On the Retrograde Condensation Behavior of Lean Natural Gas[1]

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The occurrence of liquid dropout in natural gas pipelines may cause operational problems during storage, transport, and processing. Therefore, the availability of a model that accurately predicts the amount of liquid formed is of great importance for the natural gas industry. The objective of this study is to develop a thermodynamic model for the accurate prediction of the amount of liquid formed in natural gas pipelines at transportation conditions. As input, the model requires an accurate gas analysis. A modified Peng–Robinson equation of state was selected for the phase equilibrium calculations. Interaction parameters were optimized from experimental data at conditions of practical interest, i.e., at pressures $10 < p < 70$ bar and at temperatures $250 < T < 290$ K. For a number of "keysystems," the interaction parameters were calculated from new accurate solubility data of heavy hydrocarbons in some of the main constituents of natural gas like methane and nitrogen. Also, an extensive experimental program was carried out to study the influence of minute amounts of nitrogen, ethane and carbon dioxide in methane on the solubility behavior of decane in these gas mixtures. From a sensitivity analysis, it could be concluded that the liquid dropout is influenced mainly by the concentration and characterization of C_7-C_{13} fractions. In this work, two characterization procedures to represent these fractions are compared. For two types of lean natural gas, the model predictions are compared with field measurement data, recently supplied by the Dutch natural gas industry.

KEY WORDS: characterization; equations of state; liquid dropout; natural gas; phase behavior; potential hydrocarbon liquid content; retrograde condensation; supercritical solubility.

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1. INTRODUCTION

During storage, transportation, and processing, natural gas may form small amounts of liquid. This phenomenon, occurring as a result of a pressure drop, is called retrograde condensation. To prevent operational problems, caused by the accumulation of liquid, there is a need to predict this condensation behavior of natural gas by means of an adequate thermo-dynamic model.

Oranje [1], Banell et al. [2], and Pedersen et al. [3] pointed out that the most commonly used variable for expressing the condensation behavior of a multicomponent mixture is the dew point, because it is very sensitive to the presence of traces of heavy compounds in natural gas [4]. As a result, there is a large difference between the dew-point temperature and the temperature where the amount of liquid formed may cause operational problems. In practice, this make the dew point inappropriate for estimating the amount of condensate from the pressure and temperature of natural gas along pipelines. A more appropriate property is the potential hydrocarbon liquid content (PHLC) of the gas. It is defined as the mass of condensable liquid at the pressure and temperature of the measurement, per unit volume of gas at normal conditions ($T = 273.15$ K and $p = 1.01325$ bar):

$$\text{PHLC} = 10^6 \frac{F_\text{L}}{1 - F_\text{L}} \sum_{i=1}^{N} (x_i \text{MW}_i) \frac{P_n}{Z_n \text{R} T_n} \tag{1}$$

where in the summation N is the number of components in the mixture, and where PHLC is in $\text{mg} \cdot \text{N} \cdot \text{m}^{-3}$ (here N indicates at normal conditions).

The model is supposed to predict the equilibrium temperature, at a certain pressure and PHLC yield, within ± 1 K in the range of interest, that is, $5 < \text{PHLC} < 200 \, \text{mg} \cdot \text{N} \cdot \text{m}^{-3}$, $10 < p < 70$ bar, and $250 < T < 290$ K. Under these conditions, which are far removed from the critical point of the mixture, retrograde condensation may occur.

The only input information the model requires is a detailed gas-chromatographic analysis [5]. The model consists of two distinguishable parts: an equation of state (EOS), which gives the condensation behavior of a multicomponent mixture at a specified pressure, temperature, and composition; and a suitable characterization procedure, which converts the gas-chromatographic analysis of real natural gas into a representative multicomponent mixture. To improve the EOS performance, binary experimental data are used for optimizing the interaction parameters present in the mixing rules. In addition, the validity of the model is verified by comparing it with field measurements. Depending on the result of this comparison, an optional tuning procedure can be applied to improve the
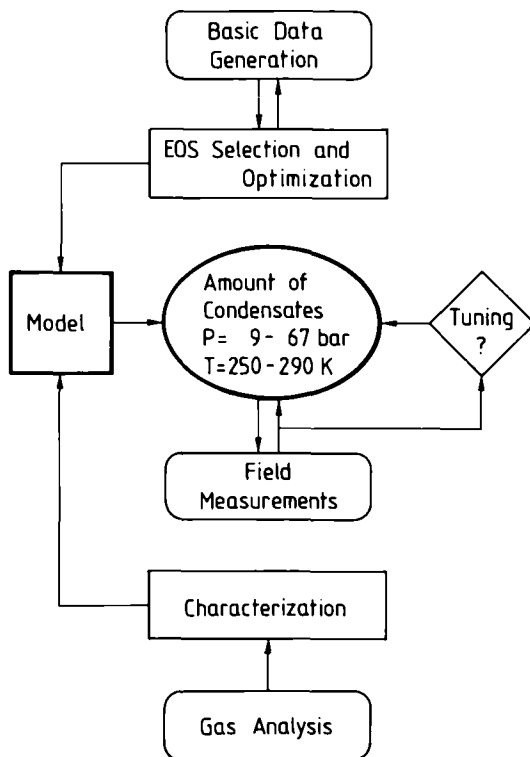
Fig. 1. Schematical overview of the procedure followed for the prediction of the potential hydrocarbon liquid content (PHLC).

performance of the model. Figure 1 shows schematically the various parts of the project.

In the following sections, we highlight aspects of the project that have not been discussed yet in the literature. For a detailed discussion we refer to Rijkers [6], Rijkers et al. [7–11], Voulgaris [12], and Peters et al. [13].

2. COMPOSITION OF LEAN NATURAL GAS

N.V. Nederlandse Gasunie has recently developed a new detailed gas-chromatographic analysis [5]. This novel method has a specified detection limit of 0.05 ppm on a molar basis for hexadecane instead of 10 ppm for octane. The latter value is the detection limit of the ISO-6974 method [14] used to determine the calorific value of natural gas. For the composition of

two typical Dutch natural gases, indicated by Gas A and Gas B, respectively, we refer to Derks et al. [15]. In general, large differences in concentration levels of the various components in the natural gas may occur. For example, methane is present in amounts 16,000,000 times larger than tetradecane. Moreover, on a molar basis the amount of carbon dioxide may vary from 1% (Gas A) to 20% (Gas B), nitrogen may vary from 5% (Gas B) to 14% (Gas A), and heavy hydrocarbons up to C_{16} (Gas A) may be present in amounts larger than 0.05 ppm or in the same amount for hydrocarbons up to up to C_{12} (Gas B). The sum of all unidentified compounds with a boiling point (T_b) between those of the n-alkanes with a carbon number $k - 1$ and k, with $k > 6$, is indicated by the $x - C_k$ fraction. A $y - C_k$ fraction has a similar definition, since, in the $y - C_7$ fraction, benzene and cyclohexane and, in the $y - C_8$ fraction, toluene and methylcyclohexane are not included because these four components are detected as individual components in the gas-chromatographic analysis [5, 15].

The large differences in composition may result in substantial differences in the condensation behavior of the various types of natural gas. This work focuses on lean natural gas, for which the amount of heavy compounds (C_7^+ fractions) is less than 0.03% of the total number of moles.

3. EXPERIMENTS

To develop the predictive thermodynamic model, three types of experiments appeared necessary:

(1)   determination of the phase behavior of a selected number of binary mixtures (bubble and dew points),

(2)   solubility measurements of heavy hydrocarbons in mixtures of gaseous components representative for natural gas, and

(3)   field measurements to test the predictive capabilities of the model.

3.1. Vapor–Liquid Equilibria of "Key" Binary Mixtures

To develop an accurate thermodynamic model for the prediction of the condensation behavior of natural gas, it is assumed that a knowledge of the phase behavior of only a limited number of carefully selected binary mixtures is required. This supposition is based on the assumption that the experimental data obtained for the "key" binary mixtures can be generalized to related binary mixtures. The main purposes of the experimental work on the "key" binary mixtures can be summarized as follows:

(1) to select an appropriate equation of state,

(2) to test mixing rules to be used in the equation of state, and

(3) to calculate binary interaction parameters.

In the literature accurate experimental data of binary mixtures of interest for this study are scarce [6, 7]. Based on the availability of experimental p, T, x- and p, T, y-data of binary mixtures of methane + n-paraffins in the temperature region $243.15 < T < 313.15$ K, the following conclusions could be drawn:

(1) the number of data points available decreases with increasing carbon number of the solute; and

(2) fewer data are available on solubilities in the gaseous phase than on solubilities in the liquid phase.

For hydrocarbons other than n-paraffins, the available experimental information relevant for this study is almost negligible, in particular, for solubilities in the gaseous phase [6, 7]. Therefore, it was decided to carry out an extensive experimental program to measure the vapor–liquid equilibria of a number of selected binary mixtures [7–11, 16, 17].

3.2. Solubility of Decane in Gas Mixtures Representative of Natural Gas

For the following reasons, the solubility of heavy hydrocarbons in gaseous mixtures representative for natural gas were experimentally determined:

(1) to obtain insight into the sensitivity of the selected equation of state used in the model to describe minute fluctuations in the concentration of heavy hydrocarbons and

(2) to obtain quantitative information about the increasing solubility effect of heavy hydrocarbons caused by ethane and carbon dioxide and the decreasing solubility effect of heavy hydrocarbons caused by nitrogen.

Therefore, it was also decided to carry out an extensive experimental program to obtain solubility data of a representative hydrocarbon in mixtures of methane, nitrogen, carbon dioxide, and ethane. Methane was the main constituent in these mixtures with smaller quantities of nitrogen, carbon dioxide, and ethane. The composition of the gas mixtures was chosen in such a way that these are representative of the extremes in composition in Dutch natural gas [15] with respect to the main volatile constituents. The selection of the representative hydrocarbon (decane) was based on a sensitivity analysis [12].

In previous papers [7, 17], experimental data on the solubility of decane in pure methane and pure nitrogen have been reported. Data on the solubility of decane in mixtures of methane (85 mol%) and nitrogen (15 mol%) have been reported by Pearce et al. [18]. In addition, the solubility of decane in the following gas mixtures has been determined experimentally:

(a)   methane (80%) + carbon dioxide (20%),

(b)   methane (80%) + carbon dioxide (5%) + nitrogen (15%), and

(c)   methane (80%) + carbon dioxide (2%) + nitrogen (15%) + ethane (3%)

All concentrations are nominal values and on a molar basis. The experimental work covers the temperature region of $260 \leqslant T \leqslant 310$ K, with pressures up to 15 MPa. These pressures are sufficiently high to meet the
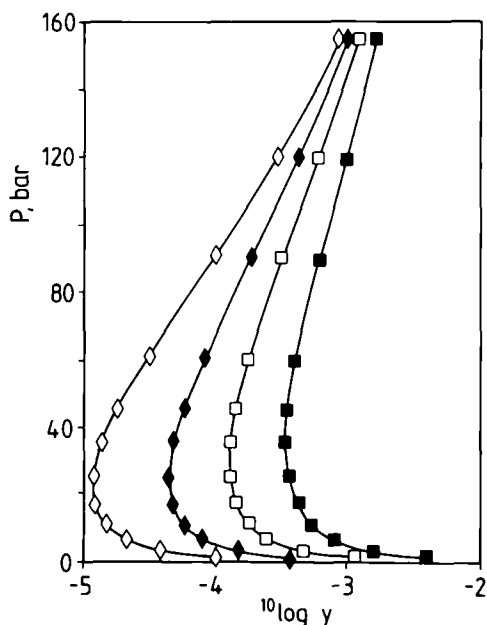
Fig. 2. Solubility of decane in a gas mixture of methane (80 mol%), ethane (3 mol%), carbon dioxide (2 mol%), and nitrogen (15 mol%). Open diamonds, 263.15 K; filled diamonds, 278.15 K; open squares, 293.15 K; filled squares, 310.85 K. Solid lines represent best fits to the experimental data.

objectives of this investigation. The experimental setup has been described elsewhere [6, 7].

As an illustration of the experimental work, isothermal data for the solubility of decane in a gas mixture of methane (80.03 mol%), nitrogen (14.95 mol%), ethane (3.02 mol%), and carbon dioxide (2.00 mol%) are shown in Fig. 2. Details of this part of the experimental work are given by Straver et al. [16].

3.3. Field Measurements

To test the predictive capabilities of the thermodynamic model, field measurements of real natural gas were required. For that purpose N.V. Nederlandse Gasunie performed these measurements. The experimental data of Gas A and Gas B at 41 bar are given by Derks et al. [15].

4. EQUATION OF STATE

4.1. Selection of the Equation of State

The accurate calculation of the PHLC of natural gas necessitates the use of an equation of state (EOS) to predict the correct fluid phase behavior. In this work for binary mixtures of natural gas components, the predictive capabilities of two EOS (the simplified perturbed-hard chain theory and the Peng–Robinson equations) were compared in the temperature and pressure range of interest. From the comparative study, it was concluded [12, 19] that the Peng–Robinson equation appeared to be sufficiently accurate. It is important to predict accurate values of the low vapor pressures of the pure components. The PR EOS in its original form is not sufficiently accurate for these predictions. A modified version of the PR EOS, introduced by Magoulas and Tassios [20], has been used. For mixture calculations, the conventional Van der Waals one-fluid mixing rules have been used [12].

4.2. Binary Interaction Parameters

After selecting the EOS, its binary interaction parameters were optimized in the pressure and temperature range of interest, by means of available binary data of the basic constituents, i.e., methane, nitrogen, carbon dioxide, and ethane with heavier hydrocarbons like paraffins, naphthenes, and aromatics. Because of their strong influence on the PHLC prediction [12], emphasis has been given to improve the representation of the asymmetrical binary mixtures. The experimental information obtained in this research was used to estimate the binary interaction parameters.

5. SENSITIVITY ANALYSIS

To design a characterization procedure for the heavy tail of natural gas (C_7^+), it is important to get insight in the factors that dominate the PHLC predictions. For that purpose a sensitivity analysis has been performed for the two natural gases A and B [12]. The sensitivity analysis has been performed with the aid of a preliminary characterization procedure. This procedure takes into account all individual compounds up to C_8 with their related physical properties. In addition, a x-C_k or y-C_k fraction, is reduced to a single n-C_k component, i.e., for that particular fraction the physical properties of the corresponding n-alkane have been used. The following aspects have been considered in the sensitivity analysis:

(1) concentration of the natural gas constituents,

(2) pure component parameters,

(3) undetectable components,

(4) fluctuations in temperature and pressure, and

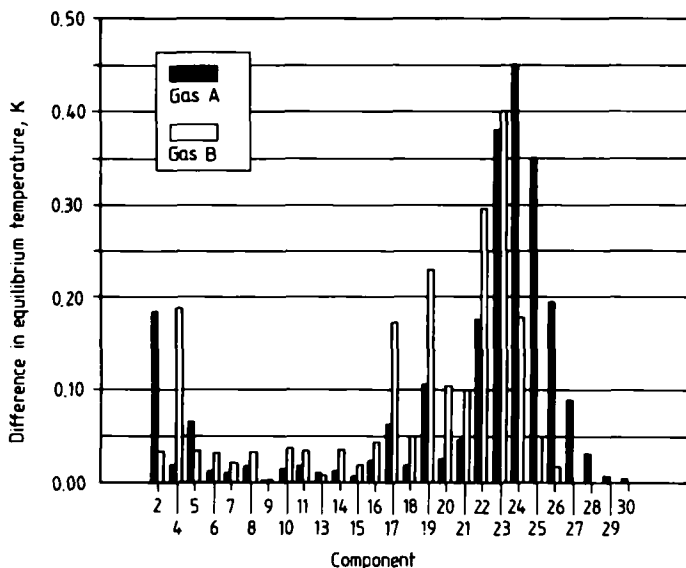(5) effect of the binary interaction parameters.

Fig. 3.   Absolute change of the equilibrium temperature at a PHLC level of $50 \text{ mg} \cdot \text{N} \cdot \text{m}^{-3}$ and a pressure of 40 bar, when the concentration of each constituent in the natural gases A and B increases 10%. For reasons of clarity, the influence of methane is not included. The numbers on the horizontal axis are explained in Table I.

Table 1. Relationship Between the Numbers on the Horizontal Axis of Fig. 3 and the Constituents of Natural Gas

Code	Component
1	Helium
2	Nitrogen
3	Methane
4	Carbon dioxide
5	Ethane
6	Propane
7	Isobutane
8	n-Butane
9	2,2-Dimethylpropane
10	Isopentane
11	n-Pentane
12	Cyclopentane
13	2,2-Dimethylbutane
14	2,3-Dimethylbutane
15	3-Methylpentane
16	n-Hexane
17	Benzene
18	Cyclohexane
19	Heptanes
20	Methylcyclohexane
21	Toluene
22	Octanes
23	Nonanes
24	Decanes
25	Undecanes
26	Dodecanes
27	Tridecanes
28	Tetradecanes
29	Pentadecanes
30	Hexadecanes

An important conclusion obtained from the sensitivity analysis was that the most important constituents for the PHLC prediction are the C_8–C_{12} and the C_7–C_{10} fractions for Gas A and Gas B, respectively [12] (see Fig. 3). Among them, C_{10} and C_9 are the most crucial ones. Therefore, the characterization of these fractions will be crucial for an accurate PHLC prediction. Details on the sensitivity analysis can be found in the thesis by Voulgaris [12].

6. CHARACTERIZATION PROCEDURE

The proposed characterization procedure for the description of natural gas, based only on the detailed gas-chromatographic analysis [5], can be separated into the following steps.

(1) Discrete components up to C_8 are taken into account with their pure component parameters and optimized binary interaction parameters with respect to the main volatile constituents (methane, nitrogen, carbon dioxide, and ethane).

(2) The r-C_7 and r-C_8 fractions include nearly all components with a boiling point T_b between that of the n-alkanes C_6–C_7 and C_7–C_8, respectively. In these fractions the aromatics, benzene and toluene, and the naphthenes, cyclohexane and methylcyclohexane, are not included because they are detected separately. Consequently, these r fractions do not show any aromaticity. There is only a small probability that a considerable amount of naphthenes will be present, since the most important ones have already been detected. For this reason, these r fractions are considered as isoparaffins.

(3) For the C_8^+ fraction, only the mole fractions of the normal alkanes and the sum of the mole fractions of all the other compounds (isoparaffins, naphthenes and aromatics), which have a T_b between that of two corresponding n-alkanes, are included. Consequently, for these fractions, a representative property or characterization procedure must be found that is directly related to the concentrations as well as to the EOS parameters.

Two properties have been tested: the boiling point (T_b) and the logarithm of the saturation pressure (p^{sat}) of the liquid pure solute at the temperature of the flash divided by the critical pressure (p_c). Solubility calculations of hydrocarbons with $N_c > 4$ in a mixture of the main natural-gas constituents (81% methane, 3% ethane, 2% carbon dioxide, and 14% nitrogen), at the pressure and temperature conditions of interest, have revealed that the logarithm of the solubility can be correlated to T_b by a second-order polynomial with a correlation coefficient equal to 0.995; see Fig. 4. Only heavy, polynuclear aromatics are not satisfactorily represented by this correlation. If only the C_8^+ n-alkanes are taken into account, the second-order polynomial reduces to a straight line. In addition, from Fig. 5 it is obvious that the logarithm of the solubility is a linear function of $\ln(p^{sat}/p_c)$. The correlation coefficient is equal to 0.998. Moreover, it is striking that all hydrocarbons (P, N, and A) satisfy this linear relationship. For further details, see Voulgaris [12] and Peters et al. [13].
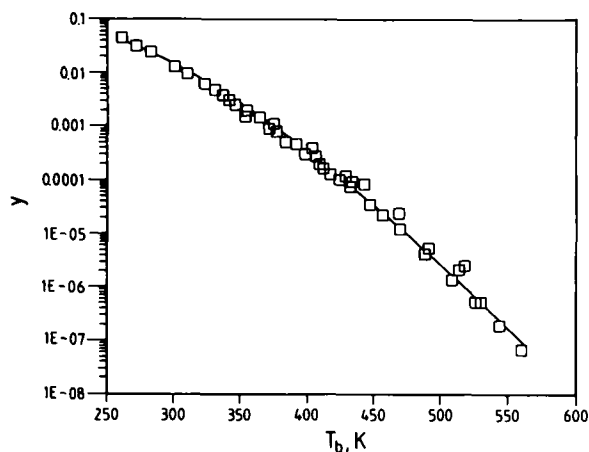
Fig. 4. Solubility of hydrocarbons as a function of their T_b (correlation coefficient $r = 0.995$) in a mixture of methane (81 %), nitrogen (14%), carbon dioxide (2%), and ethane (3%), calculated by the PR EOS at $T = 263.15$ K and $p = 60$ bar. Open squares, calculated by the PR EOS; solid curve, best fit to the filled squares.
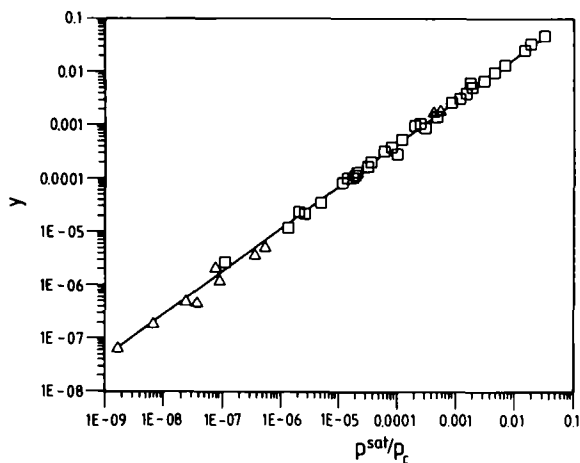

Fig. 5. Solubility of hydrocarbons as a function of their $\ln(p^{sat}/p_c)$ (correlation coefficient $r = 0.998$) in a mixture of methane (81 %), nitrogen (14%), carbon dioxide (2%), and ethane (3%), calculated by the PR EOS at $T = 263.15$ K and $p = 60$ bar. Open squares, calculated by the PR EOS; open triangles, calculated by the PR EOS, the value of p^{sat} obtained from extrapolation of the vapor pressure curve below the triple point; solid curve, best fit to the filled squares.
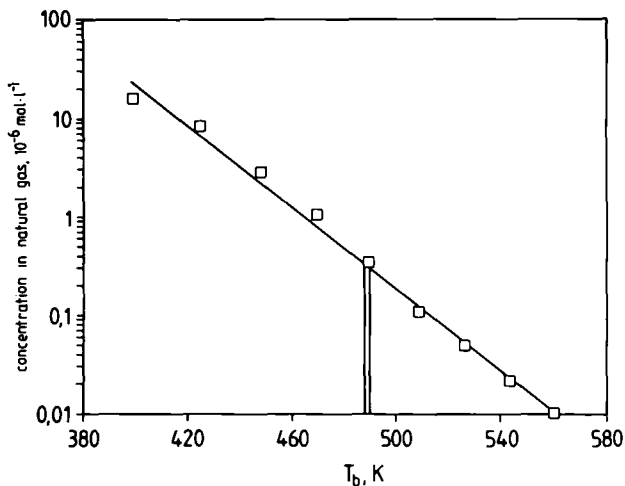
Fig. 6. Concentration of n-alkanes with $N_c \geqslant 8$ in natural gas A as a function of their T_b. Open squares, experimental data from a gas-chromatographic analysis; straight line, best correlation with slope = -0.0475 (correlation coefficient $r = 0.995$).
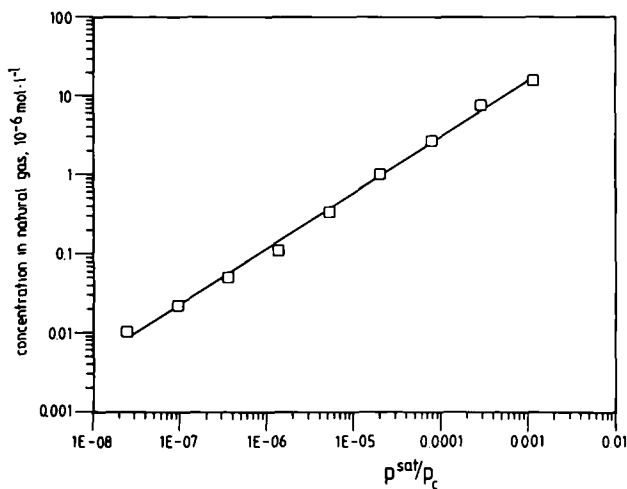

Fig. 7. Concentration of n-alkanes with $N_c \geqslant 8$ in natural gas A as a function of their $\ln(p^{sat}/p_c)$. Open squares, experimental data from a gas-chromatographic analysis; straight line, best fit with slope = 0.7133 (correlation coefficient $r = 0.997$). p^{sat} for the n-alkanes at the temperature of sampling.

For a real natural-gas mixture, it can be seen that the concentration of the C_5^+ n-alkanes follow qualitatively the same exponential decrease either as a function of T_b (Fig. 6) or as a function of $\ln(p^{sat}/p_c)$ (Fig. 7). Based on the behavior shown in Figs. 6 and 7, it is assumed that the concentrations of all compounds present in the natural gas under study follow the same exponential trend as a function of T_b or $\ln(p^{sat}/p_c)$. Both characterization procedures have been tested in this study. Further details of the characterization procedure have been discussed by Voulgaris [12].

7. DISCUSSION AND CONCLUSIONS

The best characterization procedure can be chosen only after comparing the model predictions with field measurements of lean natural gas. Field measurements for Gases A and B at 41 bar have been reported by Derks et al. [15]. Figure 8 compares the model predictions of the PHLC with the experimental data. This figure shows that the model with T_b as the characterization property gives better results. In addition, the maximum error in the equilibrium temperature does not exceed 1.2 K, i.e., the predictions are close to the accuracy required for the project. Although the performance of the characteristic parameter $\ln(p^{sat}/p_c)$ seems to be more accurate for the PNA description, T_b is found to be more accurate for the PHLC prediction. The origin of this unexpected finding is still under investigation.
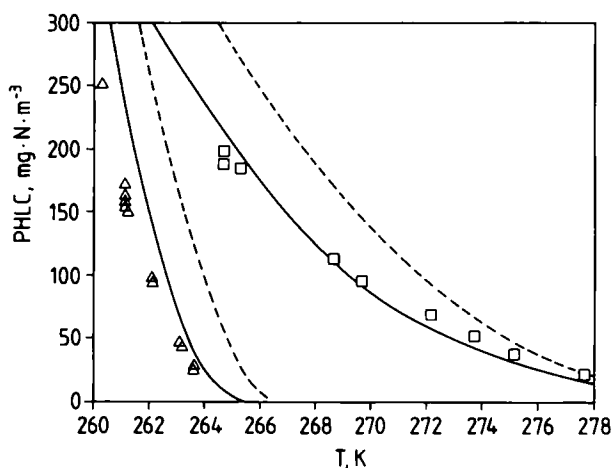

Fig. 8. Comparison of the calculated amount of PHLC with experimental field measurements as a function of equilibrium temperature at $p = 41$ bar. Open squares, Gas A; open triangles, Gas B; dashed curves, $\ln(p^{sat}/p_c)$ as characterizing parameter; solid lines, T_b as characterizing parameter.

ACKNOWLEDGMENTS

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