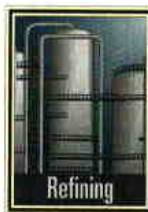


A new cubic molecular-based equation of state (MMM) accurately calculates pressure, volume, temperature (PVT) and vapor-liquid equilibrium (VLE) data for pure and mixed fluids.



Comparisons to the Redlich-Kwong (RK) equation of state, which is considered the best two-constant-param-

Equations of state

Volumetric and equilibrium calculations for oil mixtures are important in separation-equipment designs. A simple, accurate equation that calculates PVT properties of oil and gas mixtures is therefore useful for design and operation purposes.

Simple theoretical equations of state to predict fluid properties are becoming more important for industrial operators. The equations of state developed must be simple and accurate enough to replace existing empirical equations of state.

Current theoretical equations of state are based on successful theories of statistical thermodynamics.¹⁻⁴ Simple cubic equations of state, however, are still used for chemical engineering calculations especially in the oil and gas industries.⁵

We developed a molecular-based equation called the MMM equation of state.⁶ Comparisons showed the advantages of MMM vs. the RK equation as the best cubic, two-constant equation for pure and mixed fluid calculations.^{5,6}

In this article, we used the MMM equation of state to calculate the density and equilibrium states for pure, binary, ternary, and oil mixture fluids. We compared results of the volumetric calculations at different temperatures and pressures with derived results from the RK equation of state.⁷

These comparisons showed that the MMM equation of state was more accurate than the RK equation.

The Soave-Redlich-Kwong (SRK)⁸ and RK equations of state

New equation of state is accurate for VLE, PVT calculations of oil mixtures

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ter equation of state, indicated that the MMM equation of state was more accurate.

This article reports application of the MMM equation of state to pure and mixed fluid calculations of interest to the oil and gas industries. Comparison of the results to those obtained using the RK and Peng-Robinson (PR) equations of state showed that MMM is more accurate.

DENSITY OF N-HEPTANE AT 303.13 K.

Pressure, bar	Density, mole/l.		
	MMM	RK	Experimental
0	6.980	5.690	6.739
50	7.068	5.780	6.789
100	7.174	5.860	6.835
200	7.280	5.980	6.919
300	7.400	6.080	6.995
500	7.590	6.220	7.128
1,000	7.920	6.430	7.391
1,500	8.130	6.550	7.596
2,000	8.290	6.630	7.767
3,000	8.504	6.730	8.046
5,000	8.751	6.830	8.462

DENSITY OF N-NONANE AT 325.13 K.

Pressure, bar	Density, mole/l.		
	MMM	RK	Experimental
0	5.390	4.380	5.414
50	5.450	4.450	5.450
100	5.530	4.520	5.490
200	5.640	4.620	5.553
300	5.740	4.690	5.620
500	5.840	4.790	5.720
1,000	6.130	4.950	5.920
1,500	6.300	5.030	6.080
2,000	6.400	5.080	6.210
3,000	6.560	5.150	6.420
5,000	6.730	5.220	6.750

HYDROCARBON MIXTURES

Mixture	Temperature, K.	Data points	Pressure range, atm	Absolute average deviation, %	
				MMM	RK
C ₁ + nC ₆	298.15	9	10-160	2.8	15.4
C ₁ + nC ₉	273.15	18	10-318	4.2	18.8
C ₁ + nC ₉	345.15	18	10-313	1.7	19.9
C ₁ + nC ₁₀	273.15	10	10-100	3.5	22.5
C ₁ + nC ₁₀	273.15	10	20-100	3.9	25.3
C ₁ + nC ₂₀	313.15	13	1-60	19.8	51.6
C ₂ + nC ₂₀	333.15	13	1-60	18.1	55.2
C ₁ + C ₃ + nC ₁₀	277.70	23	28-280	4.1	19.7
C ₁ + C ₃ + nC ₁₀	477.60	12	28-210	10.2	21.1

EQUATIONS

$$Z = [(v + 1.3191 b) / (v - b)] - a / [RT^{3/2} (v + b)] \quad (1)$$

$$a = 0.48748 (R^2 T_c^{2.5} / P_c) \quad (2)$$

$$b = 0.064662 (R T_c / P_c) \quad (3)$$

$$Z_c = 0.333 \quad (4)$$

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (5)$$

$$a_{ij} = (1 - k_{ij}) (a_i a_j)^{1/2} \quad (6)$$

$$b = \sum_i x_i b_i \quad (7)$$

$$b = \alpha \sum_i x_i b_i + (1 - \alpha) \sum_i \sum_j x_i x_j b_{ij} \quad (8)$$

Nomenclature

a	=	Attraction parameter
α	=	Mixing rule constant
b	=	Repulsive parameter
k	=	Binary interaction parameter
P	=	Pressure, bar
R	=	Gas constant
T	=	Temperature, K
v	=	Molar volume, l./mole
x	=	Mole fraction
Z	=	Compressibility factor

Subscripts

c	=	Critical
i	=	Component i
j	=	Component j

LIQUID OIL MIXTURE AT 397 K. Table 4

Component	Mole fraction	Density, g/cc	Bubble point, bar
CO ₂	0.0133		
C ₁	0.3870		
C ₂	0.458		
C ₃	0.0315		
C ₄	0.0295		
C ₅	0.0269		
C ₆	0.0271		
C ₇	0.4386		
MMM	0.659	0.659	130.4
RK	0.495	0.495	86.4
PR	0.608	0.608	139.0
Experimental	0.648	0.648	176.0

Data source: Reference 10.

give similar results for volumetric calculations; therefore we compared MMM equation of state with RK and PR⁹ only for calculating VLE and PVT for oil mixtures.

MMM equation of state

Equations 1-4 (see Equation box) show the MMM equation of state.^{5,6}

This equation was previously used for PVT and VLE calculations of pure and mixed fluids. In this article, we

used the MMM equation to calculate the pure and mixture densities of heavy hydrocarbons, especially at high pressures.

Equations 5-7 show simple conventional mixing rules. We used a new mixing rule for the repulsive parameter, b, based on hard-sphere theoretical considerations (Equation 8).⁵

If $\alpha = 1$, Equation 8 reduces to Equation 7; therefore the popular mixing rule for b is a special form of Equation 8, the proposed mixing rule.

Calculations

Because PVT fluid properties play such an important role in the various steps of design and process operations, we used the MMM equation of state to calculate density calculations of pure components.

Tables 1 and 2 compare the results with the RK equation of state. These tables show that the MMM equation is much more accurate than the RK equation.

We also used the MMM and RK equations of state to calculate densities of binary and ternary mixtures. The calculation results in Table 3 show that MMM is more accurate than RK for density calculations of the evaluated systems.

We then applied the MMM equation to PVT and VLE calculations for oil mixtures and compared the results to data obtained using the RK and PR equations of state.

Tables 4 and 5 show the calculated results for selected oil mixtures. For all the calculations, k_{ij} equal zero.

According to our comparisons, MMM performs better than RK and PR equations for density calculations. For

LIQUID OIL MIXTURE AT 250.93 K. Table 5

Component	Mole fraction	Density, g/cc	Bubble point, bar
CO ₂	0.00184		
N ₂	0.00079		
C ₁	0.11447		
C ₂	0.06573		
C ₃	0.09115		
iC ₄	0.02639		
nC ₄	0.08337		
iC ₅	0.04814		
nC ₅	0.06281		
nC ₆	0.10205		
C ₇	0.14334		
C ₈	0.14434		
C ₉	0.06408		
C ₁₀	0.02832		
C ₁₁	0.00971		
C ₁₂	0.00364		
MMM	0.700	0.700	15.150
RK	0.514	0.514	13.190
PR	0.640	0.640	15.600
Experimental	0.685	0.685	24.125

Data source: Reference 11.

TERNARY MIXTURE C₁-C₃-C₁₀ Table 6

	Absolute average deviation, %	
	MMM	RK
Bubble point, bar	18.7	33.7
Liquid fraction, vol %	6.1	26.3
k, C ₁	3.0	5.4
k, C ₃	22.2	27.3

Temperature range = 277-477 K.
Pressure range = 27-137 bar

phase equilibrium calculations, the MMM equation of state was comparable to the PR equation; however, the MMM equation does not require accentric factor data.

For a ternary mixture (C₁-C₃-C₁₀), we compared bubble point pressure calculations using MMM and RK equations of state. Table 6 shows that MMM is the more accurate of the two equations of state.

The MMM equation of state is more suitable for extrapolation purposes due to its theoretical basis. ♦

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