Simple equation of state accurately predicts hydrocarbon densities

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A simple, cubic equation of state (EOS) for hydrocarbon systems accurately predicts densities of a variety of hydrocarbons ranging from C_1 to C_{40}.

The equation is simpler than typical industrial equations of state currently used. It produces an average error of 1.3% for density predictions of pure C_1-C_{40} hydrocarbons and 1.7% for hydrocarbon mixtures (C_1-C_{40}) at pressures as high as 700 bar and temperatures of 1,000 K. or less.

A recent article discussed uses for such equations of state (OGJ, Feb. 15, p. 76).

Usefulness

Accurate equations of state for predicting vapor pressure and pressure-volume-temperature (PVT) properties of hydrocarbons are vital to the design and operation of equipment in natural gas and other petroleum-related industries.[1]

A generalized equation for predicting vapor pressures of hydrocarbons was recently reported (OGJ, Feb. 1 p. 39). A simple, new equation of state can be used for PVT calculations of light, as well as heavy, hydrocarbons with readily available input parameters and greater accuracy than existing methods.

Because of their availability and high accuracy for PVT calculations involving hydrocarbons, the necessary input parameters are the critical properties and refractive index.

Development

Equation 1 is the Redlich-Kwong equation of state (RK-EOS)—a simple and widely used EOS (see Equations and Nomenclature). In this equation, "a" and "b" are constants defined as shown in Equations 2 and 3.

EQUATIONS

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

$$a = 0.42748\ R^2T_c^{2.5}/P_c \quad (2)$$

$$b = 0.08664\ RT_c/P_c \quad (3)$$

$$\omega = (-\log P^s_r)_{Tr=0.7-1} \quad (4)$$

$$R_m = (4\pi N_A/3)[\alpha + \mu^2 f(T)] = (1/p)(n^2 - 1)/(n^2 + 2) \quad (5)$$

$$b = (0.08664\ RT_c/P_c)\ \beta\ (R^*, T_r) \quad (6)$$

$$\beta - 1 = 1 + \{0.02[1 - 0.92\exp(-1{,}000|T_r - 1|)] - 0.035\ (T_r - 1)\}(R^* - 1) \quad (7)$$

$$T_{cm} = (\Sigma\Sigma x_i x_j T_{cij}^2/P_{cij})/(\Sigma\Sigma x_i x_j T_{cij}/P_{cij}) \quad (8)$$

$$P_{cm} = (\Sigma\Sigma x_i x_j T_{cij}^2/P_{cij})/(\Sigma\Sigma x_i x_j T_{cij}/P_{cij})^2 \quad (9)$$

$$R^*_{mix} = \Sigma\Sigma x_i x_j R^*_{ij} \quad (10)$$

$$T_{cij} = (T_{cii}T_{cjj})^{1/2}\ (1 - k_{ij}) \quad (11)$$

$$P_{cij} = 8T_{cij}/[(T_{cii}/P_{cii})^{1/3} + (T_{cjj}/P_{cjj})^{1/3}]^3 \quad (12)$$

$$R^*_{ij} = (R^*_{ii}{}^{1/3} + R^*_{jj}{}^{1/3})^3/8 \quad (13)$$

NOMENCLATURE

P = Pressure
R = Universal gas constant
T = Absolute temperature
v = Molar volume
a = Constant (see Equation 2)
b = Constant (see Equation 3)
T_r = Reduced temperature (= T/T_c)
ω = Acentric factor (see Equation 4)
R_m = Molar refraction (see Equation 5)
p = Molar density
N_A = Avogradro's number (6.023×10^{23})
α = polarizability
μ = Dipole moment (almost zero for nonpolar compounds)
n = Sodium-D light refractive index of liquid at 20° C. and 1 atm
R^* = $R_m/R_{m,ref}$
$R_{m,ref}$ = The value of molar refraction for a reference fluid (here taken to be methane) for which $\beta_{ref} = 1$
β = Dimensionless functional form defined by Equation 7 (a function of b)
β_{ref} = β for methane (a function of b, as defined in Equation 6)
T_c = Critical temperature
Z = Compressibility factor
Z_c = Critical compressibility factor

Although Equation 1 is quite accurate for the gas phase, it is not accurate enough for liquid systems or for the saturated region.[3] Many modifications of this equation—most designed to improve its accuracy for liquid-state calculations—have been reported in the literature.

A modified RK-EOS proposed by Soave, named SRK, and another cubic equation by Peng and Robinson (PR) typically are used for hydrocarbons.[4,5] The SRK and PR equations, however, break down for C_{10} and heavier hydrocarbons.

In all these equations, parameter "a" generally is considered a function of the reduced temperature and the acentric factor (Equation 4), while parameter "b" is kept constant. Parameter "b," however, is more effective for calculating liquid densities because it represents the volume of molecules.

For liquid systems in which the free space between molecules decreases, the role of "b" becomes more important than that of "a." Parameter "b" is also important for PVT prediction of dense gases and liquids.

For low-pressure gases, however, "b" becomes less important than "a" because the spacing between molecules increases and, as a re-

Table 1

HYDROCARBON PROPERTIES

Compound	T_c, K.	P_c, bar	Rm @ 20° C., cu cm/g-mole	R*	No. of data points	Temperature range, K.	Pressure range, bar	Data source (Reference No.)
Methane (C_1)	190.4	46.0	6.987	1.000	135	90-500	0.5-700	10
Ethane (C_2)	305.4	48.8	11.319	1.620	157	90-700	0.1-700	11
Propane (C_3)	369.8	42.5	15.781	2.259	130	85-700	0.1-700	12
Ethylene (C_2H_4)	282.4	50.4	10.508	1.504	90	100-500	1-400	13
Isobutane (i-C_4)	408.2	36.5	20.647	2.955	115	110-700	0.1-700	14
n-Butane (n-C_4)	425.2	38.0	20.462	2.929	183	130-700	0.1-700	15
n-Hexane (n-C_6)	507.5	30.1	29.910	4.281	100	298-1,000	1-500	8
Cyclohexane (C_6H_{12})	553.5	40.7	27.709	3.966	140	320-1,000	1-500	8
Benzene (C_6H_5)	562.2	48.9	26.186	3.748	110	310-1,000	1-500	8
Toluene (C_7H_8)	591.8	41.0	31.093	4.450	110	330-1,000	1-500	8
n-Heptane (n-C_7)	540.3	27.4	34.554	4.945	100	300-1000	1-500	8
n-Octane (n-C_8)	568.8	24.9	39.187	5.608	80	320-1,000	1-500	8
2,2,4-Trimethylpentane (C_8) [iso-octane]	544.0	25.7	39.261	5.619	70	340-1,000	1-500	8
n-Heptane (n-C_7)	540.3	27.4	34.554	4.945	35	303-373	50-500	21
n-Nonane (n-C_9)	594.6	22.9	43.840	6.274	35	303-373	50-500	21
n-Undecane (n-C_{11})	638.8	19.7	53.135	7.605	35	303-373	50-500	21
n-Tridecane (n-C_{13})	676.0	17.2	62.427	8.935	30	303-373	50-500	21
n-Heptadecane (n-C_{17})	733.0	13.0	80.948	11.585	30	323-573	50-500	21
n-Eicosane (n-C_{20})	767.0	11.1	95.418	13.656	20	373-573	50-500	21
n-Triacontane (n-C_{30})	842.0	6.7	141.298	20.223	20	373-573	50-500	21
n-Tetracontane (n-C_{40})	887.0	4.4	187.690	26.862	20	423-573	50-500	21

Table 2

COMPARISONS OF CRITICAL COMPRESSIBILITY

	Z_c				$(dP/dV)_{T_c}$ [bar-mol/cm]		$(d^2P/dV^2)_{T_c}$ [bar-mol²/cm⁶]	
Compound	Experimental	RK & SRK	PR	New	RK, SRK & PR	New	RK, SRK & PR	New
Methane	0.288	0.333	0.307	0.333	0.0	0.0	0.0	0.0
Ethane	0.285	0.333	0.307	0.293	0.0	-0.0203	0.0	0.0027
Propane	0.281	0.333	0.307	0.282	0.0	-0.0235	0.0	0.0002
Ethylene	0.276	0.333	0.307	0.295	0.0	-0.0208	0.0	0.0032
Isobutane	0.283	0.333	0.307	0.274	0.0	-0.0232	0.0	0.0014
n-Butane	0.274	0.333	0.307	0.275	0.0	-0.0229	0.0	0.0014
n-Hexane	0.260	0.333	0.307	0.264	0.0	-0.0190	0.0	0.0007
Cyclohexane	0.273	0.333	0.307	0.266	0.0	-0.0301	0.0	0.0014
Benzene	0.271	0.333	0.307	0.268	0.0	-0.0392	0.0	0.0022
Toluene	0.264	0.333	0.307	0.263	0.0	-0.0325	0.0	0.0014
n-Heptane	0.263	0.333	0.307	0.260	0.0	-0.0178	0.0	0.0005
n-Octane	0.259	0.333	0.307	0.256	0.0	-0.0164	0.0	0.0004
n-Nonane	0.260	0.333	0.307	0.253	0.0	-0.0149	0.0	0.0003
n-C_{11}	0.240	0.333	0.307	0.247	0.0	-0.0124	0.0	0.0002
n-C_{13}	0.240	0.333	0.307	0.241	0.0	-0.0111	0.0	0.0001
n-C_{15}	0.230	0.333	0.307	0.237	0.0	-0.0950	0.0	0.0001
n-C_{17}	0.220	0.333	0.307	0.233	0.0	-0.0080	0.0	0.0001
AAD*	—	**28.2%**	**18.2%**	**2.3%**	**0.0**	**0.0189**	**0.0**	**0.0010**

*Absolute average deviation

Table 3

DENSITY-PREDICTION COMPARISON

Compound	No. of data points	AAD, %			
		New	RK	SRK	PR
Methane	135	0.9	0.9	1.0	4.5
Ethane	157	1.1	2.3	2.4	4.2
Propane	130	1.4	3.4	3.5	3.9
Ethylene	90	1.3	2.4	3.4	4.5
Isobutane	115	1.4	4.7	3.9	4.9
n-Butane	183	1.1	5.0	4.7	3.4
n-Hexane	100	2.0	6.2	7.7	1.8
Cyclohexane	140	1.1	5.4	7.0	3.7
Benzene	110	1.1	5.4	4.3	1.6
Toluene	110	1.1	7.8	7.5	1.6
n-Heptane	135	1.1	8.9	9.0	1.8
n-Octane	80	1.7	9.2	9.9	2.5
2,2,4-Trimethylpentane	70	2.8	6.9	6.9	3.2
n-Nonane	35	0.6	15.5	13.4	3.4
n-Undecane	35	1.7	18.0	15.5	5.4
n-Tridecane	30	2.8	20.3	17.7	7.9
n-Heptadecane	30	1.2	27.3	24.8	16.0
n-Eicosane	20	2.8	29.5	26.7	18.2
n-Triacontane	20	0.6	41.4	39.4	32.5
n-Tetracontane	20	4.1	50.9	49.4	44.4
Overall	**1,745**	**1.33**	**7.38**	**7.28**	**4.59**

sult, the attraction energy prevails.[6] In the new RK-EOS modification presented here, "a" is kept constant while "b" is modified using the molecular theories of perturbations and refractive index.

Molar refraction (R_m), which represents the volume occupied by molecules per unit mole, is defined by Equation 5. Because "b" and "R_m" have the same physical meaning, it can be concluded that "b" must be a function of R_m. As a result, Equation 3 can be replaced with Equation 6—a general expression for "b" in terms of R_m and temperature.

Equation 7 is obtained for

Table 4

MIXTURE-PREDICTION COMPARISON

Mixtures	No. of data points	AAD, % New	RK	SRK	PR	Reference
n-Hexane + n-heptane	26	1.5	15.2	12.9	1.8	16
Benzene + cyclohexane	5	2.5	9.0	10.0	1.7	17
Benzene + n-hexane	11	0.7	12.2	10.1	1.6	18
Benzene + n-heptane	10	0.9	12.2	9.9	1.7	18
Benzene + n-octane	11	2.2	11.7	8.8	2.7	18
Toluene + n-octane	11	0.9	15.1	12.1	1.9	18
n-Octane + n-nonane	9	0.1	18.2	14.9	4.4	17
n-Octane + n-decane	9	0.5	19.2	15.9	5.2	17
n-Nonane + n-decane	9	0.6	19.6	16.3	5.4	17
n-Nonane + n-dodecane	3	0.8	21.5	18.0	9.6	17
n-Nonane + n-tetradecane	3	2.0	32.1	22.8	14.2	17
n-Nonane + n-hexadecane	3	1.8	48.8	24.5	17.6	17
Toluene + n-hexadecane	5	3.2	20.2	31.0	21.1	17
Methane + n-eicosane	13	2.8	30.5	27.2	19.2	19
Ethane + n-eicosane	13	0.3	19.2	15.6	13.9	19
Methane + propane + n-decane	44	3.1	7.9	8.5	4.9	20
Methane + propane + n-decane (at the critical state)	17	2.1	2.8	3.8	3.6	20
Total	**200**	**1.8**	**14.8**	**13.0**	**6.1**	

β, based on dense fluid data for C_2-C_8 compounds. This equation satisfies the condition $\beta = 1$ at $R^* = 1$.[7] Both "p" and "n" in Equation 7 vary with temperature, but R_m is nearly independent of temperature.

In deriving Equation 7, it was assumed that, at any given temperature, the deviation of β from unity is proportional to the deviation of R^* from unity. For all compounds, β is less than unity and, as a fluid becomes more complex, the value of β decreases.

Application to mixtures

Equations 1, 2, 6, and 7 can be applied to mixtures of known composition using the van der Waals one-fluid mixing rules.[9] This technique produces Equations 8, 9, and 10.

In these relations, summations are over all components of the mixture and x_i is the mole fraction of components i and j. Equations 11, 12, and 13 are used to represent the interaction of the terms T_{cij}, P_{cij}, and R^*_{ij}. In Equations 11-13, the term k_{ij} is the interaction parameter which, for simplicity, is considered zero in these calculations.

Equation comparability

For methane—the reference fluid here—the RK-EOS is more accurate than most other equations of state. This is demonstrated by calculating density of methane using the RK, SRK, and PR equations of state for 135 data points of methane at 90-500 K. and 0.7-700 bar.

The percentage average absolute deviation (AAD) of the density calculations using the RK equation is 0.9%. The AAD for the SRK and PR equations are 1.0% and 4.5%, respectively. The RK-EOS is therefore used as the reference EOS because it best satisfies the requirements for a simple reference fluid for hydrocarbon systems.

Table 1 presents the values of R_m (taken from TRC tables) and R^*, plus critical properties and liquid and vapor PVT data for the 20 hydrocarbons used in this study, which range from C_1 to C_{40}.[8]

A summary of the comparison of the new EOS with the RK, SRK, and PR equations is given in Tables 2 and 3. In these tables, "New" refers to calculations using Equations 1, 6, and 7.

Table 2 shows the predictions for Z_c, $(dP/dV)_{Tc}$, and $(d^2P/dV^2)_{Tc}$ for various hydrocarbons. According to Table 2, the new equation predicts the critical compressibility factor of hydrocarbons much more accurately than the other equations.

The errors of predicting the first and second derivatives of pressure, with respect to volume, at the critical point, however, are slightly increased compared to the other equations of state (Table 2).

Table 3 shows a summary of results for density calculations using the four equations of state on more than 1,700 data points. The proposed equation achieves an average error for density predictions of hydrocarbon systems, from methane to n-tetracontane (n-C_{40}), of 1.33%, for pressures as high as 700 bar.

According to Tables 2 and 3, this new modification of the RK-EOS is superior to the other equations of state for all the hydrocarbons studied. The proposed equation is also simple and more accurate than any other conventional cubic equations currently used.

A bank of density data for some binary and ternary hydrocarbon mixtures has been collected from the literature (Table 4).[16-20] The proposed EOS, along with Equations 8-13 for mixture properties, was evaluated using this data base. Results are given in Table 4.

For the 17 binary and ternary mixtures used in this evaluation, the new EOS gives an average absolute deviation of 1.8%, which is far better than the other equations tested. The Peng-Robinson equation, for example, gives an error of 6.1% for these mixtures.

Note that the last set of data in Table 4 is taken from the mixture of methane, propane, and n-decane at the critical state. Equation 4 was

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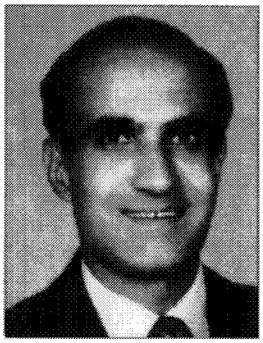

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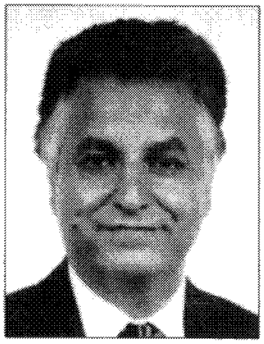

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used for the evaluations shown in Table 4 because the exponential term in Equation 6 disappears, even for mixtures at the critical state.

A major advantage of the new EOS is that, when it is applied to mixtures of undefined petroleum fractions and direct experimental data are available for molecular weight, refractive index, and density at 20° C., there is no need to calculate the mixture molar refraction. In such cases, acentric factors may not be calculated accurately.

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