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Migration Modelling of Petroleum on the Occurrence of Pyrrolic Nitrogen Compounds in the Crude Oils of Cambay Basin, India

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Summary

The ability to determine the pyrrolic nitrogen compounds, which present in trace quantities in oils, exhibit changes in both absolute and relative concentrations that correlate with migration distance. Such molecules appear promising as empirical but quantitative indicators of the relative distances of oils and present a first step towards true source to oil reservoir distance indicators. Quantitation of the transport of nitrogen compounds to reservoir surfaces during secondary migration may help in determining source rock to reservoir distances.

The abundance of pyrrolic nitrogen compounds is more in Jambusar-Broach block oils as compared to Ahmedabad-Mehsana block. The pyrrolic nitrogen distribution of Cambay basin oils indicates that the alkyl carbazoles are more abundant in most of the oils and benzocarbazoles are less abundant. The oils of Ahmedabad-Mehsana block are laterally less migrated through clay enriched rocks and Jambusar-Broach block oils are more migrated as indicated by the distribution of shielded and exposed isomers. The pyrrolic nitrogen distribution indicates that South Cambay basin oils are more enriched in alkyl carbazoles and benzocarbazoles whereas North Cambay basin oils are more enriched in alkyl carbazoles and less rich in benzocarbazoles. The total concentrations of carbazole, methyl carbazole, ethyl carbazoles and trimethyl carbazoles, benzo [a] carbazole and benzo [c] carbazole increase with increasing thermal maturity and the oils of South Cambay basin are more migrated in comparison to North Cambay basin oils. Systematic investigation of the aromatic biomarkers in oils of Cambay basin results in new generation, migration and entrapment (GME) concepts and exploration leads.

Introduction

The pyrrolic nitrogen compounds such as carbazole and benzocarbazoles are common constituents of rock extracts and crude oils. Until now, research has mainly concentrated on the use of their distribution as secondary petroleum migration markers. Larter et al. (1996) proposed the benzocarbazole parameter benzo [a] carbazole/ benzo [a] carbazole + benzo [c] carbazole as a indicator of migration distance and charging direction and suggested that the decrease in concentration of benzo [a] carbazole/ benzo [a] carbazole + benzo [c] carbazole occurs predominantly during first 100 km of petroleum migration. The rate at which the benzocarbazoles are removed from oils during migration depends on the nature and composition of the carrier bed (for example, fracture vs. capillary flow, clastic vs. carbonate content and the contents of clay and organic matter). Li et al. (1995) have reported that in crude oils, there is an enrichment of alkyl carbazoles relative to alkyl benzocarbazole. The enrichment of so called nitrogen shielded isomers to nitrogen exposed isomers suggests an enrichment of higher to lower homologues with migration distances. The present study focused on the distribution of pyrrolic nitrogen compounds in crude oils of Cambay basin to understand the migration and accumulation and their implications for petroleum exploration in the sedimentary basin.

Geological Settings

The Cambay basin, situated in the northwestern part of Indian craton is a rift graben, which came into existence in the earliest Paleocene. Basin is divided into five tectonic Blocks, which resulted as a sequel to rifiting along the west coast of India. These blocks are Narmada, Jambusar-Broach, Cambay-Tarapur, Ahmedabad-Mehsana and Sanchor-Patan blocks (Pandey et al., 1993). In the Ahmedabad- Mehsana block, two longitudinal axial trends parallel to the axis of the basin are consipcuous. These are Sobhasana- Kalol- Ahmedabad trend in the east and Mehsana- Kadi- Viraj- Jhalora- Sanand- Dholka trend in the west. The longitudinal up-lifts and depressions are (i) Eastern margin depression (ii) The eastern anticline zone (Sobhasan in North and Ahmedabad- Bakrol in south) (iii) The Central depression (iv) The Western anticline zones (v) The Western margin depression. The lithostratigraphy of different blocks of the Cambay Basin has been described by various authors (Chandra and Chaudhary, 1969, Bhandari and Chaudahary, 1975, Pandey et al., 1993). In Mehsana block the Deccan trap forms the technical basement, which is overlain unconformably by Olpad Formation. It is further subdivided in to two units designated as Older and Younger Cambay Shale formations. The Younger Cambay Shale has unconformable relationship with overlying Kalol Formation and underlying Cambay Shale Formation. The Kadi Formation restricted to Ahmedabad-Mehsana block is the stratigraphic equivalent of the younger Cambay Shale. The Kalol Formation has conformable relationship with overlain Tarapur Formation. The formation has been deposited in alternating regressive and transgressive marine influence in a deltaic depositional regime, its thickness is about 150-200m in Mehsana block. In Ahmedabad-Mehsana block two longitudinal axial trends parallel to the axis of the basin are conspicuous. These are the Sobhasan Kalol-Ahmedabad trend in the east and the Mehsana-Kadi Viraj Jholara-Sanand-Dholka trend in West. The Broach depression encompasses Tankari and Broach depression horst, the tertiary sediments over the Deccan Trap basement. A relatively smaller depression exists southwest of Nada area. The location map and generalized stratigraphy of Cambay basin is shown in Fig. 1 & 2.

Samples and Experimental

Twenty-two crude oil samples from different formations of Paleocene- Eocene age in Ahmedabad-Mehsana block of North Cambay basin and Jambusar-Broach block of South Cambay basin were selected for the study and the details of samples are given in Table- 1.

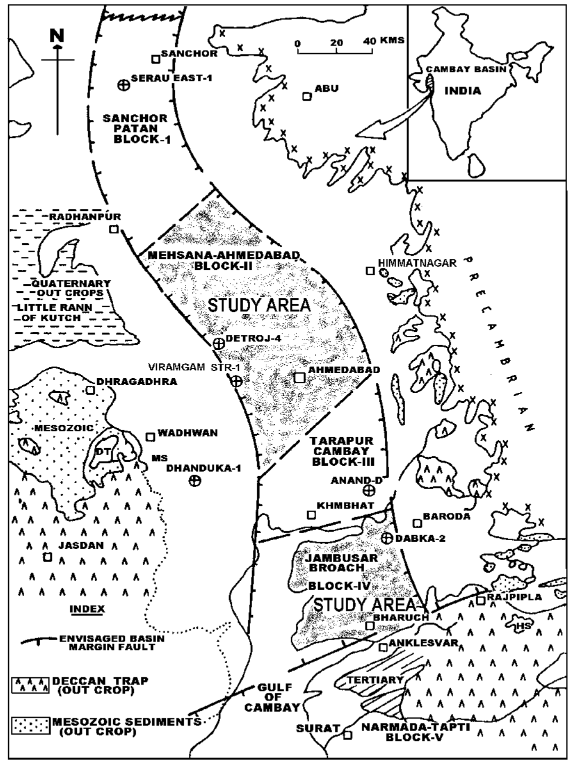

Figure 1: Location map showing the study area of Cambay basin

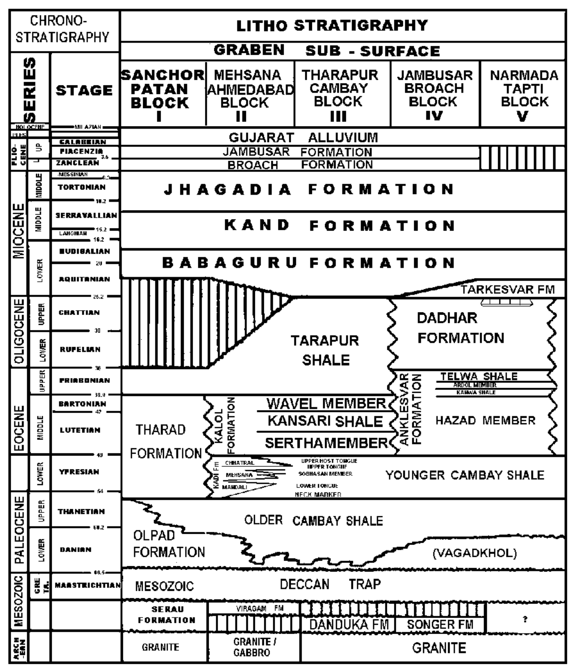

Figure 2: Generalised stratigraphy of Cambay basin

Column Chromatography

The crude oils were deasphaltened with petroleum-ether and then separated in to saturate and aromatic hydrocarbons. Briefly 0.5g of deasphaltened crude oil sample was separated by column chromatography using a 25cm X 7cm i.d. column packed with 10 g of neutral alumina and 20g of silica gel (60-120 mesh). The sequential eluting solvent is 150 ml of petroleum-ether (40-60) to obtain the saturate and 100 ml of benzene to obtain the aromatic hydrocarbons.

The deasphaltened oils (1 g) were adsorbed onto neutral alumina (40g) deactivated with 2% water and eluted with dichloromethane/ n-hexane (2:3, 50 ml) to obtain non polar compounds and aromatics, then with dichloromethane (150 ml) to obtain non basic nitrogen compounds and aromatics. These non-basic nitrogen compounds were further adsorbed onto neutral alumina (40g) deactivated with 2% water and eluted first with n-hexane/ dichloromethane (2:3, 50 ml), and then with n-hexane/ dichloromethane (1:1, 150 ml). The second fraction was further fractionated in to three subfractions by silicic acid column (2 g), eluting sequentially with n-hexane/toluene (1:1, 50 ml), toluene 30 ml and toluene/ anhydrous diethylether (1:1, 50 ml) to obtain pyrrolic nitrogen, amines and pyridinic nitrogen compounds, respectively (Li et al., 2001).

GC-MS-MS Analysis

The nitrogen compounds were analysed on Quattro-2 triple stage quadrupole GC-MS-MS coupled with HP 6890 series gas chromatograph, equipped with BP-1 fused silica capillary column (60 m X 0.25 mm X 0.25 mμ) using helium as carrier gas. The samples were injected using a split/split less injector heated at 290^{o}C. The GC oven was initially at 80^{o}C for 2 min, and then ramped to 290°C at a rate of 3°C/min. The mass spectrometer was operated routinely in selective ion monitoring mode (SIM), occasionally in full scan mode.

Carbazole and N-methylcarbazole were used as standard compounds and dimethyl carbazoles were identified with reference to Li et al. (1992), whose elution order has recently been revised by Bowler et al. (1997). Mass chromatogram obtained by monitoring the molecular ions for alkyl carbazoles show a series of these compounds. The abundance of individual pyrrolic nitrogen compounds in the samples was calculated using the peak area in the corresponding molecular ion chromatograms (m/z 167, 181, 195, 209 and 217, 231, 245).

Results and Discussion

Previous source rock studies

Extensive source rock data has been generated over the years. The geochemical studies including organic matter richness, quality, thermal maturity and source rock facies have established that the Cambay Shale is the regional major source rock in the entire basin (Banerjee et al., 2002). Tarapur, Kalol, Cambay Shale and Olpad formations are the potential source rocks in this basin. TOC ranges from 0.6 to 6.1% (average 1.6%) and 0.6 to 62.9% (average 4.8%) in Tarapur and Kalol respectively. High values of TOC in Kalol are due to the presence of coal. The Tarapur formation is immature in the entire North Cambay basin, whereas Kalol formation is presently in digenetic / catagenetic stage of maturation. Many workers have provided evidence for early generation of oils in Mehsana-Ahmedabad block (Chandra et al., 1994). Considering this concept, it is also possible that probably Kalol formation has also some contribution towards accumulation. The amount and type of organic matter and its level of thermal evolution indicate that Cambay Shale is the main source rock in the basin (Banerjee et al., 2002). TOC ranges from 0.51 to 14.3 %, HI from 40 to 316mg HC/g. TOC and maturity correlation studies indicate that generation threshold (VRo 0.5) of Cambay Shale starts around 1800-1900m (Chandra et al., 1994).

The Cambay Shale (Eocene age) contributed the major source rock in the South Cambay basin. In addition to this, Kanwa, Telwa Shale and shales of Hazad member of Ankleshwar formations are adequately rich in organic matter. TOC ranges from 1 to 2% but are immature in most of the part except along the western part where it is in early stage of catagenesis (VRo 0.5-0.6%). The Cambay Shale thickness varies in the South Cambay basin from 100m on the flanks to 1500+m in the basinal part. Moderately deep marine Upper Eocene sediments provided the regional cap in the Cambay basin. Cambay Shale extends across the South Cambay basin, including the Gulf of Cambay; TOC in shale varies from 0.51 to 27.9% (av.3.0%). HI ranges from 50 to 280mg HC/g. TOC. Entire Cambay Shale is in catagenesis stages (Tmax > 440^{o}C).

Most hydrocarbons bearing reservoir rocks in the South Cambay basin are deltaic sand stones deposited during regressive phase in the Middle Eocene- Early Oligocene. The Olpad Formation (Eocene-Paleocene) sediments are in active hydrocarbon generation stage in Ahmendabad-Meshana block. The total organic content in this formation varies from 1.5-3.5%, HI from 80-200mg HC/g. TOC and Tmax >440^{o}C. Most hydrocarbons bearing reservoir rocks are in Kalol and Kadi formations deposited under fluctuating conditions varying from marginal marine to nonmarine conditions.

Gross Composition

The oils of Balol, Santhal and North Kadi structures in the North Cambay basin of the Mehsana Horst are heavy (API gravity 14-15^o), biodegraded and the saturate/aromatic ratio ranges from 0.57 to 1.10 indicate the oil is aromatic in nature. The oils of Jotana, Nawagam and Sanand structures are medium (API gravity 20-44 ^{o}) and the saturate/aromatic ratio varies between 2.6 and 3.2 which indicate paraffinic in nature. The oils of Broach Block in South Cambay basin are comparatively lighter than North Cambay basin oils (API gravity 32-56 ^{o}) with relatively high saturate/aromatic ratios (3.1-4.7) (Table-1).

Pyrrolic Nitrogen Compounds

The pyrrolic nitrogen compounds are known to interact with the formation water and mineral surfaces, probably through hydrogen bonding between the pyrrolic N-H with hydroxyl groups in the surrounding environments (Dorban et al., 1989), and probably in immobile polar organic phases. A weaker retention and preferential movement of the more nitrogen shielded isomers such as 1-methylcarbazole and 1, 8-dimethylcarbazole during migration can be expected as compared with other isomeric counter parts. It is probably due to the shielding effect of the alkylated carbazoles that the ratio (C_2shielded/C_2exposed) increases with increasing migration. It has been demonstrated (Li et al., 1997, Larter et al., 1996) that with increasing migration distance the concentration of alkyl carbazoles and benzocarbazoles in crude oils decreases, as do the relative abundances of higher to lower molecular weight alkyl carbazoles and benzo [a] carbazole to benzo[c] carbazole. The pyrrolic nitrogen distribution of Cambay basin oils indicates that the alkyl carbazoles are more abundant in most of the oils and benzocarbazoles are less abundant (Table 2). The oils of PK-A, GN-B and LN-A contain abundance of benzocarbazole while none of the oils contain dibenzocarbazole.

PK-A and GN-B are the deepest oils in South Cambay basin are reservoired near the source but the pyrrolic nitrogen distributions of the two oils are different. The relative abundance of dimethylcarbazoles and trimethylcarbazoles are high in comparison to lower molecular weight methylcarbazoles in PK-A oil, whereas in GN-B the abundance of carbazole and methylcarbazoles are high relative to dimethylcarbazoles and trimethylcarbazoles. The ratio of C_2 shielded to exposed isomers in GN-B is lower than PK-A, which indicates that GN-B oil has less migrated as compared to PK-A oil. Similarly the GN-B and GN-C oils are generated from same source rocks but distributions of pyrrolic nitrogen isomers are quite different. GN-C oil contains no benzocarbazole and the ratio of C_2/C_2 shielded to exposed isomers are high which indicate that GN-B and GN-C oils have been derived from similar source rock and vertically/laterally migrated through clay enriched rocks. The oils of PD-B and PD-C in shallow depth are in low concentration of pyrrolic nitrogen isomers but the C_2/C_2 shielded to exposed isomers is also very low, which indicate that these oils have been derived from deeper reservoired and migrated through fault/fracture as the maturity of both the oils are similar.

The North Cambay basin oil LN-A contains no shielded isomers in C_2-dimethylcarbazoles and abundance of benzocarbazoles indicates that it has reservoired near the source bed and laterally/vertically migrated into clay enriched rocks. The other studied oils of North Cambay basin are rich in alkylated carbazoles and traces of benzocarbazoles, which indicate that these oils are reservoired by laterally/vertically short distance migration through organic rich clay minerals like kaolinite in which the pyrrolic nitrogen compounds are adsorbed in the migration path way. Hence, North Cambay basin oils contain less abundance of pyrrolic nitrogen compounds as compared to South Cambay basin oils.

The pyrrolic nitrogen distribution indicates that South Cambay basin oils are more enriched in alkyl carbazoles and benzocarbazoles whereas North Cambay basin oils are more enriched in alkyl carbazoles and less rich in benzocarbazoles. The total concentrations of carbazole,

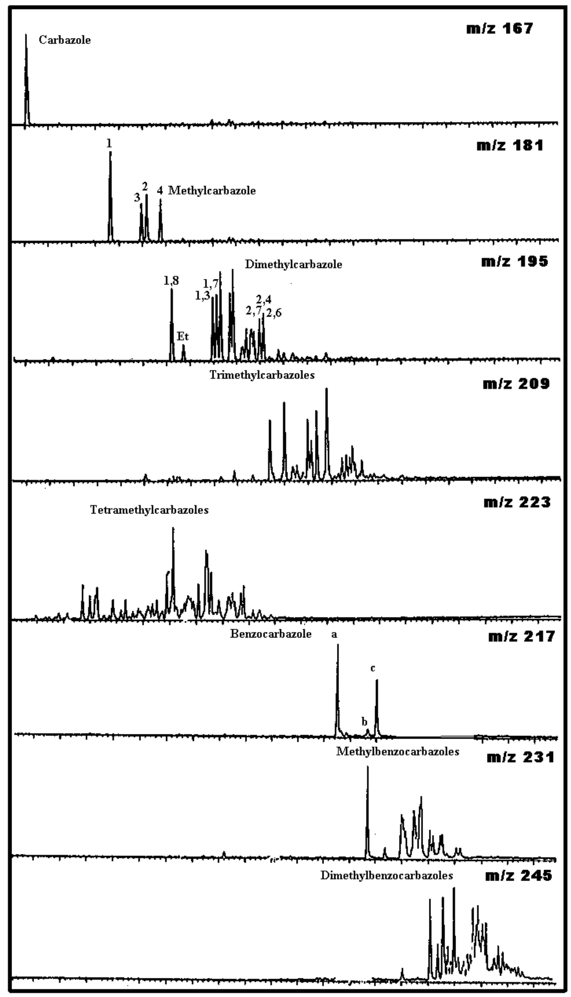

Figure 3: Mass chromatogram showing the isomeric distribution of carbazoles and benzocarbazoles in the oil of PK-A.

methyl carbazole, ethyl carbazoles and trimethyl carbazoles, benzo [a] carbazole and benzo [c] carbazole increase with increasing thermal maturity and the oils of South Cambay basin are more migrated in comparison to North Cambay basin oils.

Implications for Petrol.eum Exploration

Although the Cambay basin has well explored, the oil-source genetic relationship is not well understood because of the multiplicity of depressions, source rocks and reservoirs. The Cambay basin oils have presumed to be sourced by the Cambay Shale Formation sedimentary rocks

(Yalcin et al., 1988). Reservoirs filling were apparently a multiple charge process, which occurred over an extended period of time and little mixing of, oils occurred during migration. The multiple episodes of charging are probably due to the rifting and subsequent basin filling during sedimentation (Schull, 1988). The oils tended to move up the structure and filling the first trap they encountered deepest sand in this case. The early arrivals in this trap were less mature and heavier oils. These oils then migrated along with rejuvenated fault to shallower traps before the arrival of lighter and more mature oils. This process is repeated until all the traps were filled. Consequently, the oils with separate traps preserved the multiple episodes of filling history. So, the pyrrolic nitrogen distribution suggests that GN-C oil has more migrated than GN-B. PK-A is more mature and derived from the deeper source rock in the Broach block.

Table 1 Bulk geochemical parameters of Cambay basin oils

Well No	Depth (m)	Formation	Age	API^{o}	Sat (%)	Aro (%)	NSO (%)	S/A
Ahmedabad-Mehsana block (North Cambay basin)								
LN-A	2850-54	Olpad	Paleocene	44.0	71.23	11.95	16.82	5.96
LN-B	2023-29	Olpad	Lower Eocene	23.7	61.84	23.61	14.45	2.62
JT-A	1509-11	Cambay .Shale	Middle-Early Eocene	37.9	70.17	24.56	5.27	2.86
JT-B	1466-69	Cambay Shale	Middle Eocene	44.2	81.81	13.86	4.71	5.90
NW-A	1836-81	Olpad	Paleocene	34.1	78.76	12.65	8.58	6.30
NW-B	2131-62	Olpad	Paleocene	32.6	63.33	24.25	12.71	2.61
Broach block (South Cambay basin)								
GN-A	2968-70	Hazad	Upper-Middle Eocene	53.2	78.13	16.72	5.15	4.67
GN-B	3390-94	Hazad	Upper-Middle Eocene	43.1	70.78	25.38	3.84	2.79
PK-A	3765-75	Hazad	Upper-Middle Eocene	48.0	75.25	17.30	8.10	4.35
DB-A	1494-95	Hazad	Upper-Middle Eocene	44.9	77.38	18.56	4.06	4.17
PD-A	606-612	Olpad	Paleocene	32.6	53.85	26.92	19.23	2.00
PD-B	590-599	Olpad	Late Eocene-Paleocene	32.4	52.76	33.09	14.15	1.59
NA-A	2735-43	Hazad	Upper-Middle Eocene	39.3	67.21	21.79	11.00	3.08

API ^{o}-API Gravity: Sat-Saturate; Aro-Aromatic: NSO-Nitrogen, sulphur, oxygen; S/A-Saturate/Aromatic

Table 2 Relative percentage of carbazole, alkylated carbazoles and benzocarbazoles and their ratios in the crude oils

Well No.	CA (%)	MCA (%)	DMCA (%)	TMCA (%)	BCA (%)	DMCA/ MCA	TMCA/ MCA	TMCA/ DMCA	C_2-S / C_2-E
Ahmedabad-Mehsana block (North Cambay basin)									
LN-A	10.3	27.2	32.1	30.4	16.9	0.18	0.43	0.51	0.45
LN-B	3.60	21.4	51.9	41.7	0.50	2.42	1.95	0.80	2.71
JT-A	2.00	8.00	34.3	55.6	0.08	4.30	6.90	1.62	3.00
JT-B	0.90	6.00	35.2	57.3	0.09	5.30	8.70	1.63	1.90
NW-A	1.00	5.70	33.1	55.4	4.80	5.80	9.90	1.70	2.10
NW-C	0.50	6.60	31.3	61.6	0.07	4.70	9.30	1.96	4.90
Broach block (South Cambay basin)									
GN-A	14.7	31.4	25.3	6.9	21.6	0.80	0.22	0.27	0.96
GN-B	9.70	28.3	34.3	27.7	-	1.21	0.98	0.81	2.30
PK-A	10.3	27.3	34.1	24.4	4.60	1.31	0.96	0.72	2.38
DB-A	4.20	19.4	35.8	40.6	-	1.85	2.09	1.14	2.53
PD-A	3.10	12.2	30.1	50.6	4.00	2.47	4.20	1.68	1.20
PD-B	2.00	6.20	32.1	56.3	3.40	5.18	9.13	1.80	1.31
NA-A	3.40	21.6	33.9	41.1	-	1.57	1.90	1.21	12.6

CA-Carbazole; MCA-Methylcarbazoles; DMCA-Dimethylcarbazoles; TMCA-trimethylcarbazoles

C_2-S-Shielded isomer; C_2-E-Exposed isomer

Conclusions

The detailed geochemical study reveals that the oils of Cambay basin have been generated from similar type of source material, which is terrestrial organic matter mainly of type III kerogen. The PK-A in Broach block is the deepest oil, which has been derived from the depocenter of the depression. The pyrrolic nitrogen compounds fractionation distribution of GN-B oil suggests less migration distance as compared to Gandhar and PK-A oils. The studies further indicate that migration distance of North Cambay basin oils are believed to be generally short distance while the oils of South Cambay basin have undergone long distance migration.

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