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MEASUREMENT AND PREDICTION OF VOLUMETRIC AND TRANSPORT PROPERTIES OF RESERVOIR FLUIDS AT HIGH PRESSURE

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MESURE ET PRÉDICTION DES PROPRIÉTÉS VOLUMÉTRIQUES ET DES PROPRIÉTÉS DE TRANSPORT DES FLUIDES DE GISEMENT À HAUTE PRESSION

Les découvertes de pétrole ou de gaz dans des conditions sévères de température (plus de 150°C) ou de pression (plus de 50 MPa) se comptent dans plusieurs bassins à travers le monde. En mer du Nord, on prévoit de mettre en production des gisements dont les conditions de fond vont jusqu'à 110 MPa et 190°C. Ces caractéristiques constituent un défi pour la prédiction des propriétés des fluides de gisement, aussi bien au niveau expérimental que théorique.

Dans le but d'étudier les fluides à ces températures et pressions, l'IFP a construit un équipement à haute pression sans mercure, équipé de hublots en saphir, d'une cellule de prélèvement de phase, et d'un dispositif de mesure de viscosité par la méthode du tube capillaire. Son application est illustrée ici par des exemples de fluides réels et des mélanges synthétiques.

L'équipement a été employé en premier lieu pour mesurer les propriétés volumétriques des gaz. Il apparaît ainsi que des facteurs de compressibilité très élevés peuvent être atteints avec des gaz à condensat HP-HT. Les conséquences en sont importantes sur les taux de récupération envisageables. De manière à améliorer la prédiction des propriétés volumétriques des mélanges dans ces conditions, on propose d'utiliser une équation d'état classique, comme celle de Peng-Robinson, avec deux améliorations:

– une translation de volume améliorée, mise au point sur la base de données de masse volumique à haute pression ; cette méthode est simple, plus précise que les méthodes antérieures de translation de volume, et cohérente avec les procédures de regroupement classiques ;
– une règle de mélange quadratique sur le covolume.

Des comportements particuliers peuvent aussi se rencontrer en matière d'équilibres de phase. À basse température, les paraffines peuvent cristalliser à partir du fluide, qui est pourtant un gaz à condensat à la température du gisement. Cette caractéristique est due à l'abondance simultanée de méthane et de paraffines lourdes. Une étude de fluides synthétiques dans une cellule saphir nous a permis d'identifier les types de diagramme de phase possibles.

Bien qu'elle ne soit généralement pas considérée comme un paramètre important, la viscosité du gaz peut jouer un rôle significatif dans la production des gisements HP-HT, car les vitesses de production sont parfois très élevées. Les modèles de prédiction de la viscosité présentent des incertitudes importantes,

du fait du grand contraste de viscosité entre les constituants du fluide. De façon à tester et à améliorer ces modèles, nous avons commencé à acquérir des données dans des conditions représentatives. Un soin particulier a été apporté à l'implantation de la méthode capillaire, de sorte que nous avons pu mesurer des basses viscosités (aussi faibles que 0,02 mPa·s) avec une précision raisonnable jusqu'à des pressions de 120 MPa, sur des sytèmes simples : méthane, azote, n-pentane, mélange azote-pentane. Ces données nous ont permis d'évaluer les règles de mélange utilisées dans certains modèles de viscosité.

MEASUREMENT AND PREDICTION OF VOLUMETRIC AND TRANSPORT PROPERTIES OF RESERVOIR FLUIDS AT HIGH PRESSURE

Discoveries of oil and gas fields under severe conditions of temperature (above 150°C) or pressure (in excess of 50 MPa) have been made in various regions of the world. In the North Sea, production is scheduled from deep reservoirs at 190° C and 110 MPa. This brings with it important challenges for predicting the properties of reservoir fluids, both from an experimental and a theoretical standpoint.

In order to perform fluid studies for these reservoir conditions, IFP has developed a specific mercury-free high pressure apparatus with sapphire windows, a phase sampling device and viscosity determination by the capillary tube method. Its application is illustrated here using examples of real fluids and model mixtures.

This equipment was first used to measure volumetric properties for gases. It has been shown that very high compressibility factors can be found with HP-HT gas condensates. This has a strong influence on recovery factors during primary depletion. In order to predict more accurately the volumetric properties of mixtures under these conditions, we propose to use a conventional equation of state, such as Peng-Robinson, with two improvements:

– a modified temperature-dependent volume translation method, calibrated for high pressure density data; the method is simple, more accurate than other volume translation methods and fully consistent with lumping procedures;
– a quadratic mixing rule on the covolume.

Specific phase behavior can also be found. At low temperatures, wax crystallization can occur from a fluid which is a gas condensate at reservoir temperature. This feature is due to the simultaneous presence of abundant methane and heavy paraffins. A study of model fluids in a sapphire cell has allowed us to identify the possible types of phase diagrams.

Although generally not considered to be an important parameter, gas viscosity may have some importance in the production of HP-HT accumulations, because of high flow rates. Viscosity models exhibit significant uncertainties because of large viscosity contrasts between the individual components of the reservoir fluid. In order to test and improve prediction methods, we started the acquisition of viscosity data under representative conditions. Special care was taken in the implementation of the capillary tube method, so that low viscosities (down to 0.02 mPa·s) could be measured with high accuracy at pressures up to 120 MPa on simple systems, such as methane, n-pentane, nitrogen, and nitrogen-pentane mixtures. As a result, it was possible to evaluate mixing rules for viscosity predictions.

MEDICIÓN Y PREDICCIÓN DE LAS PROPIEDADES VOLUMÉTRICAS Y DE LAS PROPIEDADES DE TRANSPORTE DE LOS FLUIDOS DE YACIMIENTOS DE ALTA PRESIÓN

Los descubrimientos de petróleo o de gas en condiciones severas de temperatura (más de 150°C) o de presión (mas de 50 MPa) figuran en buen número de cuencas en todo el mundo. En el mar del Norte, se proyecta poner en producción yacimientos cuyas condiciones de fondo alcanzan los 110 MPa y 190°C. Estas características constituyen un reto para la predicción de las propiedades de los fluidos de los yacimientos, tanto a nivel experimental como teórico.

Con objeto de estudiar los fluidos a estas temperaturas y presiones, el IFP ha construido un equipo de alta presión sin mercurio, dotado de ventanillos de zafiro, de una célula de extracción de fase y de un dispositivo de medición de la viscosidad por el método del tubo capilar. Su aplicación figura ilustrada en este artículo mediante ejemplos de fluidos reales y mezclas sintéticas.

En primer lugar, se ha empleado este equipo para medir las propiedades volumétricas de los gases. De este modo se pone de manifiesto que los factores de compresibilidad sumamente elevados se pueden alcanzar con los gases de condensados HP-HT. En este caso, las consecuencias son importantes respecto a los porcentajes de recuperación previsibles. Así, con objeto de mejorar la predicción de las propiedades volumétricas de las mezclas en tales condiciones, se propone utilizar una ecuación convencional de estado, como la de Peng-Robinson, con dos mejoras :

– Primera : una traslación de volumen mejorada, desarrollada según la base de datos de masa volumétrica de alta presión ; este método es sencillo, más preciso que los métodos anteriores de traslación de volumen y, asimismo, coherente con los procedimientos de reagrupación convencionales ;
– Segunda : una regla de mezcla cuadrática sobre el covolumen.

También se puede tropezar con comportamientos peculiares en el aspecto de los equilibrios de fase. A baja temperatura, las parafinas pueden llegar a cristalizarse a partir del fluido, que, sin embargo, es un gas de condensados a la temperatura del yacimiento. Esta característica se deriva de la abundancia simultánea de metano y de parafinas pesadas. Así, un estudio de fluidos sintéticos en una célula zafiro nos ha permitido identificar los tipos de diagrama de fase posibles.

Pese a que, por lo general, no se considere como un parámetro importante, la viscosidad del gas puede llegar a representar un papel significativo en la producción de los yacimientos HP-HT, puesto que las velocidades de producción son sumamente elevadas en ciertos casos. Los modelos de predicción de la viscosidad presentan importantes incertidumbres, debido al fuerte contraste de viscosidad entre los componentes del fluido. Con objeto de someter a prueba y mejorar estos modelos, hemos comenzado por entrar los datos en condiciones representativas. Se ha puesto particular esmero en cuanto a la implantación del método capilar, de tal modo que nos ha sido posible medir las bajas viscosidades (tan reducidas como 0,02 mPa.s) con una precisión razonable hasta presiones de 120 MPa, utilizando sistemas simples : metano, nitrógeno, n-pentano, mezclas nitrógeno-pentano. Estos datos nos han permitido evaluar las reglas de mezcla utilizadas en ciertos modelos de viscosidad.

INTRODUCTION

In a recent article (Ungerer *et al.*, 1995) we reviewed some general characteristics of high-pressure-high-temperature (HP-HT) reservoir fluids, mainly gas condensates. In our mind, HP-HT conditions are defined by pressures or temperatures exceeding the usual range of classical PVT equipment, i.e. 500 bar and 150°C. In the most extreme cases, pressures as high as 1100 bar and temperatures up to 190°C have been found. These fluids are a challenge for production, for several reasons: lack of adapted PVT equipment, unknown prediction capability of thermodynamic models in this pressure and temperature range, the importance of water-hydrocarbon phase equilibria, the risk of paraffin crystallization, etc. In order to contribute to the solution of these problems, *IFP* has built a mercury-free apparatus (Arnaud *et al.*, 1996) which has been used on real fluids and binary systems. Here, data obtained with this equipment are used together with data from the literature to improve density and viscosity calculations.

In the first part in this paper, we briefly recall the characteristics of the HP-HT equipment. For HP-HT gas condensates, high accuracy volume measurements are required. The apparatus that we developed to meet these requirements (Arnaud, 1995) is a mercury-free apparatus called Hercules, equipped with sapphire windows to observe phase transitions. It is also equipped with a phase sampling device and the ability to measure viscosity.

In the second part, we consider volumetric properties. For HP-HT fluids, the volumetric behavior is significantly different from ordinary gas condensates, with much higher compressibility coefficients. As these features are key elements in field development and production, they must be carefully characterized and predicted. In their work on binary systems, Arnaud *et al.* (1996) have shown how to improve prediction of volumetric properties from cubic equations of state by combining an improved volume translation technique with an alternative mixing rule. Among other features, they proposed to use high pressure density data to improve the volume translation technique of Péneloux *et al.* (1982). Here, we discuss specifically this point on the basis of high pressure density data from the literature. As such data are not available for every compound, a general correlation has been developed to extend the method to all hydrocarbons (Ungerer and Batut, 1997). A preliminary evaluation of the correlation is shown.

The third part of the paper is devoted to phase behavior, which is sometimes non classical in HP-HT gas condensates since paraffin crystallization may occur at ambient temperature. In other cases, very high dew pressures are found. As these features have already been discussed in Ungerer *et al.* (1995), we will concentrate here on new information about the phase diagram of paraffin-depositing gas condensates. These diagrams have been investigated in detail for synthetic condensate gases with a sapphire cell (Jensen *et al.*, 1998). This work specifies the boundary of the three-phase region where gas, liquid and solid coexist. The water-hydrocarbon phase equilibria, which play a significant role in HP-HT fields because of the increased mutual solubilities, are discussed in another article (de Hemptinne *et al.*, 1998). We will also briefly mention the outcome of several attempts to apply non-cubic equations of state.

In the fourth part, we consider the viscosity of HP-HT fluids. This is not usually considered to be an important issue for gas, because viscosity is so low that it does not significantly influence recovery or transport processes. However, this statement must be reconsidered for HP-HT gas condensates, in order to predict well productivity during primary depletion. Indeed, the production rate is high at that stage because of the very high initial pressure. Also, primary recovery spans over a larger time interval than with ordinary gas condensates, due to the large difference between initial pressure and dew pressure. In the present work, we will demonstrate the capillary tube method used to measure gas viscosity with the HP/HT apparatus. Compared with the classical implementation of the method, gas viscosity measurement is made difficult due to the possibility of turbulent flow in the tube and to the low pressure drop. Application of the method to simple mixtures is discussed, illustrating the strong influence of pressure on gas viscosity. Such data are useful to improve viscosity models, that currently lack accuracy for HP-HT gas condensates. A preliminary comparison of mixing rules on the basis of our data illustrates this point.

1 HP-HT CHARACTERIZATION OF RESERVOIR FLUIDS

1.1 Equipment

The high pressure equipment used in this study (Fig. 1) has been designed for characterization of deep

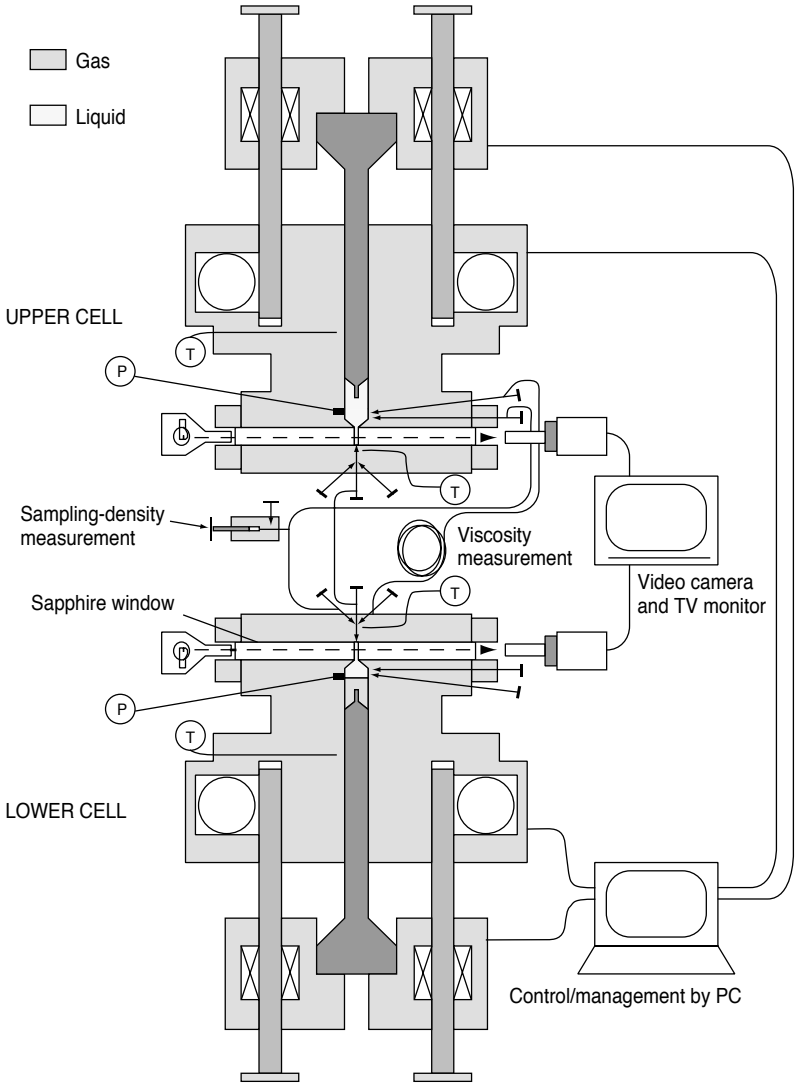


Figure 1

High pressure apparatus Hercule used for the determination of volumetric properties, phase equilibria and viscosity under HP-HT conditions (maximum operating conditions 150 MPa and 200°C). For specific studies, such as gas condensates, the cells can be placed parallel instead of opposite as shown here.

reservoir fluids, either crude oils or natural gases, which are found under conditions as extreme as 110 MPa and 470 K in some accumulations. Its maximum working pressure is 150 MPa, and the allowed temperature range is between 255 K and 470 K. It consists of two piston cells equipped with sapphire windows, so that phase changes can be visualized clearly while cell volumes are precisely known. Additional features of the equipment are the ability to determine viscosity and phase sampling at constant temperature and pressure.

Several concepts adapted for this apparatus are the same as for a previous apparatus developed by Béhar *et al.* (1990) and Moracchini *et al.* (1994) for lower pressures. The adaptations to high pressure conditions are however significant (Arnaud, 1995).

The two identical piston cells, which are located inside a large air bath, are activated by motor-driven screws, whose motors are outside the heated zone. The air bath has been designed to accommodate two positions of the cells, either opposite (as shown in Fig. 1) or parallel (both heads up or both heads down).

The maximum volume of each cell, when the piston is in its extreme position, is about 85 cm^3. Dead volumes are minimized by the design both of the pistons (same shape as the inner walls of the cells) and of the valves (seats on the body of the cells without any intermediate tubing). Nevertheless, the minimum volume is around 3 cm^3.

Two sapphire windows allow inspection of the interior of each cell, which is illuminated by an optical

fiber system. An endoscope and a small TV camera, located outside the heated zone, are used to display the inside of the cell on a TV screen. The resolution is very good, since details as small as 0.1 mm can be seen on the screen. Consequently, it is possible to set the vapor-liquid interface locus with very high precision and, thus, to measure phase volumes within +/– 0.02 cm^3. Pressure measurements are carried out with one pressure transducer (Dynesco 200 MPa) on each cell, the membrane of which is integrated into the inner wall of each cell. The sensitive element is, in fact, located outside the heated air bath, as pressure is transmitted from the cell membrane using a sealed, low compressibility hydraulic fluid. In addition to these transducers, a third pressure reading is carried out with a transducer (HBM P3MB) at the end of a tube, outside the heated air bath. The transducer is regularly calibrated, using a dead weight gauge *Desgranges et Huot* (type 5300-02). Its accuracy is +/– 0.02 MPa. For each investigated temperature, this transducer is used as a reference for non-linear calibration of the two transducers in the cells. It is usually disconnected when performing measurements, so that no segregation (such as condensation or paraffin crystallization) can occur as a result of ambient temperature in this part of the circuit. When working at a fixed temperature an accuracy of +/– 0.05 MPa is achieved in the whole pressure range.

Temperatures are measured by two platinum resistors in each cell, which penetrate half of the cell wall near the upper and lower ends of the experimental volume. They have been calibrated with a 100 Ω platinum probe connected to a high precision thermometer (AOIP, model PN5207). Reading accuracy is +/– 0.1 K.

Heating and cooling of the cells and connection tubes is performed by air venting. Temperature control is performed with standard electronics (Eurotherm 900), with a reference platinum resistance on the wall of the air bath. Temperature control is stable to +/– 0.1 K, but there are also temperature heterogeneities within the air bath; recorded temperatures are slightly greater in the upper cell than in the lower. These heterogeneities increase with increasing temperature but remain below +/– 0.5 K at 374 K.

Piston motion is controlled directly by a PC. The high resolution control of the electric motor allows highly reproducible volume readings with liquids (better than 0.01%). However, corrections must be made for the influence of valve closing, tube volumes, and cell expansion, so that the actual accuracy is not as good. Isothermal cell expansion is particularly significant at high pressure and requires careful calibration with water.

1.2 Volume Calibration

The accuracy on the dead volume is better than 0.01cm^3. Generally, the expansion coefficient M is defined as:

$$M = \frac{1}{V}\left(\frac{\Delta V}{\Delta P}\right)$$

where ΔV is the change in volume caused by a pressure variation ΔP. In this equation ΔV tends to zero when V tends to zero for a constant ΔP. However, the isothermal expansion coefficient M_T defined by the following equation was found to yield a better calibration of cell volume as a function of pressure:

$$M_T = \frac{\Delta V}{\Delta P} \qquad (1)$$

This rather surprising correlation, in which a finite expansion ΔV is found for zero volume, can be explained by the origin of volume expansion in the type of cell we are using. Indeed, most of the expansion is due to length variations of the piston and of the motorized screws that move the piston, which are submitted to the high pressure load on the piston. These length variations exist even though the volume is near zero, when the piston is in its extreme position. For a given pressure, volume expansion is nearly insensitive to the actual cell volume, because the length increase of screws under tension may be neglected compared with the decrease in piston length.

For a temperature of 374.05 +/– 0.5 K:

$$M_T = (1.45 \text{ +/– } 0.1)\cdot 10^{-2} \text{ cm}^3/\text{MPa}$$

This value accounts for the dilatation of both cells. Individual isothermal expansion coefficients have also been determined for each cell:

$$M_{T1} = (6.9 \text{ +/– } 0.5)\cdot 10^{-3} \text{ cm}^3/\text{MPa}$$

$$M_{T2} = (7.6 \text{ +/– } 0.5)\cdot 10^{-3} \text{ cm}^3/\text{MPa}$$

When the various sources of uncertainty are taken into account, the absolute accuracy of volume measurements is estimated around 0.05 cm^3.

Flow rates between the two cells may be varied in a large range, between 0.1 and 450 cm^3/hour, which is

important for circulating the fluid and for determining viscosity. Thermodynamic equilibrium is obtained by circulating fluid between the two cells, while keeping the global volume constant.

1.3 The Sampling Device (Danae)

In order to sample a phase in a two-phase system without segregation, it is essential that pressure be kept constant. As no reliable method is available for sampling very small volumes (in the range of a mm^3), we selected the option of sampling a larger volume with a small detachable variable volume cell (maximum 2 cm^3). The piston of one of the main cells is moved at the same volume rate as the piston of the sampling cell is withdrawn, so that pressure is constant during sampling (Fig. 2). The valve on the sampling cell is then closed, so that the filled cell can be detached through an opening in the wall of the air cabinet. As the sampling cell is light (about 0.5 kg), it may be weighed with reasonable accuracy to determine fluid density under sampling conditions. Its contents may then be flashed and analyzed. An application of the sampling method is given by Ruffier-Meray *et al.* (1998).

1.4 Determining Viscosity

Determining the viscosity of gases is difficult with the standard methods used for liquids, such as the rolling ball technique (Pedersen *et al.*, 1989; Werner, 1996) or the falling sinker method (Ducoulombier *et al.*, 1986). Indeed, the low viscosity of HP-HT gas

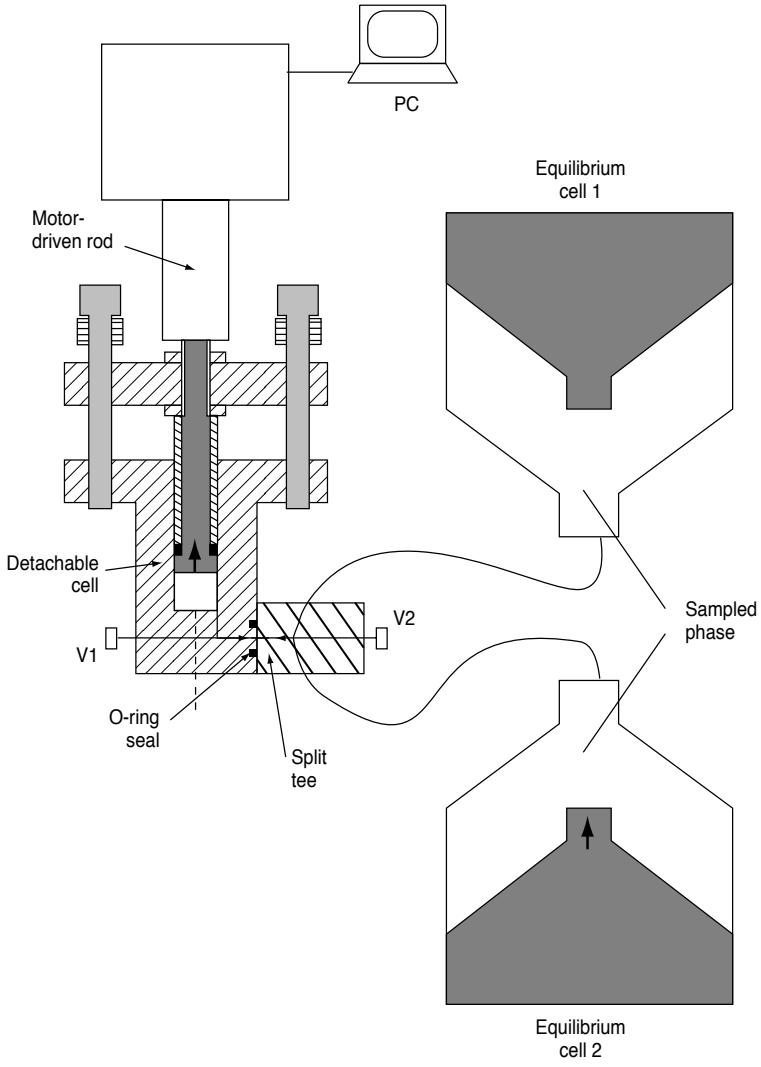


Figure 2

Sampling with the small variable volume cell Danae. The volume is reduced in the main cell and increased in the sampling cell at the same rate in order to maintain constant pressure.

condensates (an order of magnitude less than crude oils) allows the object to fall rapidly, so that the viscosity measurement is difficult with these techniques. In our apparatus, viscosity is determined by measuring the pressure drop when forcing the fluid through a capillary tube with a known flow rate. Filters are placed on both ends of the tube in order to prevent clogging. We did not use differential pressure transducers, but absolute pressure sensors. However, the signals produced by both sensors were subtracted before being amplified by an HBM electronics system, so that the signal/noise ratio is improved. The details of viscosity measurement are described in the fourth part of this article.

2 VOLUMETRIC PROPERTIES

2.1 Experimental Measurements

This apparatus has been used to investigate pure compounds, binary mixtures and real fluids, up to 120 MPa and 190°C. An example of determining a compressibility coefficient ($Z = PV/RT$) at reservoir temperature (179.5°C), taken from Arnaud (1995) is shown in Figure 3. In the high pressure range, very high values are found, exceeding 2.0.

This has important consequences for production because recovery during primary depletion is less than would be expected if classical behavior applied. When pressure drops from 110 MPa (initial pressure, P_1) to 33 MPa (dew pressure, P_d) the fraction of fluid recovered is, neglecting changes in pore volume:

$$f = \left(1 - \frac{P_d Z_1}{P_1 Z_d}\right) \approx 31\% \qquad (2)$$

For instance, a fluid showing perfect gas behavior (i.e. $Z_1 = Z_d = 1$) would have yielded much greater recovery under the same conditions ($f_{id} = 70\%$). This illustrates the particular importance of Z determination for HP-HT gas condensates. In fact, their volumetric behavior is intermediate between gas and liquid. As a result, the recovery is highly sensitive to errors in Z, because terms of similar magnitude are subtracted in Equation (2). This confirms the need for accurate measurements of this property. In our apparatus, we are quite confident that volume measurements are accurate. Indeed, we used phase volume measurements to derive phase envelopes of binary mixtures (C_1-nC_{24} and C_1-nC_{12}) in excellent agreement with data in the literature (Arnaud, 1995; Arnaud *et al.*, 1996).

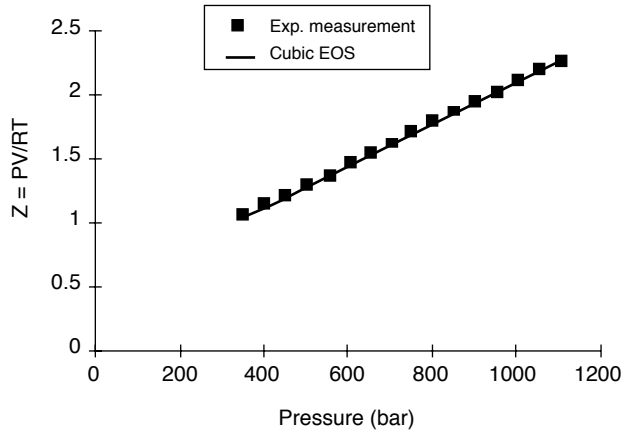


Figure 3

Compressibility coefficient of an HP-HT gas condensate (fluid A) at 179.5°C (after Arnaud, 1995).

2.2 Modeling Volumetric Properties

Cubic equations of state, although they have inherent limitations, have the advantage of being the most widely used tool in petroleum engineering, therefore allowing effective implementation in reservoir models. However, non-cubic equations of state are often inapplicable to the wide range of molecular weights that are found in crude oils and natural gases (de Hemptinne and Ungerer, 1995). In order to improve volumetric predictions for mixtures, the volume of the mixture may be expressed as the sum of pure component volumes and of an excess volume:

$$V_m = \sum_i x_i V_i + V^E \qquad (3)$$

where:

- V_m is the volume of one mole of mixture at pressure P and temperature T
- x_i is the mole fraction of component i
- V_i is the volume of pure component i at P, T
- V^E is the excess volume at constant temperature and pressure.

This expression shows that a good prediction of the volume of the mixture (V_m) requires both accurate

values for pure component volumes (V_i) and the excess volume (V^E). In a previous work (Arnaud *et al.*, 1996) it was shown that the excess volume is important for asymmetric mixtures like HP-HT gas condensates. Using a cubic equation of state with the simple linear mixing rule on the covolume, the excess volumes were predicted with an accuracy equivalent to 1 to 2% of the mixture volume. A significant improvement could be obtained with a quadratic mixing rule on the covolume. An additional interaction parameter had to be introduced for this purpose, but it was shown that it could be evaluated without ambiguity. Nevertheless, predicting pure component volumes is a still a larger source of uncertainty than excess volumes in modeling the volumetric properties of reservoir fluids. For this reason, we concentrate here on this point.

The volume translation method was introduced by Péneloux *et al.* (1982) to improve the prediction of liquid densities for pure components by a correction term *c*:

$$v_{coor} = v_{EoS} - c \quad (4)$$

where v_{coor} is the molar volume and v_{EoS} the molar volume computed from the original equation of state. In the original version, the correction *c* is a constant, calibrated at a reference temperature against the pure saturated liquid density of the component considered. Several authors have considered *c* to be temperature-dependent, calibrating the *c (T)* function by using saturated liquid densities at various temperatures (Soreide, 1989; Magoulas and Tassios, 1990; Coniglio, 1993). However, a better method is to calibrate the volume translation on high pressure liquid densities (Arnaud *et al.*, 1996). When such data are used, it appears that a simple correlation is sufficient to represent liquid densities for hydrocarbons:

$$c = AT + B \quad (5)$$

More specifically, the coefficients *A* and *B* in this relationship have been correlated with molecular weight, so that the following expression can be proposed for hydrocarbons:

$$c = -34.5 + 0.46666\,MW + (0.023 - 0.00056\,MW)T \quad (6)$$

where *c* is in cm^3/mol, *MW* is the molecular weight of the component (g/mol) and *T* the temperature (K). This correlation has proved satisfactory for hydrocarbons up to C_{13}, including aromatics (Ungerer and Batut, 1996 and 1997). An example is shown by Figure 4. Compared with other temperature-dependent volume translations, such as those proposed by Soreide (1989), Magoulas and Tassios (1990) or Coniglio (1993) the proposed method is more accurate in the high pressure region, while keeping a fair representation of saturated liquid volumes. Thanks to its simple structure and to the large pressure and temperature range of the experimental density data, this method also exhibits more reliable behavior. For instance, it is free of inconsistencies such as negative thermal expansion coefficients, which are sometimes found with other temperature-dependent volume translation methods.

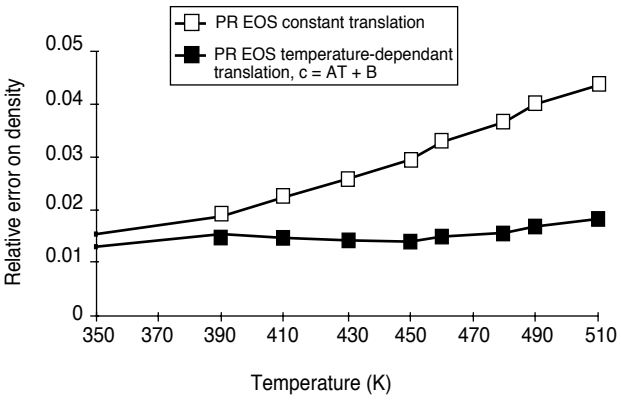


Figure 4

Relative error on *n*-hexane density at 50 MPa with the Peng-Robinson equation of state, using two methods of volume translation: constant translation and temperature-dependent translation according to Equation (6) (after Ungerer and Batut, 1997).

When this expression is used, average errors at high pressure are low (less than 3% for the C_6 to C_{13} hydrocarbons that were investigated). For heavier hydrocarbons, its predictions are sensitive to critical properties, since critical parameters are obtained by empirical extrapolation beyond the maximum temperature compatible with thermal stability. The following expression is then recommended:

$$c(T) = v(T_{ref}, P_{ref}) - \frac{MW}{\rho_{ref}} + (0.023 - 0.00056\,MW)(T - T_{ref}) \quad (7)$$

where $v\,(T_{ref}, P_{ref})$ is the liquid volume computed by the untranslated equation of state under the same conditions as those where a density measurement (ρ_{ref}) is available. With the exception of the near-critical region, the method is still accurate at low pressure.

This method does not share the inconsistencies of previous methods, and it is also shown to be consistent

with mixing rules when several pure components are grouped into a single pseudo-component. By applying the standard mixing rule of Péneloux *et al.* (1982) the volume translation of the pseudo-component (c_{ps}) can be expressed as a function of the volume translations of the pure components c_i (sums are carried over those components grouped into a given pseudo-component):

$$c_{ps} = \left(\frac{1}{\sum_i x_i} \right) \sum_i x_i c_i \quad = \frac{1}{x_{ps}} \sum_i x_i c_i \tag{8}$$

where: $$x_{ps} = \sum_i x_i$$

is the molar fraction of the pseudo-component.

By combining with Equation (5) it can easily be shown that the volume translation of the pseudo-component obeys a similar temperature dependence:

$$c_{ps} = \frac{1}{x_{ps}} \sum_i x_i \left(A_i T + B_i \right) = A_{ps} T + B_{ps}$$
$$\text{with } A_{ps} = \sum_i \frac{x_i A_i}{x_{ps}} \text{ and } B_{ps} = \sum_i \frac{x_i B_i}{x_{ps}} \tag{9}$$

This is of great practical importance since pseudo-components can consistently be represented in the same way as pure components, with the same computer code, when Equation (5) or Equation (7) is used. This is an important advantage compared to other temperature-dependent volume translations such as Magoulas and Tassios (1990) or Coniglio (1993), for which the temperature dependence is not preserved upon lumping.

This advantage extends to the dependence on molecular weight when Equation (6) is used. Indeed, combining Equations (6) and (8) rapidly yields:

$$c_{ps}(T) = (0.023 - 0.00056\, MW_{ps})\, T + (-34.5 + 0.4666\, MW_{ps}) \tag{10}$$

where the average molecular weight of the pseudo-component is simply defined by applying the conservation of mass:

$$MW_{ps} = \frac{1}{x_{ps}} \sum_i x_i MW_i \tag{11}$$

The consistency of the proposed method upon grouping can basically be explained by the linear dependence on molecular weight in Equation (6), associated with the linear dependency on mole fractions of volume translation Equation (8) and of molecular weight Equation (11)

This consistency is particularly useful for petroleum fluids at the stage of reservoir or process simulation. At this stage, the detailed characterization obtained by gas chromatography is generally unavailable, and the C_5 to C_{13} analysis is given as a list of pseudo-components together with the properties of these pseudo-components. To apply the method, it is therefore sufficient to use Equation (10) with the molecular weight of the pseudo-components taken from the global analysis. This internal consistency of the method is, here again, an advantage compared with other volume translation methods (Soreide, 1989; Magoulas and Tassios, 1990 or Coniglio, 1993). In fact, these methods introduce a non-linear dependency on mole fractions through the use of exponentiels or critical temperatures. For pseudo-components heavier than C_{13}, a density has to be provided in addition to molecular weight, so that the more accurate Equation (7) can be applied. Then density measurements are generally carried out in the standard boiling point analysis for heavy fractions, so that the implementation of this relationship is straightforward.

3 PHASE BEHAVIOR

3.1 Experimental Measurements

The phase behavior of HP-HT gas condensates has been discussed in Ungerer *et al.* (1995). Two examples taken from this work are given in Figure 5 (fluid A) and Figure 6 (fluid B) for real fluids and Figure 7 for a synthetic fluid. A specific point needed, however, clarification because the boundary between the classical two-phase region (gas + liquid) and the three-phase region (gas + liquid + solid) was unknown. For this reason, we investigated the phase behavior of additional synthetic gases in a fully transparent sapphire cell in a more recent study, the details of which will be found in Jensen *et al.* (1998). Special care was also taken to avoid departure from thermodynamic equilibrium during measurements.

The composition of these fluids differs mainly in the heavy fraction (either 0.5 mol% $n$$C_{24}$, or 0.5 mol% naphthalene, or a mixture of both) while the light fraction is the same (mostly 20% pentane and 79% methane).

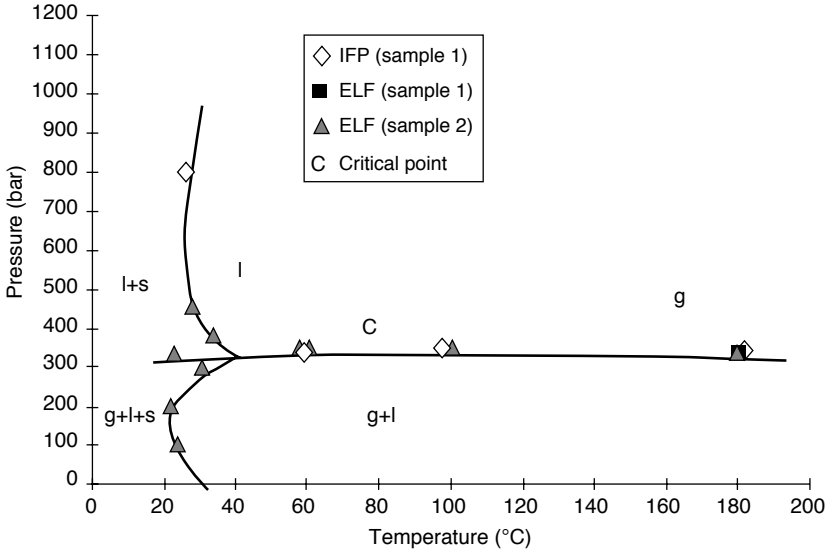


Figure 5

Phase diagram of the HP-HT gas condensate shown in Figure 3 (fluid A), which exhibits paraffin crystallization at high pressure and low temperature (after Ungerer *et al.*, 1995).

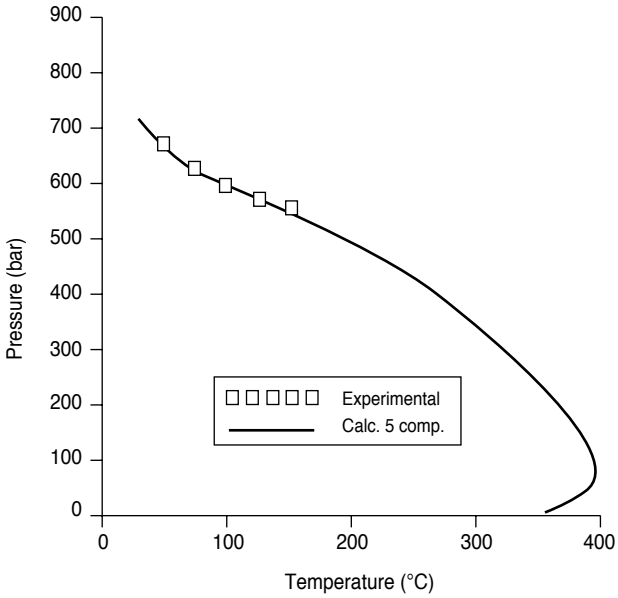


Figure 6

Phase diagram of an HP-HT gas condensate (fluid B) exhibiting very high dew pressures (after Ungerer *et al.*, 1995).

These fluids illustrate the various kinds of phase behavior that can be found for solid-depositing gas condensates. In the case of MRJ1 (Fig. 8), a classical retrograde behavior is found at high pressure and high temperature, and no bubble point is seen. At low temperature (ca. 30°C) and high pressure, the heavy paraffin crystallizes from the gas phase. Below the crystallization temperature, the (gas + solid)/(gas + liquid + solid) phase boundary corresponds to dew points in the presence of a solid phase. The real fluid B (Fig. 6) could be an example of this type, but this is not certain as its phase behavior has not been observed at temperatures lower than approximately 50°C.

In the case of MRJ2 (Fig. 9), a critical point (gas = liquid) is found above the temperature at which crystallization is observed. This behavior is similar to the real fluid A shown in Ungerer *et al.* (1995). The fluid is a gas condensate at high temperature, but the heavy hydrocarbon crystallizes from a liquid phase at lower temperature.

In the case of MRJ3 (Fig. 10), there is no longer a classical critical point (gas = liquid), since heavy hydrocarbon crystallization intervenes. However, a critical point is found in the presence of the solid phase (solid + gas = liquid). Above this critical point, the fluid has a dew point, in the presence of a solid phase, while below this critical temperature, the fluid displays a bubble point, also in the presence of a solid phase. We do not know of any gas condensates that exhibit this behavior to date but it is reasonable to assume that some do exist.

3.2 Simultaneous Modeling of Phase Equilibria and Volumetric Properties

In this article, we will not discuss in detail the modeling of phase equilibria in HP-HT gas condensates, as this problem is covered by the extensive work of Sportisse *et al.* (1997) who used continuous distribution functions to represent the

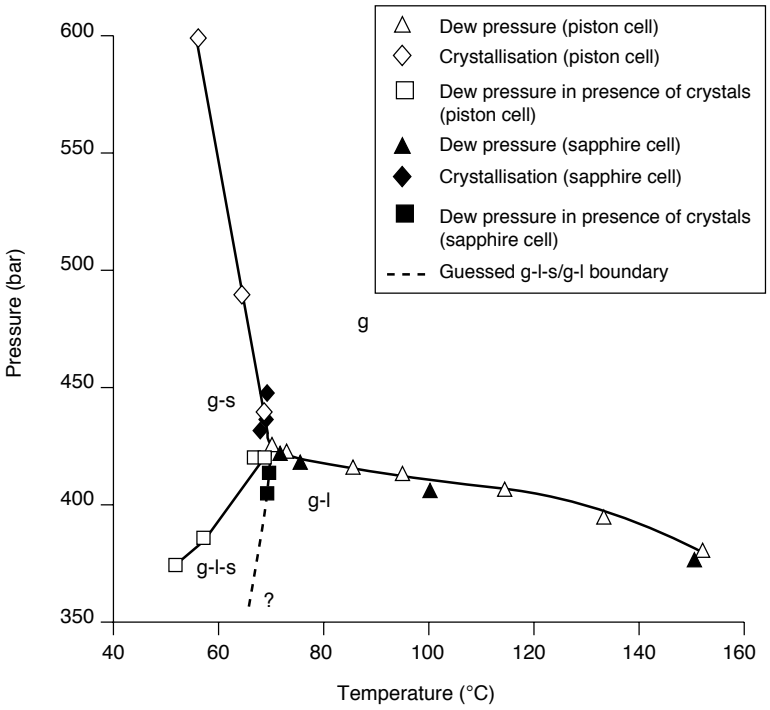


Figure 7

Phase diagram of a synthetic gas condensate containing a heavy hydrocarbon (phenanthrene) forming a solid phase at temperatures below 70°C (after Ungerer *et al.*, 1995).

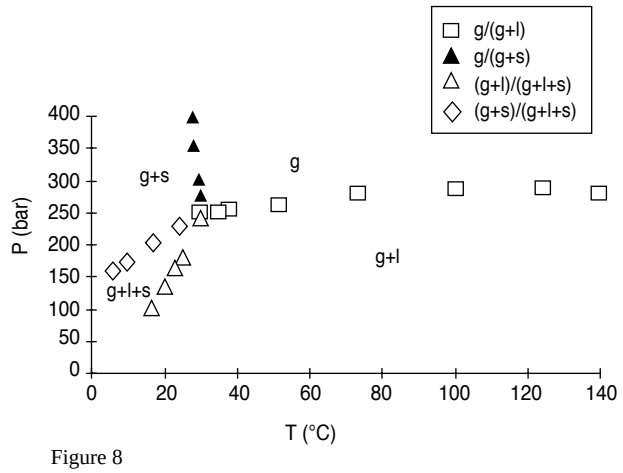


Figure 8

Phase diagram of a synthetic gas MRJ1 (molar composition approx. 79% methane, 20% *n*-pentane + 0.5% nC_{24}), showing crystallization of the heavy hydrocarbon from the fluid phase at high pressure (Jensen *et al.*, 1998).

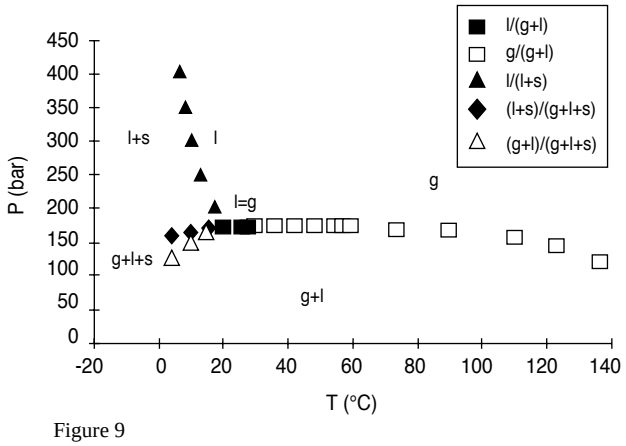


Figure 9

Phase diagram of a synthetic gas MRJ2 (molar composition approx. 79% methane, 20% *n*-pentane + 0.5% naphthalene), showing crystallization of the heavy hydrocarbon (naphthalene) from the fluid phase at high pressure (Jensen *et al.*, 1998).

composition of the heavy fraction (C_{10}^{+}). In contrast to the so-called "continuous thermodynamics" of Cotterman *et al.* (1985), the method of Sportisse *et al.* explicitly introduces three independent distributions of pure compounds for *n*-alkanes, monoaromatics and polyaromatics. This approach has been shown to possess superior flexibility and predictive capability for various condensate gases, including HP-HT fluids.

Non-cubic equations of state or corresponding states methods are often invoked as a way to improve simultaneously the prediction of phase equilibria and volumetric properties. We present here a brief outline of various attempts to implement these methods.

The corresponding states method of Lee and Kesler (1975) introduces important errors for hydrocarbons above C_{12} (de Hemptinne and Ungerer, 1995). Also,

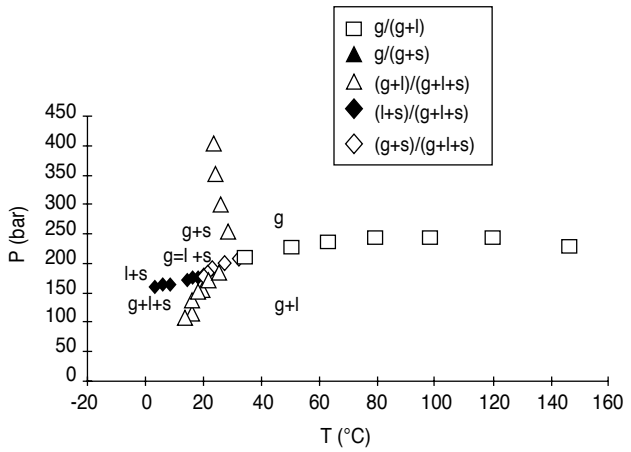


Figure 10

Phase diagram of a synthetic gas MRJ3 (molar composition approx. 79% methane, 20% *n*-pentane + 0.3 mole% naphthalene and 0.2% nC_{24}), showing crystallization of heavy hydrocarbons (nC_{24} or naphthalene) from the gas phase at high pressure (Jensen *et al.*, 1998).

numerical problems are found in the near-critical region, because a small region exists in reduced coordinates where the two reference components are in different phase states. Although this equation is sometimes very useful for gases, its fundamental flaws prohibit its use as a general method.

In the same work, de Hemptinne and Ungerer (1995) also investigated the SBR equation of state (Béhar *et al.*, 1985), with the improvements added by Jullian *et al.* (1989). It seemed that this equation would still need further development to describe the density of heavy hydrocarbons in a satisfactory way.

The COR equation, developed by Chien *et al.* (1983) gives good predictions for heavy hydrocarbons (Solimando *et al.*, 1997) but it cannot adequately reproduce the volumetric behavior of methane, even though specific adaptations were tried for this purpose.

The SAFT equation of state (Chapman *et al.*, 1989; Huang and Radosz, 1991) was found to yield somewhat disappointing vapor pressures and saturated liquid densities for liquid hydrocarbons (Chaudeur, 1995) but was found to be better than COR for methane. The increased performance seems to be too small, however, to warrant replacing cubic equations of state, which are much simpler to use. Further tests are needed with this model.

Applying the BWR-type equation of Soave (1995), we found significant positive excess volumes for the C_1-nC_{24} mixtures at high pressure, while negative values have been measured (Arnaud *et al.*, 1996). This shows that the mixing rules in this equation have to be improved.

Our present conclusion is that no existing thermodynamic model provides a serious alternative to cubic equations of state. In the next few years, we expect that further improvements will arise from an improved representation of the heavy fraction in cubic equations of state rather than from non-cubic equations of state. In the long range, perhaps the development of molecular simulation will provide standard prediction methods for volumetric and phase equilibrium properties.

4 VISCOSITY

4.1 Viscosity Measurement

When a flow rate q is imposed in a capillary tube of internal diameter D and length L, producing a pressure drop ΔP in laminar flow regime, the fluid viscosity, μ, is given by Poiseuille's law:

$$\mu = \frac{\Delta P \pi D^4}{128 q L} \tag{12}$$

Care has to be taken that the flow regime is laminar in the tube. This can be checked by computing the dimensionless Reynolds number:

$$R_e = \frac{\rho v D}{\mu} \tag{13}$$

where ρ is fluid density and $v = 4q/\pi D^2$ is the average velocity of the fluid in the tube.

In order to prevent the flow from being turbulent, the Reynolds number must remain below a threshold value (Bird *et al.*, 1960):

$$R_e \leq R_{e\max} \approx 2100 \tag{14}$$

The operating conditions (tube length and diameter, flow rate) must be optimized so that Equation (14) is satisfied and the pressure drop is sufficiently high to be measured with reasonable accuracy. Indeed, the low viscosity of gas may cause the Reynolds number to reach high values see Equation (13) if no special care is taken. As a result, the capillary tube must have a very small inner diameter, D, (approximately 0.25 mm), and

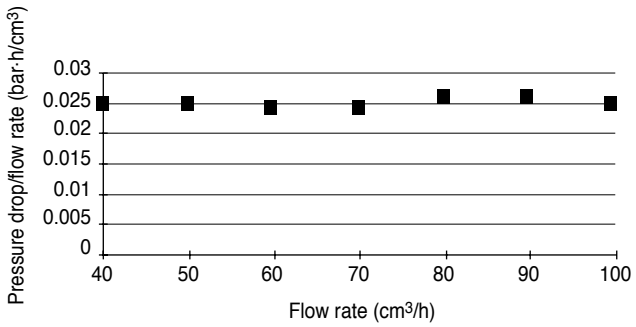


Figure 11

Test of the linear relationship between pressure drop and flow rate while measuring methane viscosity at 71°C, 400 bar by the capillary tube method. Viscosity is approximately 0.023 mPa·s.

L must be high (50 meters). An experimental check of whether Equation (14) is satisfied is to verify the linear behavior of the relationship between flow rate and pressure drop. An example is given in the case of methane at 40 MPa, 71°C, i.e. a fluid of very low viscosity for which measurement is particularly difficult (Fig. 11).

For small diameters, the uncertainty in the diameter, D, in Equation (3) is such that it cannot be applied in a predictive way. For this reason, the ratio $k = \pi D^4/128\,L$ has been treated as an adjustable constant, calibrated to *n*-pentane viscosity data from Lee and Ellington (1965) as shown on Figure 12 and Table 1. The pressure dependence of viscosity agrees with these data. When applied to methane with the same value of $k = \pi D^4/128\,L$, the method yields a viscosity in good agreement with data from Baron *et al.* (1959) (Fig. 13). Similar tests have been performed for nitrogen (Fig. 14, Table 2) in agreement with the data from Kao and Kobayashi (1967) and for the equimolar nitrogen-pentane mixture as well (Fig. 15, Table 3). These measurements clearly show increasing viscosity with increasing pressure and with decreasing temperature. In this respect, it may be noted that the temperature influence on nitrogen viscosity at high pressure (Table 2) is opposite to the low pressure behavior, where gas viscosity increases with increasing temperature. As was noted for volumetric properties, the viscosity behavior of high pressure gases is intermediate between liquid behavior and low pressure gas behavior.

TABLE 1

Viscosity of *n*-pentane at 71.3°C measured with the capillary tube method

Pressure (bar)	Viscosity (mPa·s)
310	0.210
345	0.216
414	0.232
483	0.243
552	0.253
632	0.266
710	0.278
850	0.296
982	0.307

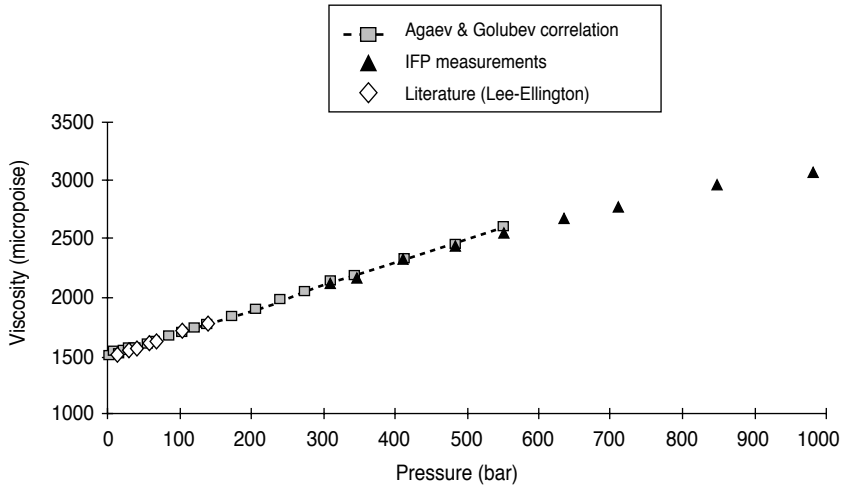


Figure 12

Example of viscosity determination at high pressure for *n*-pentane at 71°C. These data include the point (400 bar) on which the constant is calibrated.

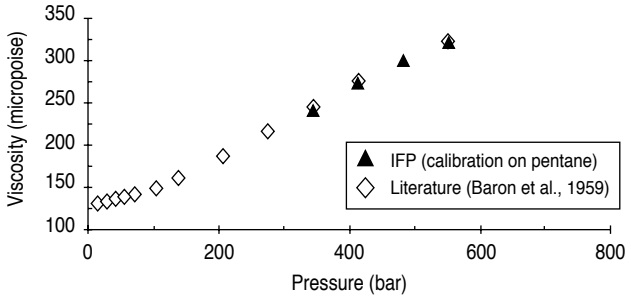


Figure 13

Viscosity of methane at 71°C.

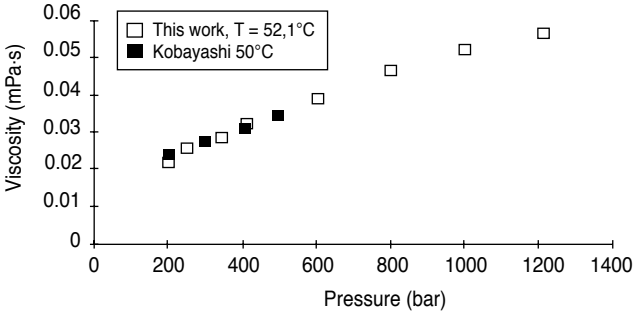


Figure 14

Viscosity of nitrogen. The scatter of data at pressures lower than 400 bar is attributed to friction and mechanical tolerance effects of the piston which disappear at high pressure.

TABLE 2

Viscosity of nitrogen measured with the capillary tube method (mPa·s)

P (bar)	Viscosity (mPa·s)			
	T = 52.1°C	T = 71.3°C	T = 98.3°C	T = 148.3°C
200.1	0.0229			
249.5			0.0255	
249.8	0.0251			
300	0.0271			
300.4		0.0278		
303.1			0.0222	
306.3				0.0298
350	0.0279			
351		0.0265		
353.9			0.0298	
356.9				0.0256
401.3		0.0297		
403.9	0.0319			
405.1			0.0306	
409.1				0.0271
603.4		0.0344		
604.6	0.0386			
608.8			0.0337	
611.9				0.0344
801.6		0.0431		
803.5	0.046			
815.7			0.04	
817.3				0.0396
994.5		0.0483		
998.2	0.0522			
1016.7			0.0428	
1021.7				0.0423
1202.5		0.0551		
1212.1	0.056			
1223.7			0.046	
1226.9				0.0455

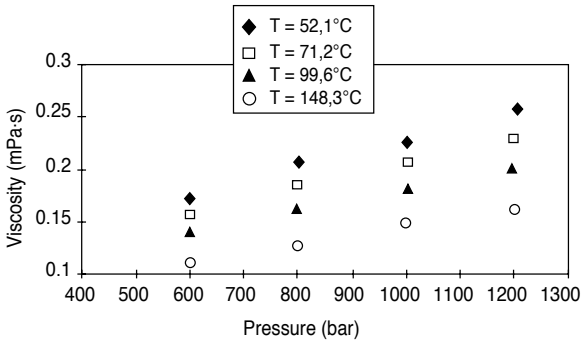


Figure 15

Viscosity of the equimolar mixture of nitrogen and *n*-pentane. No measurement has been performed below 600 bar in order to keep the mixture monophasic.

TABLE 3

Viscosity of the equimolar nitrogen-*n*-pentane mixture

P (bar)		Viscosity (mPa.s)		
	T = 52.1°C	T = 71.2°C	T = 99.6°C	T =148.3°C
599.9	0.172			
600.1			0.139	
600.5		0.157		
601.2				0.11
798.4		0.184		
799.2				0.127
799.4			0.161	
800.4	0.207			
995.9				0.149
999.3	0.226			
1000.2			0.181	
1000.4		0.207		
1197.6		0.228		
1197.9			0.201	
1200				0.162
1205	0.257			

We have not yet performed any viscosity measurement on real HP-HT condensate gases, because samples have not been available. However, we can estimate the viscosity by considering the pressure dependence of methane viscosity (Fig. 13) as well as the role of dissolved liquids and temperature (Fig. 15). It can be conjectured that viscosity should be in the vicinity of 0.1 mPa·s for a fluid such as that shown in Figure 3 in typical HP-HT conditions (1000 bars, 180°C).

4.2 Viscosity Modeling

Three main types of models are currently used to predict reservoir fluid viscosity. The most widely used is probably the method of Lohrenz *et al.* (1964). However, it has been shown to produce errors as high as 100% in gas condensates under HP-HT conditions (F. Montel, personal communication). Another type of model is based on the corresponding states principle, using either a single reference component (Pedersen *et al.*, 1989) or two reference components, namely methane and *n*-decane (Aasberg-Petersen *et al.*, 1991). These methods also suffer from important uncertainties when applied to gas condensates at high pressure (Montel, personal communication). This can be explained by the fact that the single reference component (i.e. methane) is unrepresentative in the method of Pedersen *et al.* (1989). This problem should be solved by the two-components corresponding states method of Aasberg-Petersen *et al.* (1991). However, its applicability is, in fact, limited by the small size of the domain (in reduced conditions) where methane and *n*-decane viscosities are both available. A third type of viscosity model has been proposed by Werner (1996), who used the Grunberg and Nissan (1949) mixing rule to predict the viscosity of a mixture from the viscosities of its components under the same pressure and temperature conditions. In order to test the foundations of this method, we will use our data to perform a preliminary evaluation of the mixing rule.

The viscosity behavior of a binary mixture at a given temperature (71.2°C) is illustrated in Figure 16. At this temperature, the viscosity is available for the pure components (nitrogen and *n*-pentane) and for the equimolar mixture as well. On this graph, we have reported the interpolation from the Grunberg and Nissan (1949) mixing rule, expressed in terms of molar fractions:

$$\ln \eta = x_1 \ln \eta_1 + (1 - x_2) \ln \eta_2 \qquad (15)$$

where x_i are the molar fractions and η_i are the viscosities of the pure components at the same temperature and pressure.

As can be seen in Figure 16, a significant error, of about 30%, is found in the viscosity of the equimolar mixture. When the Grunberg and Nissan mixing rule is expressed in terms of weight fractions (i.e. when we assume that x_i is a weight fraction in the above equation), much better agreement is found with our experimental data (Fig. 17).

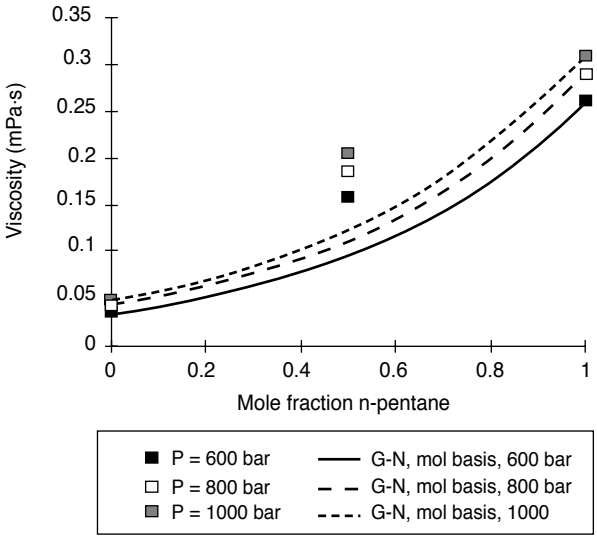


Figure 16

Viscosity of the nitrogen-*n*-pentane system at 71°C versus mole fraction of *n*-pentane. The lines represent the prediction of the Grunberg and Nissan (1949) mixing rule, expressed in terms of molar fractions.

This observation confirms the statement by Werner (1996) who found an average error of 3.1% with the weight fraction-based mixing rule, compared with 5.6 % with the molar fraction-based mixing rule. In our example, the contrast in performance between the two versions of the Grunberg-Nissan mixing rule is clearer. This shows that contrasted systems such as the nitrogen-*n*-pentane mixture investigated here are challenging for viscosity models. Although our preliminary test supports the use of the weight fraction-based mixing rule, further tests are needed. If confirmed, this mixing rule could be used to predict the viscosity of a reservoir fluid from the viscosity of the stock tank oil and of the separator gas, which are easier

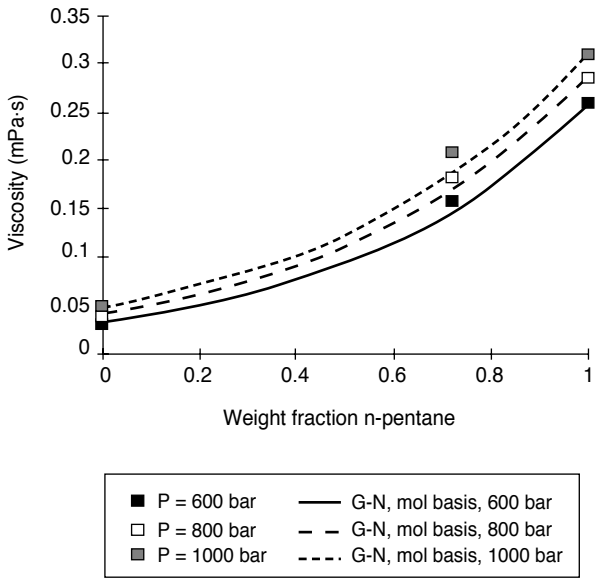


Figure 17

Viscosity of the methane-*n*-pentane system at 71°C versus weight fraction of *n*-pentane. The lines represent the prediction of the Grunberg and Nissan (1949) mixing rule, expressed in terms of weight fractions.

to measure and to predict. Also, it could be used when viscosities must be predicted over a large range of gas contents, such as in enhanced oil recovery by gas injection.

CONCLUSION

In the last five years, the perspective of developing HP-HT fields has triggered an important research and development effort. Equipment has been designed, PVT measurements have been performed, non-classical phase behaviors have been demonstrated and improved models have been developed. Part of these improvements (e.g. improved volume translation techniques) will have implications for the production of oil and gas fields in more conventional conditions. However, there is still much progress to be made in several directions.

On the experimental side, viscosity measurements of real condensate gases are still a challenge, which we will address as soon as adequate samples are available.

Another important issue is the measurement of the Joule-Thomson coefficient for HP-HT fluids. Because this coefficient may be negative at high pressure (Kortekaas *et al.*, 1998), HP-HT gas condensates could heat up upon isenthalpic expansion, so that temperatures could be higher than expected in producing wells. However, experimental measurements of the Joule-Thomson effect are necessary to validate these predictions.

Also, the adsorption on minerals or on solid organic deposits in the reservoir could be of some importance at high pressure, and experimental data are needed.

On the modeling side, a short term goal should be to test the improved volume translation described in this article on real reservoir fluids, and to examine whether specific mixing rules are useful in predicting volumetric properties. Along the line initiated by Sportisse *et al.* (1997), simultaneous prediction of phase equilibria and volumetric properties with cubic equations of state can still be improved by the use of separate distributions of paraffins and aromatics.

However, alternate thermodynamic models are desirable for precise modeling of HP-HT fluids in the future. In this respect, non-cubic equations of state appear to be successful in specific conditions (heavy hydrocarbons for COR, light hydrocarbons for Lee-Kesler, etc.) but none of them is superior to the well-known cubic equations if the whole (P, T, x) range needed for reservoir fluids is considered. Since numerous attempts, by highly qualified teams, have been made over the last fifteen years to develop non-cubic equations of state, perhaps this route will never provide a serious general alternative to cubic equations of state.

If this difficulty in founding a general non-cubic equation of state persists, the only serious alternative standard method would be molecular simulation, i.e. Monte Carlo simulation or molecular dynamics (Fuchs, 1998). Indeed, these techniques have the advantage of predicting equilibrium properties and transport properties as well, within a more rigorous framework. Of course, they will not compete with equations of state for implementation in reservoir simulators because of their heavy demand for computer time. Nevertheless, molecular simulation might become a standard method for some reservoir fluid problems in the next few years.

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