FRACTIONATION OF HYDROCARBONS BETWEEN OIL AND GAS PHASES

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FRACTIONNEMENT DES HYDROCARBURES ENTRE LES PHASES HUILE ET GAZ

L'étude du fractionnement des hydrocarbures légers entre les phases gazeuses et liquides intéresse plusieurs domaines dans le cadre de l'exploitation des gisements. En géochimie de réservoir l'évolution de la composition de la fraction légère peut expliquer certains phénomènes de migration. Lors de l'injection de gaz, la dissolution préférentielle de certains constituants dans le gaz peut modifier la composition et le comportement le l'huile en place. Le stockage souterrain de gaz dans des réservoirs contenant encore de l'huile peut également être concerné par ce problème.

Des études ont été menées à l'IFP, dans le cadre de différents projets, de façon à mettre en évidence ce phénomène et à le quantifier. Deux d'entre elles, qui concernent la géochimie de réservoir, ont été menées sur des fluides réels. La troisième étude, qui est un test de gonflement, concerne l'injection de gaz, le fluide considéré est un mélange synthétique comprenant des hydrocarbures jusqu'à C_{30}. Les équipements utilisés sont, d'une part, une cellule saphir ayant une pression maximale d'utilisation de 400 bar, et d'autre part un équipement appelé Hercule dont la pression maximale d'utilisation est de 1500 bar. Pour chacun des fluides étudiés, la pression de saturation a été mesurée. Pour plusieurs paliers, inférieurs à la pression de saturation, les phases liquides et gazeuses à l'équilibre ont été prélevées à pression constante et analysées. Dans le cas de l'injection de gaz, les compositions à l'équilibre ont été déterminées pour des mélanges contenant des quantités variables de gaz.

Par rapport aux n-alcanes de même nombre d'atomes de carbone, les hydrocarbures aromatiques restent préférentiellement dans la phase liquide, de même que les cycloalcanes pour lesquels ce phénomène est moins net toutefois. Par contre, la phase gazeuse s'enrichit légèrement en isoalcanes. Ces phénomènes de fractionnement sont moins marqués au voisinage de la région critique. Ils ont été modélisés au moyen d'une équation d'état cubique assortie d'une règle de mélange par contribution de groupes.

FRACTIONATION OF HYDROCARBONS BETWEEN OIL AND GAS PHASES

The investigation of hydrocarbon fractionation between oil and gas phases is of interest for several purposes in reservoir exploitation. In reservoir geochemistry, the evolution of light hydrocarbon fractions of oils may explain some migration phenomena. In gas injection projects, the preferred dissolution of some components in gas may alter the composition as well as the properties of the oil. Underground gas storage in depleted oil reservoirs may also be concerned by these problems.

Results of several IFP studies are described here to illustrate and to quantify the phenomenon. Two of them, using real reservoir fluids,

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concern reservoir geochemistry, while the third, which is a swelling test, aimed to study gas injection, investigated a synthetic reservoir fluid with hydrocarbon components up to C_{30}. Two pieces of equipment were used: a sapphire cell with a maximum pressure rating of 400 bar and a high pressure apparatus called Hercule with a maximum pressure of 1500 bar. For each fluid, the saturation pressure was measured. For various pressure levels below saturation, the coexisting liquid and gas phases were sampled at constant pressure, and subsequently analyzed by gas chromatography. In the gas injection study, sampling was repeated with different quantities of injection gas.

Compared to a n-paraffin with the same number of carbon atoms, aromatic hydrocarbons appear to stay preferentially in the liquid phase, as do cycloalkanes to a lesser extent. The gaseous phase is slightly enriched in isoalkanes. These fractionation effects are less pronounced near the critical region. These phenomena have been modeled with a cubic equation of state combined with a group contribution mixing rule.

FRACCIONAMIENTO DE LOS HIDROCARBUROS ENTRE LAS FASES GASEOSAS Y LÍQUIDAS

El estudio del fraccionamiento de los hidrocarburos ligeros entre las fases de gas y líquido es de interés para varios campos en el contexto de la explotación de los yacimientos. En geoquímica de yacimiento la evolución de la composición de la fracción ligera puede explicar ciertos fenómenos de migración. Durante la inyección de gas, la disolución preferente de ciertos componentes en el gas puede llegar a modificar la composición y el comportamiento del petróleo in situ. El almacenamiento subterráneo de gases en las cavidades que aún contienen petróleo puede también verse involucrado por semejante problema.

El IFP ha emprendido cierto número de estudios, en el contexto de diversos proyectos, con objeto de evidenciar este fenómeno y asimismo, cuantificarle. Dos de estos estudios, relativos a la geoquímica de yacimiento, se han efectuado mediante fluidos reales. En el tercer estudio, que constituye una prueba de hinchamiento, se ha tratado de la inyección de gas, y el fluido considerado corresponde a una mezcla sintética que está constituida por hidrocarburos hasta C_{30}. Los equipos utilizados son, en primer lugar, una célula záfiro que desarrolla una presión hasta 400 bares y en segundo lugar, un equipo denominado Hercule, cuya presión máxima puede alcanzar los 1 500 bares. Para cada uno de los fluidos estudiados, se ha medido la presión de saturación. Para varios niveles, inferiores de la presión de saturación, las fases líquidas y gaseosas en equilibrio se han extraido con presióin constante y analizadas. Al tratartse de la inyección de gases, las composiciones en estado de equilibrio se han determinado para mezclas que contienen cantidades varables de gas.

Con respecto a los n-alcanos de mismo número de átomos de carbono, los hidrocarburos aromáticos permanecen, preferentemente, en la fase líquida, lo mismo que ocurre con los cicloalcanos, para los cuales este fenómeno es, de todos modos, menos neto. En cambio, la fase gaseosa se enriquece ligeramente en isoalcanos. Estos fenómenos de fraccionamiento son menos señalados en las inmediaciones de la región crítica y se han modelizado por medio de una ecuación de estado cúbica acompañada de una regla de mezcla por contribución de grupos.

INTRODUCTION

The investigation of hydrocarbon fractionation between oil and gas phases is of interest for several fields in reservoir production.

The main goal in reservoir geochemistry is to understand the origin of heterogeneities in reservoir fluid composition. Light hydrocarbons can easily be displaced as dissolved components in a migrating gas. These compounds can be removed from pre-existing oil and transported through seals or faults by migrating gas. Under the effects of pressure and/or temperature variations, they can condense and subsequently accumulate as light oil.

In the gas injection process, the preferential dissolution of some components in gas alters the composition as well as the properties of the oil. This phenomenon must be taken into account while the production process is being determined, whatever the gas injection mechanism is condensing gas drive, vaporizing gas drive or mixed condensing/vaporizing gas drive. Some investigations have already been done by Danesh (1990) on a synthetic mixture (with components up to nC_{24}). The purpose of the paper was, however, to evaluate a cubic EoS for phase behavior calculations regarding gas injection. Hence, the distribution of components between the two phases was not studied in this paper; only saturation pressure and volumetric properties were calculated.

Finally, underground gas storage in depleted oil reservoirs may be concerned by these problems. If the lighter components of oil are dissolved in the gas phase, the proportion of heavy components in the gas may become significant. This provides an opportunity because of the value of condensate, but it also brings with it a constraint because of the need for more complex production facilities than with dry gas.

Results of several *IFP* studies are described here to illustrate and to quantify the phenomenon. Two of them, using real reservoir fluids, concern reservoir geochemistry, while the third, concerning gas injection, investigated a 15-component synthetic reservoir fluid with hydrocarbon components up to C_{30}.

The equipment used was a sapphire cell with a maximum pressure rating of 400 bar (Ungerer *et al.,* 1995) and a high pressure cell called Hercule with a maximum pressure of 1500 bar (Arnaud *et al.,* 1996). In the first two experiments, the coexisting liquid and gas phases were sampled at various pressure levels

below saturation, and subsequently analyzed by gas chromatography. In the third experiment, a swelling test, which was designed to study gas injection, sampling was repeated with different quantities of injection gas, at the same pressure.

1 SAMPLES

The samples will hereafter be called "synthetic oil", "live oil" and "near-critical fluid". The synthetic oil was investigated for the swelling test, while the live oil and the near-critical fluid were investigated for geochemistry purposes. The composition of the different mixtures is reported in Tables 1 to 3, where F_1, F_2...F_{20} are boiling point fractions. In the synthetic fluid, squalane (2,6,10,15,19,23-hexamethyltetracosane) was selected because it is liquid at ambient temperature, which facilitates preparation of the mixture.

TABLE 1

Composition of injection gas and synthetic oil used in the swelling test

Component	Injection gas (mole %)	Synthetic oil (mole %)
CO_2	3.07	
methane	75.83	42.87
ethane	15	8.27
propane	5.12	4.72
n-butane	0.98	3.53
n-hexane		4.96
methylcyclohexane		4.19
toluene		4.14
n-decane		5.44
decalin		4.46
1-methylnaphthalene		4.39
n-hexadecane		6.54
n-eicosane		2.32
n-tetracosane		0.56
squalane (iC_{30})		3.61

Monophasic fluids were obtained by combining liquid samples (stock tank oil or liquid mixtures of pure components) with a gas (separator gas or synthetic gas) in a high pressure cell. For the swelling test, mixtures were prepared directly in the Hercule high pressure cell, which will be described hereafter, with different gas concentrations.

The sample was analyzed by combining the analyses of the gas and liquid phases that were obtained by flashing the sample at atmospheric pressure.

TABLE 2

Composition of gas and liquid used to recombine natural fluid 1 (live oil)

Component or fraction	Gas (mole %)	Oil (mole %)	Recombined sample (mole %)
CO_2	7.44		5.21
F_1	68.05		49.55
F_2	11.83		8.46
F_3	6.94	0.29	5.09
F_4	5.74	2.38	4.60
F_5		4.97	1.44
F_6		6.06	1.66
F_7		7.12	1.89
F_8		7.80	2.02
F_9		7.31	2
F_{10}		6.91	1.94
F_{11}		5.78	1.64
F_{12}		4.99	1.45
F_{13}		4.37	1.27
F_{14}		3.72	1.09
F_{15}		3.40	0.98
F_{16}		3.03	0.87
F_{17}		2.51	0.72
F_{18}		2.20	0.64
F_{19}		2.02	0.59
F_{20}		1.76	0.52
$F_{20}+$		23.37	6.37

TABLE 3

Composition of recombined natural fluid 2 (near-critical fluid)

Component or fraction	Recombined sample (mole %)
N_2	2.13
CO_2	2.14
F_1	65.91
F_2	10.42
F_3	5.49
F_4	2.63
F_5	1.26
F_6	1.27
F_7	1.39
F_8	1.18
F_9	0.86
F_{10}	0.81
F_{11}	0.57
F_{12}	0.40
F_{13}	0.31
F_{14}	0.23
F_{15}	0.19
F_{16}	0.16
F_{17}	0.09
F_{18}	0.11
F_{19}	0.07
F_{20}	0.07
$F_{20}+$	2.31

2 ANALYSES

Liquid and gas analyses were performed by gas chromatography. The gases were analyzed twice (two samples) using a HP 5890 chromatograph equipped with two packed columns (Porapak Q and molecular sieves) and a TCD (Thermal Conductivity Detector) detector. To measure the heaviest components of both gas and liquid samples, a second HP 5890 chromatographer was used. It was equipped with a PONA (Paraffins Olefines Naphthenes Aromatics) capillary column and a FID (Flame Ionisation Detector) detector, and used the Carburane, method developed at *IFP* (Durand, 1993) with 2,4,4-trimethyl pentene as the internal standard. The quantity of heavy fraction (F_{20+}) was not measured directly but obtained from mass balance.

3 EQUIPMENT

The first apparatus, used for the live oil study, was a high pressure PVT sapphire cell equipped with a rotating stirring rod. As the entire fluid volume is visible, this equipment is particularly suited for observing phase transitions. It can be used up to 400 bar and 145°C. Temperature control is provided by a windowed air bath. The stirring rod floats on mercury, which is used as hydraulic fluid. Pressure is provided by a mercury pump, so that gas and liquid phases can be flashed while maintaining constant pressure in the cell.

The second apparatus, used for the swelling test and for the near-critical fluid, is a high pressure—high temperature PVT equipment. It has been designed to study the characteristics of deep reservoir fluids, either crude oils or natural gases. Its maximum working pressure is 1500 bar and the temperature range is between –10°C and +200°C. It is made of two mercury-free piston cells equipped with sapphire windows, so that phase changes can be precisely observed and cell volumes can be accurately known. This apparatus can

also be used to determine viscosities and perform phase sampling at constant temperature and pressure. The second phase sampling device is a small high pressure—high temperature cell (called Danae) made of titanium with a variable volume of 2 cm^3 which was connected to the Hercule cell. This cell can be isolated from the main cell, once it has been filled, and detached to allow analysis without interrupting the experiment. A known volume of gas or liquid sample was transferred at constant pressure to the Danae cell after which it was flashed under ambient conditions in a special gas meter.

4 RESULTS

4.1 Synthetic Fluid (Swelling Test)

A swelling test consists of studying several mixtures with different quantities of injection gas. Five mixtures (Table 4) were studied at 120°C in the Hercule apparatus. The quantity of injected gas varied between 0 and 87.7 mole %. Analyses of the recombined samples were made using the Danae sampling cell and gas chromatography as described above. Saturation pressures were determined by visual observation. Liquid and gas volumes were measured at constant temperature for several pressures below the saturation pressure. At one of these pressures the density and composition of the liquid and gas phases at equilibrium were measured, and the results are reported in Table 5.

In order to compare gas and liquid phase compositions, a thermodynamic model was used to calculate mixture properties at a fixed pressure of 150 bar at 120°C. The behavior of the mixture was calculated using the Peng-Robinson EoS (Peng and Robinson, 1976) combined with the group contribution method of Abdoul (1987, 1991). For the initial calculation, the binary interaction coefficients (k_{ij}) were calculated using the Abdoul mixing rules. Under those conditions, the calculated saturation pressure of mixture 1 (with 0% volume of injection gas) was

TABLE 4

Saturation pressure vs quantity of injection gas at 120°C (synthetic fluid - swelling test)

Quantity of injection gas (mole %)	Mixture 1 0	Mixture 2 39.3	Mixture 3 65.7	Mixture 4 69.8	Mixture 5 79.7	Mixture 6 87.7
Saturation pressure (bar)	209 Bubble point	320.1 Bubble point	386 Bubble point	389 Bubble point	403.9 Dew point	414.4 Dew point

TABLE 5

Composition of the liquid and the gas phases at equilibrium (synthetic fluid - swelling test)

| Component | Mixture 2 (39.3% of injection gas) | | Mixture 3 (65.7% of injection gas) | | Mixture 6 (87.7% of injection gas) | |
| | Flash at 292 bar and 120°C | | Flash at 383.4 bar and 120°C | | Flash at 327.1 bar and 120°C | |
	Gas phase (molar %)	Liquid phase (molar %)	Gas phase (molar %)	Liquid phase (molar %)	Gas phase (molar %)	Liquid phase (molar %)
CO_2	1.62	1.28	2.22	2.23	2.90	2.45
methane	77.12	51.78	65.03	62.50	73.79	54.28
ethane	11.19	11.28	13.17	13.84	14.20	14.09
propane	4.36	5.45	4.90	5.46	5.33	5.64
n-butane	1.70	2.80	1.55	1.79	1.35	1.53
n-hexane	0.96	3.39	1.62	1.40	0.44	1.08
n-decane	0.67	3.33	1.86	1.75	0.35	1.94
n-hexadecane	0.33	4.01	2.10	2.25	0.33	3.80
n-eicosane	0.08	2.01	0.92	1.12	0.10	2.45
n-tetracosane	0.01	0.87	0.35	0.48	0.02	1.23
methylcyclohexane	0.66	2.80	1.23	1.33	0.32	1.22
toluene	0.62	2.81	1.07	1.34	0.32	1.30
decaline	0.39	2.71	1.47	1.50	0.26	2.10
alpha-methylnaphthalene	0.26	2.67	1.39	1.50	0.23	2.53
squalane (iC_{30})	0.03	2.81	1.12	1.51	0.06	4.36

185 bar at 120°C, while the experimental value was 209 bar. All critical parameters were from DIPPR (Data Compilation of Pure Compound Properties) or the Reid and Sherwood (1958) data bank. In a second calculation, the critical parameters (critical temperature, critical pressure and the acentric factor) of the heavier components (nC_{24} and iC_{30} (squalane)) were fitted in order correctly to calculate the saturation pressure of the initial mixture. After fitting, the calculated saturation pressure was 203 bar compared to the experimental value of 209 bar. The fitted critical properties are reported in Table 6 and the results in Table 7.

It is known that the EoS is inadequate at predicting liquid density. One way to correct for this is to shift the predicted volume by a constant value which is component dependent (Peneloux *et al.,* 1982). We used this technique to calculate correctly the density of mixture 1. Using the volume translation as defined by Péneloux for each component, the calculated density was unsatisfactory. In order to calculate correctly the density of the initial mixture, we fitted the volume translations of heavy components. Better results were obtained when the volume translations for nC_{16}, nC_{20}, nC_{24} and iC_{30} are equal to zero.

Then, k_{ij}, critical properties and volume translations estimated for the first mixture were used to calculate saturation pressures, densities and phase compositions

of all the other mixtures. Differences between calculated and experimental values are presented in Table 8. Equilibrium constant (K_i) between gas and liquid phases for each component was calculated and compared to the experimental value; results are presented in Figures 1 to 3.

TABLE 6

Critical properties of pure components present in the synthetic fluid

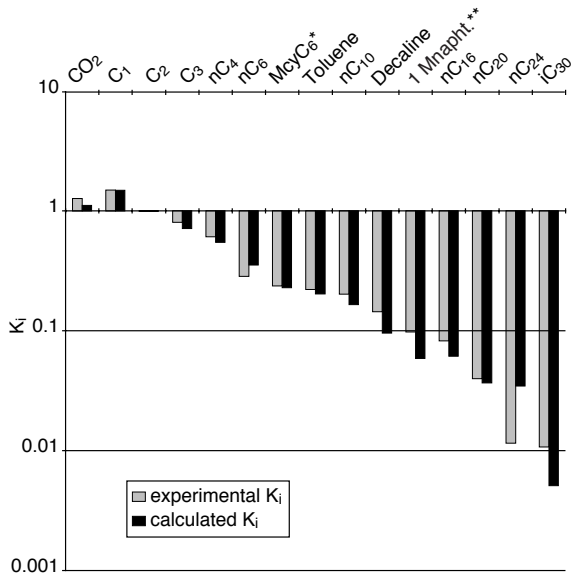| Component	Critical Temperature (K)	Critical Pressure (Pa)	Acentric factor	Origin
CO_2	304.1	73.8E+05	0.239	Reid & Sherwood
methane	190.4	46.0E+05	0.0111	Reid & Sherwood
ethane	305.4	48.8E+05	0.099	Reid & Sherwood
propane	369.8	42.5E+05	0.153	Reid & Sherwood
n-butane	425.2	38.0E+05	0.199	Reid & Sherwood
n-hexane	507.5	30.1E+05	0.299	Reid & Sherwood
n-decane	617.7	21.2E+05	0.489	Reid & Sherwood
n-hexadecane	722.0	14.4E+05	0.742	Reid & Sherwood
n-eicosane	767.0	11.1E+05	0.907	Reid & Sherwood
n-tetracosane	891.0	11.4 E+05	1.133	fitted parameters
methylcyclo-hexane	572.2	34.7D+05	0.235	Reid & Sherwood
toluene	591.8	41.0D+05	0.264	Reid & Sherwood
decaline	702.3	32.0D+05	0.286	Reid & Sherwood
alpha-methyl-naphthalene	772.0	36.0D+05	0.31	Reid & Sherwood
squalane (iC_{30})	901.0	7.2 D+05	1.286	fitted parameters

Figure 1

Synthetic oil (swelling test). Mixture 2 (39.3% mole injection gas), equilibrium constants ($K_i = y_i/x_i$) at 120°C and 293 bar.

* methylcyclohexane.
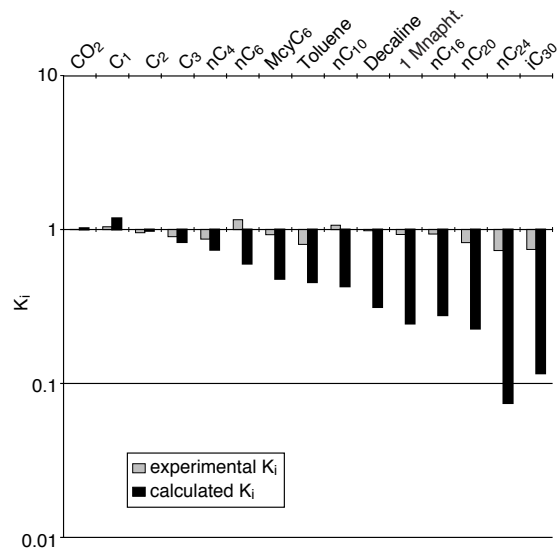** α-methylnaphthalene.

Figure 2

Synthetic oil (swelling test). Mixture 3 (65.7% mole injection gas), equilibrium constants ($K_i = y_i/x_i$) at 120°C and 383.4 bar.
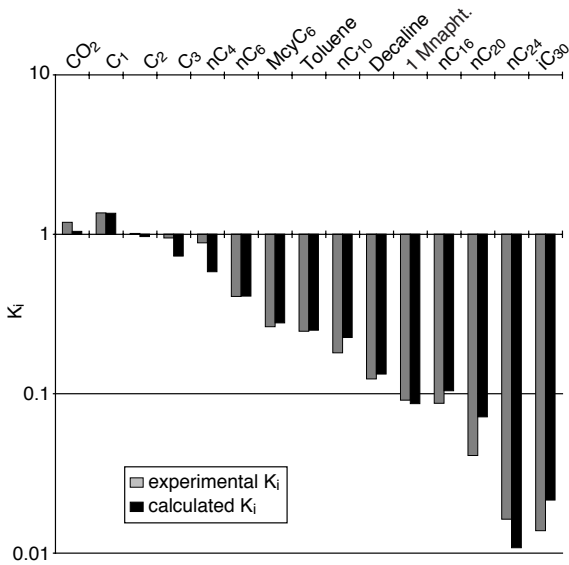

Figure 3

Synthetic oil (swelling test). Mixture 6 (87.8% mole injection gas), equilibrium constants ($K_i = y_i/x_i$) at 120°C and 327.1 bar.

The calculated properties are in good agreement with experimental values except for the critical mixture. However, it is well known that cubic equations of state are not suitable for the critical region.

In order to be able to compare fractionation of hydrocarbons between oil and gas phases, the composition of oil and gas phases was calculated at 150 bar and 120°C for all mixtures using the parameters estimated above. The results are presented in Figures 4 to 6. It can be seen that modeling results are in good agreement with experimental ones and that aromatics and naphthenes are preferentially in the liquid phase.

It will be noted that the equilibrium constant of the C_{11} aromatic (α-methylnaphthalene) is much lower than for nC_{10}, whereas it is close to the constant of nC_{16}. Generally, such differences are attributed to the higher boiling points of aromatics compared with *n*-alkanes. However, the equilibrium constant of

TABLE 7

Experimental and modeling results after fitting for mixture 1 of the swelling test (synthetic oil)

	All $k_{ij} = 0$	Abdoul-Rauzy-Péneloux mixing rules	Abdoul-Rauzy-Péneloux mixing rules + fitted parameters (nC_{24} - iC_{30})
Experimental results	209 bar	209 bar	209 bar
Modeling results	157.5 bar	185 bar	203 bar

TABLE 8

Comparison between calculated and experimental values (for all mixtures of the swelling test)

% mole of injection gas	Mixture 1 0	Mixture 2 39.3						Mixture 3 65.7					
	Monophasic fluid	Monophasic fluid		Gas and liquid phases at 293 bar and 120°C liquid-vapor equilibrium				Monophasic fluid		Gas and liquid phases at 383.4 bar and 120°C liquid-vapor equilibrium			
			Δ (%)	Gas	Δ (%)	Liquid	Δ (%)		Δ (%)	Gas	Δ (%)	Liquid	Δ (%)
Experimental saturation pressure (bar)	209	320.1						386					
Calculated saturation pressure (bar)	203	314.3	1.8					393.8	2				
Experimental density (g/cm³)	(370 bar) 0.644	(700 bar) 0.601						(700 bar) 0.510					
Calculated density (g/cm³)	(370 bar) 0.596	(700 bar) 0.572	4.8					(700 bar) 0.520	2				
Experimental density at equilibrium pressure (g/cm³)				0.241		0.562				0.438		0.486	
Calculated density at equilibrium pressure (g/cm³)				0.230	4.6	0.521	7.3			0.312	28.8	0.468	3.7
Experimental molecular weight (g)	84.4	59.4		24.4		66.3				42		45.3	
Calculated molecular													

TABLE 8 (continued)

Comparison between calculated and experimental values (for all mixtures of the swelling test)

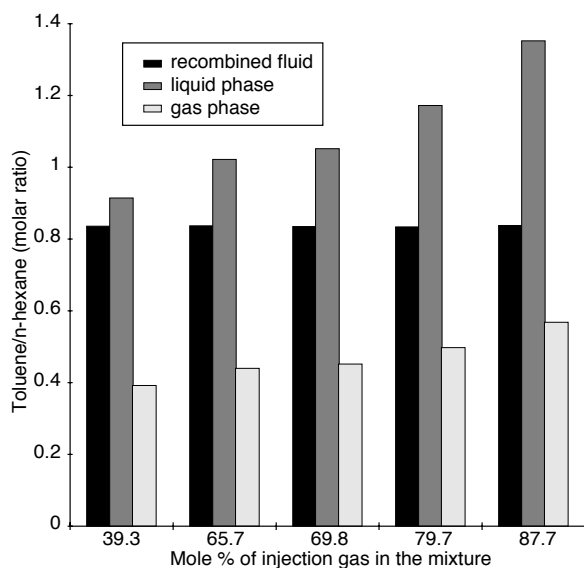| % mole of injection gas	Mixture 4 69.8	Mixture 5 79.7				Mixture 6 87.7					
	Monophasic fluid	Monophasic fluid		Gas and liquid phases at 395.5 bar and 120°C liquid-vapor equilibrium		Monophasic fluid		Gas and liquid phases at 327.1 bar and 120°C liquid-vapor equilibrium			
			Δ (%)	Liquid	Δ (%)		Δ (%)	Gas	Δ (%)	Liquid	Δ (%)
Experimental saturation pressure (bar)	389	403.9				414.4					
Calculated saturation pressure (bar)	405.3	422.4	4.6			423.0	2				
Experimental density at 700 bar (g/cm³)		0.447				0.403					
Calculated density at 700 bar (g/cm³)		0.466	4.3			0.417	3.5				
Experimental density at equilibrium pressure (g/cm³)				0.497				0.263		0.578	
Calculated density at equilibrium pressure (g/cm³)				0.449	9.7			0.255	3	0.494	14.5
Experimental molecular weight (g)	40.0	33.8						24.1		68.1	
Calculated molecular weight (g)				42.5		27.9		23.7	1.7	59.5	12.6

Figure 4

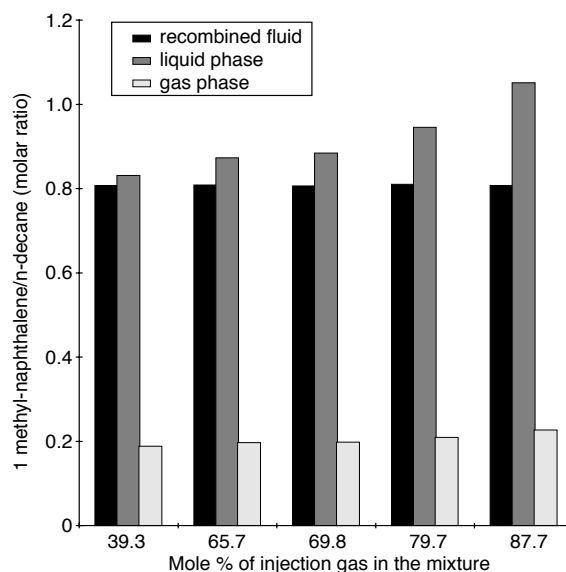Synthetic oil, calculated values. Flash at 120°C and 150 bar, toluene/*n*-hexane molar ratio.

Figure 5

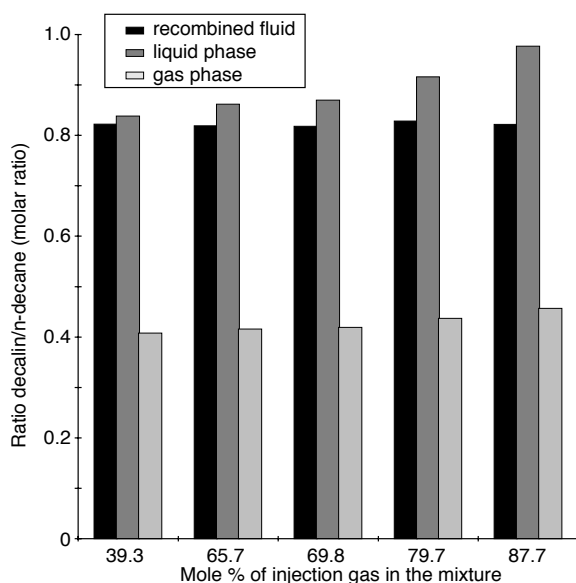Synthetic oil, calculated values. Flash at 120°C and 150 bar, 1 methylnaphthalene/*n*-decane molar ratio.

Figure 6

Synthetic oil, calculated values. Flash at 120°C and 150 bar, decalin/*n*-decane molar ratio.

α-methylnaphthalene cannot be explained solely by its boiling point. Indeed, it has a boiling point of 517.9 K, which is intermediate between that of nC$_{13}$ (508.6 K) and nC$_{14}$ (526.7 K). A similar statement can be made about the equilibrium constants of the other cyclic hydrocarbons in our synthetic mixture (methyl-cyclohexane, toluene, decalin). This is coherent with an observation by Savvina and Velikovsky (1956) who performed a well-documented study of several methane-hydrocarbon mixtures. Indeed, they concluded that methane-cycloalkanes and methane-aromatics showed higher critical pressures than methane-n-alkane mixtures, even though the cyclic hydrocarbon had the same boiling temperature as the n-alkane being studied. We suspect that such effects are even stronger with triaromatic hydrocarbons or polycyclic cyclo-alkanes, which exhibit considerable immiscibility with gas, as illustrated by the extremely high saturation pressures of methane-phenanthrene mixtures (Flöter *et al.,* 1997).

As a practical consequence, it is important to separate aromatics, cycloalkanes and paraffins in the representation of crude oils in thermodynamic models. Incorporation of polyaromatics in the representation of the heavy fraction is also supported by the analysis of Sportisse *et al.* (1997). If hydrocarbons are grouped within boiling point fractions without consideration of chemical family, the equilibrium constants are systematically overestimated.

4.2 Live Oil

As reported in a previous paper (Carpentier *et al.,* 1996), a synthetic gas and a natural stock tank oil

(Arabian light) were mixed in order to prepare the recombined sample. Gas and stock tank oil composition are reported in Table 2. The bubble pressure of the recombined sample was 335 bar at 134.2°C. The recombined sample was studied in the sapphire cell at 134.2°C. Saturation pressure was determined visually, and pressure was subsequently lowered to 240 bar. Gas and liquid phases in equilibrium at 240 bar and 134.2°C were sampled and analyzed. Distribution of the different chemical families between the two phases is presented in Figures 7, 8 and 9. For the same carbon atom number, it can be seen that isoalkanes seem to have slightly greater affinity for the gas phase. Naphthenes and aromatics show more fractionation and have more affinity than *n*-alkanes for the liquid phase.

4.3 Near-Critical Fluid

A natural gas separator and a natural stock tank oil were used to prepare the recombined sample. The saturation pressure of the recombined sample was measured at various temperatures (101.4, 122.3 and 142.5°C) by visual observation through the sapphire window in the Hercule PVT apparatus. The measurement at 101.4°C was difficult because the

mixture was very close to the critical point. At 122.3°C, the saturation pressure was 422.5 bar. Then, pressure was lowered to 388.5 bar. Gas and liquid phases at equilibrium were sampled using Danae, then analyzed. Results are presented in Table 9 and in Figures 10, 11 and 12. As for the live oil, it can be seen that naphthenes and aromatics stay preferentially in the liquid phase but the fractionation is less pronounced than in the previous case. No conclusion can be made about isoalkanes.

CONCLUSION

The three studies reported in the present paper allowed us to quantify fractionation of hydrocarbons between oil and gas phases in a consistent way. In all three cases, we show that naphthenes and aromatics stay preferentially in the liquid phase. However, the gas phase is enriched in *n*-alkanes. These fractionation effects are less pronounced in the vicinity of the critical region, which is normal as gas and liquid compositions tend to be identical at the critical point.

The Peng-Robinson EoS combined with the Abdoul mixing rules was used to calculate behavior of the
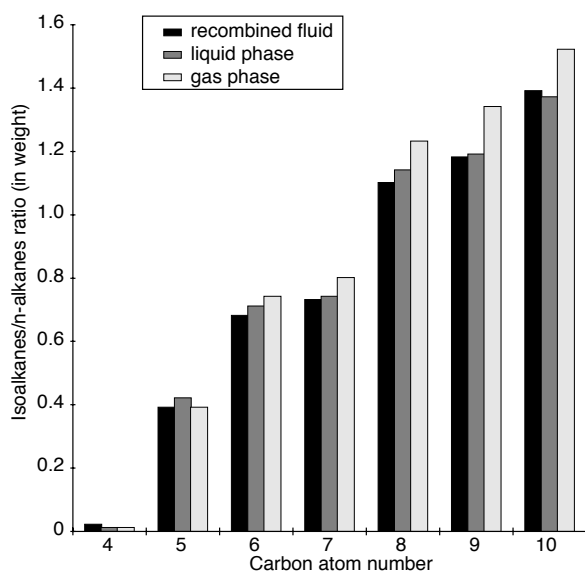
Figure 7

Live oil, experimental data. Flash at 134.2°C and 240 bar, isoalkanes/*n*-alkanes weight ratio.
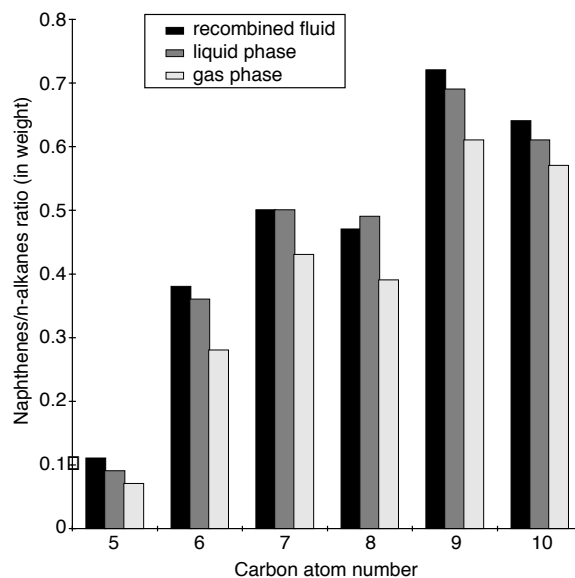
Figure 8

Live oil, experimental data. Flash at 134.2°C and 240 bar, naphthenes/*n*-alkanes weight ratio.

TABLE 9

Composition of the liquid and gas phases at equilibrium (122.3°C - 388.5 bar) (near critical fluid).
Chemical families have not been quantified above C_{10}

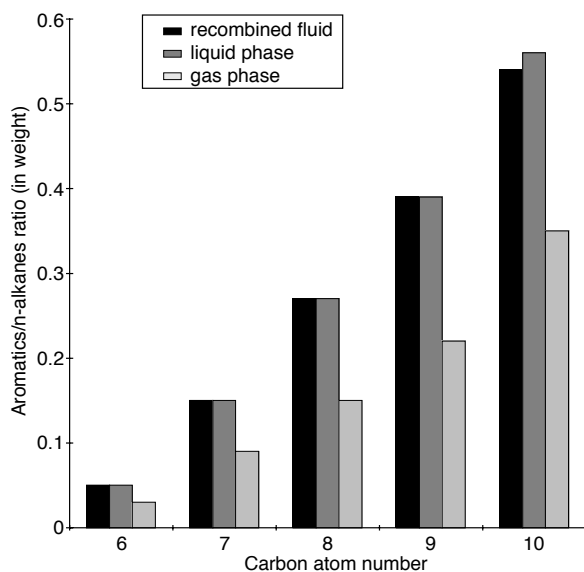| Fraction	Nonhydrocarbons (weight %)		n-alkanes (weight %)		Isoalkanes (weight %)		Cycloalkanes (weight %)		Aromatics (weight %)	
	Gas phase	Liquid phase	Gas phase	Liquid phase	Gas phase	Liquid phase	Gas phase	Liquid phase	Gas phase	Liquid phase
N_2	1.39	0.3								
CO_2	2.74	1.35								
C_1			31.59	14.62						
C_2			8.46	4.33						
C_3			4.57	2.96						
C_4			2.12	1.93	0.81	0.64				
C_5			1.12	1.19	0.73	0.77	0.10	0.12		
C_6			0.97	0.92	0.83	0.82	1.01	1.05	0.42	0.49
C_7			0.88	0.77	0.74	0.65	1.37	1.32	0.95	1.03
C_8			0.82	0.71	1.02	0.87	0.64	0.61	1.03	1.09
C_9			0.70	0.59	0.89	0.72	0.61	0.58	0.74	0.77
C_{10}			0.64	0.55	0.89	0.81	0.57	0.55	0.92	0.95
C_{10}-C_{20}			12.52	13.49						
C_{20}+			17.21	42.45						

Figure 9

Live oil, experimental data. Flash at 134.2°C and 240 bar, aromatics/n-alkanes weight ratio.
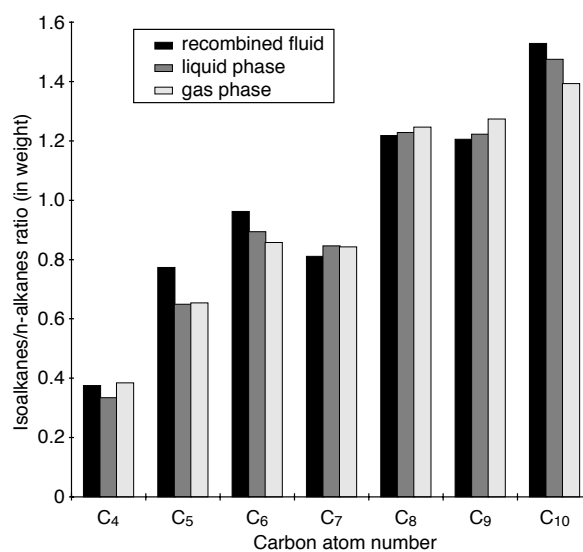

Figure 10

Near-critical fluid, experimental data. Flash at 122.3°C and 388.5 bar, isoalkanes/n-alkanes weight ratio.

various mixtures. Using k_{ij} calculated with the Abdoul method and after limited modification of the thermodynamic properties of the heavier components (nC_{24} and iC_{30}) it has been possible to calculate behavior of the mixture correctly.

The major conclusion that can be drawn from this work about gas injection studies is the important role of chemical families. In particular, aromatics and cycloalkanes have lower equilibrium constants than alkanes with identical carbon number or boiling point. As suggested by Sportisse *et al.* (1997) for gas condensates, the representation of the heavy fraction in thermodynamic models should account for differences among aromatics, cycloalkanes and paraffins in order to produce a satisfactory prediction of phase behavior in gas injection tests. Otherwise the
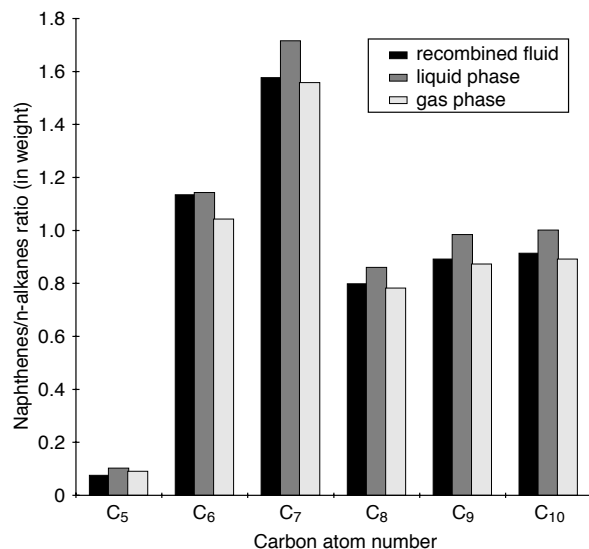
Figure 11

Near-critical fluid, experimental data. Flash at 122.3°C and 388.5 bar, naphthenes/*n*-alkanes weight ratio.
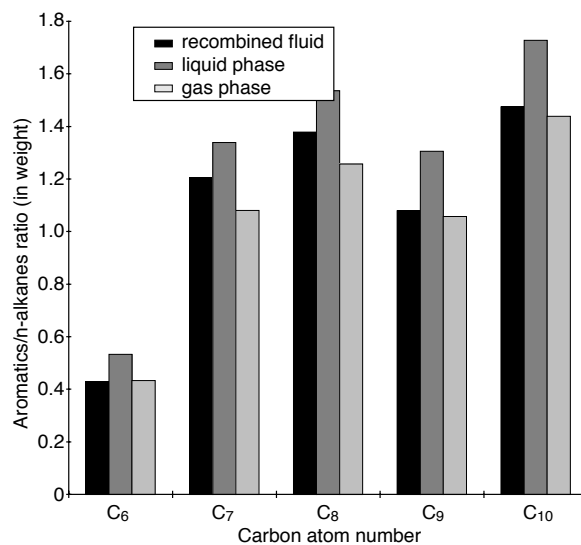

Figure 12

Near-critical fluid, experimental data. Flash at 122.3°C and 388.5 bar, aromatics/*n*-alkanes weight ratio.

model will overestimate the extent of stripping of heavy hydrocarbons by gas.

The present study confirms the wide applicability in reservoir geochemistry of equation of state models to quantify evaporative fractionation effects under various conditions. It also illustrates the lower extent of fractionation for near-critical fluids.

For both applications however, the difficulty in predicting the location of the critical point is still a delicate problem. Adequate models and optimization techniques (for instance, using continuous distribution functions) are needed to improve predictions in the near-critical regions.

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