Vapor Liquid Equilibrium in the Ternary System

Methane-n-Hexane-n-Tetradecane

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ABSTRACT

The paper presents the results of new measurements of the phase behavior of the ternary system methane-n-hexane-n-tetradecane. The measurements have extended over the range of compositions at 348.15 K and 383.15 K for pressures from 2 MPa up to the vicinity of the critical pressure of around 25 MPa. As well as the phase envelope itself, measurements of the density of both phases have been carried out simultaneously.

The experimental data provide the opportunity to examine the effectiveness of three different thermodynamic models for the prediction of the properties of ternary mixtures from prescribed information on the constituent binary systems. The models employed for the tests include the cubic equation of Peng-Robinson, the one-fluid corresponding-states model and the more flexible, multiple-reference fluid corresponding-states model. It will be shown that only the multiple-reference fluid model provides a satisfactory description of the fluid density. The same model also represents the phase compositions moderately well but not quite as well as the Peng-Robinson equation.

KEY WORDS: alkanes; density; experimental method; mixture; model; vapor-liquid equilibrium.

1. INTRODUCTION

The thermodynamic behavior of multicomponent systems, including hydrocarbons, is of considerable interest to the petroleum extraction and refining industry. With respect to extraction, the temperatures and pressures of reservoirs from which it is expected that exploitation will take place in the future, are likely to be much higher than those encountered routinely hitherto. Of the thermodynamic properties of the fluid mixtures in reservoirs that are of significance, the density is of especial importance because it determines the estimated total mass of a field from a knowledge of its extent (volume). During exploitation of such a reservoir the phase behavior of the fluid becomes important at certain stages of the process and it is certainly of vital importance during refining and transportation, albeit at somewhat lower pressures.

For these reasons we have embarked upon a program of measurement of the phase behavior and density of hydrocarbon mixtures that contain components of greatly different volatilities. The studies are to include binary and multicomponent mixtures that are representative models of the systems encountered in practice; our prototype system is methane-n-hexane-n-tetradecane. We have already reported studies of the binary pair methane-n-hexane and preliminary studies of the ternary system [1]. In the current text we provide the experimental results of more detailed studies of the ternary system carried out with our purpose-built, high-pressure phase equilibrium apparatus [2]. The apparatus permits the simultaneous measurement of liquid and vapor compositions and densities.

In this paper we examine the performance of three different thermodynamic models that have varying degrees of statistical-mechanical rigour [3-8]. The examination consists of a comparison of the predictions of the models with our experimental data.

2. EXPERIMENTAL

The high-pressure, high-temperature phase equilibrium equipment employed for the present work has been described in detail elsewhere [2]. Here it is sufficient to note that the equipment makes use of independent chromatographic analyses of samples taken at high pressures for both gas and liquid and vapor phases. It also permits measurement of the density of each phase by means of high-pressure vibrating-tube densimeters. In our earlier work [1, 2] we confirmed the estimated uncertainty in mole fraction measurements to be $\pm 3 \times 10^{-3}$ for the liquid phase and $\pm 9 \times 10^{-4}$ for the vapor phase. The estimated uncertainty in the density is one of ± 0.8 kg m^{-3}.

In order to conduct the measurements reported here the two liquid components were added to the evacuated equilibrium cell held at the desired equilibrium temperature, with a metering pump and then degassed *in situ*. Subsequently, methane from a cylinder was compressed into the equilibrium cell until a prescribed pressure was attained. Following agitation of the contents of the cell, both mechanically and by phase recirculation [2], composition and density measurements were carried out on the equilibrium system. A new measurement cycle was then initiated by adding further methane, then changing the overall composition of the mixture and increasing the pressure. This measurement procedure leads to a sequence of isothermal measurements of the phase compositions and densities for various methane fractions in the system for an essentially constant ratio of content of n-hexane to that of n-tetradecane in the overall system.

To conserve space two sets of results will serve to illustrate the quality and extent of the experimental data and the performance of the various thermodynamic models but a more comprehensive representation of the results will have to be given elsewhere.

3. THERMODYNAMIC MODELS

In the interests of brevity we present the experimental data in Figures 1 to 6 in conjunction with the comparisons with various thermodynamic models. In this section, brief details of the three thermodynamic models explored are presented.

3.1 Peng-Robinson Model

The cubic, Peng-Robinson equation has two disposable parameters, for each pure fluid *i*, and the values of these two parameters are known for all components of interest here [3]. In the case of a mixture containing an arbitrary number of components the equation of state is assumed to be the same, but the parameters for the mixture are derived from mixing rules given elsewhere [3]. For a ternary mixture, therefore, there are three parameters that can be used to fit the equation of state to experimental data. In fact, the parameter for the methane-n-hexane system is fixed from the experimental information on the binary pair reported elsewhere [2, 9]. Thus, in the present work we have varied the remaining two interactions parameters to obtain an optimum fit of the experimental data for the ternary system.

3.1 One-Fluid Corresponding-States Model

The essence of the one-fluid model introduced by Leland [4] is that for a fluid mixture in which the intermolecular potentials are conformal, there exists an equation of

state which is a scaled version of the equation of state for a single reference substance. There are two scaling parameters for each binary mixture, one for energy and the other for length, and they can be deduced from the appropriate scaling parameters for the pure fluids using the van der Waals mixing rules [4]. Thus, for our case there are six disposable parameters arising from the three binary interactions that can be varied to attempt to describe the experimental data on a ternary system. We have sought for an optimum description of our experimental data on the ternary system by variation of these six parameters using as the single reference equation of state that for methane [10].

3.3 Modified Multiple-Reference Fluid Corresponding States

The basic hypothesis of the multiple-reference fluid corresponding-states model is that instead of seeking to find a hypothetical single fluid that represents the equation of state of a mixture, one seeks to identify a number of pseudo-substances that mix ideally to form the equation of state for the mixture. The advantages of this technique are that it allows the use of several equations of state for the different substances to be employed and can ensure satisfactory representation of the properties of mixtures in the limit of any of the pure components.

Recent studies by Cha *et al.* [7, 8] have shown that for mixtures involving molecules of very different size, the multiple-reference-fluid model benefits from a semi-empirical modification which seeks to improve its representation of the radial distribution function. The modification to the original scheme is characterised by the value of a single parameter denoted by Cha *et al.* as l [7, 8]. For the present purposes, it is sufficient to note that for $l = 0$ the original multiple-reference-fluid model is recovered, while for $l = 1$ a model equivalent to the Lebowitz-Percus-Yevick equation of state is

obtained [7 ,8]. We have sought to represent the experimental data for the ternary system methane-n-hexane-n-tetradecane by means of the modified multiple-reference fluid model. We have not yet sought to optimise the parameters in such a representation but, rather, intend to demonstrate here that even without such an optimisation the model has distinct advantages over the other models examined.

Accordingly, we have first fixed the parameter l for each binary interaction in the system. For methane-hexane we have fixed it at $l = 0$, whereas for the other two interactions we have adopted the value $l = 1$. Next we have fixed the values of the binary interaction parameters for methane-n-hexane at those given in the literature [11], $x_{ij} = 0.97$, $h_{ij} = 1.0$. For the other two binary pairs we have adopted the values $x_{ij} = 1.0$ and $h_{ij} = 1.0$ throughout. With these fixed parameters we have chosen to consider a number of different reference fluids for each of the pseudocomponents in the mixture.

In all of our calculations with this model the reference substance for pseudo-methane has been methane itself [12], whereas for pseudo-n-hexane we have tried both the equation of state for methane [12] and that for n-butane [13] as reference substances. For pseudo-n-tetradecane we have uniformly employed the reference equation of n-butane [13].

4. DISCUSSION

Figures 1 and 2 contain a comparison of the prediction of the Peng-Robinson and one-fluid model with the experimental compositions of the two phases present in the methane-n-hexane-n-tetradecane system as a function of methane mole fraction at a temperature of 348.15 K and 383.15 K. The mole fractions of the other constituents in

the mixture have, of course, been measured but their numerical values are not important for the present discussion.

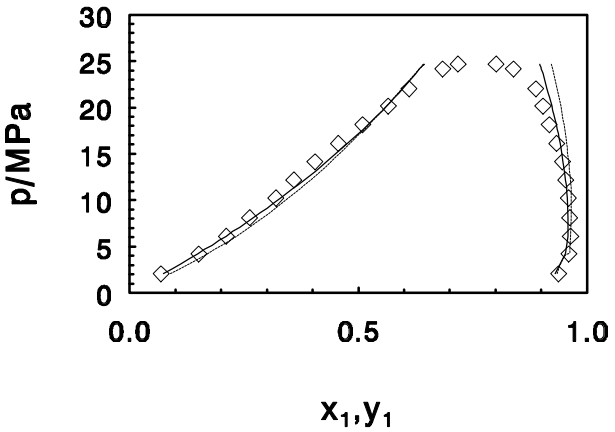

Fig. 1 Comparison of the experimental mole compositions for the ternary system methane-n-hexane-n-tetradecane at 348.15 K with prediction results from the Peng-Robinson e.o.s. and the one-fluid corresponding states model.

◊: experimental points;

ÄÄÄÄ PR, $d_{1,6}$ = 0.0475, $d_{1,14}$ = 0.15, $d_{6,14}$ = 0.02.

- - - - - 1-F, $x_{1,6}$ = 0.97, $x_{1,14}$ = 1.02, $x_{6,14}$ = 1.006, all h_{ij} = 1.

It can be seen that at 348.15 K both models overpredict the methane mole fraction in both phases. They also succeed rather better in the liquid phase than in the gas phase but fail most dramatically near the critical point. As the temperature is increased, the predictions in the liquid phase improve marginally, whereas those in the gas phase become worse. There is very little to choose between the Peng-Robinson and one-fluid models at either temperature.

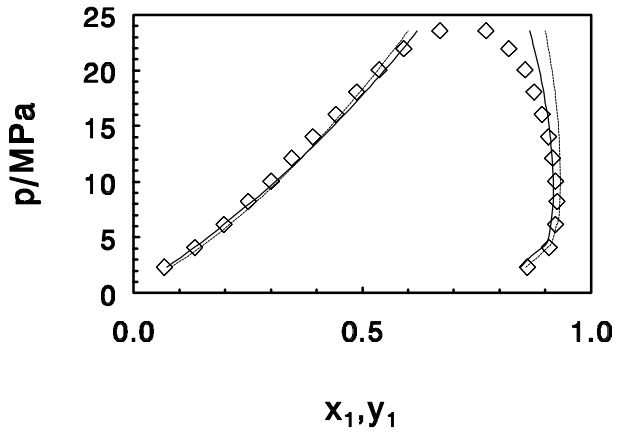

Fig. 2 Comparison of the experimental mole compositions for the ternary system methane-n-hexane-n-tetradecane at 383.15 K with prediction results from the Peng-Robinson e.o.s. and the one-fluid corresponding-states model.

◊: experimental points;

ÄÄÄÄ PR, $d_{1,6}$ = 0.0475, $d_{1,14}$ = 0.15, $d_{6,14}$ = 0.02.

- - - - - 1-F, $x_{1,6}$ = 0.97, $x_{1,14}$ = 1.02, $x_{6,14}$ = 1.006, all h_{ij} = 1.

Figures 3 and 4 show comparison of the results for the same two models with the measurements of density. Here we see that the one-fluid model underestimates the vapor phase density but overestimates the liquid phase density, while the Peng-Robinson equation has predictions that intersect the experimental data in both phases. These characteristics pertain to both temperatures and the predictions of density are rather poor, particularly in the liquid phase.

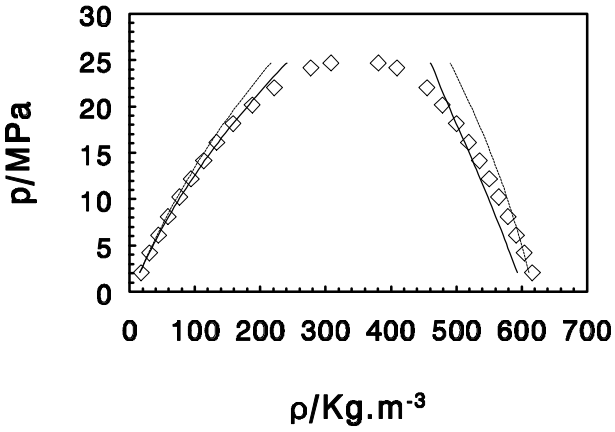

Fig.3 Comparison of the experimental densities for the ternary system methane-n-hexane-n-tetradecane at 348.15 K with prediction results from the Peng-Robinson e.o.s. and the one-fluid corresponding-states model.

◊: experimental points;

ÄÄÄÄ PR, $d_{1,6}$ = 0.0475, $d_{1,14}$ = 0.15, $d_{6,14}$ = 0.02.

- - - - - 1-F, $x_{1,6}$ = 0.97, $x_{1,14}$ = 1.02, $x_{6,14}$ = 1.006, all h_{ij} = 1.

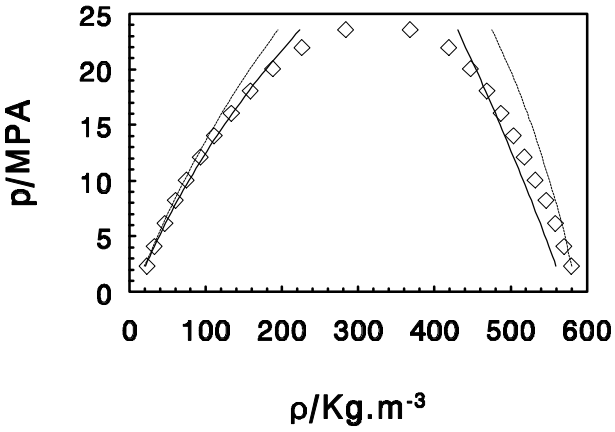

Fig. 4 Comparison of the experimental densities for the ternary system methane-n-hexane-n-tetradecane at 383.15 K with prediction results from the Peng-Robinson e.o.s. and the one-fluid corresponding-states model.

◊: experimental points;

ÄÄÄÄ PR, $d_{1,6}$ = 0.0475, $d_{1,14}$ = 0.15, $d_{6,14}$ = 0.02.

- - - - - 1-F, $x_{1,6}$ = 0.97, $x_{1,14}$ = 1.02, $x_{6,14}$ = 1.006, all h_{ij} = 1.

Figures 5 and 6 contain comparisons of the same experimental data for phase composition and densities respectively with predictions of the multiple-reference-fluid model using a variety of different reference equations for the pseudo-components. Figure 5 contains the comparison for the composition of the phases at 383.15 K. For these calculations in which pseudo-n-hexane is represented by methane, the predictions of the phase compositions are essentially as good as those for the Peng-Robinson and one-fluid model. When pseudo-n-hexane is represented by butane, the predictions are significantly worse. Figure 6 contains the comparison of the same two models with the

experimental density data. Again, we see that the use of the methane equation of state as a reference for n-hexane has considerably better results than when n-butane is used as the reference. More importantly, for practical applications, we note that the multiple-reference-fluid model yields very much better predictions of the density of the system than any other model tried, a result achieved without a complete optimisation of parameters.

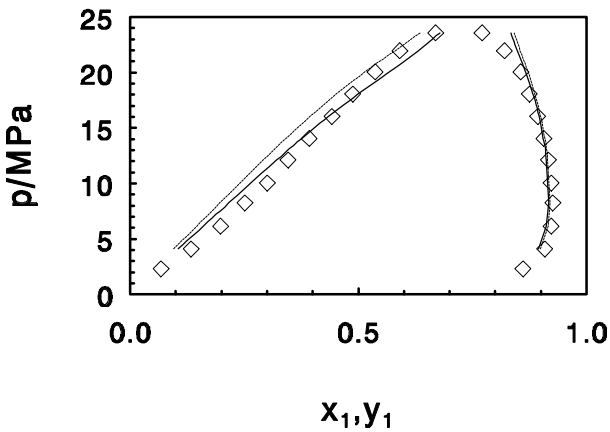

Fig. 5 Comparison of the experimental mole compositions for the ternary system methane-n-hexane-n-tetradecane at 383.15 K with prediction results from the modified multireference fluid corresponding-states model, using two different reference fluids for pseudo-hexane (see text for values of binary interaction parameters and other reference fluid substances).

◊: experimental points; ÄÄÄÄ reference fluid: methane; - - - - - reference fluid: n-butane

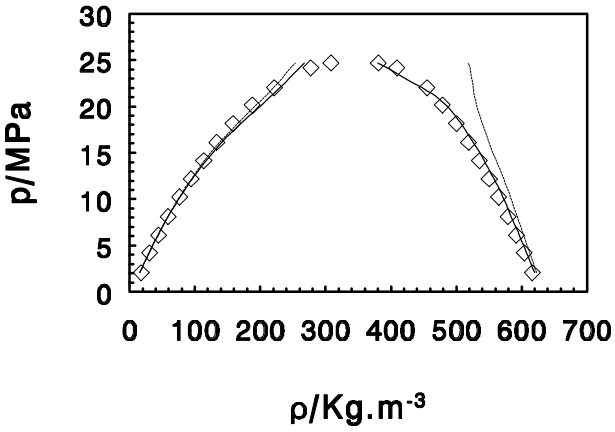

Fig. 6 Comparison of the experimental densities for the ternary system methane-n-hexane-n-tetradecane at 348.15 K with prediction results from the modified multireference fluid corresponding-states model, using two different reference fluids for pseudo-hexane (see text for values of binary interaction parameters and other reference fluid substances).

◊: experimental points; ÄÄÄÄ reference fluid: methane; - - - - - reference fluid: n-butane

5. CONCLUSIONS

Extensive new experimental data for the phase compositions and densities in a ternary mixture of hydrocarbons at elevated pressures have been obtained. The measurements have been used to demonstrate that relatively simple thermodynamic models can give an adequate description of the phase compositions except near the critical point. However, more complex thermodynamic models involving a number of reference substances are required to secure a good description of both the phase behavior and the density simultaneously.

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