

Predicting Phase Behavior of Condensate/Crude-Oil Systems Using Methane Interaction Coefficients

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Introduction

Prediction of phase behavior of complex hydrocarbon systems has improved gradually. Recent papers using equations of state for predicting phase fugacities of constituents have extended their usefulness to higher boiling components. Using extended analysis with boiling points of higher boiling hydrocarbon groups and their densities and molecular weights provides a basis for improvement when predicting phase behavior. At the high pressure of reservoir conditions, properties of these C_6^+ groups are important.

Using the Peng-Robinson⁵ equation of state has the advantage of improving accuracy when calculating liquid density. When used by Bergman $et\ al.^{4,6}$ with extended gas analyses, the equation gave good prediction of dew points and liquid yield at pipeline conditions. Bergman $et\ al.$ used interaction coefficients but did not completely explore their usage since phase behavior of condensates at pipeline conditions appeared rather insensitive to the C_6^+ interaction coefficients.

This paper reports the extension of the Peng-Robinson-AGA procedure⁶ for phase prediction of condensates and natural-gas/crude-oil systems at reservoir conditions. New interaction coefficients were found necessary for methane and C_6^+ constituents (especially the highest boiling group, such as C_{20}^+) so that experimental behavior could be matched by prediction. Steps for developing interaction parameters are presented. Then, agreement between measured and predicted phase

0149-2136/78/0011-6721\$00.25 ©1978 Society of Petroleum Engineers of AIMS behavior up to pressures of 64 121 kPa (9,300 psia) is shown for several crude oil and condensate systems.

Calculations of Phase Behavior

The equation of state, using the relationship of fugacity to partial molal volumes, is used to compute the fugacity of each component in both liquid and gaseous phases. At equilibrium the fugacity of each component in liquid equals its fugacity in the gaseous state.

Basic parameters for each constitutent are the critical properties, normal boiling point or vapor pressure. For hexane and heavier groups present in natural-gas and crude-oil systems, average normal boiling point, liquid density, and molecular weight are used? instead of measured properties available for pure components.

For systems containing various molecular families, the interaction coefficients between the primary constituents must be included to account for the degree of compatibility. Here methane and higher boiling C_6^+ groups are the principal components for which interaction coefficients appear significant.

Since properties of C_6^+ groups in crude oil and condensates are needed here, generalized properties are given in the absence of measured values.

Properties of Hexanes and Heavier Groups

Average boiling points, liquid densities, and molecular weights were reported by Bergman *et al.*⁶ from C₈ through C₁₅, based on analysis of 26 condensates and naturally occurring liquid hydrocarbons. This correlation

This paper extends the Peng-Robinson-AGA procedure for computing phase behavior to include gas-condensate and crude-oil systems at reservoir conditions. Interaction coefficients from methane to the C_6^+ groups were correlated with liquid density. With these coefficients, the 'rehavior of gas condensate systems may be predicted reliably.

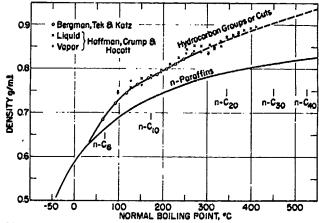


Fig. 1—Density vs bolling points of hydrocarbon groups in crude oil and condensate systems.

was extended to a normal boiling point of 500°C using added data^{8,9} for use with reservoir condensates and crude oils. Table 1 and Figs. 1 and 2 give average properties for groups of compounds boiling between 0.5°C above the previous n-paraffins¹⁰ and 0.5°C above the carbon number used to identify the group. The higher boiling point properties are only best estimates and are used for systems for which properties and/or analyses have not been performed at these high boiling points.

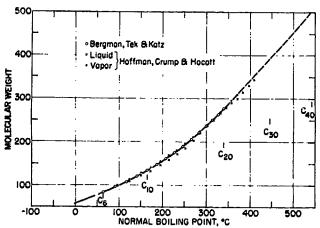


Fig. 2—Molecular vs boiling points of hydrocarbon groups in crude oil and condensate systems.

Development of Interaction Coefficients

Initial trials of predicting bubble points of crude oils with the Peng-Robinson-AGA procedure failed to give good agreement, even though extended analyses up to C_{20}^+ were used. The interaction coefficient, used earlier by Zudkevitch and Joffe, 11 was inserted in the equation of state by Peng-Robinson. 5 Using alternative interaction coefficients showed promise as a way of modifying the

TABLE 1—GENERALIZED PROPERTIES OF PETROLEUM HEXANE PLUS GROUPS

Average

			erage			
Hydrocarbon	Boiling	Boilin	ig Point	Density '	Molecular	
Group	(°C)	(°F)	(°C)	(°F)	(g/ml)	Weight
C ₆	36.5 to 69.2	97.9 to 156.7	63.9	147	0.685	84
C,	69.2 to 98.9	156.7 to 210.1	91.9	197.5	0.722	96
C _s	98.9 to 126.1	210.1 to 259.1	116.7	242	0.745	107
C,	126.1 to 151.3	259.1 to 304.4	142.2	288	0.764	121
C ₁₀	151.3 to 174.6	304.4 to 346.4	165.8	330.5	0.778	134
C ₁₁	174.6 to 196.4	346.4 to 385.5	187.2	369	0.789	147
C ₁₂	196.4 to 216.8	385.5 to 422.2	208.3	407	0.800	161
Cı3	216.8 to 235.9	422.2 to 456.7	227.2	441	0.811	175
C,4	235.9 to 253.9	456.7 to 489.2	246.4	475.5	0.822	190
C ₁₅	253.9 to 271.1	489.2 to 520	266	511	0.832	206
C16	271.1 to 287.3	520 to 547	283	542	0.839	222
C ₁₇	287 to 303	547 to 577	300	572	0.847	237
C ₁₈	303 to 317	577 to 603	313	595	0.852	251
C ₁₉	317 to 331	603 to 628	325	617	0.857	263
C ₂₀	331 to 344	628 to 652	338	640.5	0.862	275
C ₂₁	344 to 357	652 to 675	351	664	0.867	291
C ₂₂	357 to 369	675 to 696	363	686	0.872	305
C ₂₃	369 to 381	696 to 717	375	707	0.877	318
C ₂₄	381 to 392	717 to 737	386	727	0.881	331
C ₂₅	392 to 402	737 to 756	397	747	0.885	345
C ₂₆	402 to 413	756 to 775	408	766	0.889	359
C ₂₇	413 to 423	775 to 793	419	784	0.893	374
C ₂₈	423 to 432	793 to 810	429	802	0.896	388
C ₂₉	432 to 441	810 to 826	438	817	0.899	402
C₃₀	441 to 450	826 to 842	446	834	0.902	416
C ₃₁	450 to 459	842 to 857	455	850	0.906	430
C32	459 to 468 468 to 476	857 to 874	463	866	0.909	444
C ₃₃		874 to 888	471	881	0.912	458
C₃₄		888 to 901	478	895	0.914	472
C₃₅ C₃₅	483 to 491	901 to 915	486	908	0.917	486
C ₃₇			493	922	0.919	500
C ₃₆			500	934	0.922	514
C ₃ ,			508	947	0.924	528
C ₄₀			515 522	959	0.926	542
C ₄₁			522 528	972	0.928	556 670
C ₄₂			526 534	982 993	0.930	570 504
C ₄₃			540	1,004	0.931	584 609
Č.,			540 547	1,004	0.933	598 612
C ₄₅		•	553	1,017	0.935	612
-45			JUJ	1,027	0.937	626

procedure. Accordingly, interaction coefficients for methane binaries were compiled based on bubble points along with descriptive properties that might allow a correlation related to known properties of the C_8^+ groups. The interaction coefficients obtained are the values that gave minimum error for the bubble point for the range of temperature and pressure indicated in Table 2, using data from Refs. 12 through 20.

The use of liquid density at 15.5°C (60°F) for the binary component in the methane binary gave a correlation of the interaction coefficients for these systems (Fig. 3).

Interaction coefficients for nonhydrocarbons used here are 0.12 for nitrogen hydrocarbons, 20,21 and 0.15 for CO_2 hydrocarbons. Ethane and propane interaction coefficients were considered with other hydrocarbons. Because of the variation found with temperature and pressure, and the relatively small influence on the predictions, the value of 0.01 used in the Peng-Robinson-AGA procedure was continued. The interaction coefficients between methane and ethane through n-pentane were zero. Later, the significance of the interaction coefficients for methane and the last composite group, such as C_{20}^+ , will be discussed.

Natural-Gas Condensate Systems

The natural-gas condensate system used when comparing experimental data with calculated values is listed in Table 3. The measured dew-point pressure at stated temperatures, the liquid yield when flashed at given temperatures and pressures, and the corresponding equilibrium ratios are used to give three methods for comparison. For each system, the extended analysis was available. The predictions for the condensates were based on the interaction coefficients of Fig. 3, which is correlated on liquid density of the hydrocarbon groups as developed here. For natural-gas condensates, none of the experimental data being compared were used to generate the calculation procedure. Each comparison will be discussed in turn.

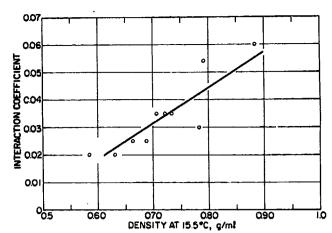


Fig. 3—Interaction coefficient from methane to other hydrocarbons as a function of the density of the iteavier hydrocarbon.

Hoffman et al. 8 Lean-Gas Condensate

Hoffman et al.'s data on the gas-cap material at the reservoir temperature of 93.9°C (201°F) are the most complete because true boiling-point distillations with densities and molecular weights were determined on cuts corresponding to n-paraffins up to C₂₂. The analysis given and the densities and molecular weights for each cut were used to predict (1) dew-point pressure, (2) liquid yield as a function of pressure down to 3551 kFa (515 psia), and (3) vapor-liquid equilibrium ratios all at 93.9°C. Table 4 compares experimental data, predicted values in this study, and published predictions by Starling.¹ Fig. 4 compares equilibrium ratios. The dewpoint pressure and liquid-yield predictions are excellent, and predicted equilibrium ratios for methane have an average absolute error of 0.76% with experimental data.

Starling¹ Rich-Gas Condensate (Fluid B)

Starling reported the analysis on a rich-gas condensate

TABLE 2-INTERACTION COEFFICIENTS FOR BINARY METHANE/HYDROCARBON SYSTEMS

Heavier Component	Interaction Coefficient	Boiling Point (°C)	Density (g/ml, 15.5°C)	Molecular Weight	Pressure Range (kPa)	Temperature Range (°C)	Ref.
nC ₄	0.02	-0.50	0.584	58.12	4100 to 12 400	71.1.87.8,104.4,121.1	12
nC ₅	0.02	36.07	0.6312	72.15	4100 to 16 100	71.1,104.4,137.8	12
nC ₆	0.025	68.74	0.6640	86.18	4050 to 16 200	75,100,150	13
nC ₂	0.025	98.43	0.6882	100.20	4100 to 20 600	71.1,104.4,137.8	14
nC _a	0.035	126.66	0.7068	114.23	4050 to 7090	75,100,150	15
nC,	0.035	150.80	0.7217	128.26	4050 to 30 400	75,100,150	16
nC ₁₀	0.035	174.12	0.7341	142.28	4100 to 32 750	71.1,104.4,137.8	12
nC ₂	0.054	343.8	0.795	282.57	500 to 6080	40	17
Benzene	0.06	80.09	0.8844	78.11	9970 to 24 200	37.8,71.1,104.4	18,19
Cyclohexane	0.03	80.72	0.7834	84.16	4100 to 24 100	71.1,104.4,137.8	20

TABLE 3—GAS-CONDENSATE/CRUDE-OIL SYSTEMS USED IN COMPARISONS OF EXPERIMENTAL WITH PREDICTED BEHAVIOR

		Temperature	Range	Pressure Range		
Authors	System	(°C)	(°F)	(kPa × 10 ⁻³)	(psia)	
Hoffman, et al.*	Condensate, crude	83.89	201	26.49 to 3.55	3,842-to 515	
Starling ¹	Condensate	101.11, 121.11	214, 250	26.16 to 3.55	3,795 to 515	
Roland ²³ Standing and	Crude oil	48.89, 93.33	120, 200	7.22 to 64.63	1,047 to 9,374	
Katz ²⁴ Katz and	Crude oil	48.89, 121.11	120, 250	6.96 to 38.13	1,010 to 5,530	
Hachmuth ²⁵	Crude oil	93.33	200	0.813 to 16.54	118 to 2,399	
Evans and Harris*	Crude oil	87.78	190	7.65 to 41.37	1,110 to 6,000	

TABLE 4—COMPARISON OF PREDICTED WITH EXPERIMENTAL DATA FOR GAS-CAP COMPOSITION OF HOFFMAN et al. • AT 98.9 ℃

		Liquia Yield*							
Pressure		Experimental		This Work		Starling ¹			
(kPa)	(psia)	(m^3/m^3x10^6)	(bbl/MMscf)	(m^3/m^3x10^6)	(bbl/MMscf)	(m³/m³x10°)	(bbl/MMscf)		
20 098	2,915	51.02	9.07	54.50	9.69	63.56	11.3		
17 340	2,515	69.97	12.44	70.25	12.49	77.62	13.8		
13 893	2,015	87.52	15.56	84.49	15.02	90.56	16.1		
10 445	1,515	95.51	16.98	92.87	16.51	98.44	17.5		
6998	1,015	95.29	16.94	94.50	16.80	97.31	17.3		
3551	515	84.82	15.08	86.00	15.29	83.81	14.9		

Experimental dew-point pressure is 36 490 kPa (3,842 psia).

Predicted dew point for this study is 26 682 kPa (3,870 psia), Starling 1 > 35 267 kPa (5,115 psia).

Average absolute deviation between experimental and predicted yields for this study is 2.6%, and 8.2% for Starling.

with extended analysis to C₂₀, but did not include liquid densities and molecular weights for the groups. His analysis with generalized liquid densities and molecular weights of Table 1 were used with the interaction coefficients in Fig. 3. Dew-point measurements at temperatures of 101.1°C and 121.1°C (214°F and 250°F) are compared with predictions along with liquid yields at these temperatures in Table 5. The method in this study showed no improvement when predicting dew-point pressure, but a modest improvement when predicting liquid yield. Note that the Starling method involved re-

PRESSURE, psia 500 1000 2000 4000 Experimental Experimental Smoothed Data) (Raw Data) C₂= Predicted EQUILIBRIUM RATIO, 0. 0.01 0.00 40,000 1000 10,000 PRESSURE, kPa

Fig. 4—Comparison of predicted with experimental K values of Hoffman et al.* condensate at 93.9°C (201°F).

gression analysis on measured equilibrium ratios to determine parameters for the common Bendict-Webb-Rubin equation of state and then predictions were made on the same systems.

Crude-Oil/Natural-Gas Systems

Data available for crude-oil/natural-gas systems are listed in Table 3. Before making phase calculations, extended analyses had to be prepared for some systems by converting distillations to individual hydrocarbon groups using the generalized properties in Table 1. Density and molecular weight of the last fraction were adjusted to provide an over-all match of reported density and molecular weight of the C_7^+ fraction.

Preliminary trials when predicting the behavior of crude-oil/natural-gas systems indicated that the interaction coefficient relationship with density did not give satisfactory results when extended to the last fraction. We knew that asphaltic and high-boiling constituents occurring in the "last fraction," such as C_{20}^+ , were not likely to have a continuous volatility behavior when measured in terms of liquid density. In the work of Roland²³ and Standing and Katz,24 the downward curvature of the vapor-liquid equilibrium ratios with increased pressure was unexpected. At that time, the explanation was that concentration of the high-boiling and asphaltic fractions in the liquid state by retrograde vaporization of the intermediate constituents was responsible for the behavior; equilibrium cell contents were approaching dew points at increased pressure. One might, therefore, expect to have a discontinuity in the interaction-coefficient/density function as the last constituent is reached. Accordingly, the interaction coefficient for the last group was determined from even a single reliable point (a bubble point, for example) because its use for predicting equilibria for other conditions is shown to be reliable.

Hoffman et al. 8 Crude-Oil System

Data are composed of composition of the equilibrium liquid and gas phases at 93.9°C (201°F) and 26 455 kPa (3,837 psia) at reservoir conditions. The interaction coefficient of the last group, C_{22}^+ , is computed using the bubble-point pressure of the liquid of 0.17. Using this value, the gas-condensate composition calculated as part of the bubble-point computation is compared with the measured composition of the gas-cap fluid in Table 6.

Roland²³ Natural-Gas/Crude-Oil System

Based on the distillation curve, density and molecular

^{*}Liquid volume at reported pressure and temperature; gas standard conditions for metric units are 15°C and 101.325 kPs.

TABLE 5—COMPARISON OF PREDICTED WITH EXPERIMENTAL DATA FOR STARLING¹ CONDENSATE AT TEMPERATURES OF 101.1 and 121.1°C (214° and 250°C)

			Liquid Yield*						
Pressure		Temperature	Experimental		This Work		Starling		
(kPa)	(psia)	(°C)	(m^3/m^3x10^6)	(bbl/MMscf)	(m^3/m^3x10^6)	(bbl/MMscf)	(m³/m³x10°)	(bbl/MMscf)	
13 893	2.015	101.1	880.2	156.5	823.50	146.4	1056.9	187.9	
10 445	1.515	101.1	877.5	156.0	780.7	138.8	990.0	176.0	
6998	1.015	101.1	822.9	146.3	706.5	125.6	872.4	155.1	
3551	515	101.1	648.8	115.3	576.0	102.4	872.4	119.7	
13 893	2.015	121.1	672.2	119.5	690.2	122.7	830.8	147.7	
8722	1,265	121.1	711.0	126.4	633.9	112.7	755.4	134.3	
Des	w-Point Te	emperature	Measur	ed (kPa)	This Stu	idy (kPa)	Starlin	g (kPa)	
101	.1°C	(214°F)	26 166 (3	,795 psia)	26	641	24 235	to 25 614	
	.1°C	(250°F)		,515 psia)	25	786	23 546	to 24 235	

^{*}Liquid volume at reported pressure and temperature, and gas standard conditions for metric units are 15°C and 101.325 kPa. Average absolute deviation for this study is 9.4% and 12.1% for Starting

weight of the C_7^+ residue, and the generalized properties in Table 1, an extended analysis up to the C_{28}^+ group was conducted for the crude oil of constant composite composition of Roland.²³

The interaction coefficient for methane through C_{28}^+ was computed by adjusting methane K values for the 24 587-kPa (3,566 psia) and 38 480-kPa (5,581 psia) runs at 120°F. The equilibrium ratios of all other runs of constant composition then were computed. Predicted equilibrium ratios at 93.3°C (200°F) are compared with experimental data in Fig. 5. The average absolute deviation of 14 runs at 93.3°C (200°F) for methane K values is 2.30%. However, if the K value of the run at 54 917 kPa

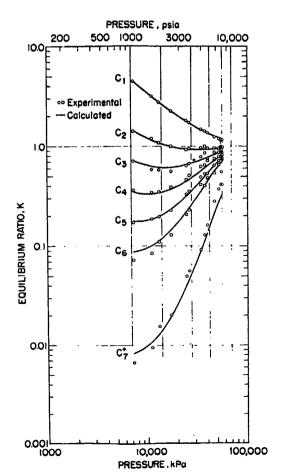


Fig. 5—Comparison of predicted with experimental K values for Roland²³ crude oil at 93.9°C (200°F).

(7,965 psia), which seems to be in some error, is excluded, the absolute deviation will improve to 1.68%. Furthermore, for 13 runs of 48.9°C (120°F) and 93.3°C (200°F) and below 46 471 kPa (6,740 psia), absolute deviation for methane equilibrium ratios is only 0.83%. Methane K values and components through C_8^+ (Table 7) indicate excellent agreement between predicted and measured values.

Standing and Katz²⁴ Natural-Gas/Crude-Oil System

Six runs were selected from Standing and Katz data. These runs belong to 49.9°API crude oil with a GOR of 650 m³/m³ (3,660 scf/bbl) at 48.9°C (120°F) and 121.1°C (250°F). Standing²6 gives extended analysis for crude oil with cut intervals of 37.8°C (100°F), and also data for molecular weight and density of high-boiling constituents vs boiling point.

The interaction coefficient between methane and the last group, with boiling points starting at 371.1°C (700°F), was obtained by using the methane K values for two runs at 121.1°C (250°F) with pressures of 21 960 kPa (3,185 psia) and 29 715 kPa (4,310 psia). Fig. 6 compares predicted with experimental K values for three runs at 48.9°C (120°F). The proposed procedure is capable of predicting downward curvature of ethane through heptane plus K values at high pressures. Deviation of the K values is given in Table 7.

Katz and Hachmuth²⁵ Crude-Oil/Natural-Gas System

Although the composite composition is not provided for this set of early data on the equilibrium ratios of the

TABLE 6—COMPARISON OF PREDICTED WITH MEASURED GAS-CAP PHASE COMPOSITION WITH HOFFMAN et al.*

Measured Composition of Gas-Cap Well Effluent (mol %)	Bubble Point Calculation on Crude Oil (mo! %)
91.35	92.12
4.03	3.504
1.59	1.52
0.19	0.16
0.158	0.116
0.050	0.046
0.004	0.0036
0.002	0.0019
	Composition of Gas-Cap Well Effluent (mol %) 91.35 4.03 1.55 0.19 0.158 0.050 0.004

TABLE 7—AVERAGE ABSOLUTE PERCENTAGE DEVIATION FOR METHANE THROUGH C_7 + K VALUES FOR CRUDE-OIL SYSTEMS

Component	Roland ²³	Standing and Katz ²⁴	Katz and Hachmuth ²⁸	Evans and Harris*
C ₁	2.4*	2.2	2.3	2.8
C ₂	3.0	4.8	2.3	9.6
C ₃	3.4	8.1	3.6	6.8
C,	6.0	4.7	1.7	10.3
C ₅	4.3	15.0	7.3	13.1
C ₆	8.7	13.6	10.1	13.9
C ₇ +	19.8	18.9	33.5	37.2
Equilibria compared	20	6	7	10

^{*}Average absolute deviations as percent of experimental values.

crude-oil/natural-gas system, the smoothness of the measured K values indicates that the composite composition change is negligible. Based on this assumption, one can compute the composite composition in the cell. Vapor- and liquid-phase compositions of the run at 12 024 kPa (1,744 psia) and 93.3°C (200°F) were selected to compute the composite composition. Liquid and vapor phases of this run were combined as 2 mol gas and 1 mol liquid. Extended analysis was conducted the same way as for Roland crude oil. The interaction coefficient for methane and the last fraction (i.e., C_{28}^+) was obtained by matching predicted vaporization to equal 66.67%. With this value of interaction coefficient, K values were predicted for other rur at 93.3°C (200°F). Table 7 indicates that predicted values agree well with experimental measurements.

PRESSURE, psia 1,000 0000 100 C, 1.0 EQUILIBRIUM RATIO, Ce 00 C² ○ □ Experimento: Predicted 0.001 1,000 10,000 PRESSURE, kPo

Fig. 6—Comparison of predicted with experimental K values for 650-m³/m³ (3,660 scf/bbi) gas-to-oil ratio of Standing and Katz²⁴ crude oil at 48.9°C (120°F).

Evans and Harris⁹ Crude-Oil/Natural-Gas System

Extended analysis for the crude oil was conducted for up to C_{28}^+ ; the interaction coefficient between this last fraction and methane was obtained by adjusting methane K values for runs of Mixture B. Fig. 7 compares predicted with experimental K values for constituents of Mixture A, and Table 7 shows percentage deviations.

General Comparison

Table 8 assembles the interaction coefficient between methane and the last group for crude oils, accompanied by properties of the last fraction. All extended analysis, except for Hoffman *et al.* crude oil, did not have true boiling-point distillation analyses. Extended analyses were improvised using judgment and generalized ex-

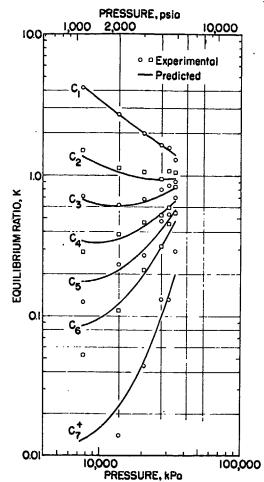


Fig. 7—Comparison of predicted with experimental K values for Mixture A crude oil of Evans and Harris^o at 87.8°C (190°F).

TABLE 8—INTERACTION COEFFICIENTS BETWEEN METHANE AND LAST FRACTION OF CRUDE-OIL SYSTEMS

			Last Fraction		
Crude Oil	Last Fraction	Interaction Coefficient	Density, at 15.5°C (g/ml)	Molecular Weight	
Hoffman et al.	C ₂₂ +	0.17	0.902	361	
Roland ²³	C ₂₅ +	0.17	0.928	492	
Standing and Katz ²⁴	C23+	0.25	1.008	622	
Katz and Hachmuth ²⁵	C28+	0.20	0.939	508	
Evans and Harris®	C22+	0.25	0.914	342	

tended hexane plus its properties. Therefore, any correlation of methane with the last group's interaction coefficient should wait for more data with systems, including true boiling-point analyses.

Recommendation

When obtaining composition data for crude-oil reservoirs, bubble-point pressure customarily is obtained at the reservoir temperature on a bottom-hole or recombined sample. The composition with extended analyses to C_{20}^+ or more, using a true boiling distillation along with bubble point, Peng-Robinson-AGA procedure, and our proposed technique (including properties of the groups, if necessary) can be used to assess the interaction coefficient for methane and the last fraction. The interaction coefficient then will give the information required for predicting phase behavior at other conditions.

Conclusions

Proper estimation of methane K values in both crude-oil and condensate systems is essential for an accurate estimate of bubble point, dew point, and flashing of these systems. Using our proposed procedure, predicted methane K values agree well with measured values.

For gas-condensate systems, the Peng-Rand and AGA procedure with extended analysis and interaction coefficients for methane and C₆+ constituents correlated with density seems to give reliable results. For crude-oil/natural-gas systems, the interaction coefficient for methane and the last fraction should be determined with a bubble point, or selected from Table 8. Gathering data with true boiling-point analyses of crude oils should help correlate the interaction coefficients for the last fraction containing the high boiling-point material and asphalt.

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