Thermodynamics of Petroleum Mixtures Containing Heavy Hydrocarbons. 1. Phase Envelope Calculations by Use of the Soave–Redlich–Kwong Equation of State

Karen Schou Pedersen,[†] Per Thomassen,[‡] and Aage Fredenslund*[†]

Instituttet for Kemiteknik, Danmarks Tekniske Højskole, DK-2800 Lyngby, Denmark, and STATOIL, Den Norske Stats Oljeselskab a.s., N-4001 Stavanger, Norway

Analytical data for various North Sea oils and gas condensates have been measured. The data include compositional measurements, TBP analyses, molecular weights, PNA analyses and specific gravities of most fractions. In addition, some dew and bubble points have been measured for each mixture establishing a few points on the phase envelopes. The corresponding phase envelopes are computed with the SRK (Soave–Redlich–Kwong) equation of state. Different methods of representing the heavy components by subfractions and different methods for computing the properties of the subfractions (T_c, P_c, and ω) are compared. It is found that the phase envelopes can be accurately represented if the TBP residue ($C_{21}+$) is split into approximately 20 subfractions and the C_6–C_{20} interval is treated as one subfraction for each carbon number. A logarithmic dependence of the mole fraction against carbon number may be assumed for the residue. The best results are obtained by using the Cavett relations for T_c and P_c of the subfractions and the Lee–Kesler relations for ω. The results are improved when the paraffinic, naphthenic, and aromatic parts of each subfraction are treated separately rather than lumped. No "matching" or "tuning" to experimental phase equilibrium data is needed.

1. Introduction

Phase equilibrium computations for mixtures containing heavy hydrocarbon fractions are usually regarded as being difficult and mysterious, somewhat reminiscent of the methods of the alchemists. Lack of experimental data for these mixtures and the necessity of representing the highly complex heavy fractions by means of relatively few model compounds or parameters are some of the main reasons for this.

The Norwegian State Oil Company, STATOIL, has measured a large amount of experimental analytical and phase equilibrium data for different North Sea oils. The aim of this project is to evaluate and develop procedures for equation of state descriptions of phase equilibria in such oils which contain heavy hydrocarbon fractions. The project is necessarily empirical in nature, both because of the unknown nature of the heavy hydrocarbons and because the simple equations of state, at least in their original forms, were not intended for components which differ much from sphericity. The difficulties of representing complex hydrocarbon mixtures have resulted in simulation procedures where the EOS parameters are adjusted to match the saturation points (Coats and Smart, 1982; Whitson, 1982; Wilson et al., 1978). It has been our goal to develop a purely predictive method and in this contribution we describe phase envelope calculations.

A phase envelope program (TERM) has been developed by Michelsen (1980, 1982). The program can treat mixtures of H_2O, N_2, CO_2, H_2S, and hydrocarbons from C_1 to C_9. This program has been extended to mixtures containing hydrocarbons heavier than C_9. The vapor–liquid equilibria are represented in TERM by either the Soave–Redlich–Kwong (Soave, 1972) or the Peng–Robinson (1976) equations of state. The necessary input parameters are a critical temperature and pressure and an acentric factor for each component and a binary interaction parameter between each pair of components. Since it is

generally only possible to make a component analysis for the lighter components, one is left with the problem of how to characterize the heavy fraction. Instead of an analysis for pure components, it has been split into a number of subfractions with different mean boiling points by a distillation process.

Acentric factors and critical properties of each subfraction have then been estimated from specific gravity, molecular weight, and boiling points using different correlations as described below. However, the heaviest fraction, i.e., the one left in the flask when the distillation is finished, probably contains a large number of different hydrocarbons, and the properties of these may vary considerably. This causes problems because the final result is sensitive to even minor changes in the estimated critical properties of the latter fraction. Various procedures have been tried and the calculated phase envelopes have been compared with experimental results.

2. Data

2.1. Analytical Data. For a given petroleum mixture, data obtained by gas chromatographic (GC) analysis, a true boiling point (TBP) distillation process, and measurements of molecular weights are put together to give a molar composition. The C_4 and C_5 fractions are analyzed for both normal and isoparaffins while no such distinction is made for the heavier hydrocarbons, i.e., the C_6+ fraction. The latter is split into what is roughly C_6, C_7, and C_8 fractions, etc. by a TBP distillation. Measurements of specific gravity, molecular weight, and refractive index are carried out on each boiling point fraction. STATOIL's distillation equipment permits separation into carbon number (C_N) fractions up to about C_{20}, where the process must be stopped to avoid cracking. The remaining part, the $C_{21}+$ fraction, might be further fractionated in a GC, but at present STATOIL does not consider the method reliable enough for quantitative analyses. For some of the samples there exists a PNA analysis which is a determination of the content of paraffins, naphthenes, and aromatics in each fraction. The analysis is based on measurements of refractive index and density (Nes and Western, 1951).

[†] Instituttet for Kemiteknik.
[‡] STATOIL.

The analytical data which have been used in this work are listed in the supplement. Note the supplement includes data for both heavy oil systems and gas condensates.

2.2. Dew and Bubble Point Data. Saturation pressures for hydrocarbon mixtures are determined at constant temperature in high-pressure steel vessels. Both dew and bubble points are determined visually at equilibrium conditions.

2.2.1. Dew Points. Dew points in this study are determined in a Sloan type gas condensate cell developed at Elf research center, Boussens. The main features of this cell are its large volume, high working pressure, low liquid readability (less than 0.1 cm³), and dual piston type operation. The cell is fitted with two sapphire windows in the bottleneck part of the cell which permit observations of the hydrocarbon system. The pressure of the recombined hydrocarbon system can be varied via a double piston mercury pump and the temperature can be controlled to within ±0.1 °C in the air bath surrounding the cell.

The hydrocarbon system is subjected to a constant mass expansion and at each pressure point the system in equilibrium is inspected for two phases. The pressure at which trace amounts of liquid are formed is noted as the dew point of the system.

2.2.2. Bubble Points. Bubble points of hydrocarbon mixtures are determined in much the same way as dew points, although the equipment used is different. We use a Ruska, visual PVT cell, submerged in a silicone oil bath for temperature control (±0.1 °C). The volume of this cell can be controlled with mercury via a 250-cm³ Ruska mercury pump. The cell is charged with the hydrocarbon mixture and subjected to a constant mass expansion experiment. The total volume of the hydrocarbon mixture is determined at each pressure point via the mercury pump readings. The hydrocarbon system can be inspected through the cell window and we can see the last bubble of gas go into solution. The pressure at which this occurs is the bubble point of the system.

The bubble point is also determined from a pressure vs. volume plot of the hydrocarbon mixture. The change from two phases to one phase can clearly be seen as a discontinuity in the P–V curve.

3. Correlations for Characterization of the Heavy Fraction

To use an equation of state like the Soave–Redlich–Kwong (SRK) or the Peng–Robinson (PR) equations on a petroleum mixture, the critical temperature, T_c, critical pressure, P_c, and the acentric factor, ω, are needed for each component. A number of pure-component data are available (Reid et al., 1977), but since the heavy fraction is normally split in boiling point fractions, each of which may comprise many different components, one is instead obliged to estimate the necessary parameters from the properties which have been measured on each fraction. Specific gravity, viscosity, and molecular weight can easily be measured and the boiling range is known from the distillation process. A number of correlations have been published which convert this information into critical properties.

1. Lee–Kesler Correlations (Kesler and Lee, 1976).

$$T_c = 341.7 + 811SG + (0.4244 + 0.1174SG)T_B +$$
$$(0.4669 - 3.2623SG) \times 10^5/T_B \quad (1)$$

$$\ln P_c = 8.3634 - 0.0566/SG -$$
$$(0.24244 + 2.2898/SG + 0.11857/SG^2) \times 10^{-3}T_B +$$
$$(1.4685 + 3.648/SG + 0.47227/SG^2) \times 10^{-7}T_B^2 -$$
$$(0.42019 + 1.6977/SG^2) \times 10^{-10}T_B^3 \quad (2)$$

$$\omega = (\ln P_{Br} - 5.92714 + 6.09648/T_{Br} +$$
$$1.28862 \ln T_{Br} - 0.169347T_{Br}^6)/(15.2518 - 15.6875/T_{Br}$$
$$- 13.4721 \ln T_{Br} + 0.43577T_{Br}^6) \quad \text{(for } T_{Br} < 0.8) \quad (3)$$

$$\omega = -7.904 + 0.1352K - 0.007465K^2 + 8.359T_{Br} +$$
$$(1.408 - 0.01063K)/T_{Br} \quad \text{(for } T_{Br} > 0.8) \quad (4)$$

$$MW = -12272.6 + 9486.4SG + (4.6523 -$$
$$3.3287SG)T_B + (1 - 0.77084SG - 0.02058SG^2) \times$$
$$(1.3437 - 720.79/T_B) \times 10^7/T_B + (1 - 0.80882SG +$$
$$0.02226SG^2) \times (1.8828 - 181.98/T_B) \times 10^{12}/T_B^3 \quad (5)$$

The boiling point, T_B, and the critical temperature, T_c, are in degrees Rankine and the specific gravity, SG, in 60 °F/60 °F. The critical pressure, P_c, is in psia. $T_{Br} = T_B/T_c$ and $P_{Br} = P_B/P_c$ where P_B is the pressure where T_B has been measured. K is the Watson characterization factor which equals $T_B^{1/3}/SG$. MW is the molecular weight.

2. Winn Relations (Winn, 1957; Sim and Daubert, 1980).

$$T_c = \frac{\exp[4.2009T_B^{0.08615}SG^{0.04614}]}{1.8} \quad (6)$$

$$P_c = 6.1483 \times 10^{12}T_B^{-2.3177}SG^{2.4853} \quad (7)$$

$$MW = 5.805 \times 10^{-5}\left[\frac{T_B^{2.3776}}{SG^{0.9371}}\right] \quad (8)$$

T_B and T_c are in K, SG in 15 °C/15 °C, and P_c in Pa.

3. Cavett (1964) Relations.

$$T_c = 768.071 + 1.7134T_{50} - 0.10834 \times 10^{-2}T_{50}^2 +$$
$$0.3889 \times 10^{-6}T_{50}^3 - 0.89213 \times 10^{-2}T_{50}API + 0.53095 \times$$
$$10^{-6}T_{50}^2API + 0.32712 \times 10^{-7}T_{50}^2API^2 \quad (9)$$

$$\log P_c =$$
$$2.829 + 0.9412 \times 10^{-3}T_{50} - 0.30475 \times 10^{-5}T_{50}^2 +$$
$$0.15141 \times 10^{-8}T_{50}^3 - 0.20876 \times 10^{-4}T_{50}API +$$
$$0.11048 \times 10^{-7}T_{50}^2API + 0.1395 \times 10^{-9}T_{50}^2API^2 -$$
$$0.4827 \times 10^{-7}T_{50}API^2 \quad (10)$$

where

$$API = 141.5/SG - 131.5 \quad (11)$$

The critical temperature, T_c, and the mid-volume boiling point of the fraction, T_{50}, are given in °F, P_c in psia, and SG in 60 °F/60 °F.

Erbar (1977) has used these relations and a PNA analysis to determine the critical point of the paraffinic, naphthenic, and aromatic components of each fraction and these parameters are then combined to a T_c and a P_c of the total fraction

$$T_c = X_PT_{cP} + X_NT_{cN} + X_AT_{cA} \quad (12)$$

$$P_c = X_PP_{cP} + X_NP_{cN} + X_AP_{cA} \quad (13)$$

X_P, X_N, and X_A are the molar fractions of P, N, and A in the total fraction.

The following relations are used for the specific gravities of the P, N, and A components

$$SG_P = 0.5892 + 0.5446 \times 10^{-3}T_{50} - 0.5446 \times 10^{-6}T_{50}^2 \quad (14)$$

$$SG_N = 0.7224 + 0.2817 \times 10^{-3}T_{50} - 0.1902 \times 10^{-6}T_{50}^2 \quad (15)$$

$$SG_A = 0.9103 - 0.1816 \times 10^{-3}T_{50} - 0.1575 \times 10^{-6}T_{50}^2 \quad (16)$$

4. Edminster's (1958) Acentric Factor.

$$\omega = \frac{3}{7}\left[\frac{\log P_c}{T_c/T_B - 1}\right] - 1 \qquad (17)$$

where P_c is in atmospheres.

4. Binary Interaction Parameters

To use the SRK or the PR equations on a mixture it is necessary to correct for binary interactions between different components by means of empirically derived interaction parameters. For interactions between hydrocarbons these are set to zero. For interactions between nonhydrocarbons and between hydrocarbons and nonhydrocarbons the values in Reid et al. (1977, p 77) may be used.

5. Estimation of the PNA Distribution

In those cases where no PNA analysis is available, the refractive index of each fraction is estimated from the density and the boiling point (Riazi and Daubert, 1980), and an approximate PNA distribution is then determined as described in section 2.

6. Characterization of the Residue of the TBP Distillation

As explained in section 2, the composition of the oils is given for each component up to C_6 and, by distillation, for each carbon number from C_6 to approximately C_{20}.

Most naturally occurring hydrocarbon mixtures contain a heavy fraction which cannot be split by a standard TBP distillation. In the mixtures which have been considered, the latter fraction constitutes up to 10 mol % of the total mixture. Since no boiling point is available, it is difficult to characterize this fraction. Various attempts are described below.

6.1. Attempts to Characterize the TBP Residue as One Single Fraction.
Measurements of specific gravity, SG, and of the molecular weight, MW, are often available for the heaviest fraction. A boiling point can, therefore, be estimated from either eq 5 or 8. Once T_B and SG have been determined, the correlations for T_c, P_c and ω given in section 3 can be applied to the fraction (cf. methods 1 and 2 of section 7).

To get an idea about the accuracy of eq 5 and 8 for the actual mixtures, a comparison has been made between the experimental boiling points (see supplement) and those determined from the two equations. It turns out that eq 8 generally leads to better results than eq 5.

6.2. Division of the TBP Residue into Subfractions.
Since the fraction left in the flask when the distillation is stopped may contain a large number of components covering a wide range in boiling points, it is perhaps too optimistic to believe that it can be properly characterized as one single fraction and it has therefore been tried to treat it as a number of subfractions. We use up to 20 $C_{21}+$ fractions.

6.2.1. Molar Composition.
It has been suggested (Wilson et al., 1978) that naturally occurring hydrocarbon mixtures should exhibit a logarithmic relationship between the mole fraction, z_N, and the corresponding carbon number, C_N, for $C_N \geq 7$

$$C_N = A + B \ln (z_N) \qquad (18)$$

A and B are constants. If that is the case, it means that an approximate composition of the TBP residue can be achieved from the analysis for the lighter fractions. If the constants, A and B, of eq 18 are determined by a least-squares fit to the experimental data, the results can be used to calculate the molar content of each of the heavier fractions by extrapolation.

Various ways may be employed to check whether the final result is reasonable. The subfractions should sum
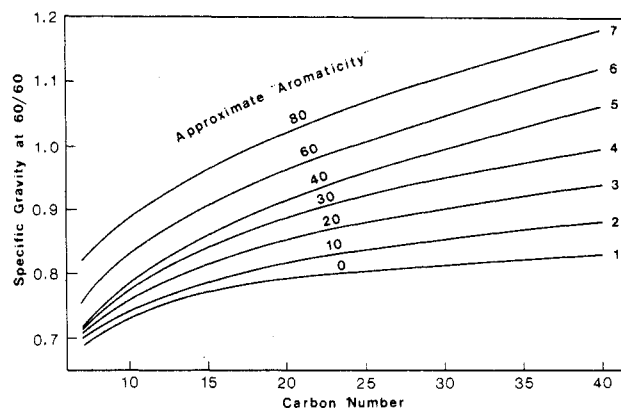

Figure 1. Yarborough's curves relating specific gravity to carbon number fraction which allow for different molecular types of hydrocarbons (Yarborough, 1978).

up to a fraction which is identical with the original one. This means that not only the quantity but also the specific gravity and average molecular weight should be right.

It is not obvious at which carbon number the compositional extrapolation based on eq 18 should be terminated. One possibility could be to continue until the sum of the calculated heavy subfractions equals the total TBP residue. However, it turns out that the sum goes asymptotically towards a limit and that this limit in most cases is smaller than the measured fraction.

C_{40} (methods 3–4 of section 7) and C_{100} (methods 5–7 of section 7) have been tried as the heaviest carbon number fraction considered. If the measured TBP residue is larger than the calculated one when using the A and B values determined from the fit to the experimental data, A and B are changed to obtain agreement between the two quantities. The z_N value (eq 18) found for the heaviest fraction which was distilled off is kept as the starting point for the extrapolation.

For the heavy oil systems a different procedure for estimation of the molar composition of the TBP residue has been tried (method 8 of section 7). The TBP distillation curve is extrapolated to 100% distilled off by fitting a 5th degree polynomium to the experimental TBP data plus the following two artificially generated data points

$$T_{80w\%} = 10^{-0.2127} T_{50w\%}{}^{1.103} SG^{-0.6495} \qquad (19)$$

$$T_{100w\%} = 10^{1.083} T_{50w\%}{}^{0.7097} SG^{0.6717} \qquad (20)$$

$T_{50w\%}$, and $T_{80w\%}$, and $T_{100w\%}$ are the temperatures in K at which 50, 80, and 100 wt % have been distilled off. Relation 19 is founded on experimental TBP data, partly from Aalund (1976), partly supplied by STATOIL, whereas the extrapolation to 100 wt % expressed in eq 20 is purely empirical. The TBP curve is related to carbon number fractions as explained in section 6.2.4.

6.2.2. Specific Gravity.
A measured average specific gravity (SG) of the TBP residue may be available. If the residue is treated as a number of subfractions (refer to section 6.2.1) the specific gravity of each of these must be estimated. SG is mainly governed by the PNA distribution. The aromatic compounds are heavier than the naphthenes and the naphthenes are heavier than the paraffins. Yarborough (1978) has suggested that in a naturally occurring hydrocarbon mixture the deviation from paraffinic behavior can be expressed as a smooth function of carbon number, and he names this deviation, the "aromaticity". In Figure 1 (from Yarborough, 1978) the specific gravity is shown against carbon number for various "aromaticities". The suggestion is then that in a certain mixture all the carbon number fractions should follow the

same curve. It has been tried out on a number of STAT-OIL's compositions. The general trend seems to be curves more flat than those of Figure 1. Nevertheless, since no other information is available about the specific gravity of the heavy hydrocarbons it has been tried to use the curves of Figure 1.

1. Fit to *SG* of the TBP Residue. A fitting procedure is established which determines the "aromaticity" (refer to Figure 1) which brings the specific gravity in agreement with the measured value. It turns out that this method in most cases leads to a discontinuity in *SG* when passing from the carbon number fractions for which measured values are available to those for which the specific gravity must be estimated. This was of generating *SG* data is used in method 3 of section 7.

2. Fit to the "Aromaticity" of the Carbon Number Fractions for Which *SG* Data Are Available. To avoid the above-mentioned discontinuity in *SG*, another approach has been tried. Based on Figure 1 and the *SG* data which are available for the TBP fractions, an average "aromaticity" of these fractions is determined. It is done by minimizing the sum of the squared deviations from the measured values. The same "aromaticity" is then used to generate the *SG* values for the heavier fractions. This generally leads to a specific gravity of the total fraction which is above the measured value. In method 4 of section 7 the specific gravities of the heaviest fractions are generated in this way.

3. *SG* Data Generated by a Logarithmic Fit against Carbon Number. As explained in section 6.2.1, the fractionation is sometimes extended to C_{100}, and in those cases the curves of Figure 1 cannot be used because they stop at C_{40}. The *SG* data for the lighter fractions could suggest a logarithmic dependence of SG against carbon number. In the latter cases, therefore, the specific gravities of the heavy fractions are generated from the following equations (refer to methods 5–8 of section 7)

$$SG(C_N) - SG(C_{N_0}) = D(\ln (C_N) - \ln (C_{N_0})) \quad (21)$$

$$\sum_{C_N=C_{N_0+1}}^{C_{N_{max}}} z_N MW(C_N) / \sum_{C_N=C_{N_0+1}}^{C_{N_{max}}} z_N MW(C_N) / SG(C_N) =$$
$$SG \text{ of TBP residue} \quad (22)$$

D is a constant, $SG(C_N)$ is the specific gravity, and $MW(C_N)$ is the molecular weight of the carbon number fraction, C_N. Equation 21 expresses the logarithmic dependence of *SG* against carbon number and that the starting point should be the specific gravity, $SG(C_{N_0})$, of the heaviest carbon number fraction for which a measured value is available.

4. P, N, and A Specific Gravities. When Erbar's method of generating T_c and P_c (see eq 9–13) is used, a specific gravity must be determined for the P, N, and A components of each fraction. Erbar suggests relations 14 to 16, but it turns out that these relations are only suitable up to about C_{11}. For heavier hydrocarbons, these relations predict specific gravities which decrease with increasing carbon number, while in reality *SG* is an increasing function of carbon number. The P, N, and A specific gravities, SG_P, SG_N, and SG_A, are instead estimated as follows from the specific gravity, *SG*, of the total fraction (methods 7 and 8 of section 7)

$$SG_A = 1.16 SG_N \quad (23)$$

$$SG_N = 1.12 SG_P \quad (24)$$

$$SG = X_P SG_P + X_N SG_N + X_A SG_A \quad (25)$$

X_P, X_N, and X_A are the molar fractions of P, N, and A in the total carbon number fraction.
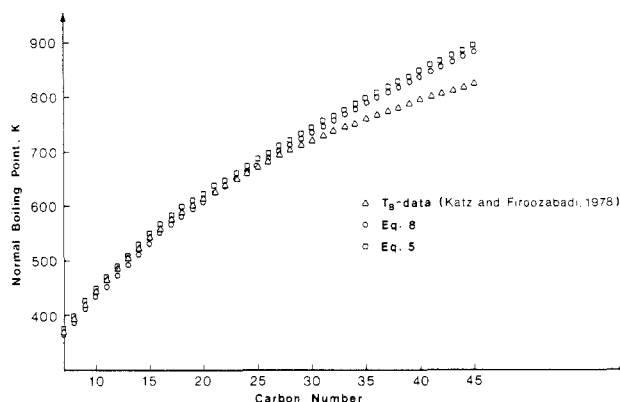
Figure 2. Boiling points for hydrocarbon fractions.

6.2.3. Molecular Weight. If the boiling point is known for a certain C_N fraction, it is not necessary to know the molecular weight to perform the phase envelope calculations. On the other hand, the molecular weight of a heavy C_N fraction is almost independent of the PNA distribution, and the measured molecular weight of the TBP residue can, as explained below, be used as an overall check of the fractionation procedure (refer to section 6.2.1). An approximate molecular weight, MW, of a given $C_{21}+$ fraction can be obtained from the carbon number, C_N, as follows (Katz and Firoozabadi, 1978)

$$MW = -4.0 + 14.0 C_N \quad (26)$$

When the TBP residue has been divided into subfractions, an average molecular weight, MW, of the total fraction can be calculated

$$MW = \sum_{C_N=C_{N_0+1}}^{C_{N_{max}}} z_N MW(C_N) / \sum_{C_N=C_{N_0+1}}^{C_{N_{max}}} z_N \quad (27)$$

and a comparison can be made with the experimentally determined molecular weight.

6.2.4. Boiling Points. Katz and Firoozabadi (1978) have published boiling points, specific gravities, and molecular weights of petroleum fractions up to C_{45}. Their T_B values may be used for the carbon number fractions C_7–C_{45}. Since no data are available for the $C_{46}+$ fraction, it has been checked whether it is reasonable to use either eq 5 or 8 to generate T_B of heavy hydrocarbons up to C_{45}.

The specific gravities and molecular weights of Katz and Firoozabadi are used, and subsequently the calculated boiling points are compared with those of this reference. The results are shown in Figure 2. Both equations lead to boiling points which are above the experimental values for the $C_{30}+$ fractions. To find a T_B correlation which is more suitable for the heavy hydrocarbons, the boiling points, molecular weights, and specific gravities of Katz and Firoozabadi for the C_{31}–C_{45} fractions were fitted to the following expression

$$MW = a \left[\frac{T_B^{\ b}}{SG^{0.9371}} \right] \quad (28)$$

A least-squares fit gives $a = 2.4519 \times 10^{-7}$ and $b = 3.2156$. The result is thus

$$MW = 2.4519 \times 10^{-7} \left[\frac{T_B^{3.2156}}{SG^{0.9371}} \right] \quad (29)$$

where T_B is measured in K and *SG* in 15 °C/15 °C.

If the molar composition of the TBP residue has been estimated from eq 18, the boiling points of the $C_{46}+$ fractions are found from eq 29, while the weight based

TBP curve is related to carbon numbers by assuming 6 K boiling point intervals per carbon number for each fraction heavier than C_{45}.

7. Results of the Phase Envelope Calculations

The methods which have been tried are summarized below. The methods 1–8 have in common that the calculations are based on the SRK equation of state and that T_c, P_c, and ω of the nonhydrocarbons and of C_1–C_6 are found from Reid et al. (1977). T_c, P_c, and ω for each of the carbon number fractions which have been split by a TBP distillation (i.e., C_7 to $\sim C_{20}$) are obtained from correlations in SG and T_B as specified below. Experimental T_B and SG data for each fraction are used.

Method 1. T_c, P_c, and ω for $C_N \geq 7$: eq 1–4 (Lee–Kesler). The TBP residue is treated as one fraction. The measured SG is used and T_B is found from eq 5.

Method 2. T_c and P_c for $C_N \geq 7$: eq 6 and 7 (Winn). ω for $C_N \geq 7$: eq 3 or 4 (Lee–Kesler). The TBP residue is treated as one fraction. The measured SG is used, and T_B is found from eq 8.

Method 3. T_c and P_c for $C_N \geq 7$: eq 6 and 7 (Winn). ω for $C_N \geq 7$: eq 3 or 4 (Lee–Kesler).

The TBP residue is treated as a number of subfractions. A logarithmic dependence of mole fraction against carbon number is assumed. C_{40} is the heaviest carbon number fraction considered. The specific gravities of the subfractions are found from the "aromaticity" curve of Figure 1 which brings SG of the total fraction in agreement with the measured value. The boiling points of Katz and Firoozabadi are used.

Method 4. T_c and P_c for $C_N \geq 7$: eq 6 and 7 (Winn). ω for $C_N \geq 7$: eq 3 or 4 (Lee–Kesler).

The TBP residue is treated as a number of subfractions. A logarithmic dependence of mole fraction against carbon number is assumed. C_{40} is the heaviest carbon number fraction considered. The average "aromaticity" of the fractions which were split by a distillation is determined from Figure 1. The specific gravities of the heavier fractions are found by assuming the same "aromaticity". The boiling points of Katz and Firoozabadi are used.

Method 5. T_c and P_c for $C_N \geq 7$: eq 6 and 7 (Winn). ω for $C_N \geq 7$: eq 3 or 4 (Lee–Kesler).

The TBP residue is treated as a number of subfractions. A logarithmic dependence of mole fraction against carbon number is assumed. C_{100} is the heaviest carbon number fraction which can be included. The specific gravities of the subfractions are found by a logarithmic fit. The starting point is the specific gravity of the heaviest fraction which was distilled off. The calculated SG of the total fraction equals the experimental value (refer to eq 21 and 22). The T_B's of Katz and Firrozabadi are used up to C_{45}. For heavier fractions T_B is found from eq 29.

Method 6. T_c and P_c for $C_N \geq 7$: eq 9 and 10 (Cavett). ω for $C_N \geq 7$: eq 3 or 4 (Lee–Kesler). TBP residue: as method 5.

Method 7. T_c and P_c for $C_N \geq 7$: eq 9 to 13 (Cavett and Erbar). ω for $C_N \geq 7$: eq 3 or 4 (Lee–Kesler). The TBP residue is treated as a number of subfractions as explained under method 5.

For all the C_7+ fractions the PNA distribution is used. T_c, P_c, and ω of the total fractions are found by a summation on molar basis of the values found for the P, N, and A parts (see eq 11 and 12). The P, N, and A specific gravities are found from eq 23 to 25.

Method 8. T_c and P_c for $C_N \geq 7$: eq 9 to 13 (Cavett and Erbar). ω for $C_N \geq 7$: eq 3 or 4 (Lee–Kesler).

The TBP residue is treated as a number of subfractions. The molar composition is found by extrapolation of the
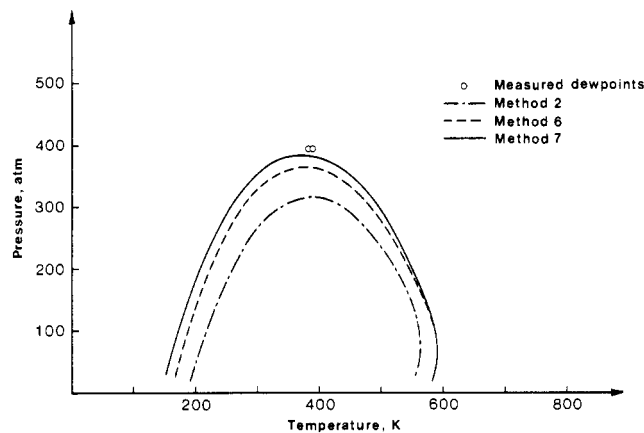
Figure 3. Calculation of phase envelopes for sample no. 1.

TBP curve using eq 19 and 20. Up to C_{45}, the T_B values of Katz and Firoozabadi are used while a 6 K increase in boiling point per carbon number is assumed for the heavier fractions. The procedure explained under method 5 is used for the specific gravities. The PNA distribution is taken into consideration as explained under method 7.

Method 9. This procedure was developed by Robinson (1981) and is fully described in this reference. It is based on the Peng–Robinson equation of state. P_c is found from a group contribution correlation and ω is assumed to be a linear function of carbon number. T_c is determined from eq 17, where T_B is found from a 5th degree polynomium in carbon number. Binary interaction parameters different from zero are used for light paraffin–nonparaffin hydrocarbon pairs. As the results for T_B become unreasonably large for hydrocarbons heavier than C_{50}, the method has only been tried for gas condensate systems.

PNA analyses are available for samples no. 1–3 and 10–12. For the remaining samples, the results obtained with methods 7 and 8 are based on estimated PNA distributions as explained in section 2.

Phase envelope calculations have been made for mixtures no. 1–12 listed in the supplement. Methods 1–5 have not been tried for samples 2 and 10–12.

The supplement gives a survey of results generated by methods 7 and 8 comprising mole fractions, specific gravities, molecular weights, boiling points, critical temperatures and pressures, and acentric factors.

A comparison between experimental and calculated dew and bubble points is made in Table I. Figure 3 shows the phase envelopes calculated for sample no. 1 (a gas condensate) using methods, 2, 6, and 7.

In methods 1 and 2 the measured molecular weight of the TBP residue is used directly. In the other methods, a molar composition of the TBP residue is estimated. That means that a molecular weight of the total fraction can be calculated (refer to eq 27). Table II lists measured and calculated molecular weights.

To get an idea of the influence of the TBP residue on the phase behavior, phase envelopes were calculated for samples no. 1 and 3–9 neglecting the TBP residue. T_c and P_c were determined from eq 6 and 7 and ω from eq 3 or 4 (see method 2). The resulting dew and bubble points are listed in Table III. The results should be compared with those of method 2 in Table I.

A few other phase envelope calculations have been made. It was tried to use eq 17 for ω instead of the eq 3 and 4. For the lighter fractions it makes little difference while for the heaviest fractions where T_c/T_B comes close to 1, relation 17 predicts acentric factors which appear unreasonably large.

Table I. Experimental and Calculated Dew and Bubble Points

compn no.	exptl dew or bubble point P, atm	exptl dew or bubble point T, K	calcd dew or bubble point pressure at temp of the expt — method 1 P, atm	method 1 % dev[a]	method 2 atm	method 2 % dev	method 3 atm	method 3 % dev	method 4 atm	method 4 % dev	method 5 atm	method 5 % dev	method 6 atm	method 6 % dev	method 7 atm	method 7 % dev	method 8 atm	method 8 % dev	method 9 atm	method 9 % dev
1	392.8	384.3	314.3	-20.0	330.1	-16.0	347.3	-11.6	427.7	8.9	343.9	-12.4	362.6	-7.7	383.2	-2.4			360.9	-8.1
1	392.8	392.1	314.0	-20.1	327.8	-16.5	348.3	-11.4	429.6	9.4	344.8	-12.1	361.6	-7.9	381.3	-2.9			361.7	-7.9
2	155.8	303.2											134.8	-13.5	142.1	-8.8	142.4	-8.6		
2	200.4	373.2											183.3	-8.5	191.4	-4.5	192.6	-3.9		
2	217.2	423.2											202.9	-6.6	210.8	-2.9	212.3	-2.3		
3	157.3	340.9	134.2	-14.7	114.2	-27.4	198.4	26.1	242.3	54.0	124.7	-20.7	148.2	-5.8	154.1	-2.0			132.4	-15.8
4	259.6	363.7	214.6	-17.3	222.3	-14.4	223.8	-13.8	223.8	-13.8	223.5	-13.9	245.4	-5.5	245.4	-5.3			211.8	-18.4
5	184.4	387.6	135.0	-26.8	161.3	-12.5	162.2	-12.0	161.2	-12.6	160.0	-13.2	168.2	-8.8	175.3	-5.0	175.1	-5.1		
6	241.1	345.4	130.0	-46.1	182.6	-24.3	197.6	-18.0	203.3	-15.7	195.7	-18.8	207.5	-13.9	221.8	-8.0	226.8	-5.9		
7	232.9	351.0	143.4	-38.4	184.1	-21.0	189.7	-18.5	191.0	-18.0	185.4	-20.4	203.9	-12.5	212.0	-9.0	213.4	-8.4		
8	187.5	346.2	121.4	-35.3	162.2	-13.5	171.0	-8.8	173.6	-7.4	168.2	-10.3	182.3	-2.8	192.0	2.4	193.4	3.1		
9	206.8	346.2	119.2	-42.4	163.3	-21.0	173.4	-16.2	176.9	-14.5	172.8	-16.4	185.6	-10.3	196.3	-5.1	198.9	-3.8		
10	357.3	394.2											339.8	-4.9	354.4	-0.8			309.0	-16.3
10	369.1	303.2											314.5	-14.8	332.5	-9.9			264.4	-24.8
11	351.4	394.2											335.7	-4.5	352.4	0.3			322.9	-8.1
12	247.2	366.5											227.3	-8.1	239.3	-3.2	242.3	-2.0		

a % dev = [(calcd pressure) − (exptl pressure)]/(exptl pressure) × 100%.

The calculations of methods 7 and 8 have been repeated using the PR equation of state instead of the SRK equation. Generally the PR equation predicts lower dew and bubble points than the SRK equation, i.e., pressures which deviate more from the experimental values than those found with the SRK equation.

The effect of setting all binary interaction coefficients (refer to section 4) equal to zero has been checked for samples no. 1–9. Sample no. 1 has the largest content of nonhydrocarbons and it is for that mixture that the most marked effect is observed. The maximum pressure at which two phases can exist is reduced by 4.5% (based on method 7). For the other mixtures the decrease in maximum pressure is less than 1.1%.

9. Discussion

The best match of the measured dew and bubble points is obtained with methods 7 and 8, i.e., by using the Cavett relations (9) and (10) for T_c and P_c, a Lee–Kesler relation (3) or (4) for ω, and by treating the TBP residue as a number of subfractions. The molar contents of the latter are determined either by a logarithmic fit against carbon number or from an extrapolated TBP curve. A comparison of the results of method 6 with those of method 7 reveals a marked improvement when the PNA distribution is taken into consideration.

In methods 3–5, the TBP residue was also treated as a number of subfractions. T_c and P_c were found from the Winn relations (6) and (7). The most marked differences in the critical properties predicted by the Cavett and the Winn relations are found for T_c of the heavy components for which the Cavett relations predict lower T_c's than the Winn relations. The picture for P_c is more complicated. In most cases the Cavett relations predict higher P_c's than the Winn relations for the lighter fractions, lower P_c's in the range $C_{20}-C_{50}$, and higher P_c's for the heaviest fractions. The critical properties found by methods 6–8 result in larger acentric factors than those found by methods 3–5.

In practice, it would be preferable if the TBP residue could be treated as one single fraction as in methods 1 and 2. Method 2, which makes use of Winn relations, gives better results than method 1, which is based on Lee–Kesler relations. Still, the results of method 2 are not satisfactory. One could imagine that a proper description of the phase behavior could be achieved by making a modified version of the T_c and P_c relations, (6) and (7), specially adapted for the TBP residue. Since for all the samples too low dew or bubble point pressures were obtained, attempts were made to change T_c and P_c in a direction which would result in higher pressures. This means to lower T_c and to raise P_c. The resulting phase envelopes were in disagreement with both the experimental values and those found by any of the method 1–9.

In all the methods, even no. 7 and 8, the trend is dew and bubble point pressures below the measured ones. An analysis of the influence of the various input parameters shows that the most influential parameter is the specific gravity, SG. An increase in SG results in lower T_c and higher P_c and thus a higher dew point pressure. The marked influence of SG is also reflected in the fact that the results are improved if the PNA analysis is taken into account; i.e., if each fraction is treated as a mixture of lighter and heavier components. This stresses the importance of PNA analyses. One point which needs further consideration is the specific gravities of the subfractions constituting the TBP residue. The logarithmic fitting procedure for SG of each subfraction and the method for determination of SG of the P, N, and A parts (refer to section 6.2.2) were founded on results obtained for the

Table II. Measured and Calculated Molecular Weights of TBP Residue

compn no.	measd MW	calcd MW, methods 3 and 4	% dev[a]	calcd MW, methods 5, 6, and 7	% dev	calcd MW, method 8	% dev
1	318	326	2.5	334	5.0	–	–
2	453	–	–	419	−7.5	444	−2.0
3	167	176	5.4	163	−2.4	–	–
4	264	268	1.5	265	0.4	–	–
5	444	393	−11.5	458	3.2	452	1.8
6	580	408	−29.7	428	−26.2	514	−11.4
7	550	400	−27.3	426	−22.5	497	−9.6
8	570	412	−27.2	458	−19.6	498	−12.6
9	580	409	−29.5	450	−22.4	507	−12.6
10	377	–	–	326	−13.6	–	–
11	377	–	–	337	−10.5	–	–
12	465	–	–	417	−10.5	452	−2.8

[a] % dev defined in Table I.

Table III. Dew and Bubble Points Found Experimentally and Calculated by Method 2 Neglecting the TBP Residue

compn no.	exptl dew or bubble point P, atm	exptl dew or bubble point T, K	calcd dew or bubble point pressure at the temp at which the expt was made P, atm	calcd dew or bubble point pressure at the temp at which the expt was made % dev[a]
1	392.8	384.3	205.4	−47.7
1	392.8	392.1	198.0	−49.6
3	157.3	340.9	$T > T_{max}$	–
4	259.6	363.7	209.0	−19.5
5	184.4	387.6	154.4	−16.3
6	241.1	345.4	235.3	−2.4
7	232.9	351.0	195.5	−16.1
8	187.5	346.2	167.1	−10.9
9	206.8	346.2	176.2	−14.8

[a] % dev defined in Table I.

lighter fractions. For the heaviest fractions problems are encountered with the Cavett relation for P_c (eq 10). An unexpected minimum is predicted at about C_{50}.

Methods 6 and 7 assume a logarithmic relationship between the mole fractions and the corresponding carbon numbers for $C_N \geq 7$. To get agreement with the measured quantities, the slope of the logarithmic curve for the heavy fractions for most of the samples must be changed to smaller values than those found for the lighter fractions. This problem is related to the molecular weight of TBP residue. For the oil samples large discrepancies between experimental and calculated values are found (refer to Table II). Better results are obtained with method 8, which also represents a slight improvement compared to method 7 with respect to bubble point pressures. The latter trend might have been more marked with a P_c relation adapted for the heaviest fractions.

The problems which are encountered stem from the characterization of the heaviest fractions. Complete data for the C_{21}–C_{40} fractions comprising mole fractions, boiling points, specific gravities, and PNA distributions would be of great value. There is also a need for more experimental points of the phase envelopes. At present it is impossible to tell which of the methods is most accurate for lower pressures.

10. Conclusion

The best agreement between experimental and calculated phase envelopes is obtained with methods 7 and 8. This means that T_c and P_c of each of the carbon number fractions heavier than C_6 should be determined from the Cavett relations (9) and (10) and ω from the Lee–Kesler relations (3) and (4). The results are improved when the

paraffinic, naphthenic, and aromatic parts of each fraction are treated separately instead of using the properties of the total fraction. The TBP residue must be treated as a number of subfractions. In this work we have used 20 subfractions; in a forthcoming publication, methods of reducing this number will be discussed.

For the gas condensate systems, a logarithmic dependence of mole fraction against carbon number can be assumed, while for the heavy oil systems slightly better results are obtained by extrapolating the TBP curve to 100% distilled off. The specific gravity and the boiling point are needed for each of the carbon number fractions to use the relations for T_c, P_c, and ω. Measured T_B and SG data are normally available for the TBP fractions, whereas they must be estimated for the subfractions of the TBP residue. For T_B the values of Katz and Firoozabadi (1978) are used up to C_{45} and the T_B data for the heavier fractions are found by extrapolation of these literature data. For SG the best approximation seems to be a logarithmic dependence of SG against carbon number. Part 2 of this contribution will concentrate on PVT and flash calculations.

Acknowledgment

Nomenclature

A, B = parameters in composition distribution function
C_N = carbon number
D = parameter in specific gravity distribution function
MW = molecular weight
P_c = critical pressure
SG = specific gravity
T_B = boiling point
$T_{Br} = T_B/T_c$
T_{50} = midvolume boiling point
$T_{50w\%}$ = midweight boiling point
T_c = critical temperature
X = mole fraction
z_N = mole fraction of carbon numer fraction C_N
ω = acentric factor

Literature Cited

Aalund, L. "A Guide to World Export Crudes"; The Petroleum Publishing Co.; Tulsa, OK (Collection of articles from *Oil Gas J.*), 1976.
Coats, K. H.; Smart, G. T. Society of Petroleum Engineers of AIME Report 11197, 1982.
Cavett, R. H. "Physical Data for Distillation Calculations, Vapor–Liquid Equilibria"; 27th Midyear Meeting, API Division of Refining, San Francisco, CA, May 15, 1964.
Edminster, W. C. *Pet. Refiner.* **1958**, *37*(4), 173.
Erbar, J. H. Research Report 13, Gas Processors Association, Tulsa, OK, 1977.
Katz, D. L.; Firoozabadi, A. *Pet. Technol.* **1978**, *20*, 1649.
Kesler, M. G.; Lee, B. I. *Hydrocarbon Process.* **1976**, *55*, 153.
Michelsen, M. L. *Fluid Phase Equilib.* **1980**, *4*, 1.

Michelsen, M. L. *Fluid Phase Equilib.* **1982**, *9*, 1.
Nes, K. van; Westerns, H. A. van "Aspects of the Constitution of Mineral Oils"; Elsevier: New York, 1951.
Peng, D. Y.; Robinson, D. B. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59.
Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. "The Properties of Gases and Liquids"; McGraw-Hill: New York, 1977.
Riazi, M. R.; Daubert, T. E. *Hydrocarbon Process.* **1980**, *59*, 115.
Robinson, D. B. Research Report 22, Gas Processors Association, Tulsa, OK, 1981.
Sim, W. J.; Daubert, T. E. *Ind. Eng. Chem. Process Des. Dev.* **1980**, *19*, 386.
Soave, G. *Chem. Eng. Sci.* **1972**, *27*, 1197.
Whitson, C. H. Society of Petroleum Engineers of AIME Report 11200, 1982.
Wilson, A.; Maddox, R. N.; Erbar, J. H. *Oil Gas J.* **1978**, *76*, 76.
Winn, F. W. *Pet. Refiner* **1957**, *36*, 157.

Yarborough, L. "Application of a Generalized Equation of State to Petroleum Reservoir Fluids"; Paper presented at the 176th National Meeting of the American Chemical Society, Miami Beach, FL, 1978.

Supplementary Material Available: Analytical data for the compositions used and results from methods 7 and 8 (26 pages). Ordering information is given on any current masthead page.

Prediction of Henry's Constants in Mixed Solvents from Binary Data

Jack K. Kung, Frank N. Nazario, Joseph Joffe, and Dimitrios Tassios*

The Foundation at NJIT and New Jersey Institute of Technology, Newark, New Jersey 07102

A method for the prediction of Henry's constants of single gases in mixed solvents, from the corresponding binary data and by using a one-parameter form of the Wilson equation, is presented. Good results are obtained when the degree of gas solubility in each solvent is moderate to high. For 40 such systems, the overall error in 5.9%. Good extrapolations with respect to temperature are also realized for such systems. For systems of low gas solubility, mainly water containing, the results are unreliable. An empirical extension of the proposed method, however, provides improved results.

Introduction

While the solubility of single gases in mixed solvents is of industrial importance, most experimental work has dealt with solubilities in single solvents. For mixed solvents, therefore, prediction schemes are often used. The typical approach is to relate the Henry's constant of a gas in a mixed solvent, $H_{1,m}$, to the Henry's constants of the gas in the individual single solvents, $H_{1,i}$.

The simplest relationship, first proposed by Krishchevsky (1937) and often used in practive, is

$$\ln H_{1,m} = \sum_{i=2}^{M} x_i \ln H_{1,i} \qquad (1)$$

where M is the number of components including the gaseous one.

Equation 1 is limited to the cases of ideal solution behavior, of the gas in the solvents and their mixture, as demonstrated by the following general expression (Prausnitz, 1969)

$$\ln H_{1,m} - \sum_{i=2}^{M} x_i \ln H_{1,i} = \ln \gamma^\infty_{1,m} - \sum_{i=2}^{M} x_i \ln \gamma^\infty_{1,i} \qquad (2)$$

Here, $\gamma^\infty_{1,m}$ is the infinite dilution activity coefficient of the gas in the mixed solvent (symmetric convention), and $\gamma^\infty_{1,i}$ is the infinite dilution activity coefficient of the gas in each individual solvent. Depending on the model used for describing these activity coefficients different forms of eq 2 are realized. For example, for a gas dissolved in a mixture of two solvents, use of the two-suffix Margules expansion yields

$$\ln H_{1,m} - x_2 \ln H_{1,2} - x_3 \ln H_{1,3} = -\alpha_{23} x_2 x_3 \qquad (3)$$

where α_{23} is the Margules parameter for the two-solvents binary. Such a simplified model is a good approximation only for solutions consisting of simple, nonpolar molecules (O'Connell and Prausnitz, 1964).

On the other hand, use of the Wilson equation leads to

$$\ln H_{1,m} - x_2 \ln H_{1,2} - x_3 \ln H_{1,3} =$$
$$-\ln \left[x_2 \left(\frac{\Lambda_{12}}{\Lambda_{13}} \right)^{x_3} + x_3 \left(\frac{\Lambda_{13}}{\Lambda_{12}} \right)^{x_2} \right] -$$
$$\frac{x_2 x_3 (1 - \Lambda_{23}) \Lambda_{21}}{x_2 (1 - \Lambda_{23}) + \Lambda_{23}} - \frac{x_2 x_3 (1 - \Lambda_{32}) \Lambda_{31}}{x_3 (1 - \Lambda_{32}) + \Lambda_{32}} \qquad (4)$$

Prausnitz et al. (1967) suggested that $\Lambda_{21} \ll \Lambda_{12}$ and $\Lambda_{31} \ll \Lambda_{13}$ and hence they can be neglected. O'Connell (1971) showed that under this assumption $(\Lambda_{12}/\Lambda_{13}) = (H_{1,3}/H_{1,2})$ and eq 4 becomes

$$\ln H_{1,m} - x_2 \ln H_{1,2} - x_3 \ln H_{1,3} =$$
$$-x_3 \ln (H_{1,3}/H_{1,2}) - \ln [1 + x_3(H_{1,2}/H_{1,3})] \qquad (5)$$

which contains no parameters reflecting the solvent–solvent interaction (Λ_{23} and Λ_{32}). O'Connell indicates, in addition, that the right-hand side of eq 5 is always negative, which is in variance with experimental evidence. Equation 5 was considered in this study, however, because of its simplicity.

In the same study, O'Connell derived a semiempirical expression for $H_{1,m}$ from the Kirkwood–Buff solution theory, which takes the following form for a binary solvent

$$\ln H_{1,m} - x_2 \ln H_{1,2} - x_3 \ln H_{1,3} =$$
$$(x_3/2) \left(\frac{\partial \ln \gamma_3}{\partial x_3} \right)_{T,P,N_2} + A_{23} z_2 z_3 \qquad (6)$$

where

$$A_{23} = \frac{1050|V_2 - V_3|}{T^{1/2} V_2 V_3} \qquad (7)$$

and z_2 is the volume fraction of solvent 2

$$z_2 = \frac{x_2 V_2}{x_2 V_2 + x_3 V_3} \qquad (7a)$$

z_3 is defined similarly and V_2 and V_3 are the molar vol-