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ABSTRACT

Experimental and calculated phase equilibria are reported for two systems containing propane and petroleum-derived oil mixtures near 400K and pressures to 55 bar; these conditions are close to the critical. In the first system, the oil is rich in saturated hydrocarbons; in the second system, the oil is rich in aromatic hydrocarbons. For both oils, number-average molecular weights are in the range 300-350. Solubilities in two equilibrium phases, measured with a flow-cell apparatus, are correlated with the perturbed-hard-chain equation of state wherein the composition of the heavy hydrocarbon is described by a continuous distribution function. A simple procedure is proposed to derive a molecular-weight distribution from boiling-point data. Calculated and experimental equilibria agree well when small empirical corrections are introduced into the perturbed-hard-chain equation of state to obtain characteristic potential-energy parameters for oil-propane interactions.

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INTRODUCTION

For design and evaluation of supercritical-fluid extraction processes, it is necessary to have quantitative phase-behavior data. We report here a study of vapor-liquid equilibria for two propane-oil mixtures at temperatures near 400 K and pressures to 55 bar, near the mixtures' critical conditions. The first mixture contains an oil rich in saturated hydrocarbons; the second mixture contains an oil rich in aromatic hydrocarbons. Both oils have number-average molecular weights in the range 300-350.

These phase equilibria are of interest because for many years, low-molecular-weight paraffin solvents (typically, propane) have been used to extract valuable components from heavy crude residua. In many cases, such a process is operated as a liquid-liquid extraction. More recently, however, there is increased interest (Gearhart and Garwin, 1976; Zosel, 1978; Eisenbach et al., 1983) in a concept of operating such extraction processes at elevated pressures and temperatures, near the solvent's critical point, as first proposed by Godlewicz (1938). Regardless of the extraction conditions, solvent recovery from the extracted oil is known to be much more efficient at supercritical conditions, compared to conventional subcritical evaporation (Gearhart and Garwin, 1976). In addition, when the extraction step is near the mixture critical conditions, the solvent can be regenerated with small changes in temperature and pressure (Cotterman, Dimitrelis and Prausnitz, 1984). The key input needed to design such supercritical separations is the equilibrium composition of both solvent-rich and oil-rich phases, which is the subject of this study.

Numerous studies have been concerned with design of supercritical-fluid-extraction processes (for example, Brulé et al., 1983; Cotterman, Dimitrelis and Prausnitz, 1985) and many articles have described results for model systems (for comprehensive reviews, see Paulaitis et al., 1983; Williams, 1981). While industrial supercritical-fluid processes are almost always concerned with mixtures that contain a large number of components, most model studies for supercritical-fluid processes have been restricted to binary or ternary systems. In this work, the heavy-hydrocarbon fraction is represented as a continuous mixture wherein the composition is given by two continuous distribution functions, one for paraffins and one for aromatics. This representation, called continuous thermodynamics (see, for example, Cotterman, Bender and Prausnitz, 1985; Cotterman and Prausnitz, 1985; Kehlen, Rätzsch and Bergmann, 1985), is here combined with a new perturbed-hard-chain equation of state to correlate experimental phase-equilibrium data for propane/heavy-hydrocarbon mixtures.

EXPERIMENTAL APPARATUS AND PROCEDURE

Phase-equilibrium measurements for heavy oils should generate relatively large samples because these are needed for subsequent chemical analyses such as boiling-point data, molecular weight, specific gravity and retention times from liquid chromatography. For that reason, a flow method was chosen for the propane-oil systems, as shown in Figure 1. In this method, all the feed components flow through an equilibrium cell at steady state. In contrast to batch techniques, the flow techniques (Chao et al., 1984; Simnick et al., 1977; Wilson and Owens, 1977) not only can generate large samples but also allow for short residence times as required for thermally-unstable liquids.

The flow cell shown in Figure 1 serves as a high-pressure separator in which it is possible to observe phase separation visually. Upstream of the cell, two high-pressure metering pumps feed the condensable components to a Kenics static mixer. This mixer provides the mixing energy needed to promote mass transfer. Downstream of the cell, two low-pressure separators, one for each the phase, separate the depressurized effluents into vapor and liquid. In this way, four samples are generated: vapor and liquid from each of the equilibrium phases.

During equilibration, which takes up to 30 minutes, both effluent streams are directed to a knockout pot to bypass the sampling section. After equilibrium is reached, the three-way valves are turned to direct the product streams to the sampling section. For the next 10 to 30 minutes the low-pressure separating vessels are filled with the liquid components and the vapor components pass through the wet test meters to measure their volume. The amount of liquid is determined gravimetrically. Three pairs of samples are usually collected from each run. Typically, the vapor samples are GC analyzed (if the vapor contains more than one component) whereas the liquid samples are subjected to chemical analyses such as molecular-weight determination and liquid chromatography. The equilibrium-phase compositions are calculated from the material balance based on the measured vapor volume and liquid weight.

Both equilibration and sampling require careful control of pressure, temperature and liquid level. The cell pressure is adjusted using a micrometering valve mounted on the upper phase line. The liquid level is adjusted using another micrometering valve mounted on the lower phase line. Mixer and cell temperatures are maintained constant using an air bath. Detailed description of the apparatus and procedure, and test results for carbon dioxide and decane, are given elsewhere (Radosz, 1985).

MATERIALS

Prior to use, the oils were filtered through a 10-micron filter. Propane of C.P. purity was obtained from Matheson and used without further purification.

Table 1 shows properties for the two petroleum-derived oils. These oils were obtained from extraction of a single vacuum distillate with N-methylpyrrolidone. Therefore, as indicated in Table 1, the two oil samples have similar boiling-point characteristics but have significantly different chemical composition; one oil is rich in saturates (paraffins and naphthenes) and the other is rich in aromatics.

The saturates and aromatics concentrations were determined with High-Performance Liquid Chromatography (HPLC) using hexane as a solvent. Other properties measured for the oils are specific gravity, carbon-to-hydrogen ratio and number-average molecular weight. Molecular weights are measured using vapor-pressure osmometry, using toluene as a solvent.

Table 1 also shows a boiling-point analysis for each oil; this analysis is determined from a gas-chromatographic(GC) simulated distillation. The normal boiling point is indicated at several distillation points. Figure 2 shows the total boiling-point curve for the saturates-rich oil. Detailed distillation analyses for each oil and for the aromatic and saturate fractions of each oil are deposited as supplementary material.

EXPERIMENTAL RESULTS

Tables 2 and 3 give experimental phase equilibria for the two mixtures with propane. The first two columns indicate the temperature and pressure for each experimental run. The last two columns give the solubilities in each phase: first, the solubility (in weight percent) of the oil in the propane-rich (vapor) phase and second, the solubility (in weight percent) of the propane in the oil-rich (liquid) phase. The middle column gives the propane-to-oil weight ratio in the flow-cell feed stream for each run.

Weight-percent compositions given in Tables 2 and 3 are averages from at least three measurements. Reproducibility for the propane-rich phase was typically better than 0.005 wt% except near the critical conditions (392.2 K and 55.14 bar) where reproducibility was 0.03 wt% due to extreme sensitivity to small variations in pressure. Reproducibility for the oil-rich phase was typically better that 0.1 wt% and always better than 0.2 wt%. Overall accuracy is estimated to be twice the reproducibility.

CORRELATION USING AN EQUATION OF STATE

To correlate the phase-equilibrium data for the propane-heavy hydrocarbon mixtures, two separate, but related, problems must be addressed: first, an equation of state must be chosen to represent thermodynamic properties and second, a procedure must be developed to relate equation-of-state parameters to measurable properties of the heavy-hydrocarbon fraction. Phase equilibria are then calculated using continuous thermodynamics.

The perturbed-hard-chain (PHC) theory (Beret and Prausnitz, 1975; Donohue and Prausnitz, 1978) is useful for representing the thermodynamic properties of fluid mixtures containing both small and large molecules. A recent modification (Cotterman et al., 1986) significantly improves the accuracy of PHC theory for pure fluids and mixtures.

Other multiparameter equations of state, (e.g. the extended Benedict-Webb-Rubin equation, Starling, 1971) may offer advantages over simpler equations [e.g. Soave-Redlich-Kwong (SRK) or Peng-Robinson] for representing thermodynamic properties of heavy-hydrocarbon systems. However, multiparameter equations introduce uncertainty due to the large number of arbitrary mixing rules. Recent attempts to correlate SRK equation-of-state parameters for heavy-hydrocarbon systems have met with only limited success (Alexander et al., 1985) whereas PHC parameters appear to correlate well for high-molecular-weight fluids (Wilhelm and Prausnitz, 1985).

To use an equation of state for complex mixtures, it is necessary to characterize the mixture through analytical measurements and, subsequently, to relate characterization data to equation-of-state constants. As discussed by Brulé et al.(1985), a characterization procedure requires three steps. The first is concerned with the composition representation of a high-molecular-weight fraction; this representation is classically provided by a finite number of pseudocomponents, or equivalent "pure" components. For a narrow-boiling fraction, the somewhat arbitrary choice of a few pseudocomponents is sufficient; however, as the boiling-point range of the fraction becomes large, calculated results become sensitive to the selection of pseudocomponents. Continuous thermodynamics provides a procedure whereby the composition of a wide-boiling fraction may be represented by a continuous distribution function.

The second characterization step is concerned with the relation of the correlations for equation-of-state constants to measurable properties of the oil fraction. Cotterman et al.(1986) present equation-of-state parameter correlations for several hydrocarbon homologous series as a function of molecular weight. In this work, each hydrocarbon fraction is represented as the sum of two homologous series: one for paraffins and another for fused-ring aromatics. The molecular weight distributions for each oil are determined from a boiling-point analysis.

The final characterization step requires introduction of binary (or higher) parameters to correlate experimental phase behavior. In this work we adjust binary parameters between propane and each hydrocarbon class to correlate the flow-cell experimental results.

Equation of State

The equation of state used in this work is based upon the PHC theory, as presented elsewhere (Cotterman et al., 1986). Only a brief overview is given here.

The molar residual Helmholtz energy $\mathbf{a}^r$ is given by the sum of a reference term and a perturbation term. For the reference term, we use a form based on the Carnahan-Starling expression (1972). We divide the perturbation term $\mathbf{a}^{pert}$ into two parts, each corresponding to a density region:

$$\mathbf{a}^{pert} = \mathbf{a}^{sv}(1-F) + \mathbf{a}^{df}F \tag{1}$$

where $\mathbf{a}^{sv}$ is the low-density (second-virial) limit of the perturbation term and $\mathbf{a}^{df}$ is the dense-fluid limit of the perturbation term; F is a smooth function which interpolates between these two limits. The expression for the low-density term is determined by correlating experimental second-virial coefficients; the expression for the dense-fluid term is derived from computer-simulation studies. This division of the perturbation term, as suggested by Dimitrelis and Prausnitz (1982), allows us to represent accurately the thermodynamic properties of a pure component or a mixture for the entire fluid-density range, using a single equation of state.

The pressure-explicit equation of state is obtained by differentiating the residual Helmholtz energy with respect to volume V at constant temperature T and mole number n:

$$P = \frac{nRT}{V} - \left(\frac{\partial n a^r}{\partial V}\right)_{T, \text{all } n} \tag{2}$$

For a pure fluid, this extended version of PHC theory contains three molecular parameters: v^*, $\varepsilon q / k$ and c; these are, respectively, characteristic of the soft-core volume, the potential energy and the number of external degrees of freedom of the molecule. Characteristic temperature is defined $T^* \equiv \varepsilon q / ck$ where ε is the potential energy per unit area, q is the external molecular surface area and k is Boltzmann's constant. These pure-component parameters are fit to second-virial-coefficient, vapor-pressure and liquid-density data.

For large molecules, the pure-component parameters may be expressed as continuous functions of molecular weight for various hydrocarbon classes. Figures 3 and 4 show equation-of-state parameters for two hydrocarbon classes: normal alkanes and fused-ring aromatics. The parameters are correlated by

$$v^{*} = a^{(1)} + a^{(2)}MW \tag{3a}$$

$$cT^{*} = \varepsilon q / k = a^{(3)} + a^{(4)}MW \tag{3b}$$

$$T^{*} = a^{(5)} - a^{(6)}\, exp\,(-a^{(7)}MW^{1/2}) \tag{3c}$$

where *MW* is molecular weight. Coefficients for these and other homologous series are reported by Cotterman et al. (1986).

The PHC equation of state is extended to mixtures through suitable mixing rules that relate mixture parameters to composition and to pure-component parameters. Two binary parameters are used to correlate binary-mixture behavior: one in the low-density region and one in the dense-fluid region. The binary parameters k_{ij}^{sv} and k_{ij}^{df} correct the geometric mean assumption for the cross energetic parameter ε_{ij}:

$$\varepsilon_{ij}(virial\ limit) = (\varepsilon_{ii}\varepsilon_{jj})^{1/2}(1 - k_{ij}^{sv}) \tag{4a}$$

$$\varepsilon_{ij}(dense\ fluid) = (\varepsilon_{ii}\varepsilon_{jj})^{1/2}(1 - k_{ij}^{df}) \tag{4b}$$

These parameters are independent of temperature, pressure and composition.

Characterization of Oil Samples

A simple procedure is used to generate molecular-weight distributions for the oils investigated in this study. The composition of each oil is considered to be the sum of two hydrocarbon homologous series: one for the saturates-rich fraction and another for the aromatics-rich fraction. The saturates are represented by the normal-paraffin series and the aromatics by the fused-ring aromatic series. Each fraction in each oil is experimentally characterized by a normal-boiling-point curve.

To represent the composition of the oil fraction with a continuous distribution function, it is necessary to relate experimental characterization data for that oil to some characterizing property. In this work, we choose molecular weight as a characterizing property; hence, the boiling-point curve for each oil is converted to a molecular-weight distribution. As shown in Figure 5, the normal boiling point is correlated for each hydrocarbon class as a function of molecular weight. This correlation is given by an empirical function:

$$T_b(K) = b^{(1)} - b^{(2)}\exp(-b^{(3)}MW) \tag{5}$$

where T_b is normal boiling point. Table 4 gives the coefficients for Eq. 5.

Boiling-point data are converted to a molar molecular-weight distribution by numerically differentiating the boiling-point curve, converting the boiling-point axis to molecular weight using Eq. 5 and finally, normalizing the resulting distribution. A smoothed continuous representation of this molecular-weight distribution is obtained with a statistical distribution function; in this work, the beta distribution is chosen since that distribution resembles the experimental distribution. The beta distribution $f(u)$ is a continuous function defined over a finite interval:

$$f(u) = \frac{\Gamma(\alpha+\beta)}{\Gamma(\alpha)\Gamma(\beta)} u^{\alpha-1}(1-u)^{\beta-1} \tag{6}$$

where Γ is the gamma function, u is the distributed variable, scaled to the range $0<u<1$, and α and β are adjustable parameters. These parameters are related to the mean Θ and variance σ^2 through:

$$\Theta = \frac{\alpha}{\alpha + \beta} \tag{7a}$$

$$\sigma^2 = \frac{\alpha\beta}{(\alpha+\beta)^2(\alpha+\beta+1)} \tag{7b}$$

To a good approximation, the parameters in the beta distribution are determined from the experimental mean and variance as obtained from the converted boiling-point distribution. The initial and final values of the molecular-weight distribution are determined from the experimental initial and final boiling points.

Figures 6 and 7 show the smoothed molar distributions of heavies in the saturates-rich oil and in the aromatics-rich oil. Since the beta distribution is a probability density whose integral is normalized to unity, the quantity *molar distribution* is defined to indicate relative amounts of each hydrocarbon class. The molar distribution is the product of the normalized molecular-weight distribution and the mole fraction of the hydrocarbon class within the oil fraction. In both figures, the distribution is distinctly bimodal with respect to molecular weight, as dictated by the particular assumptions made for the boiling point of each hydrocarbon class. The distributions of the aromatics and the saturates within each oil are nearly symmetric. This symmetry results from the experimental boiling-point analysis for each fraction and does not depend on the form of our analytical distribution function.

The number-average molecular weight and variance for the saturates-rich oil are 321.8 and 1532, respectively for the saturates and 202.0 and 341.0, respectively for the aromatics. For the aromatics-rich oil, the corresponding numbers are 321.4 and 1256 for the saturates and 202.5 and 253.8 for the aromatics.

Continuous-Thermodynamics Framework

To perform a flash calculation for a continuous or semicontinuous mixture, we must solve simultaneously the phase-equilibrium and mass-balance equations. These equations are solved using Gaussian quadrature techniques as discussed elsewhere (Cotterman and Prausnitz, 1985). Gaussian quadrature provides a convenient method to represent accurately integral properties of a continuous feed distribution.

Upon specifying the number of quadrature points, the Gaussian integration formulae estimate the optimal values of molecular weight at which to integrate our molecular-weight distribution. The number of quadrature points is determined by the required precision of the phase-equilibrium calculations. Our experience with fixed-interval distribution functions using Chebyshev-Gauss quadrature indicates that five quadrature points are adequate. There are five quadrature points for each hydrocarbon class (ensemble), or a total of ten points for each total oil fraction.

At each quadrature point, the molecular weight is used to calculate equation-of-state constants from Eqs. 3a-3c.

COMPARISON OF CALCULATED AND EXPERIMENTAL RESULTS

Figures 8 through 11 compare calculated and experimental results for the two propane-oil mixtures. Calculated results are based on a 4:1 propane-to-oil weight ratio in the feed. These figures show solubility of the propane in the liquid phase and solubility of the heavies (as the total of both hydrocarbon classes) in the vapor phase. For each isotherm, two calculated results are shown. First, calculations are shown as dashed lines for the case where all binary parameters are set to zero. Second, calculations are indicated by a solid line for the case where binary parameters between the propane and each hydrocarbon class were adjusted to correlate the experimental results.

The critical temperature and critical pressure of pure propane are 369.8 K and 42.5 bar, respectively. At the two lowest pressures investigated (near 30 bar and 40 bar), agreement between calculation and experiment is good for all isotherms. This region is removed from the mixture's critical and the inclusion of binary parameters has a relatively small effect. However, at the highest pressure (near 55 bar) the calculations indicate that we are beginning to approach the mixture critical region where binary parameters have a large effect. Particularly in the vapor phase, the solubility of heavies increases dramatically over the pressure range (note the logarithmic scale). The vapor-phase solubility of heavies is therefore difficult to correlate well because essentially all equations of state, including the PHC, are poor in the critical region.

The two oil mixtures exhibit qualitatively similar solubility behavior; however, due to the different chemical nature of the two oils, the equilibrium solubilities of propane in the liquid and of the heavies in the vapor are systematically different. Mutual solubilities of propane and heavies are greater in the propane/saturates-rich oil mixture than in the propane/aromatics-rich oil mixture since propane is chemically more similar to the saturates-rich oil than to the aromatics-rich oil.

Table 5 gives the binary parameters used for the calculated results shown in Figures 8 through 11.

Typically, binary parameters k_{ij} are positive when evaluated from binary vapor-liquid equilibrium data. The slightly negative binary-parameter values obtained here suggest that binary information is not sufficient to predict phase equilibria for multicomponent mixtures near the critical region. Qualitatively similar results have been reported by Radosz (1985) using a version of the Redlich-Kwong equation of state.

CONCLUSIONS

Phase equilibrium compositions have been measured for two systems containing propane and oil mixtures with a flow-cell apparatus at temperatures near 400 K and pressures to 55 bar, near the mixture critical region. Such data provide the key to understanding and designing supercritical separation processes.

The two oils investigated in this study cover moderate ranges of molecular weight and have similar boiling-point characteristics but are chemically different: one oil is rich in aromatics, the other is rich in saturates. As a result, measured solubilities of propane in each oil are systematically different at the same temperature and pressure. Similar differences exist for the solubilities of the oils in the propane-rich phase.

Measured solubilities are correlated with a new version of the perturbed-hard-chain equation of state. The compositions of the oils are described by continuous distribution functions derived from a boiling-point analysis. Calculated and experimental results are in good agreement when small empirical corrections are applied to the equation of state, except for regions near the critical region of the mixture, where most equations of state fail.

The PHC equation of state and continuous-thermodynamics framework are applicable to other molecular-weight ranges. However, oil mixtures having much higher molecular-weight ranges require different experimental methods for characterization, which are the subject of work now in progress.

The calculation procedures presented here are suitable for computer-aided design of supercritical-fluid extraction processes. Computer programs are available upon request to the last-named author.

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NOTATION

Symbols

$\mathbf{a}$	molar Helmholtz energy
$a^{(1)},a^{(2)}$,*etc.*	coefficients for molecular-parameter correlations
$b^{(1)},b^{(2)},b^{(3)}$	coefficients for boiling-point correlation
c	external-degrees-of-freedom parameter
f	beta distribution function
F	interpolation function
k	Boltzmann's constant
MW	molecular weight
n	number of moles
P	absolute pressure
q	external molecular surface area
R	gas constant
T	absolute temperature
T°	characteristic temperature, $T^{\circ}=\varepsilon q / ck$
u	distributed variable
v	molar volume
v°	hard-core molar-volume parameter
V	total volume

Subscripts and Superscripts

b	normal boiling point
df	dense-fluid density limit
ii	characteristic of component i
jj	characteristic of component j
ij	characteristic of component i and component j interaction
r	residual property
sv	second-virial density limit

Greek Symbols

α	beta-distribution parameter
β	beta-distribution parameter
ε	potential energy per unit surface area
Γ	gamma function
Θ	number-average molecular weight
σ^2	variance

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Table 1. Properties for the Two Oils.

Property	Saturates-Rich Oil	Aromatics-Rich Oil
Specific Gravity at 60°C	0.8355	0.9237
Carbon/Hydrogen Ratio	6.23	7.56
Saturates, Wt %	88.6	37.9
Aromatics, Wt %	11.4	62.1
Number-Average Molecular Weight	340	310
GC Simulated Distillation Normal Boiling Point, K		
Initial	575.5	581.5
10 Wt % Off	622.4	624.0
50 Wt % Off	670.6	668.4
90 Wt % Off	711.7	707.7
Final	744.2	746.9

Table 2. Experimental Two-Phase Equilibria for Propane and Saturates-Rich Oil.

Temperature (K)	Pressure (bar)	Propane/Oil Weight Ratio in Feed	Propane-Rich Phase Oil Wt %	Oil-Rich Phase Propane Wt %
374.4	31.02	3.5	0.012	26.9
392.5	31.02	3.5	0.022	18.0
392.6	41.36	3.7	0.056	28.2
392.2	55.14	4.1	0.840	55.4
413.5	31.02	3.4	0.051	13.1
413.5	41.36	3.8	0.090	19.3
413.5	55.14	4.1	0.305	29.7

Table 3. Experimental Two-Phase Equilibria for Propane and Aromatics-Rich Oil.

Temperature (K)	Pressure (bar)	Propane/Oil Weight Ratio in Feed	Propane-Rich, Phase Oil Wt %	Oil-Rich Phase Propane Wt %
392.7	31.02	3.4	0.022	14.5
392.7	41.36	3.7	0.041	22.7
392.4	55.14	3.8	0.780	42.9
413.5	31.02	3.5	0.052	10.7
413.5	41.36	3.8	0.083	15.6
413.5	55.14	3.8	0.292	23.9

Table 4. Coefficients for Boiling-Point Correlation.

Class	$b^{(1)}$	$b^{(2)}$	$b^{(3)}$
Normal Paraffins	962.3	733.6	2.6580×10^{-3}
Fused-Ring Aromatics	1537.5	1417.3	2.3889×10^{-3}

Table 5. Binary parameters k_{ij}.

Oil	Hydrocarbon Class			
	Saturates		Aromatics	
	Virial Limit	Dense Fluid	Virial Limit	Dense Fluid
Saturates-Rich	-0.040	-0.010	-0.080	0.000
Aromatics-Rich	0.000	-0.015	0.000	-0.015

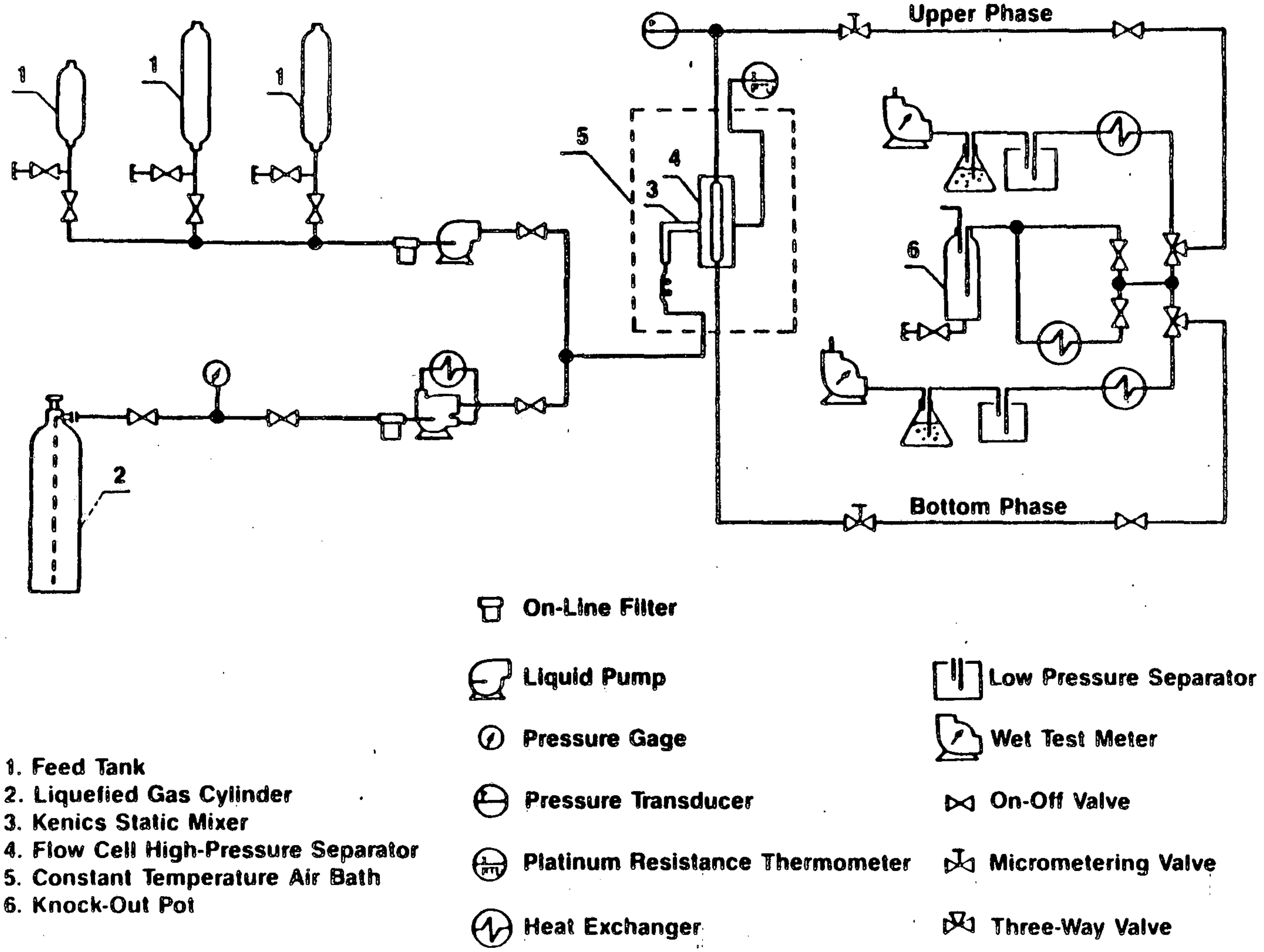

Figure 1. Flow-cell apparatus for phase-equilibrium measurements.

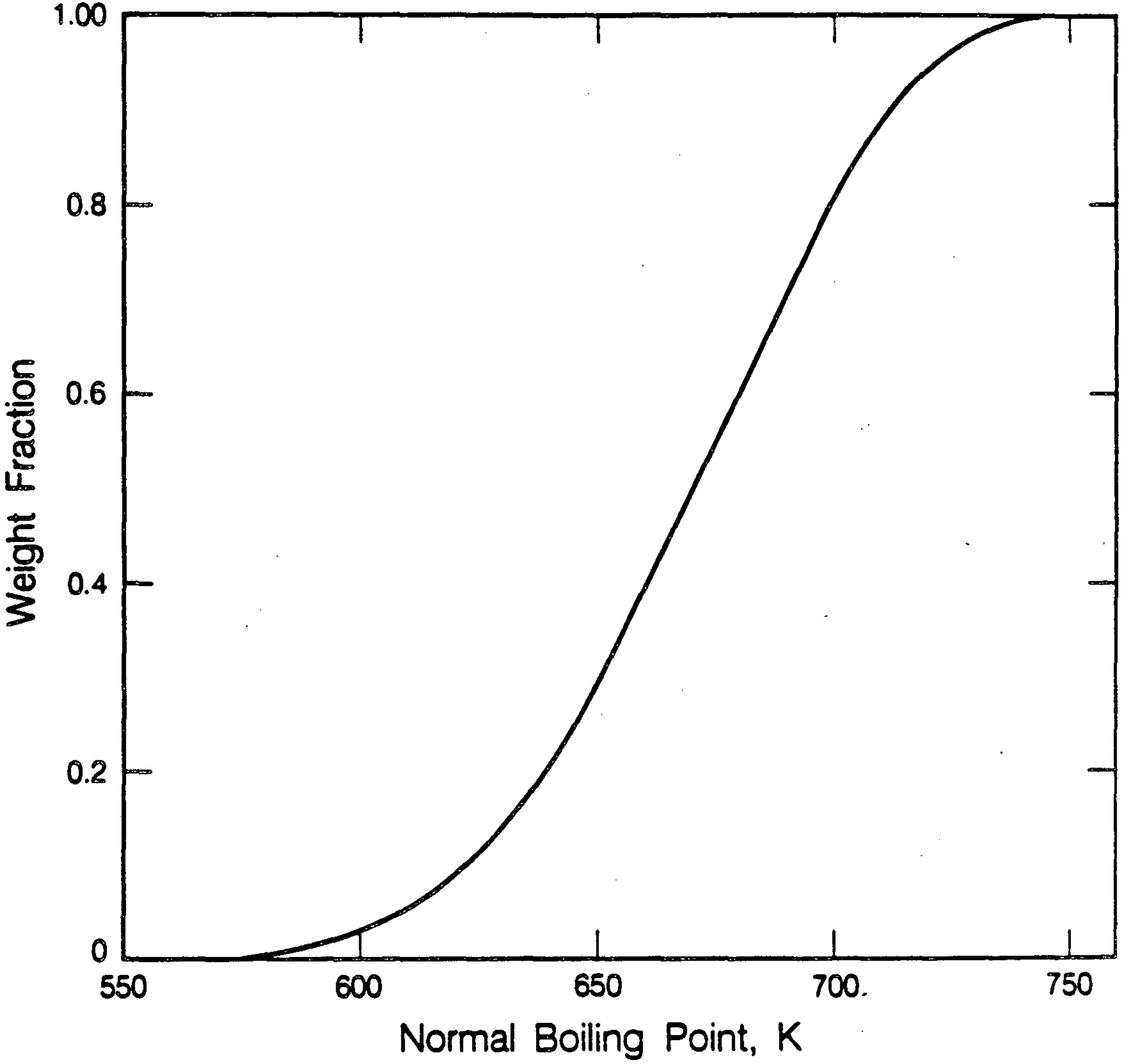

Figure 2. Gas-chromatographic simulated analysis of saturates-rich oil.

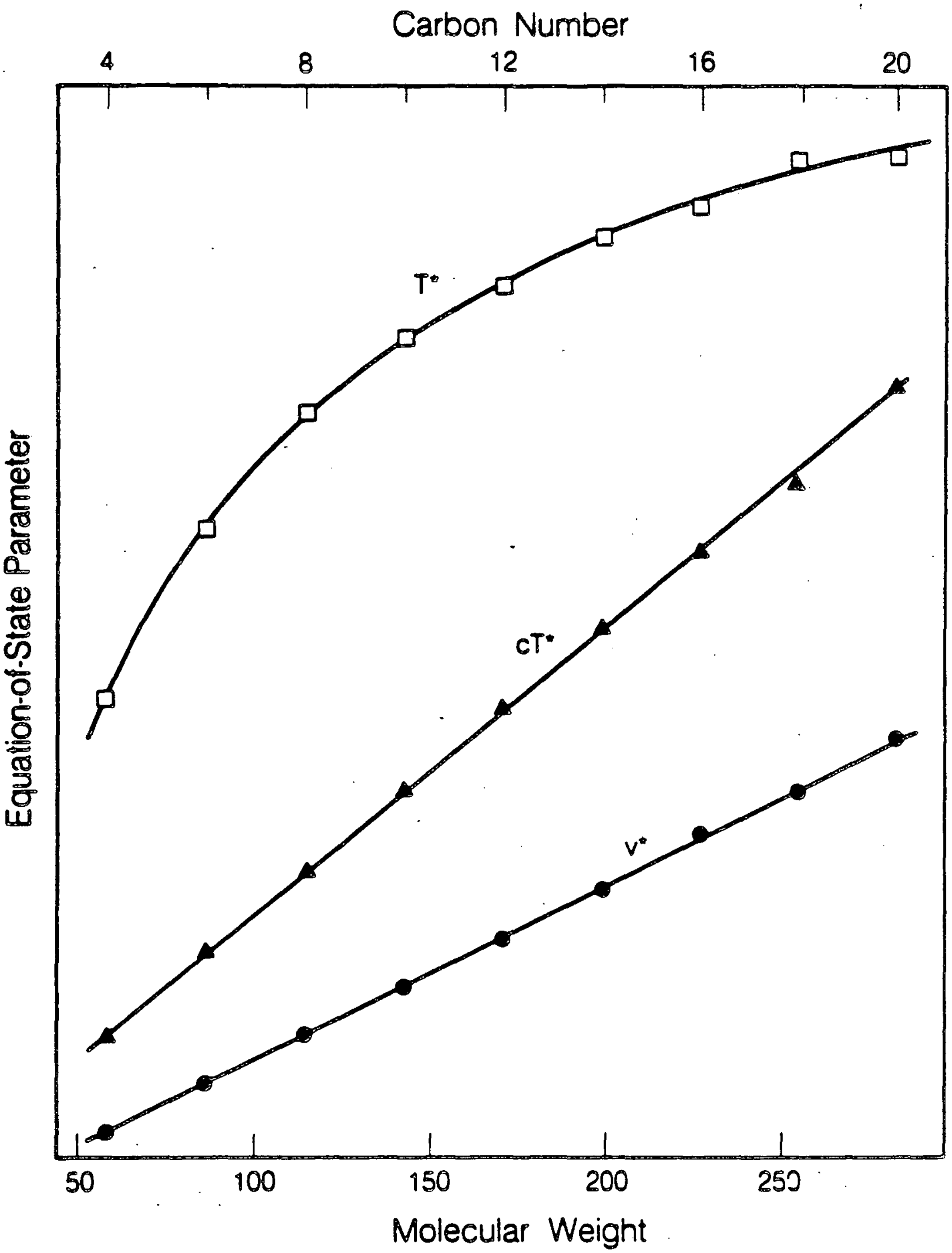

Figure 3. Correlation of equation-of-state parameters with molecular weight for normal alkanes. Figure drawn to scale.

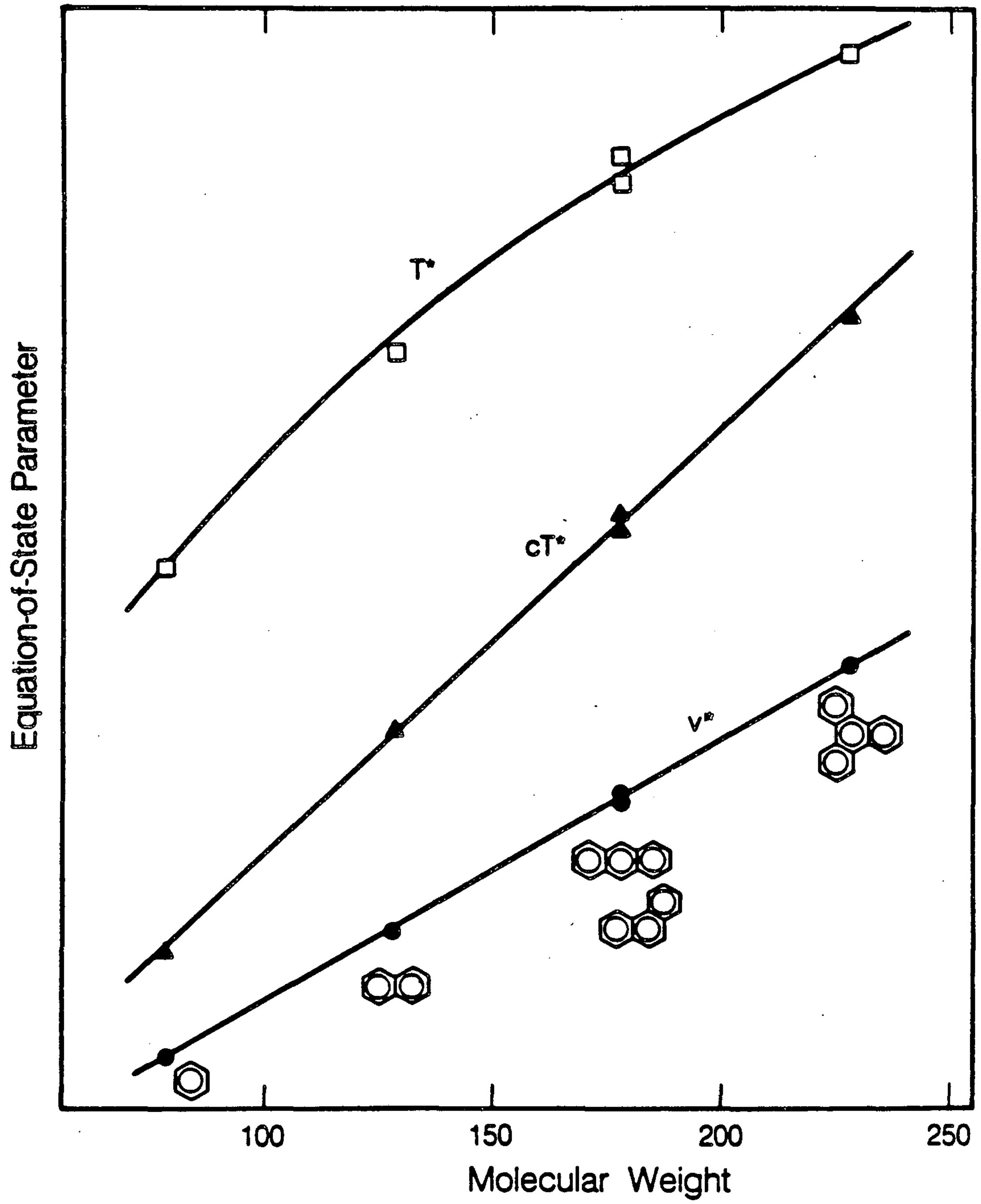

Figure 4. Correlation of equation-of-state parameters with molecular weight for fused-ring aromatics. Figure drawn to scale.

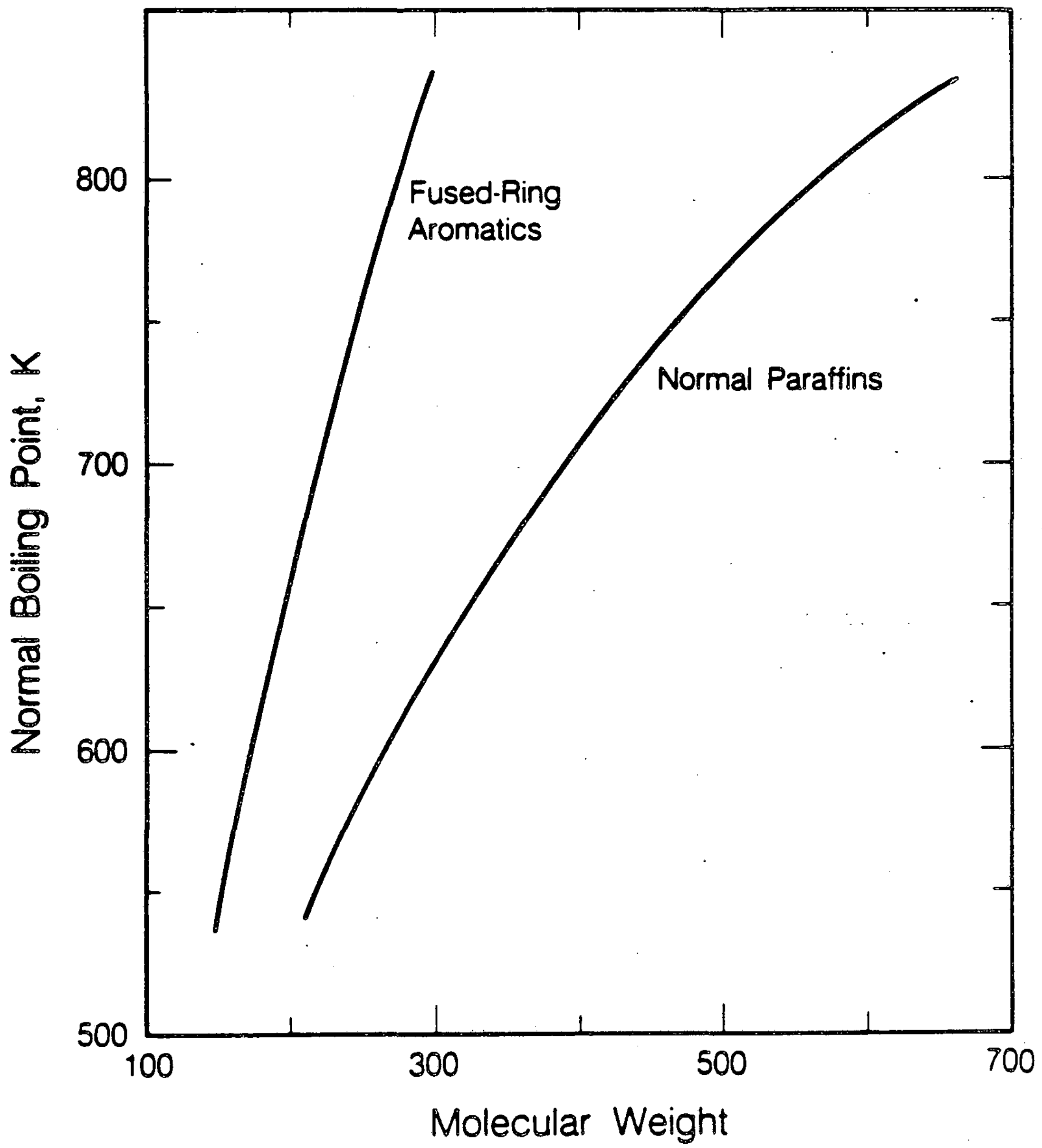

Figure 5. Correlation of normal boiling point with molecular weight for two hydrocarbon classes.

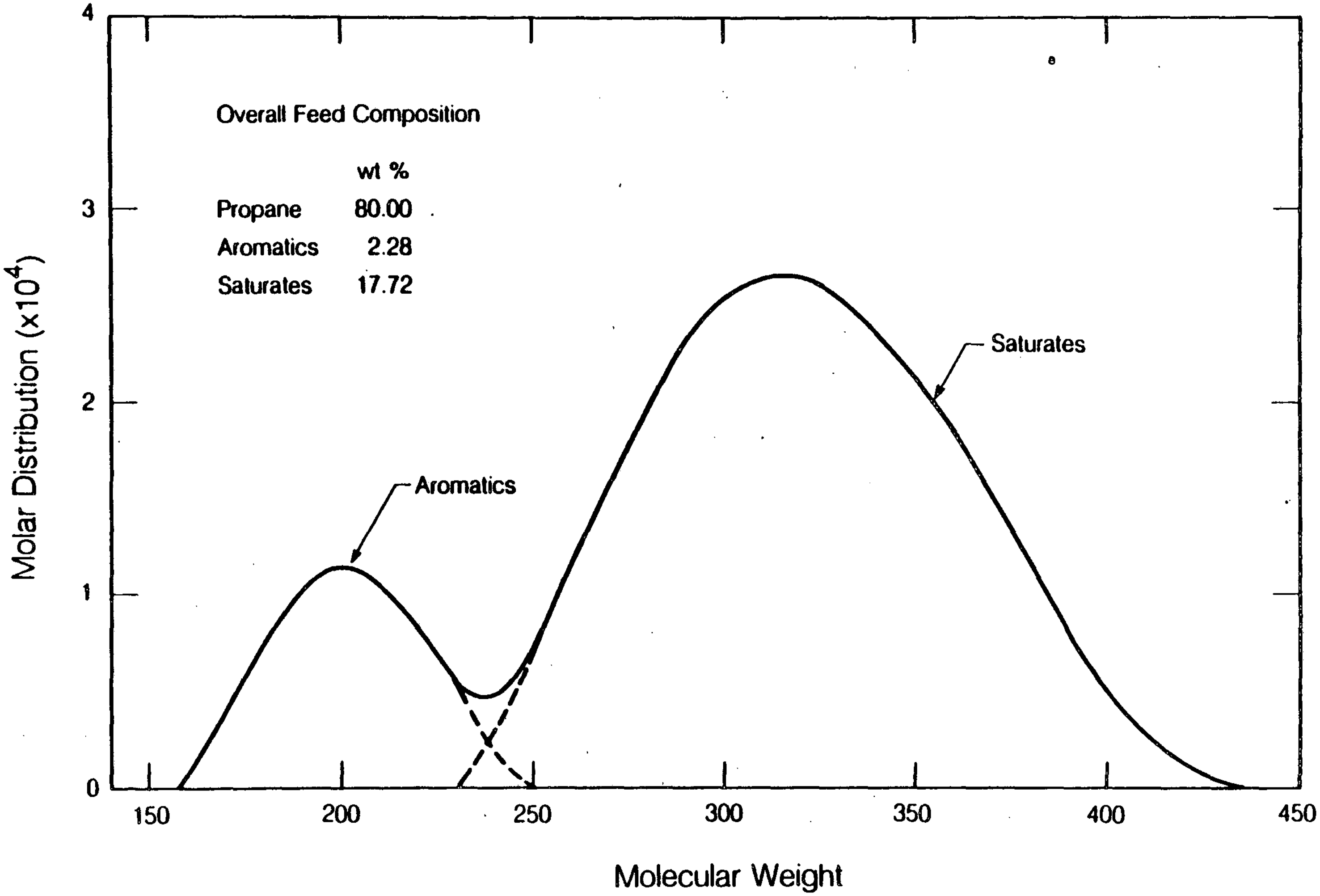

Figure 6. Molar distribution of heavies for saturates-rich oil.

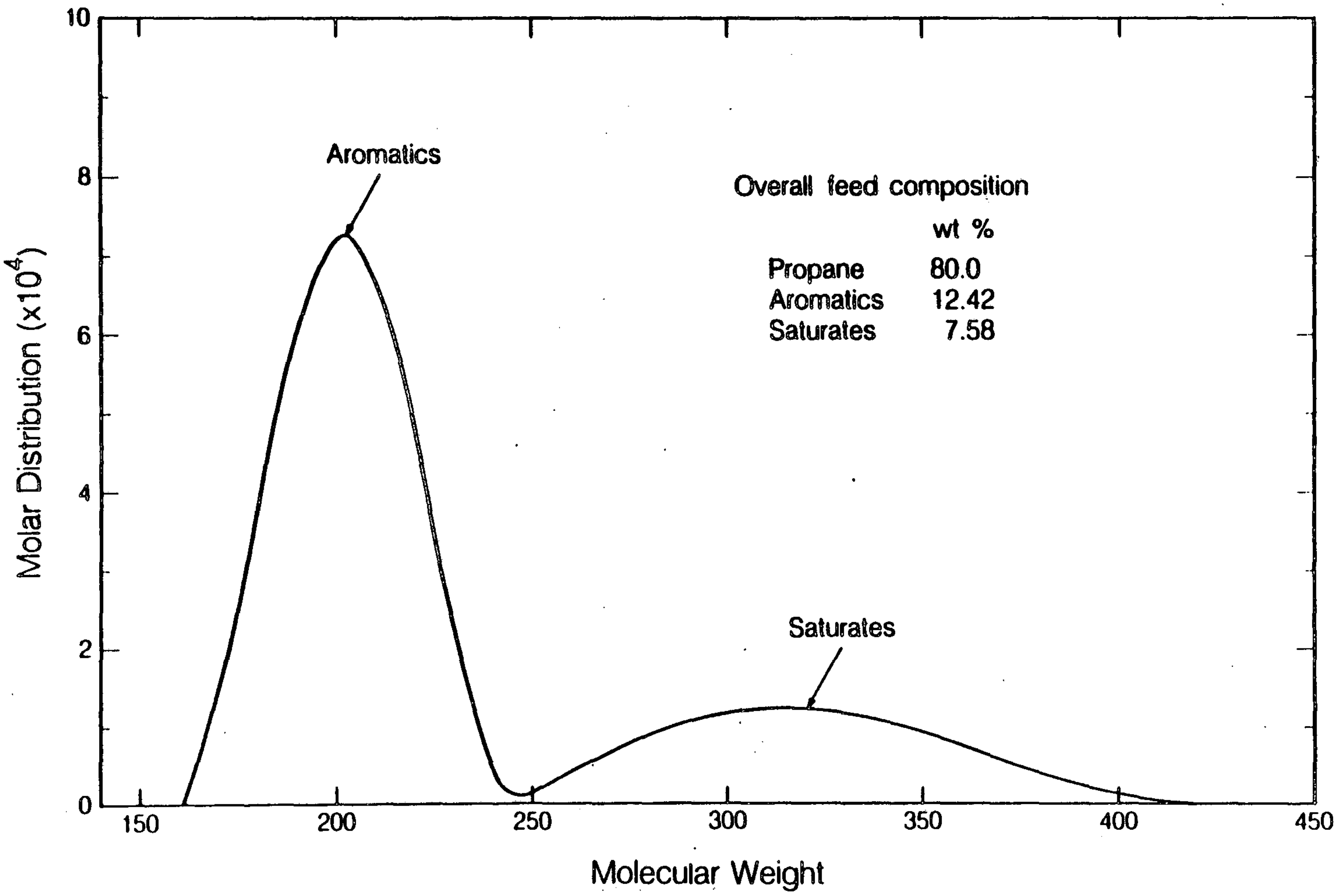

Figure 7. Molar distribution of heavies for aromatics-rich oil.

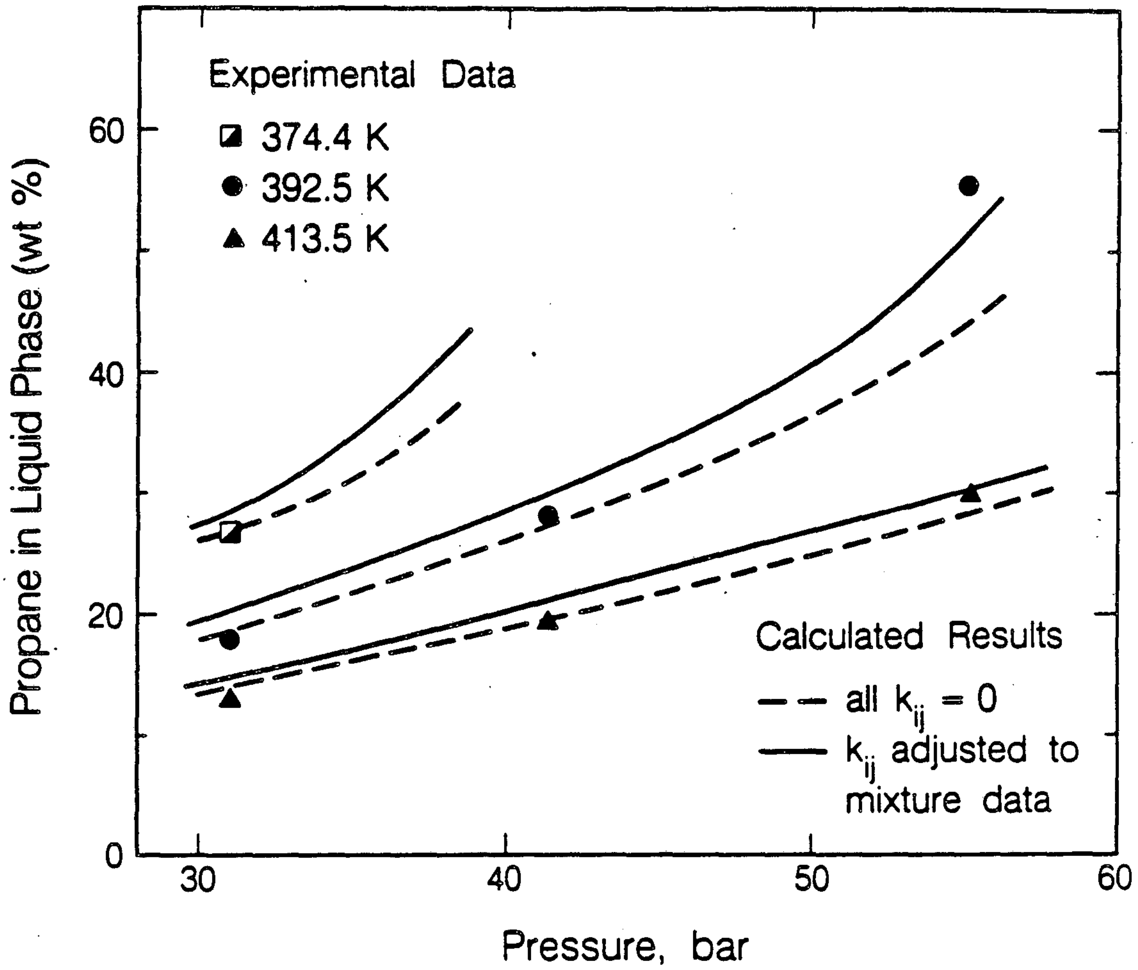

Figure 8. Calculated and experimental solubility of propane in liquid phase for saturates-rich oil.

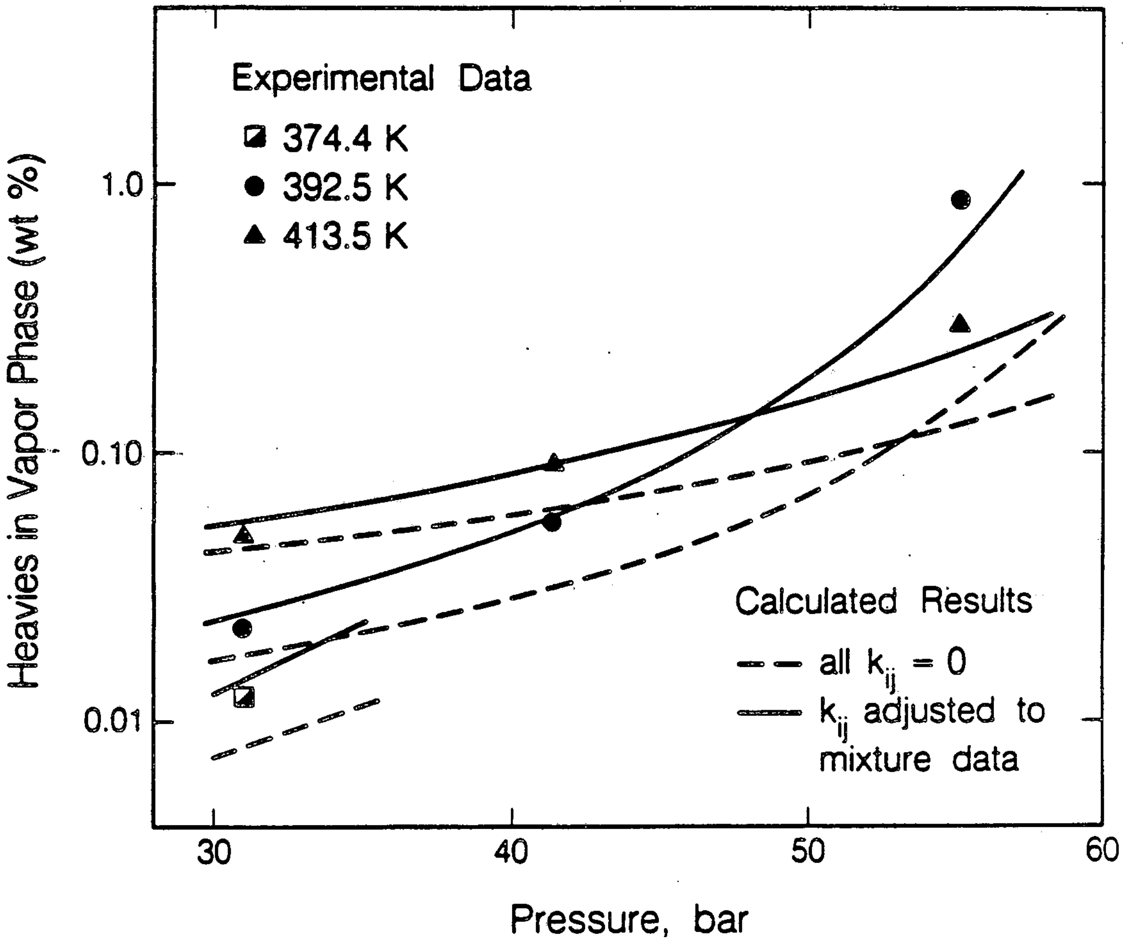

Figure 9. Calculated and experimental solubility of heavies in vapor phase for saturates-rich oil.

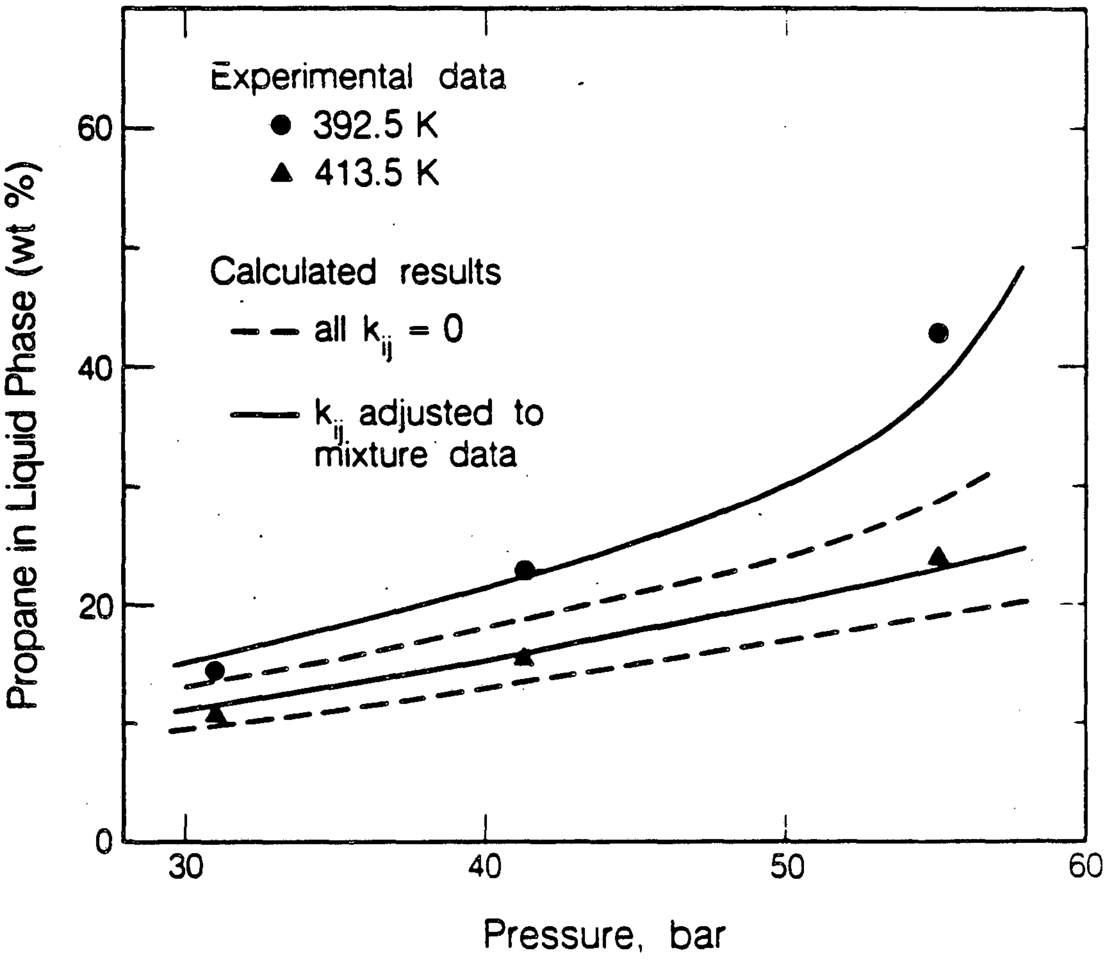

Figure 10. Calculated and experimental solubility of propane in liquid phase for aromatics-rich oil.

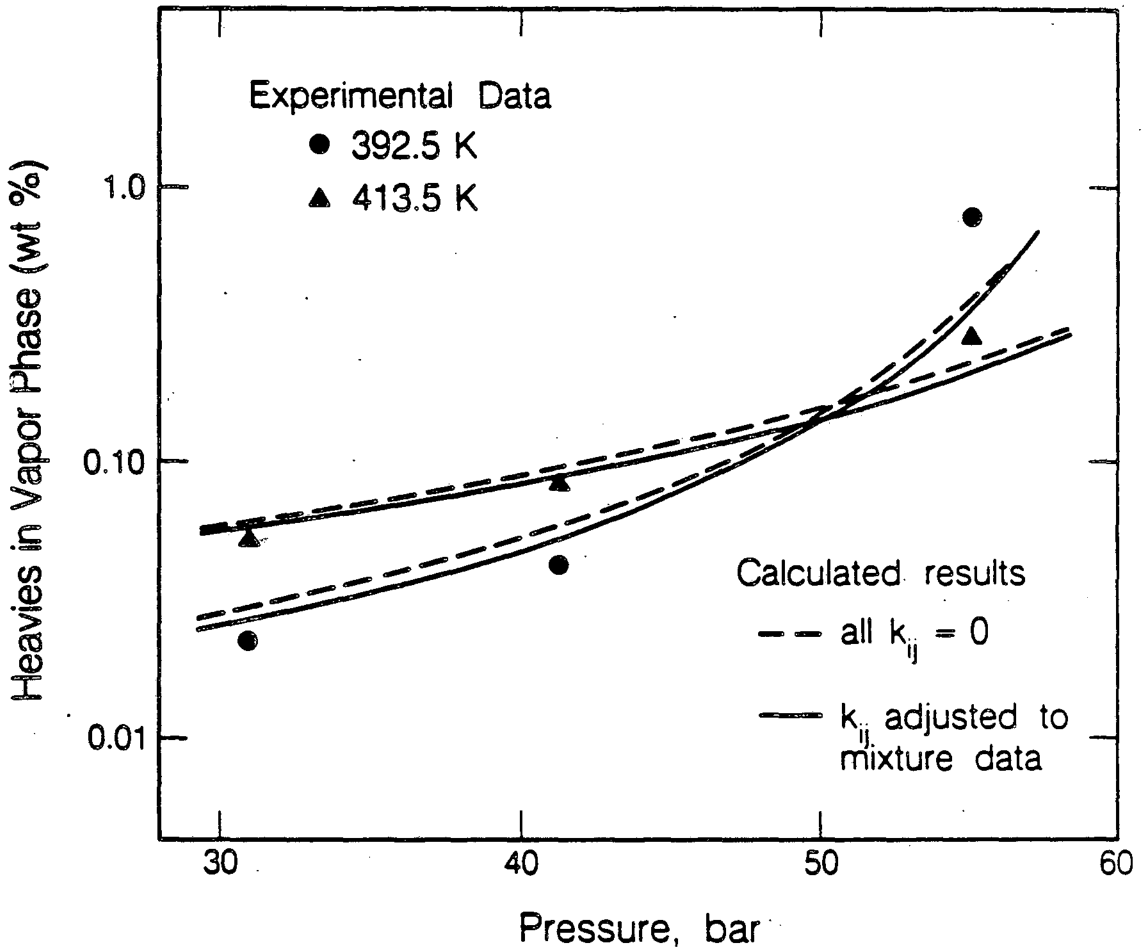

Figure 11. Calculated and experimental solubility of heavies in vapor phase for aromatics-rich oil.

APPENDIX I

Boiling-Point Analyses for Two Oils

Table I-1. Boiling-point distribution for saturates-rich oil.

	Normal Boiling Point, K		
Wt. % Off	Total Oil	Saturates Fraction	Aromatics Fraction
0.0	575.5	576.6	567.3
2.0	593.3	596.9	586.2
4.0	604.3	607.8	597.1
6.0	612.2	615.9	604.0
8.0	617.8	620.3	609.7
10.0	622.4	625.5	614.2
12.0	626.8	629.1	618.1
14.0	630.5	631.6	621.8
16.0	633.0	634.9	625.1
18.0	636.3	637.9	628.1
20.0	639.2	640.5	631.0
22.0	642.1	642.4	633.8
24.0	644.5	644.2	636.6
26.0	646.3	646.5	639.1
28.0	648.8	648.8	641.5
30.0	651.0	651.0	644.0
32.0	653.3	652.9	646.5
34.0	655.7	654.4	648.9
36.0	657.5	655.9	651.3
38.0	659.1	657.9	653.6
40.0	661.2	659.9	655.9
42.0	663.2	661.9	658.3
44.0	665.2	663.8	660.5
46.0	667.4	665.2	662.7
48.0	669.2	666.5	664.8
50.0	670.6	668.2	667.0

Table I-1 (cont). Boiling-point distribution for saturates-rich oil.

	Normal Boiling Point, K		
Wt. % Off	Total Oil	Saturates Fraction	Aromatics Fraction
52.0	672.4	670.2	669.2
54.0	674.3	672.2	671.3
56.0	676.3	674.0	673.4
58.0	678.3	675.5	675.5
60.0	680.2	676.9	677.5
62.0	681.6	678.5	679.6
64.0	683.4	680.6	681.7
66.0	685.4	682.6	683.8
68.0	687.4	684.5	685.9
70.0	689.4	686.1	688.0
72.0	691.2	687.7	690.2
74.0	692.8	689.8	692.4
76.0	694.9	692.0	694.7
78.0	697.1	694.2	697.0
80.0	699.3	696.2	699.4
82.0	701.3	698.3	702.0
84.0	703.7	701.0	704.7
86.0	706.2	703.8	707.6
88.0	709.0	706.4	710.8
90.0	711.7	709.7	714.3
92.0	715.2	713.5	718.3
94.0	718.9	717.5	723.2
96.0	724.1	723.4	729.6
98.0	731.6	732.0	740.0
100.0	744.2	747.7	758.8

Table I-2. Boiling-point distribution for aromatics-rich oil.

	Normal Boiling Point, K		
Wt. % Off	Total Oil	Saturates Fraction	Aromatics Fraction
0.0	581.5	587.9	573.0
2.0	598.0	604.3	595.7
4.0	607.9	614.8	607.0
6.0	614.4	620.2	614.0
8.0	619.5	625.5	618.8
10.0	624.0	629.1	623.2
12.0	627.7	631.8	626.8
14.0	630.9	635.0	629.9
16.0	633.7	637.8	632.8
18.0	636.6	640.2	635.4
20.0	639.2	641.9	637.9
22.0	641.5	643.6	640.1
24.0	643.9	645.7	642.2
26.0	645.9	647.7	644.4
28.0	648.0	649.6	646.4
30.0	650.2	651.4	648.5
32.0	652.2	652.9	650.4
34.0	654.1	654.2	652.2
36.0	656.0	655.6	654.0
38.0	657.8	657.3	655.8
40.0	659.4	659.0	657.5
42.0	661.3	660.8	659.3
44.0	663.0	662.4	661.1
46.0	664.8	663.8	662.8
48.0	666.6	665.0	664.5
50.0	668.4	666.4	666.2

Table I-2 (cont). Boiling-point distribution for aromatics-rich oil.

	Normal Boiling Point, K		
Wt. % Off	Total Oil	Saturates Fraction	Aromatics Fraction
52.0	670.0	668.0	667.9
54.0	671.5	669.8	669.5
56.0	673.3	671.5	671.3
58.0	675.0	673.2	673.0
60.0	676.8	674.7	674.7
62.0	678.5	675.9	676.5
64.0	680.3	677.4	678.3
66.0	681.9	679.4	680.0
68.0	683.7	681.3	681.9
70.0	685.5	683.2	683.8
72.0	687.4	684.9	685.7
74.0	689.3	686.4	687.7
76.0	691.2	688.4	689.7
78.0	693.1	690.6	691.9
80.0	695.2	692.9	694.1
82.0	697.4	694.9	696.5
84.0	699.7	697.1	699.0
86.0	702.0	699.9	701.8
88.0	704.7	702.9	704.8
90.0	707.7	705.7	708.2
92.0	710.9	709.4	712.2
94.0	714.9	713.8	716.9
96.0	720.1	719.4	723.3
98.0	728.5	728.0	733.4
100.0	746.9	743.3	751.0

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