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SEPARATION AND SPECTROSCOPIC CHARACTERIZATION OF N-PARAFFIN WAXES AND ISOPARAFFINS FROM THREE LOCAL CRUDES IN KURDISTAN REGION OF IRAQ

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ABSTRACT

Samples of light, medium and extra heavy Kurdistan crude oils and have been de-asphalted and separated into fractions of saturates by elution liquid chromatography technique. The fractions obtained were separated into n-paraffins, isoparaffins by urea adduction and analyzed using FTIR spectroscopy. The infrared data confirmed the presence of methyl and methylene groups in the saturate fractions of the crude oils. Tawke paraffins fraction have highest value of methyl index, while Jamjamal have the lowest, it means that it has the longest chains of saturate hydrocarbon more than others, while Taqtaq isoparaffins have the highest value, Jamjamal has the lowest.

KEY WORDS: *Crude oils, elution chromatography, FTIR, urea adduction.*

Introduction

Hydrocarbon compounds, usually, with minor amounts of nitrogen-, oxygen-, and sulfur-containing compounds as well as trace amounts of metal-containing compounds like nickel and vanadium (porphyrins) (Considine and Considine, 1984; Francis and Peters, 1980; Hobson and Pohl, 1973; Speight, 1990, 1999; Thornton, 1977). The crude oils have compounds belonging to different families (paraffins, naphthenes and aromatics, PNA) or polarities (saturates, aromatics, resins and asphaltenes, SARA) (Altgelt and Boduszynski, 1994).

The isolation, identification, and characterization of the constituents in heavy oil fractions is a very complicated task (Ryan et al., 2004). For this reason, the standard analysis usually performed in refinery laboratories is not sufficient to give a good quantitative and qualitative prediction of chemical composition of a given feedstock. In order to analyze thoroughly the components of the crude, a separation procedure has to be applied. For the separation of the aromatics and nonaromatics, the elution chromatography procedure (using many absorbents) was used from the literature. The techniques of applying these absorbents to petroleum samples usually consist of separating the oil into a saturate portion and an aromatic portion by adsorption on silica or on alumina (or on both of them). The further separation of the aromatic portion is followed by adsorption on alumina. Both steps utilize elution chromatography with solvents of different polarity (ASTM, 1985; ASTM, 1986; Hirsh et al., 1972; Surinder, 2010).

The n-paraffins are separated either by selective adsorption with 5A molecular sieves or adduction with urea. The ratio of n-paraffins to isoparaffins, aromatics and naphthenic hydrocarbons varies widely and depends upon the type of oil. The formers are used as light lubricants in industry, in alkylation process (detergents industry) and many various applications. Urea crystallizes from solutions in a matrix where the *n*-paraffins, but not the branched or cyclic compounds, are included within urea’s cylindrical pores. For this process, various reaction temperatures have been used in the literature. Subsequent recovery of the *n*-paraffins is by decomposition of the urea clathrate by heat or by simply adding water. In this way, the urea reverts to its original form. For effecting complex formation, the presence of a polar compound (activator) such as water, aliphatic alcohol, or ketone expedites the complex formation. Thiourea has been shown to form similar adducts with branched paraffin’s under a similar procedure (Lappas et al., 1997; Obali, 1988; Shiping and Yongge, 2005).

The aim of this research is to investigate an improved method for the complete separation of saturate fraction of crude by elution chromatography then separate this fraction into normal paraffin’s and isoparaffins by urea adduction. The identification of these fraction is carried out by FTIR spectroscopy (Odebunmi and Adeniyi, 2007; Said et al., 1988).

2. Experimental

2.1. Crude oil samples:

The study was carried out on three crude oil samples which are collected from the fields of JamJamal, TaqTaq and Tawke located in the Kurdistan region of Iraq.

2.2. Physicochemical properties

The physicochemical characterizations of the three studied crude oils were carried out using the standard test methods of analysis ASTM (ASTM, 2003), UOP (UOP, 1985) and IP (IP, 2002) and the results are listed in Table (1).

2.3. Elution column chromatography

Asphaltenes were removed by precipitation with n-heptane followed by filtration. The de-asphaltened oils were separated into saturate and non saturate fractions using column chromatography with a mixture of pre-activated silica gel and alumina (9:1, v/v) as stationary phase, with n-hexane, as the eluting solvent, respectively. The saturated fractions were then ready for further separation by urea adduction (Obali, 1988; Shiping and Yongge, 2005).

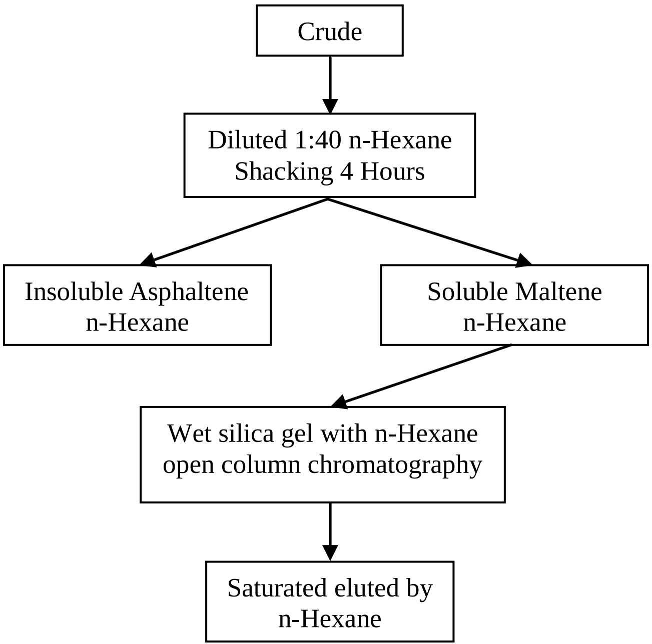

Figure (1): Diagram of the separation procedure by open column chromatography technique

2.4. Traditional urea adduction

10 g of urea and aliphatic hydrocarbons (isolated by elution chromatography) are placed in a 250 mL flask and stirred for 0.5 h at 30-40 °C by adding 5 mL of methanol and the mixture is stirred for 1.5 h and allowed to stand for 24 h at room temperature for complete adduction. The urea crystals were rinsed several times with cold petroleum ether (30/60) and dried under a nitrogen stream. The straight chain waxy n-paraffin's were recovered by dissolving the crystals with distilled water and extracting with petroleum ether (30/60). The isoparaffins fraction was obtained by removing the methanol with a nitrogen stream and extracting with petroleum ether (30/60) (Shiping and Yongge, 2005).

2.3. FT-IR measurements

Infrared spectra of the fractions were obtained from Perkin Elmer Spectrum One B FTIR spectrophotometer. Thin films between KBr windows at a sample thickness of 0.1 mm and resolution at 4 cm^{-1}. FT-IR spectroscopy was used to characterize the saturate fractions of these three crudes. The comparison between these spectra fractions is done by calculating the methyl index (the ratio of intensity peak of methyl group to the methylene groups, which gives an idea of the length of the alkyl chains) (Gonzalez et al., 2001).

$$\text{Methyl Index} = I_{CH_2/CH_3} = \frac{I_{at\ 2925}}{I_{at\ 2950}}$$

3. Results and discussion

The physicochemical characteristics of the three studied crude oils are given in Table (1). The results indicate that Jamjamal crude oil belong to the extra heavy crude oil types with API gravity of about 8.53 (Sp.Gr. 1.010494), while Tawke is a heavy crude oil type with API 24.78 (Sp.Gr. 0.9054) and Taqtaq is a light crude oil with API 147.52 (Sp.Gr. 0.7904).

Table (1): Physicochemical Properties of the three Studied Crude Oils.

Physical properties	Jamjamal	Tawke	Taq-Taq	Method
Density at 15.5 ºC	1.009484	0.9046	-	ASTMD-1298
Sp.Gr. at 15.6	1.010494	0.9054	0.7904	ASTMD-1298
APIº	8.53	24.78	47.52	ASTMD-1298
Pour point ºC	-8	<-40	<-36	ASTM D-97
Kin. Viscosity at 100 ºC	19.5583	4.1505	-	ASTM D-445
Kin. Viscosity at 40 ºC	-	19.11	1.93	ASTM D-445

The analysis of the three studied crude oils for their components has been carried out by deasphalting the crude through precipitation in normal heptane, then resolving the maltene by silica-alumina column chromatography into saturates and non saturates. The saturates were separated into n-paraffins (straight chain) and isoparaffins (branched alkane fractions using urea adduction. The results are given in Table (2). The Jamjamal crude oil has the highest content of saturates while Tawke crude oil has the lowest content. Taqtaq crude has the highest content of n-paraffins, while Tawke has the lowest. An increase in asphaltenes is from Taqtaq, Tawke to Jamjamal.

Table (2): Weight percent of hydrocarbon fractions

	Jamjamal	Tawke	Taq-Taq
Saturate %	60.9	11.85	50.53
n-parafine %	9.24	1.18	14.56
Iso-parafine %	52.26	50.12	46.23
Asphatene %	10	5.6	0.15

The IR spectra of the saturate fractions (n-paraffins and isoparaffins) are presented in Figure (2). The most useful information from FT-IR spectra of crude oil fractions mixture is in the range of 3200–2700 cm^{-1} and 1800–650 cm^{-1} region. Generally, all FT-IR spectra of the fractions fractionated from three crude oils are relatively similar except their differences in intensity (Khadim and Sarbar, 1999).

The aliphatic C–H stretching at the range of 2955 cm^{-1} for CH_3 methyl groups, the presence of several methyl groups in a molecule results in strong absorption at these positions, whereas CH_2 methylene groups have bands at 2924 and 2853 cm^{-1}. The bending vibration of methyl appears at 1377 cm^{-1}, while the methylene appears at 1462 cm^{-1}. The out-of-plane vibration band from methylene groups appears near 721 cm^{-1} which indicate the straight-chain alkanes for four or more carbon atoms and in the lower members of the n-paraffins series, the bands appears at somewhat higher frequencies. The isoparaffinic bands are similar to those in n-paraffins as mentioned the literatures (Mystry, 2009; Silverstein et al., 2005).

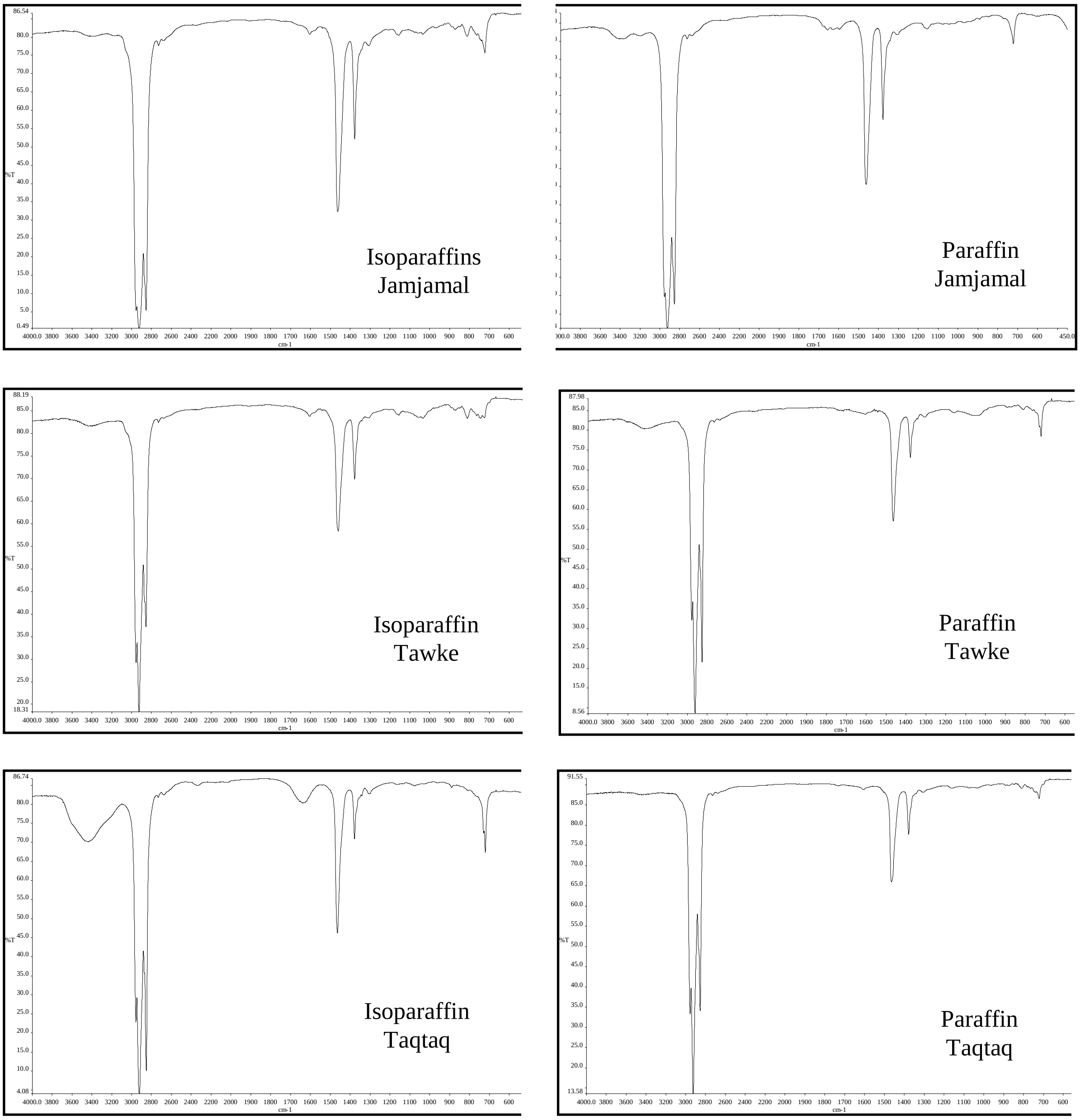

Figure (2): Infrared spectrum for the saturate fractions of the three crudes

Intensities of saturate fraction spectra were listed in Table (3). The methyl index of Tawke paraffins fraction have highest value (2.62), while Jamjamal have the lowest (1.36), respectively this explains that Tawke has long chain of saturate hydrocarbon more than others, while Taqtaq isoparaffins have the highest value (2.28) Jamjamal has the lowest (0.71). This conclusion confirmed from the literatures (Adedosu and Sonibare, 2005; Gonzalez et al., 2001; Khadim and Sarbar, 1999)

Table (3): Intensities of saturate fractions spectra

Crude oil samples		Stretching bands			Bending bands		Rocking	Methyl index
		$-CH_3$	**$-CH_2-$**		**$-CH_3$**	**$-CH_2-$**	**$-CH_2-$**	
			Asym.	**Sym.**				
Jamjamal	n-P	0.25	0.34	0.87	0.51	1.00	0.17	1.36
	Iso-p	0.30	0.21	0.75	0.52	1.00	0.13	0.71
Tawke	n-P	0.31	0.81	1.00	0.23	0.62	0.17	2.62
	Iso-p	0.58	0.82	1.00	0.51	0.98	0.07	1.41
Taq-Taq	n-P	0.35	0.67	1.00	0.26	0.83	0.31	1.91
	Iso-p	0.40	0.91	1.00	0.29	0.63	0.07	2.28

4.Conclusions

Traditional urea adduction gives a clear separation of straight chain and branched alkanes despite some loss of light alkanes due to the influence of temperature, it is faster and more convenient. IR spectroscopy seems to perform slightly good technique in predicting the saturate and other fractions of crude oils.

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فصل وتشخيص البارافينات والايزوبارافينات لثلاث خامات نفطية في أقليم كردستان العراق

الخلاصة

تم التعامل مع ثلاثة نماذج نفطية من منطقة كوردستان العراق موزعة ما بين خفيف ومتوسط وثقيل، بعد فصل الأسفلتين من الخامات، تم فصل الهيدروكاربونات المشبعة بواسطة تقنية كروماتوكرافيا شطف السائل، بعد ذلك تم عزل هذه البارافينات إلى متفرعة ومستقيمة بواسطة تقنية الفصل باليوريا. تم تحليل هذه البارافينات بواسطة طيف الاشعة تحت الحمراء، ومن خلاله تم التأكد من وجود مجموعة المثيل والمثيلين في المقاطع البارافينية المشبعة للخامات، وقد كان خام طاوكي يحوي على اعلى نسبة من البارافينات المشبعة ذات السلاسل الطويلة بينما خام طق طق يملك اعلى نسبة من البارافينات المتفرعة، أما خام جمجمال فيملك أوطأ النسب.

پوختە

پشتی سەرەدەری هاتیە کرن دگە ل سێ نمونێن پترولێ ژکوردستانا عیراقێ دابە شکری دناڤبەرا سڤك و ناڤنجی و گران، وپشتی جوداکرنا اسفلتینێ ژ پترولا ژێر ئەرد و جوداکرنا هیدرو کاربوناتێت تێر ب هاریکاریا تێکنیکا گوروماتوگرافیا پشتی ڤێ چەندێ ئەڤ پارافینە هاتنە جودا کرن ب کار هاتە کرن دگەل سێ نمونێت پترولێ ژ ناوچێن کوردستانا ئیراقێ دناڤ بەرا سڤك مامناوەند و کران پشتی جوداکرنا وو چەند تایەکا ب هاریکاریا تەکنیکا جوداکرنا ب یوریایی پاش هاتینە شیکارکرن ب تیشکا ژێر سوری ئو ب ڤێ چەندێ جەخت ل سەر هندێ کر کو کومەلێن (مەسیل و مەسلین) د ناڤا پارچێن پارافینێن تێر هەنە هەروەسا پترولا تاوکێ بلندترین رێژا پارافینێن تێر یێن زنجیرەیێن درێژ تێ دا بوون بەلێ پترولا تەق تەق بلندترین رێژا پارافینێن لق دار تێ دا بوو بەلێ یا پترولا چەمچەمال رێژا وێ ژ هەر دوو یێن دی کێم تر بوو.