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PHASE EQUILIBRIA FOR HIGH-BOILING FOSSIL-FUEL DISTILLATES. 2. CORRELATION OF EQUATION-OF-STATE CONSTANTS WITH CHARACTERIZATION DATA FOR PHASE-EQUILIBRIUM CALCULATIONS.

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December 1984

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PHASE EQUILIBRIA FOR HIGH-BOILING FOSSIL-FUEL DISTILLATES

2. CORRELATION OF EQUATION-OF-STATE CONSTANTS WITH CHARACTERIZATION DATA FOR PHASE-EQUILIBRIUM CALCULATIONS

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December 4, 1984
ABSTRACT

The Redlich-Kwong-Soave equation of state is used to calculate phase-equilibria for systems containing characterized high-boiling fossil-fuel distillate fractions. Equation-of-state constants are calculated from structural-characterization data (carbon number, hydrogen distribution, and heteroatom content). Limited experimental data for a few petroleum fractions, indicate that calculated vapor pressures using structural data are comparable to those using specific gravity and normal boiling point; in both calculations, additional use of one boiling-point datum improves the accuracy of vapor-pressure calculations by an order of magnitude. The results of this study suggest that, for petroleum fractions, structural data for characterization do not provide significantly improved correlation of vapor-pressures when that correlation is based on a simple model like the Soave equation. For effective utilization of structural characterization data, it may be advantageous to direct attention to coal-derived liquids and to base correlations on a better molecular model, more suitable for mixtures of large molecules.
Thermodynamic properties of high-boiling fossil-fuel liquids are required to design efficient phase-separation operations for production of liquid fuels from coal, petroleum residua, and other high-molecular-weight fossil-fuel sources. Traditional methods for estimating thermodynamic properties of paraffinic feedstocks may be inappropriate for those aromatic and heteroatom-rich feedstocks which are slowly replacing conventional paraffinic sources. Characterization of complex liquid mixtures may be useful so that common computational methods for calculating thermodynamic properties of well-defined mixtures of identified components can be extended to complex mixtures of unknown composition.

In recent years, increased attention has been given to thermodynamic properties of systems containing heavy fossil fuels. For example, vapor-pressures of heavy hydrocarbons and hydrocarbon derivatives, and solubilities of gases in such liquids have been reported by Sebastian, et. al. (1981), Chappelow and Prausnitz (1974), Cukor and Prausnitz (1972), Macknick and Prausnitz (1979), van de Rostyne and Prausnitz (1980), Brulé, et. al. (1979), Tremper and Prausnitz (1976), Wilson, et. al. (1981), and others. Correlations for vapor-pressures of heavy-fossil fuel fractions have been proposed; for example, SWAP (Smith, et. al., 1976; Edwards and Prausnitz, 1981) provides an alternative to the older Maxwell-Bonnell method (Lee and Kesler, 1980; Maxwell and Bonnell, 1957) and corresponding-states methods have been reported by Mentzer, et. al. (1981), Teja and Sandler (1980), Brulé, et. al. (1982), and others. Ruzicka, et. al. (1983) have extended the UNIFAC group-contribution method to low-boiling fossil-fuel fractions; however, current published data are insufficient to extend UNIFAC to high-boiling fuels. Unfortunately, few experimental data have been published for physical properties of well-characterized, high-boiling fossil-fuel fractions.
The current state of the art suffers from two major deficiencies. First, traditional characterization techniques often fail to use modern analytical methods, depending instead on the 50-year-old Watson characterization factor K and on API gravity, which were established for predominantly paraffinic materials and which reveal little about the molecular structure of the compounds in the fuel. Second, experimental studies tend to be restricted to pure compounds or to wide-boiling fuels which are not well characterized.

Improved techniques are needed for correlating phase equilibria of high-boiling \((T_{\text{aut}}>150^\circ\)) distillates and nondistillables. The distinction between these two classes depends on the thermal stability of the substance but generally implies a cut-off atmospheric boiling point between 350 and 550°C. As nondistillables and even some distillables decompose at temperatures below their hypothetical critical temperatures, the use of critical-property correlations for estimating equation-of-state parameters may be misleading. Atmospheric boiling points and 60/60°F specific gravities are difficult to measure for many high-boiling fuels, and must be estimated by extrapolation from data at other conditions. With nondistillables, it may be impractical to measure a boiling point or liquid density at any temperature.

This work discusses preliminary efforts toward a possible method for calculating vapor-liquid equilibria for mixtures containing high-boiling fossil-fuel distillates, as well as "normal" components such as methane, ethane, carbon dioxide, etc. We restrict attention to distillables with the expectation that what we learn about these fuels may be useful for the more difficult task of correlating phase equilibria for nondistillables. In the method discussed here, narrow-boiling distillates are considered to be pseudocomponents in a conventional equation of state that is applicable to both vapor and liquid phases. Equation-of-state parameters are derived not from estimated critical constants, but from
experimental characterization data obtained from modern analytical procedures, as discussed in the preceding paper. While these characterization data fall short of precise chemical analysis, they give molecular-structure information toward calculating equation-of-state parameters; an equation of state can then be used to calculate thermodynamic properties for fractions as well as for mixtures of fractions with light gases.

We report here results for a correlation using the Redlich-Kwong-Soave (RKS) equation of state. When compared with limited experimental data for petroleum fractions, the results suggest that the Soave equation may be inadequate for representing the thermodynamic properties of heavy fractions. Unfortunately, experimental data are not available for well-characterized fractions from coal-derived liquids.

**EQUATION OF STATE FOR HEAVY-FOSSIL-FUEL FRACTIONS**

Sim and Daubert (1980) and Pedersen, et. al. (1984 and 1984) have indicated that the Redlich-Kwong-Soave equation of state may be a suitable cubic equation of state for correlating phase equilibria in systems containing heavy-fossil-fuel fractions. Following their example, we also use the RKS equation of state, but unlike previous authors, we correlate equation-of-state parameters with average molecular-structure characterization data obtained for high-boiling, fossil-fuel distillates.

The RKS equation of state is

\[ P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \]  

where \( P \) is the total pressure and \( v \) is the molar volume. Parameter \( b \) is independent of temperature but parameter \( a(T) \) depends on temperature \( T \) according to
\[ a(T) = a_c \alpha(T) \]  
\quad (2)

where \( a_c \) is a constant and \( \alpha(T) \) is given by

\[ \alpha(T) = \left[ 1 + m \left( 1 - \sqrt{T/T^*} \right) \right]^2 \]  
\quad (3)

where \( T^* = 0.2027 \frac{a_c}{(R \beta)} \)  
\quad (4)

and \( m \) is a constant. For pure fluids, \( T^* \) is equal to \( T_c \) (the critical temperature) and

\[ a_c = 0.42747 R^2 T_c^2 / P_c \]  
\quad (5)

\[ b = 0.08664 R T_c / P_c \]  
\quad (6)

\[ m = 0.480 + 1.574 \omega - 0.176 \omega^2 \]  
\quad (7)

where \( P_c \) is the critical pressure and \( \omega \) is the acenptic factor. However, for heavy-fossil-fuel fractions, the three adjustable constants \( (a_c, b, \text{ and } m) \) are determined from characterization data as shown below.
CALCULATION OF EQUATION-OF-STATE CONSTANTS

To evaluate constants \( a_c, b, \) and \( m \) for narrow-boiling fractions (pseudo-components), we relate them to characterization data, using model fluids. When evaluated from critical data, \( \sqrt{a_c}, m^2, \) and \( b \) are approximately linear in number of carbon atoms per molecule for normal alkanes larger than butane, although \( \sqrt{a_c} \) seems to level off at high molecular weights. In general, however, these constants depend not only on molecular size, but also on molecular shape and charge distribution. These features can be well represented by functional-group compositions as in UNIFAC. For undefined mixtures, detailed information on functional groups is difficult to obtain. Rather than make the measurements necessary to obtain the detailed carbon-type functional-group distributions, we correlate equation-of-state constants directly to hydrogen-type distributions. The number of each type of hydrogen atom represents, in an approximate and simplified way, the number of each of various carbon-structural types present in the molecules. To represent the effects of size, shape, and charge distribution, the number of each type of hydrogen atom per molecule is included in the correlations in linear terms, terms relative to the number of carbon atoms per molecule, and a few nonlinear terms found useful for small molecules. The correlation for \( a_c \) includes a denominator to force \( a_c \) to level off for high-molecular-weight paraffins.

The correlating equations immediately below are based on critical data and characterization data for 80 pure, hydrocarbon model fluids. (Corrections for heteroatoms are considered later.) From experimental values for \( T_c \) and \( P_c, \) we calculate \( b \) and \( a_c \) using Equations 5 and 6. Characterization data for these fluids are obtained by inspection of the known molecular structure. Characterization data are
C = number of carbon atoms per number-average molecule (PAM)

\( H_{\text{aro}} = \) number of hydrogen atoms bonded to aromatic carbon atoms PAM

\( H_a = \) number of hydrogen atoms bonded to aliphatic carbon atoms which are in turn bonded to aromatic carbon atoms PAM

\( H_\beta = \) number of hydrogen atoms bonded to aliphatic carbon atoms which are not alpha and do not terminate a chain PAM

\( H_\gamma = \) number of hydrogen atoms bonded to aliphatic carbon atoms which are not alpha and terminate a chain PAM

The correlating equations are

\[
b = -0.1707 + 0.3929 / \sqrt{C} + 0.033131 H_{\text{aro}} + 0.020902 H_a \\
+ 0.015881 H_\beta + 0.012906 H_\gamma \\
\quad - (0.10759 H_{\text{aro}} + 0.06224 H_a + 0.03939 H_\beta + 0.02355 H_\gamma) / C
\]

where \( b \) is in liter mole\(^{-1}\),

\[
\sqrt{a_c} = (-3.437 + 3.990 / C + 2.5930 \sqrt{C} + 0.20437 H_{\text{aro}} + 0.04809 H_a \\
+ 0.10936 H_\beta + 0.09500 H_\gamma - 0.2534 \sqrt{H_{\text{aro}}} + 0.2176 \sqrt{H_a} \\
/ (1.000000 - 0.004973 H_{\text{aro}} + 0.0009645 H_a + 0.002973 H_\beta)
\]

where \( a_c \) is in bar liter\(^2\) mole\(^{-2}\).

From vapor-pressure data for 115 hydrocarbon fluids, we obtain for \( m \)

\[
m = -3.010 + 0.6621 \sqrt{C} - 0.1258 \sqrt{H_\beta} - 0.0425 \sqrt{H_\gamma} \\
+(2.223 H_{\text{aro}} + 1.388 H_a + 1.318 H_\beta + 1.086 H_\gamma) / C
\]

For those heavy-fossil-fuel fractions containing heteroatoms, corrections are required. We consider heteroatoms nitrogen, sulphur, and oxygen. We distinguish among primary-amine, secondary-amine, and pyridinic-nitrogen atoms; and between hydroxyl and ether-oxygen atoms. We assume that all sulphur
atoms are thiophenic. To determine these corrections, we used critical and vapor-pressure data for 33 heteroatom-containing model compounds. These comprised 14 hydroxyl-containing, 10 ether-containing, 1 sulphur-containing, 1 secondary-amine-containing, 3 primary-amine-containing, and 4 other-nitrogen-atom-containing model compounds. The resulting corrections to the correlations are useful, but may be limited in scope; they are based on data for small molecules (<C\textsubscript{12}) because critical data are not available for larger compounds. Further, the corrections for nitrogen and sulphur are based on severely limited data.

For each equation-of-state constant, the correction is relative to the constant (b\textsubscript{HC}, a\textsubscript{e,HC}, and m\textsubscript{HC}) for the corresponding hydrocarbon which is defined as the hypothetical hydrocarbon which has the same carbon and hydrogen characterization data as does the heteroatom-containing compound. The corrections are

\begin{equation}
 b - b_{HC} = 0.00191 \text{NH} + 0.03853 \text{NH}_2 + 0.01276 N_p \frac{H_{aro}}{C} + 0.00486 \text{OH} + 0.02261 O_e + 0.02034 S 
\end{equation} \hspace{1cm} (11)

\begin{equation}
 a_e - a_{e,HC} = [ 2.189 \text{NH} + 3.430 \text{NH}_2 + 2.246 N_p + 1.950 \text{OH} + 2.680 O_e + 2.674 S ]^2 
\end{equation} \hspace{1cm} (12)

\begin{equation}
 m - m_{HC} = 0.4026 \text{NH} + 0.5389 \text{NH}_2 + 0.1064 N_p + 0.8935 \text{OH} - 0.0445 O_e + 0.2545 S 
\end{equation} \hspace{1cm} (13)

Equations 8-13 can be used to calculate Redlich-Kwong-Soave constants for high-boiling fossil-fuel fractions characterized with the experimental procedure discussed previously.

To illustrate these correlations, Table 1 gives RKS constants for dibutyl ether obtained from critical constants, from hydrocarbon structural data and from structural data using the heteroatom corrections. Note that for dibutyl
ether, the corrections are too large; however, the corrections improve the accuracy of vapor-pressure calculations using structural data.

For several representative compounds, Table 2 compares constants \( a_c \) and \( b \) calculated from critical data with those calculated from structural data.

CALCULATED AND EXPERIMENTAL VAPOR PRESSURES FOR PETROLEUM FRACTIONS

The RKS equation of state may be used to calculate vapor pressures of pure compounds (model fluids) and crude-oil fractions. Equation-of-state constants \( b, a_c, \) and \( m \) can be obtained from characterization data, as shown above. Constants \( b \) and \( a_c \) can also be obtained from critical data. For pure fluids, characterization data are obtained from known molecular structures; for crude-oil fractions, they are obtained from experimental measurements as discussed previously. Alternatively, the constant \( m \) can be obtained from one vapor-pressure datum. For a fraction, that datum was obtained by averaging the initial and final atmospheric bubble points. Atmospheric bubble points were estimated from fractionation data using the Maxwell-Bonnell method (Maxwell and Bonnell, 1957).

Table 3 summarizes results for vapor-pressure calculations for several classes of model compounds using structural data. Included for each class are the number of compounds, the minimum and maximum number of carbon atoms per molecule, and the average absolute percent error in calculated vapor pressure for two cases: (1) \( m \) obtained from structural data, and (2) \( m \) chosen to minimize the sum of the squared errors in calculated vapor pressure. In case 1, the large errors are due primarily to the uncertainty in the \( m \) correlation (Equations 10 and 13). Case 2 shows that the errors are much reduced by fitting \( m \) to minimize the sum of squared error in vapor pressure. It is prefer-
able to fit \( m \) to one boiling-point datum rather than to use Equations 10 and 13. If \( m \) is fit to one boiling-point datum, the accuracy in calculating vapor pressures depends on the accuracy of the datum and the extent of extrapolation from that datum. Each \( m \) used in Case 2 is approximately the same as that from fitting the median vapor-pressure datum measured for the corresponding compound. The range of vapor-pressure data used in Table 3 varies from compound to compound, but is generally 10 to 1000 millibar. Details of the correlation method and compound-by-compound results for vapor-pressure calculations are given elsewhere (Alexander 1984).

A traditional method for estimating vapor pressures of fossil-fuel fractions is to obtain equation-of-state constants from effective critical temperatures and critical pressures as determined from experimental normal-boiling-point and specific-gravity data. Table 4 presents these data for ten petroleum fractions. Using correlations proposed by Twu (1984), the data in Table 4 give critical temperatures and pressures. The critical constants are then used to obtain Redlich-Kwong-Soave equation-of-state constants \( b \) and \( a_c \) using Equations 5 and 6.

Vapor pressures were calculated for eight of the fractions using the Soave equation of state with equation-of-state constants \( a_c \) and \( b \) obtained in two ways: (1) from specific gravity and normal boiling point as described above and (2) from structural data (Equations 8, 9, 11, and 12). Table 5 compares vapor-pressure data (Alexander 1984) for the eight petroleum fractions with calculations using these two methods. The estimated normal boiling point is used to find \( m \). The errors are large for both methods, perhaps due to the boiling-point data used to obtain \( m \)’s.

Table 6 also compares vapor-pressure calculations for these two methods; however, calculations are now based on values of \( m \) which minimize the sum of
the squared error in vapor pressure. For the fractions considered here, the results show that when calculations are based on the Redlich-Kwong-Soave equation of state, Twu's method gives vapor pressures similar to those obtained from structural-characterization data. It appears that Soave's equation does not take full advantage of the information available in the structural-characterization data. Comparison of Tables 5 and 6 suggests that some of the error in calculated vapor pressures is due to the choice of m; however, the large errors in Table 6 suggest that the Redlich-Kwong-Soave equation of state may not be adequate for representing phase equilibria for multicomponent mixtures containing large molecules, using average structural data.

We expect that structural characterization may be advantageous for highly aromatic or heteroatom-rich fractions. Unfortunately, published experimental data for such fractions are rare and typically they do not include the characterization data necessary for using a correlation based on structural characterization. For example, Henson, et. al. (1982) measured hydrogen-distribution data along with vapor-pressure and solubility data for two fossil-fuel fractions; however, since molecular-weight and normal boiling-point data were omitted, we could not use their data for comparison with calculated results. For typical published experimental studies, the most common omission is hydrogen-distribution data.

Pseudocomponents are mixtures of many fluids; thus, there is always some error when assuming that a fossil-fuel fraction behaves as a pseudocomponent. When the fraction is flashed, the composition of the fraction in the vapor phase differs from that in the liquid phase and from that in the unflashed fraction. The characterization data for the fraction do not accurately describe the structure of the portion of the fraction in either phase. Because the fraction is a mixture, the vapor pressure of the fraction depends on the percentage of the
fraction in each phase; the bubble point does not equal the dew point. These errors are greatest at low pressures and for wide-boiling fractions. The error may be reduced by using chromatographic carbon-distribution data to divide characterized wide-boiling fractions into several characterized narrow-boiling fractions, as briefly described in the previous paper. The number of narrow-boiling fractions (or "microfractions") may be chosen to obtain an optimum compromise between accuracy and computational difficulty. For example, if Belridge-Crude-Oil fraction 4 is considered to be a single pseudocomponent, its calculated bubble and dew-point pressures at 500 K are both about 13 millibar. However, when Belridge-Crude-Oil fraction 4 is divided into 23 microfractions, we obtain the same bubble point, but the calculated dew-point pressure is 0.4 millibar, and the 13-millibar dew-point temperature is more than 550 K, much higher than that calculated by assuming that the fraction is one pseudocomponent.
MIXTURES

Conventional mixing rules can be used for extending the equation of state to mixtures containing a heavy fraction and a light gas; these mixing rules include a binary constant $k_{ij}$. Figure 1 shows calculated equilibrium ratios (K-factors) for binary mixtures of Belridge-Crude-Oil fraction 3 and each of three gases (methane, ethane, carbon dioxide). The Redlich-Kwong-Soave equation of state is used with equation-of-state constants obtained from characterization data for the fraction and obtained from critical data and acentric factors for the gases. Parameters $a_c$ and $b$ for the oil fraction were obtained from Equations 8, 9, 11, and 12; $m$ was fit to the average estimated normal boiling point of the fraction. The binary parameter $k_{ij}$ was fit to Henry’s-constant data (Alexander, 1984).

CONCLUSIONS

This work presents initial efforts toward a method for calculating thermodynamic properties of characterized, narrow-boiling, heavy fossil-fuel fractions and of mixtures of such fractions with light gases such as methane or carbon dioxide. The calculations are based on the Redlich-Kwong-Soave equation of state modified such that characterization data are used to obtain equation-of-state constants. A generalized correlation is given for these constants as a function of molecular structural-characterization data. When available, one vapor-pressure datum is used to obtain the constant $m$.

The method described here is in its early stages; modifications are required to obtain better results. These modifications will follow as experience grows along with availability of more experimental data for characterized fractions rich in aromatics and heteroatomic hydrocarbons. It appears likely that improved results can be obtained with an equation of state more suitable than...
that of Soave for fluids containing large molecules. Nevertheless, the limited results reported here suggest that the method, even in its present incomplete form, may be useful for engineering design to upgrade heavy fuels for energy applications and for chemical feed stocks.

ACKNOWLEDGEMENTS

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**NOMENCLATURE**

Roman

\[ a_c = \text{Redlich-Kwong-Soave constant} \]

\[ a(T) = \text{Redlich-Kwong-Soave attractive energy} \]

\[ b = \text{Redlich-Kwong-Soave repulsive constant} \]

\[ C = \text{number of carbon atoms per average molecule} \]

\[ H_{aro} = \text{number (per average molecule) of hydrogen atoms which are bonded to aromatic carbon atoms} \]

\[ H_a = \text{number (per average molecule) of hydrogen atoms which are bonded to aliphatic carbon atoms bonded to aromatic carbon atoms} \]

\[ H_s = \text{number (per average molecule) of hydrogen atoms which are bonded to non-methyl, non-alpha, aliphatic carbon atoms} \]

\[ H_\gamma = \text{number (per average molecule) of hydrogen atoms which are bonded to non-alpha, methyl carbon atoms} \]

\[ k_{ij} = \text{binary interaction parameter for molecules i and j} \]

\[ m = \text{Redlich-Kwong-Soave constant} \]

\[ P = \text{pressure} \]

\[ \text{PAM} = \text{Per number-Average Molecule} \]

\[ R = \text{gas constant} \]

\[ T = \text{absolute temperature} \]

\[ T^* = \text{characteristic temperature} \]

\[ v = \text{volume per mole} \]
Greek

\[ \alpha(T) = \text{temperature-dependent factor in } a(T) \]
\[ \omega = \text{acentric factor} \]

Subscripts

\[ c = \text{critical} \]
\[ \text{HC} = \text{hydrocarbon} \]
LITERATURE CITED


TABLE 1

REDLICH-KWONG-SOAVE EQUATION-OF-STATE CONSTANTS
AND AVERAGE ABSOLUTE PERCENT ERROR IN CALCULATED VAPOR PRESSURES
FOR DIBUTYL ETHER

<table>
<thead>
<tr>
<th>Type of Data Used</th>
<th>(a_c)</th>
<th>b</th>
<th>m</th>
<th>AAPE in (P^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Critical Temperature</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Critical Pressure</td>
<td>39.2</td>
<td>0.165</td>
<td>1.22</td>
<td>1.2</td>
</tr>
<tr>
<td>and Acentric Factor</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Structural Data</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No Heteroatom Correction</td>
<td>37.2</td>
<td>0.160</td>
<td>1.11</td>
<td>50</td>
</tr>
<tr>
<td>Structural Data</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>With Heteroatom Correction</td>
<td>44.4</td>
<td>0.182</td>
<td>1.07</td>
<td>12</td>
</tr>
</tbody>
</table>
TABLE 2

REDLICH-KWONG-SOAVE EQUATION-OF-STATE CONSTANTS
FROM CRITICAL DATA AND FROM STRUCTURAL DATA
FOR SELECTED MODEL FLUIDS

<table>
<thead>
<tr>
<th>Model Compound</th>
<th>$\alpha_a$ [bar liter$^2$ mole$^{-2}$]</th>
<th>$b$ [liter/mole]</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-octane</td>
<td>35.5</td>
<td>37.2</td>
</tr>
<tr>
<td>n-hexadecane</td>
<td>107.</td>
<td>107.</td>
</tr>
<tr>
<td>2,2,5-trimethylhexane</td>
<td>40.9</td>
<td>41.5</td>
</tr>
<tr>
<td>1-methyl-1-ethylcyclopentane</td>
<td>34.6</td>
<td>34.8</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>31.2</td>
<td>31.7</td>
</tr>
<tr>
<td>tetralin</td>
<td>43.4</td>
<td>44.1</td>
</tr>
<tr>
<td>1-methylnaphthalene</td>
<td>49.4</td>
<td>49.8</td>
</tr>
<tr>
<td>pyridine</td>
<td>20.2</td>
<td>21.8</td>
</tr>
<tr>
<td>aniline</td>
<td>27.2</td>
<td>27.9</td>
</tr>
<tr>
<td>N-methylaniline</td>
<td>27.9</td>
<td>27.9</td>
</tr>
<tr>
<td>ethyphenylether</td>
<td>36.1</td>
<td>36.7</td>
</tr>
<tr>
<td>p-cresol</td>
<td>26.5</td>
<td>26.0</td>
</tr>
<tr>
<td>thiophene</td>
<td>17.45</td>
<td>16.86</td>
</tr>
</tbody>
</table>
TABLE 3

ERROR IN VAPOR-PRESSURE CALCULATIONS FOR MODEL FLUIDS USING STRUCTURAL-DATA CORRELATIONS

CASE 1: m FROM STRUCTURAL DATA

CASE 2: m FIT TO VAPOR-PRESSURE DATA

<table>
<thead>
<tr>
<th>Class of Compounds</th>
<th>Number of Compounds</th>
<th>Min Carbon</th>
<th>Max Carbon</th>
<th>AAPE in P°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Paraffins</td>
<td>17</td>
<td>6</td>
<td>44</td>
<td>24</td>
</tr>
<tr>
<td>Branched Paraffins</td>
<td>28</td>
<td>6</td>
<td>42</td>
<td>18</td>
</tr>
<tr>
<td>Naphthenes</td>
<td>32</td>
<td>6</td>
<td>27</td>
<td>23</td>
</tr>
<tr>
<td>Aromatics</td>
<td>34</td>
<td>6</td>
<td>31</td>
<td>50</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>111</td>
<td>6</td>
<td>44</td>
<td>30</td>
</tr>
<tr>
<td>Nitrogen-Containing</td>
<td>8</td>
<td>5</td>
<td>8</td>
<td>61</td>
</tr>
<tr>
<td>Oxygen-Containing</td>
<td>19</td>
<td>5</td>
<td>12</td>
<td>76</td>
</tr>
<tr>
<td>Sulphur-Containing</td>
<td>1</td>
<td>4</td>
<td>4</td>
<td>11</td>
</tr>
<tr>
<td>Heteroatom-Containing</td>
<td>28</td>
<td>4</td>
<td>12</td>
<td>69</td>
</tr>
<tr>
<td>Total</td>
<td>159</td>
<td>4</td>
<td>44</td>
<td>38</td>
</tr>
</tbody>
</table>

AAPE = Average Absolute Percent Error (in calculated vapor pressure)
### TABLE 4

NORMAL BOILING POINT (R) AND SPECIFIC GRAVITY (60/60°F) FOR FOSSIL-FUEL FRACTIONS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fraction</th>
<th>Boiling Point</th>
<th>Specific Gravity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beiridge</td>
<td>1</td>
<td>810</td>
<td>0.8085</td>
</tr>
<tr>
<td>Crude</td>
<td>2</td>
<td>810</td>
<td>0.8473</td>
</tr>
<tr>
<td>Oil</td>
<td>3</td>
<td>1035</td>
<td>0.8906</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1190</td>
<td>0.9412</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1365</td>
<td>0.9551</td>
</tr>
<tr>
<td>Hendrick</td>
<td>1</td>
<td>810</td>
<td>0.7945</td>
</tr>
<tr>
<td>Station</td>
<td>2</td>
<td>810</td>
<td>0.8243</td>
</tr>
<tr>
<td>Pipeline</td>
<td>3</td>
<td>1035</td>
<td>0.8684</td>
</tr>
<tr>
<td>Mix</td>
<td>4</td>
<td>1197.5</td>
<td>0.9029</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1372.5</td>
<td>0.9338</td>
</tr>
</tbody>
</table>
TABLE 5

ERROR IN VAPOR-PRESSURE CALCULATIONS
USING THE REDLICH-KWONG-SOAVE EQUATION OF STATE
METHOD 1: a_c AND b FROM SPECIFIC-GRAVITY/BOILING-POINT DATA
METHOD 2: a_c AND b FROM STRUCTURAL-CHARACTERIZATION DATA
BOTH METHODS: m FIT TO ESTIMATED NORMAL-BOILING-POINT DATUM

<table>
<thead>
<tr>
<th>Sample</th>
<th>No.</th>
<th>AAPE in Vapor Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Frac.</td>
<td>Data</td>
</tr>
<tr>
<td>Belridge</td>
<td>1</td>
<td>17</td>
</tr>
<tr>
<td>Crude</td>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>Oil</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>14</td>
</tr>
<tr>
<td>Hendrick</td>
<td>1</td>
<td>21</td>
</tr>
<tr>
<td>Station</td>
<td>2</td>
<td>22</td>
</tr>
<tr>
<td>Pipeline</td>
<td>3</td>
<td>21</td>
</tr>
<tr>
<td>Mix</td>
<td>4</td>
<td>15</td>
</tr>
</tbody>
</table>
TABLE 6

ERROR IN VAPOR-PRESSURE CALCULATIONS USING THE REDLICH-KWONG-SOAVE EQUATION OF STATE

METHOD 1: $a_c$ AND $b$ FROM SPECIFIC-GRAVITY/BOILING-POINT DATA

METHOD 2: $a_c$ AND $b$ FROM STRUCTURAL-CHARACTERIZATION DATA

BOTH METHODS: $m$ FIT TO VAPOR-PRESSURE DATA BY LEAST SQUARES

<table>
<thead>
<tr>
<th>Sample</th>
<th>Frac.</th>
<th>No.</th>
<th>AAPE in Vapor Pressure Method 1</th>
<th>Method 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Belridge</td>
<td>1</td>
<td>17</td>
<td>3.4</td>
<td>6.2</td>
</tr>
<tr>
<td>Crude</td>
<td>2</td>
<td>12</td>
<td>7.2</td>
<td>4.4</td>
</tr>
<tr>
<td>Oil</td>
<td>3</td>
<td>5</td>
<td>9.8</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>14</td>
<td>19</td>
<td>16</td>
</tr>
<tr>
<td>Hendrick</td>
<td>1</td>
<td>21</td>
<td>34</td>
<td>25</td>
</tr>
<tr>
<td>Station</td>
<td>2</td>
<td>22</td>
<td>23</td>
<td>19</td>
</tr>
<tr>
<td>Pipeline</td>
<td>3</td>
<td>21</td>
<td>18</td>
<td>14</td>
</tr>
<tr>
<td>Mix</td>
<td>4</td>
<td>15</td>
<td>32</td>
<td>35</td>
</tr>
</tbody>
</table>
CAPTIONS FOR FIGURES

Figure 1: Calculated Equilibrium Ratios at 375 K
for Binary Mixtures of Belridge-Crude-Oil Fraction #3 (1) and Methane, Ethane, and Carbon Dioxide (2)
Figure 1

Calculated Equilibrium Ratios at 375 K
for Binary Mixtures of Belridge-Crude-Oil Fraction #3 (1) and Methane, Ethane, and Carbon Dioxide (2)
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