	5.10	2.10	0.17	11.51
KMC	7.06	5.07	3.11	1.08	0.06	16.38

40°C fraction. Whereas DK, SL and JN have non-linear distribution of wax content in different wax fractions. DK and JN shows similar wax distribution pattern, i. e. maximum at 20°C. In KMC and SL the maximum is at 0°C. Pierre et al.<sup>[15]</sup> demonstrated that n-alkane molar concentration distribution is of 'normal logarithmic' type. Lira-Gaieana et al.<sup>[16]</sup> developed a thermodynamic framework for calculating wax precipitation in petroleum mixtures over a wide range of temperatures. The location of wells from where crude oil samples collected for present study is shown in figure 1. In this present communication the distribution of n-paraffins present in wax separated at different temperatures are presented in figure 2(a-d) respectively for DK, SL, JN and KMC wax. It is observed from the figures

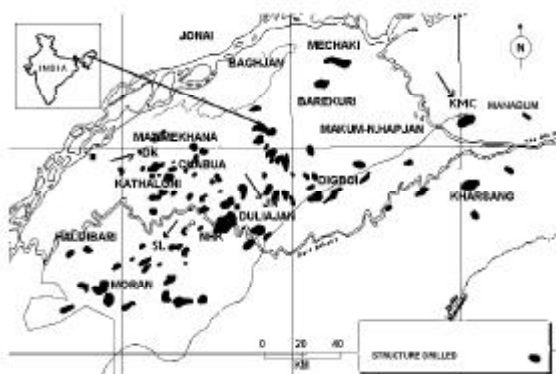


Figure 1 : Oilfield map of Assam and Arunachal Pradesh

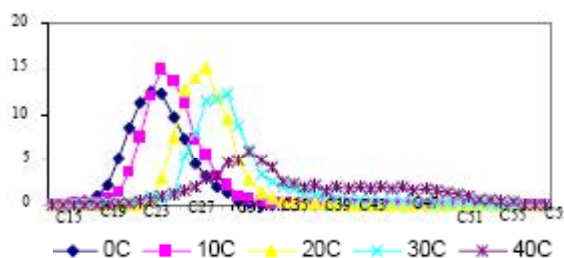


Figure 2(a) : C-No. distribution of DK wax separated at different temperatures

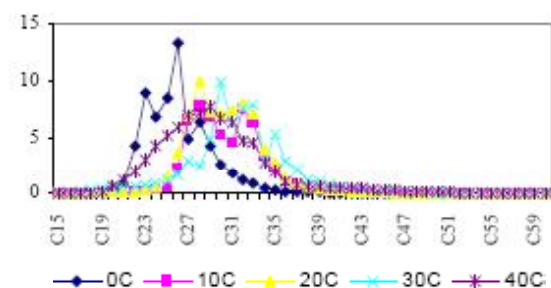


Figure 2(c) : C-No. distribution of JN wax separated at different temperatures

that at higher temperature of dewaxing, high molecular weight alkanes are separated. The distribution range of alkane carbon number present in different waxes is tabulated in TABLE 2. The data in TABLE 2 indicates that lower molecular weight waxes  $C_{17}$ - $C_{25}$  followed by  $C_{26}$ - $C_{35}$  predominates for DK waxes separated at 0°C whereas higher molecular weight alkanes  $C_{26}$ - $C_{35}$  predominates at higher dewaxing temperatures. So, the average carbon number increases with increase of separation temperature of the waxes. For DK the average carbon number of wax fractions is 25.1, 26.9, 29.2 and 32.1 respectively for the waxes separated at 0, 10, 20 and 30°C. Even the peak carbon number of waxes shifted from lower to higher as presented in figure 2(a-d). The interesting feature is that some of the separated waxes contain more than 50 n-alkane carbon number particularly for DK.

### Composition of wax fractions

The wax fractions were further characterized for their iso+cyclo paraffins content and tabulated in TABLE 3. The data in the TABLE indicates that n-paraffin content decreases with increase of separation temperature for DK and SL. But it is not so for the other two. For DK the total wax content at 30 and 40°C having more than 45 carbon numbers is about 2.2 and 15.3% (TABLE 2). The iso- and cyclo-paraf-

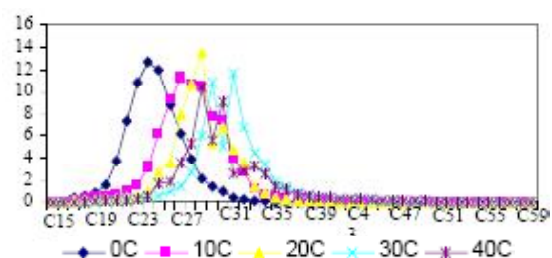


Figure 2(b) : C-No. distribution of SL wax separated at different temperatures

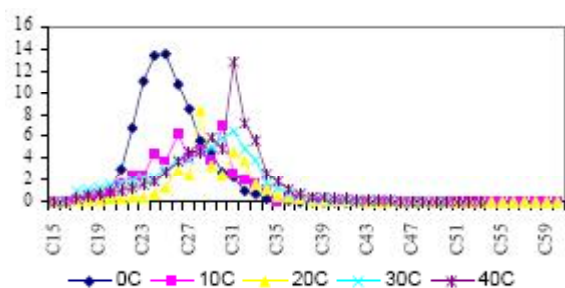


Figure 2(d) : C-No. distribution of KMC wax separated at different temperatures

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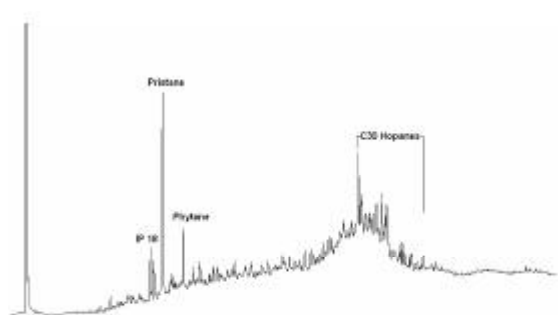


Figure 3(a) : GC fingerprints of DK iso and cyclo alkanes

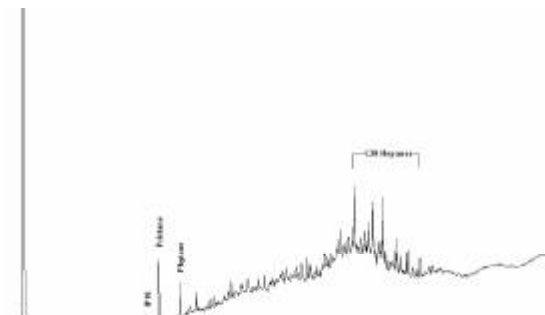


Figure 3(b) : GC fingerprints of SL iso and cyclo alkanes

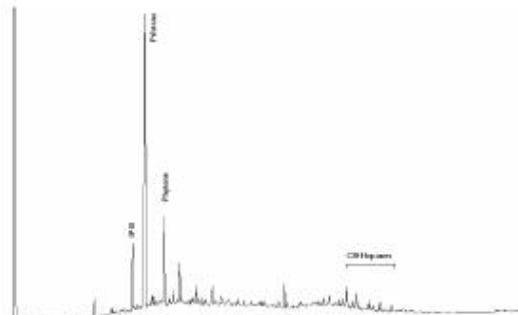


Figure 3(c) : GC fingerprints of JN iso and cyclo alkanes

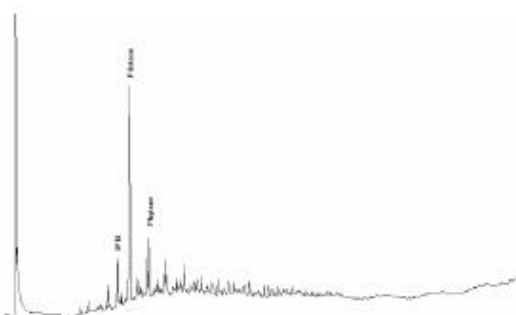


Figure 3(d) : GC fingerprints of KMC iso and cyclo alkanes

TABLE 2: N-alkane carbon number distribution range in waxes

N-alkane C no.	Sample	0°C		10°C		20°C		30°C		40°C	
		Conc.(%)	Av.C no.	Conc.(%)	Av.C no.	Conc.(%)	Av.C no.	Conc.(%)	Av.C no.	Conc.(%)	Av.C no.
C17-C25	DK	59.5	25	43.3	27	6.0	29	4.1	32	2.5	37
	SL	56.2	25	19.7	28	15.7	32	8.7	31	5.7	-
	JN	52.5	26	38.1	27	30.0	29	15.1	30	10.4	31
	KMC	39.6	26	3.8	29	4.6	28	8.3	32	24.1	29
C26-C35	DK	39.3	-	53.0	-	88.8	-	89.0	-	45.2	-
	SL	41.8	-	75.7	-	78.9	-	80.3	-	80	-
	JN	41.6	-	59.5	-	68.0	-	79.5	-	78.4	-
	KMC	51.7	-	89.4	-	76.2	-	77.3	-	69.1	-
C36-C45	DK	0.37	-	1.2	-	2.3	-	10.3	-	35.1	-
	SL	0.70	-	1.7	-	3.0	-	7.7	-	0.6	-
	JN	1.4	-	1.5	-	1.0	-	2.7	-	7.6	-
	KMC	1.0	-	4.1	-	3.5	-	11.2	-	6.4	-
C46-C55	DK	-	-	0.3	-	0.1	-	2.2	-	15.3	-
	SL	-	-	0.04	-	0.08	-	0.6	-	1.0	-
	JN	0.3	-	0.09	-	0.07	-	0.31	-	0.31	-
	KMC	2.6	-	0.3	-	0.3	-	0.7	-	1.2	-

TABLE 3: Chemical composition of wax fractions

Crude oil	Total wax (%)	Wax separation temperature(°C)									
		0	10	20	30	40	0	10	20	30	40
		Wax (%)	I+C Alk. (%)	Wax (%)	I+C Alk. (%)	Wax (%)	I+C Alk. (%)	Wax (%)	I+C Alk. (%)	Wax (%)	I+C Alk. (%)
DK	9.26	2.01	17.19	1.45	17.33	5.56	22.55	0.17	58.11	0.07	0.07
SL	11.52	3.27	24.28	3.36	32.29	2.0	32.70	2.23	55.15	0.66	0.66
JN	11.51	2.36	16.23	1.78	29.18	5.1	43.71	2.1	27.05	0.17	0.17
KMC	21.60	10.5	25.05	6.2	14.49	3.3	29.36	1.5	16.89	0.1	0.1

fin content of this wax at 30°C is 58% (TABLE 3). This

iso- and cyclo paraffin content of the wax increases with the increase of separation temperature of waxes. Probably DK wax separated at 30°C may be suitable as microcrystalline/mixed grade wax. The increase of cyclo and iso-paraffin at higher temperature indicates their better commercial viability. Since these waxes consist of iso-alkanes and cyclo-alkanes they will have appreciable flexibility, ductility, adhesiveness and the higher viscosity.

**TABLE 4: Iso- and cyclo- alkanes identified in wax fractions by HTGC**

Sample	IP18 (%)	Pristane (%)	Phytane (%)	Pristane/Phytane	C <sub>29</sub> Hopane (%)	C <sub>30</sub> Hopanes (%)
DK	6.34	29.22	9.03	3.2	0.88	4.40
SL	1.73	19.72	10.37	1.9	17.93	19.83
JN	9.04	35.07	11.70	3.0	0.63	2.36
KMC	1.77	8.77	2.86	3.0	Nil	Nil

**TABLE 5: DSC data for wax fractions**

Waxes	Wax separation temperature (°C)							
	0		10		20		30	
	Tran. Temp (°C)	Energy J/g mw	Tran. Temp (°C)	Energy J/g mw	Tran. Temp (°C)	Energy J/g mw	Tran. Temp (°C)	Energy J/g mw
DK(s-s)	42.8	6.8	46.5	8.8	-	-	-	-
(s-l)	56.5	20.3	59.7	21.2	68.5	19.8	66.2	26.3
SL(s-s)	45.4	3.6	-	-	-	-	-	-
(s-l)	56.1	4.9	63.3	28.1	66.3	21.1	62	19.6
JN(s-s)	44.2	10.3	-	-	-	-	-	-
(s-l)	58.7	24.0	63.4	19.7	64.2	20.6	70.2	24.1
KUM	40.1	7.3	-	-	-	-	-	-
(s-s)	57.9	22.4	46.1	8.7	57.1	11.5	62.3	17.7
(s-l)								

### Analysis of iso+cyclo alkanes by HTGC

The presence of tri terpenoids particularly hopanes are detected in crude oil<sup>[17,18]</sup>. The iso- and cyclo paraffins obtained as above were analyzed by HTGC using the same procedure as mentioned above. Some of the iso- and cyclo-paraffins of geochemical interest like pristane, phytane, hopanes and C18 isoprenoid could be identified due to their higher peak intensities. The analyzed data are presented in TABLE 4. From the study of GC chromatograms it was observed that DK, SL and JN contain significant amount of C-30 and above hopanes whereas KMC contains negligible quantity of hopanes. The exact quantity of the individual hopanes could not be obtained due to poor separation of the peaks. The concentration of C<sub>18</sub> isoprenoid, pristane and phytane are more in JN and DK than in SL and KMC. The identification of these compounds was done by comparing with the retention times of their standard compounds. The high pristane/phytane ratio (TABLE 4) indicates that the source matter for the oil was deposited under oxic conditions and probably included abundant material of higher plant origin.

### Analysis of wax fractions by DSC

Differential scanning calorimetry (DSC) can be used to detect the physical or chemical changes in a material that are accompanied by absorption (endothermic) or

liberation of heat (exothermic). It can quantify the thermal events, if the original mass of sample is known. It is a further aid to the investigation of petroleum wax properties and composition<sup>[4,9-13]</sup>. It provides the characteristics record of melting and crystallization behaviour of wax. Moreover the energies associated during transformation of solid-solid, solid-liquid transition state can also be evaluated by these studies. DSC analysis of wax fractions was carried out to determine the melting point of wax fractions.

DSC data for all the waxes are presented in TABLE 5. At 0°C both solid-solid as well as solid-liquid transition state of wax is observed. But when the wax separation temperature is higher than 0°C, only one transition i.e. solid-liquid transition state is observed. It is reported that<sup>[9,10]</sup> only lower molecular weight wax fraction can produce multiple transition state. This shows that molecular weight of wax separated at 0°C are of lowest molecular weight. The carbon number distribution pattern as presented in TABLE 2 also shows that lower average carbon number exists in the wax separated at 0°C. It is also observed from the TABLE that DK wax separated at 10°C, also exhibit solid-solid as well as solid-liquid transition. The average carbon number of the separated wax is 26.9, i. e. lower molecular weight. The energy associated during transition from one form to another is also presented in the TABLE. The solid-liquid transition i. e. the melting point of waxes increases with the increase of separation temperature of wax. The same is true for average carbon number of separated wax.

Another interesting behaviour of these waxes is their solid-liquid transition temperature as determined by DSC technique. Waxes separated at higher temperature should have higher solid-liquid transition temperature. In case of DK, wax separated at 20°C has solid-liquid transition temperature 68°C whereas that of separated at 30°C, is 66°C. The decrease in their solid-liquid transition temperature at higher separation temperature is probably due to their cyclo and iso-alkane content in wax. At 20°C separation temperature the cyclo and iso-alkane content of the wax is 22.5% whereas it is 58.1% in case of 30°C wax (TABLE 3). Similar is the case with SL wax separated at 20 and 30°C. Wax melting point largely depends on the type of paraffins present in the wax.

## CONCLUSION

The crude oils of different geological origins produce wax to different extents. In the present study it was found that the amount of wax in crude oils increases from the deepest to shallowest origins. The physical and chemical characteristics of the wax fractions separated at different temperatures from the heavier fractions of crude oils of different geological origins also are quite different. Wax fraction separated at a particular temperature for the crude oils of different geological origins can show different physical and chemical properties. On increasing the temperature of dewaxing there is increase in average carbon number, peak carbon number and also the molecular weight of the separated wax. At higher temperature like 40°C, negligible amount of wax was obtained. Major portion of the separated waxes have n-alkane carbon number from 17-25 followed by 26-35. The presence of higher amount of iso- and cyclo- paraffin in DK and SL wax separated at and above 30°C is of commercial importance because of their use as mixed grade/microcrystalline wax. DK, SL and JN contain significant amount of C<sub>30</sub> and above hopanes. C18 isoprenoid, pristane and phytane are detected in all the four crude oils. The solid-liquid transition was found to be increases with increase of separation temperature to different extent for all the wax fractions. The findings of the present study will be of immense importance for oil fields to formulate flow improver suitable for oils of different geological origins.

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