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025397 An Accurate Equation of State for Hydrocarbon Systems
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Abstract:

A simple modification has been introduced to parameter b in the original Redlich-Kwong equation of state in terms of molar refraction and temperature. While the proposed modification is simpler than any other modified equation of state, it produces an average error of 1.3% for density predictions of hydrocarbons from C_1 to C_{40} at pressures to 700 bar and temperatures to 1000 K. This new simple equation seems to be the most accurate equation of state ever developed for non-polar and hydrocarbon systems and it greatly improves phase behavior studies of reservoir fluids.

Introduction:

Since 1949 when Redlich and Kwong (RK) formulated their two-parameter cubic equation of state (EOS), many investigators have introduced various modifications to improve ability of RK-EOS. Two other well-known cubic equations are Soave (SRK) (1972) and Peng-Robinson (PR) (1976) equations. Although many modified forms of RK-EOS are reported in the literature, but at least for hydrocarbon systems and their mixtures, only SRK and PR equations have been widely accepted. However, these equations break-down at C_{10} - C_{11} and heavier compounds. Peneloux and Rauzy (1982) introduced a constant for each substance to be subtracted from the volume obtained in the SRK equation. Their modification greatly improves liquid density predictions, but it requires a fourth parameter beside critical temperature, critical pressure and acentric factor required by SRK equation. Reid et. al. (1987) give a good summary of these cubic equations of state.

Both SRK and PR equations use Pitzer acentric factor as the third parameter to obtain parameter a in their equations. Acentric factors are calculated through critical properties, therefore, for heavy compounds where critical properties should be estimated, errors in critical properties will be contributed to acentric factor.

The main objective of this paper is to introduce a simple equation of state which can be applied to heavy hydrocarbons with readily available input parameters and higher degree of accuracy. Refractive index parameter is considered in this paper because of its availability and high accuracy for hydrocarbon systems.

Technical Development:

One of the most widely used and simple two-parameter cubic equation of state is the original Redlich-Kwong equation (RK-EOS) given by the equation

$$P = \frac{RT}{V - b} - \frac{a}{T^{1/2} V(V + b)} \quad (1)$$

where T is absolute temperature and V is the molar volume. R is the gas constant and a and b are two constants given by the following equations in terms of critical temperature and pressure:

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

$$b_{RK} = \frac{0.08664 RT_c}{P_c} \quad (3)$$

Most modifications of RK-EOS such as Soave (1972) use parameter a as a function of reduced temperature and Pitzer's acentric factor. The main purpose for modification of RK-EOS by many investigators was to improve accuracy of eq. 1 for liquid systems. However the parameter which is more effective on liquid densities is parameter b and not a . Because parameter b represents the volume of molecules themselves and for liquid systems where the free space between molecules becomes smaller, the role of parameter b becomes more important than parameter a . The role of parameter b is important for PVT prediction of dense gases and liquids (dense fluids). Parameter b becomes less important than parameter a for low pressure gases since the space between molecule is larger and as a result the attraction energy prevails in this case as discussed by Haile and Mansoori (1983).

Eq. 1 can be written in terms of molar density (ρ) and compressibility factor (Z) in the following form:

$$Z = \frac{1}{1 - b\rho} - \frac{a\rho}{RT^{3/2}(1 + b\rho)} \quad (4)$$

It is clear from this equation that for gases where values of ρ are small, parameter a is the governing parameter in eq. 4 while for liquids and dense gases (dense fluids) where values of ρ are large, parameter b becomes more important than parameter a . Therefore in order to improve accuracy of eq. 1 for dense fluid systems parameter b should be modified.

In this work we only consider non-polar compounds especially hydrocarbon systems which constitute petroleum mixtures and reservoir fluids. An accurate equation of state is a vital tool in phase behavior calculations of reservoir fluids in reservoir simulations as well as estimation of many thermodynamic properties of

petroleum fractions necessary in design and operation of equipments in petroleum related industries.

As discussed by Hirschfelder et. al. (1964), for non-polar compounds one of the parameters which represent intermolecular forces is the polarizability (α) given by the equation

$$\alpha = \frac{3}{4\pi N_A} \frac{1}{\rho} \frac{n^2 - 1}{n^2 + 2} \cdot \mu^2 f(T) \quad (5)$$

where N_A is the Avogadro's number, n is the refractive index (normally Sodium-D light) and μ is the dipole moment of the molecules which for non-polar compounds is almost zero. Molar refraction (R_m) is defined as:

$$R_m = \frac{1}{\rho} \frac{n^2 - 1}{n^2 + 2} \quad (6)$$

where ρ is the molar density. Parameter R_m represents the volume occupied by molecules per unit mole while $\frac{1}{\rho}$ represents the total (or apparent) molar volume

including the free space between molecules. Therefore, $\frac{n^2 - 1}{n^2 + 2}$ represents the fraction of total volume occupied by molecules and is one of the powerful parameters in prediction of many physical and thermodynamic properties as shown by Riazi and Daubert (1987). It should be noted that parameter b in the van der Waals equation and parameter R_m have the same physical meaning and investigation of data shows that there is a strong relationship between parameter b and the molar refraction, R_m for non-polar compounds.

Both ρ and n in eq. 6 vary with temperature, but R_m is nearly independent of temperature especially over a narrow temperature range. Values of R_m for many hydrocarbon compounds up to n-tetracontane (C_{40}) have been reported in TRC Tables (1986) at two different temperatures of 20 and 25°C. The difference between values of R_m at these two temperatures for most compounds is less than 0.05%. Both ρ and n are easily measurable for hydrocarbons at 1 atm with high degree of accuracy and usually are reported at 20°C and 1 atm for liquid systems as reference state. These properties can also be estimated with very good accuracy both for pure compounds and mixtures as discussed by Riazi and Danbert (1980, 1987) and Riazi (1989).

For simple fluids such as methane where its acentric factor is small, the original Redlich-Kwong equation of state is the most accurate one among various other equations of state. Table 1 shows a simple comparison among RK, SRK and PR equations for two relatively simple fluids of methane and oxygen. Therefore, we take RK-EOS as our reference equation of state which best satisfies a reference simple fluid such as methane for the case of hydrocarbon systems.

If we indicate actual value of b in the RK equation which best represents the equation for a given substance by b_{act} we define a parameter β as:

$$\beta \equiv \frac{b}{b_{RK}} \quad (7)$$

where b_{RK} is parameter b in the original RK equation and is given by eq. 3. Provided the RK-EOS is exact for a given fluid, then the value of β for that fluid is unity. Since we assume RK-EOS is the best equation for the reference fluid (methane), therefore we can assume:

$$\beta_{ref} = 1 \quad (8)$$

For other compounds β is not equal to unity and normally is less than one. As a fluid becomes more complex, value of β becomes smaller.

Since parameter R_m (or the polarizability α) represents parameter b , therefore we can assume that for a non-polar fluid:

$$\frac{\beta}{\beta_{ref}} = \frac{\alpha}{\alpha_{ref}} \quad (9)$$

Combining eqs. 5, 6, 8 and 9 would result

$$\beta = f(r, T_r) \quad (10)$$

in which T_r is the reduced density and parameter r is defined as:

$$r \equiv \frac{R_m}{R_{m,ref}} \quad (11)$$

Function f in eq. 10 yet to be determined later. In Table 2 values of R_m for some compounds used in this study are given. They are all taken from TRC Tables (1986). For methane, our reference fluid at 20°C and 1 atm the system is not at liquid state and value of R_m is not reported in TRC Tables. However, based on the values for n and ρ at 20°C and 1 atm for n-alkanes from C_2 to n- C_{20} given in TRC Tables a relatively accurate value for R_m of methane at 20°C at a hypothetical liquid state can be estimated through eq. 6 as given in Table 2. However as we can see later this value of R_m for the reference fluid does not affect our calculations in any way, since for the reference fluid the value of β is assumed to be unity. Values of r calculated through eq. 11 are also given in Table 2. For more complex fluids, r becomes larger and larger. Eq. 10 assumes that at any given temperature deviation of β from unity is proportional to deviation of r from unity or β is only a function of r so that as $r \rightarrow 1$ we have $\beta \rightarrow 1$.

A bank of P, ρ, T data on 20 compounds from different hydrocarbon groups ranging from C_1 to C_{40} was collected from mainly three different sources as given in Table 2. Data for C_1 to C_4 were taken from various National Bureau of Standard (NBS) Technical reports and for C_6 to C_8 data have been taken from TRC Tables (1986). These data cover the temperature and pressure ranges from gaseous to liquid state as specified in Table 2. The last data set for normal alkanes from $n-C_7$ to $n-C_{40}$ are taken from data reported by Doolittle (1964) which are only for liquid state and does not contain any gas data. It should be noted that we have two sets of data for normal heptane ($n-C_7$), one taken from TRC Tables and the other one taken from Doolittle (1964) data set. These data do not, in general, agree with each other. In some instances these values differ up to 3%. For example at 500 bar and 300°C value of molar density reported by Doolittle for $n-C_7$ is 5.56 g-mole/L while at the same condition value of ρ from TRC Tables is 5.73 g-mole/L. However, we will use Doolittle data set only for the purpose of evaluation of various equations of state for heavy compounds. Data on P, ρ, T reported in Table 2 for compounds from C_2 to C_8 were used for the determination of f function in eq. 10.

As discussed earlier for the gaseous systems (low pressure) RK-EOS is the most accurate equation and does not require any modification. In fact in the region where $|Z - 1| \leq 0.1$, RK - EOS is superior to any other equation of state. Therefore we use data on P, ρ, T in the region $|Z - 1| > 0.1$ to find f function in eq. 10. In this region data normally represent liquid and dense gas systems. However, as discussed earlier, modified values of b do not significantly change the nature of equation of state for gaseous systems at low pressures. With respect to the above points, the following form for eq. 10 was obtained based on the dense fluid data set for $C_2 - C_8$ compounds:

$$\beta^{-1} = 1 + [0.02 - 0.035 (T_r - 1)] (r - 1) \quad (12)$$

Although many other functional forms may be used instead of eq. 12, but eq. 12 is one of the simplest forms which satisfies the condition of $\beta = 1$ at $r = 1$.

Results and Discussion:

A summary of evaluation of this proposed equation of state with original RK-EOS, SRK and PR equations as well as modified SRK equation (MSRK) proposed by Peneloux and Rauzy (1982) is given in Table 3 for $C_1 - C_8$ compounds. The same comparison for $n - C_7$ to $n - C_{40}$ data set of Doolittle (1964) which have not been used in obtaining eq. 12 is shown in Table 4. Data on critical properties, acentric factor and Rackett parameter given in Table 2 are all taken from Reid, et. al. (1987) book. Coefficients a and b for SRK and PR equations as well as the volume translation parameter needed in MSRK equation of Peneloux and Rauzy (1982) are also taken from Reid et. al. (1987). MSRK method requires that volume obtained in the SRK should be subtracted from parameter c given by the following correlation:

$$c = 0.40768 (0.29441 - Z_{RA}) RT_c/P_c \quad (13)$$

where Z_{RA} is the Rackett compressibility factor parameter.

Tables 3 and 4 show summaries of all results for density calculations through various equations of state for over 1700 data points collected from the literature. In these tables "NEW" refers to eqs. 7 and 12 together with eq. 1. In other words in the method proposed in this work, for parameter b in eq. 1 the following equation is recommended:

$$b = \frac{0.08664 RT_c/P_c}{1 + [0.02 - 0.035 (T_r - 1)] (r - 1)} \quad (14)$$

Eq. 14 is derived from eqs. 3, 7 and 12. As it can be seen from Tables 3 and 4, the new modified RK-EOS is superior than other equations of state especially for heavier compounds. It should be emphasized again that Table 4 represents evaluation of data which were not used in obtaining eq. 12. The only equation which is comparable with the new proposed method is MSRK method using eq. 13 together with SRK equation. PR-EOS is better than MSRK equation only for compounds C_6 to C_9 . Overall, the new proposed equation (eq. 14) gives an average error nearly half of that from MSRK method.

Point by point density predictions from various equations of state for normal alkanes from C_1 to C_8 at 500 bar and 400 K are shown in Figure 1. Similar results for heavy compounds from $n - C_9$ to $n - C_{30}$ at 500 bar and 373 K are shown in Figure 2. Note that since parameter Z_{RA} for $n - C_{30}$ and $n - C_{40}$ were not available, the MSRK method (eq. 13) cannot be applied to heavy compounds. Use of critical compressibility (Z_c) instead of Z_{RA} in MSRK leads to significant errors for $n - C_{30}$ and $n - C_{40}$ (47% and 87% respectively). Although the MSRK method gives relatively good results especially for light compounds, this method requires four parameters, one of which, Z_{RA} , is neither available for heavy compounds nor for the mixtures.

Another advantage of this method is its application to mixtures. For mixtures both p and n at 20 °C are easily measurable with high degree of accuracy and therefore parameter r can be obtained directly from experimental measurements. While in other equations of state values of acentric factor for mixtures should be calculated through critical properties which are not measurable. Whitson (1984) has shown how various equations of state are sensitive to their input parameters.

Conclusions:

Based on the theory of intermolecular forces for non-polar compounds and hydrocarbon systems, parameter b in the original Redlich-Kwong equation of state has been modified in the form of eq. 14 in terms of molar refraction ratio with respect to

a reference simple fluid and reduced temperature. The proposed equation reduces average error for density predictions of hydrocarbon systems from methane to n-tetracontane (n - C₄₀) to 1.3% for pressures to 700 bar. The proposed equation is also simple while more accurate than any other conventional cubic equations currently being used in reservoir simulations and does not require acentric factor as an input parameter.

NOMENCLATURE:

a = parameter in the original Redlich-Kwong equation of state.

b = parameter in the original Redlich-Kwong equation of state (eq. 1).

b_{RK} = original Redlich-Kwong b parameter defined in eq. 3.

c = volume translation parameter defined in eq. 13.

n = Sodium-D light refractive index of liquid at 20°C and 1 atm.

N_A = Avogadro's number.

P_c = critical pressure

R = gas constant

R_m = molar refraction defined in eq. 6.

r = molar refraction defined in eq. 11.

T = absolute temperature

T_c = critical temperature

T_r = reduced temperature (= T/T_c)

v = molar volume

Z = compressibility factor

Z_c = critical compressibility factor

Z_{RA} = Rackett compressibility factor parameter

Greek Letters:

α = polarizability

β = dimensionless b parameter defined in eq. 7 ($= b/b_{RK}$)

ρ = molar density ($= 1/V$)

μ = dipole moment

Units: P_c in bar, T in $^{\circ}K$, ρ in g-mole/mL,
 $R = 83.1432$ bar cm^3 /g-mole, $^{\circ}K$

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Table 1

Evaluation of RK, SRK and PR Equations of State for Density Prediction of Two Simple Fluids

| Compound | No. of Data Points | Temperature Range, °K | Pressure Range, Bar | AAD%* | | | Data Source |
|----------|--------------------|-----------------------|---------------------|-------|-----|-----|----------------|
| | | | | RK | SRK | PR | |
| Methane | 135 | 90 - 500 | 0.7 - 700 | 0.88 | 1.0 | 4.5 | Goodwin (1974) |
| Oxygen | 120 | 80 - 1000 | 1 - 500 | 1.1 | 1.4 | 4.0 | TRC (1986) |

*RK: Redlich-Kwong; SRK: Soave-Redlich-Kwong;
PR: Peng-Robinson

$$\text{AAD\%: \%average absolute deviation} = \frac{1}{N} \sum \left| \frac{\rho_{\text{calc}} - \rho_{\text{exp}}}{\rho_{\text{exp}}} \right| \times 100$$

N: no. of data points.

Table 2
Density Data Bank and Properties of Compounds Used in This Work

| Compound | T_c , K | P_c , bar | ω | Z_{RA} | R_m , 20°C cm ³ /g-mole | r | No. of Data Points | Temperature Range, K | Pressure Range, Bar | Data Source |
|--|-----------|-------------|----------|----------|---|--------|-----------------------|-------------------------|------------------------|-----------------------------|
| Methane (C ₁) | 190.4 | 46.0 | 0.011 | 0.2892 | 6.987 | 1.000 | 135 | 90 - 500 | 0.5 - 700 | Goodwin (1974) |
| Ethane (C ₂) | 305.4 | 48.8 | 0.099 | 0.2808 | 11.319 | 1.620 | 157 | 90 - 700 | 0.1 - 700 | Goodwin et. al. (1974) |
| Propane (C ₃) | 369.8 | 42.5 | 0.153 | 0.2766 | 15.781 | 2.259 | 130 | 85 - 700 | 0.1 - 700 | Goodwin and Haynes (1982) |
| Ethylene (C ₂ H ₄) | 282.4 | 50.4 | 0.089 | 0.2815 | 10.508 | 1.504 | 90 | 100 - 500 | 1 - 400 | McCarty and Jacobsen (1981) |
| Isobutane (iC ₄) | 408.2 | 36.5 | 0.183 | 0.2754 | 20.647 | 2.955 | 115 | 110 - 700 | 0.1 - 700 | Goodwin and Haynes (1982) |
| n-Butane (n - C ₄) | 425.2 | 38.0 | 0.199 | 0.2730 | 20.462 | 2.929 | 183 | 130 - 700 | 0.1 - 700 | Haynes and Goodwin (1982) |
| n-Hexane (n - C ₆) | 507.5 | 30.1 | 0.299 | 0.2635 | 29.910 | 4.281 | 100 | 298 - 1000 | 1 - 500 | TRC Tables (1986) |
| Cyclohexane (C ₆ H ₁₂) | 553.5 | 40.7 | 0.212 | 0.2729 | 27.709 | 3.966 | 140 | 320 - 1000 | 1 - 500 | " |
| Benzene (C ₆ H ₆) | 562.2 | 48.9 | 0.212 | 0.2698 | 26.186 | 3.748 | 110 | 310 - 1000 | 1 - 500 | " |
| Toluene (C ₇ H ₈) | 591.8 | 41.0 | 0.263 | 0.2644 | 31.093 | 4.450 | 110 | 330 - 1000 | 1 - 500 | " |
| n-Heptane (n - C ₇) | 540.3 | 27.4 | 0.349 | 0.2604 | 34.554 | 4.945 | 100 | 300 - 1000 | 1 - 500 | " |
| n-Octane (n - C ₈) | 568.8 | 24.9 | 0.398 | 0.2571 | 39.187 | 5.608 | 80 | 320 - 1000 | 1 - 500 | " |
| 2,2,4-Trimethylpentane (C ₈) (iso-octane) | 544.0 | 25.7 | 0.303 | 0.266 | 39.261 | 5.619 | 70 | 340 - 1000 | 1 - 500 | " |
| n-Heptane (n - C ₇) | 540.3 | 27.4 | 0.349 | 0.2604 | 34.554 | 4.945 | 35 | 303 - 373 | 50 - 500 | Doolittle (1964) |
| n-Nonane (n - C ₉) | 594.6 | 22.9 | 0.445 | 0.2543 | 43.840 | 6.274 | 35 | 303 - 373 | 50 - 500 | " |
| n-Undecane (n - C ₁₁) | 638.8 | 19.7 | 0.535 | 0.2499 | 53.135 | 7.605 | 35 | 303 - 373 | 50 - 500 | " |
| n-Tridecane (n - C ₁₃) | 676.0 | 17.2 | 0.619 | 0.2473 | 62.427 | 8.935 | 30 | 303 - 373 | 50 - 500 | " |
| n-Heptadecane (n - C ₁₇) | 733.0 | 13.0 | 0.770 | 0.2343 | 80.948 | 11.585 | 30 | 323 - 573 | 50 - 500 | " |
| n-Eicosane (n - C ₂₀) | 767.0 | 11.1 | 0.907 | 0.2281 | 95.418 | 13.656 | 20 | 373 - 573 | 50 - 500 | " |
| n-Triacontane (n - C ₃₀) | 842.0 | 6.7 | 1.210 | ----- | 141.298 | 20.223 | 20 | 373 - 573 | 50 - 500 | " |
| n-Tetracontane (n - C ₄₀) | 887.0 | 4.4 | 1.500 | ----- | 187.690 | 26.862 | 20 | 423 - 573 | 50 - 500 | " |

*Data on T_c , P_c , ω , and Z_{RA} are taken from Reid et. al. (1987). Data on R_m are taken from TRC Tables (1986).

Table 3

Comparison of Various Equations of State for Density Prediction of Light Compounds

| Compound | No. of Data Points | AAD% | | | | |
|------------------------|-----------------------|------------|------------|------------|------------|------------|
| | | New* | RK | SRK | MSRK | PR |
| Methane | 135 | 0.9 | 0.9 | 1.0 | 1.0 | 4.5 |
| Ethane | 157 | 1.1 | 2.3 | 2.4 | 1.3 | 4.2 |
| Propane | 130 | 1.4 | 3.4 | 3.5 | 2.3 | 3.9 |
| Ethylene | 90 | 1.3 | 2.4 | 3.4 | 1.6 | 4.5 |
| Isobutane | 115 | 1.4 | 4.7 | 3.9 | 2.6 | 4.9 |
| n-Butane | 183 | 1.1 | 5.0 | 4.7 | 2.0 | 3.4 |
| n-Hexane | 100 | 2.0 | 6.2 | 7.7 | 2.6 | 1.8 |
| Cyclohexane | 140 | 1.1 | 5.4 | 7.0 | 3.2 | 3.7 |
| Benzene | 110 | 1.1 | 5.4 | 4.3 | 1.3 | 1.6 |
| Toluene | 110 | 1.1 | 7.8 | 7.5 | 1.9 | 1.6 |
| n-Heptane | 100 | 1.3 | 7.8 | 8.5 | 3.0 | 1.9 |
| n-Octane | 80 | 1.7 | 9.2 | 9.9 | 2.7 | 2.5 |
| 2,2,4-Trimethylpentane | 70 | 2.8 | 6.9 | 6.9 | 3.7 | 3.2 |
| TOTAL | 1520 | 1.3 | 4.9 | 5.1 | 2.2 | 3.3 |

*New refers to the method developed in this work: eqs. 1, 2, & 14.

RK, SRK & PR are defined in Table 1.

MSRK refers to the volume translation method: eq. 13 & SRK.

AAD% defined in Table 1.

Data sources and other information are given in Table 2.

Table 4

Comparison of Various Equations of State for Density Prediction of Heavy Compounds

| Compound | No. of Data Points | AAD% | | | | |
|-----------------------------|-----------------------|-------------|-------------|-------------|--------------|-------------|
| | | New | RK | SRK | MSRK | PR |
| n-Heptane | 35 | 0.6 | 12.1 | 10.5 | 3.4 | 1.4 |
| n-Nonane | 35 | 0.6 | 15.5 | 13.4 | 3.1 | 3.4 |
| n-Undecane | 35 | 1.7 | 18.0 | 15.5 | 3.0 | 5.4 |
| n-Tridecane | 30 | 2.8 | 20.3 | 17.7 | 2.2 | 7.9 |
| n-Heptadecane | 30 | 1.2 | 27.3 | 24.8 | 1.8 | 16.0 |
| n-Eicosane | 20 | 2.8 | 29.5 | 26.7 | 2.2 | 18.2 |
| n-Triacontane | 20 | 0.6 | 41.4 | 39.4 | — | 32.5 |
| n-Tetracontane | 20 | 4.1 | 50.9 | 49.4 | — | 44.4 |
| TOTAL | 225 | 1.6 | 24.3 | 22.1 | 2.7* | 13.3 |
| Overall with Table 3 | 1745 | 1.33 | 7.38 | 7.28 | 2.22* | 4.59 |

*For MSRK method due to lack of values for Z_{RA} , last two compounds (C_{30} & C_{40}) were not included in AAD% calculation.

Fig. 1. Densities of Light n-Alkanes at 500 Bar & 400 K from Various Equations

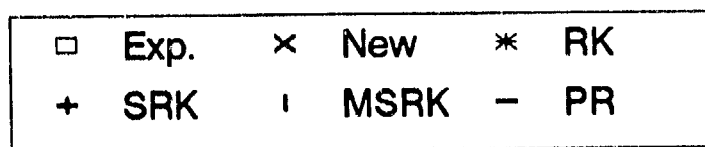
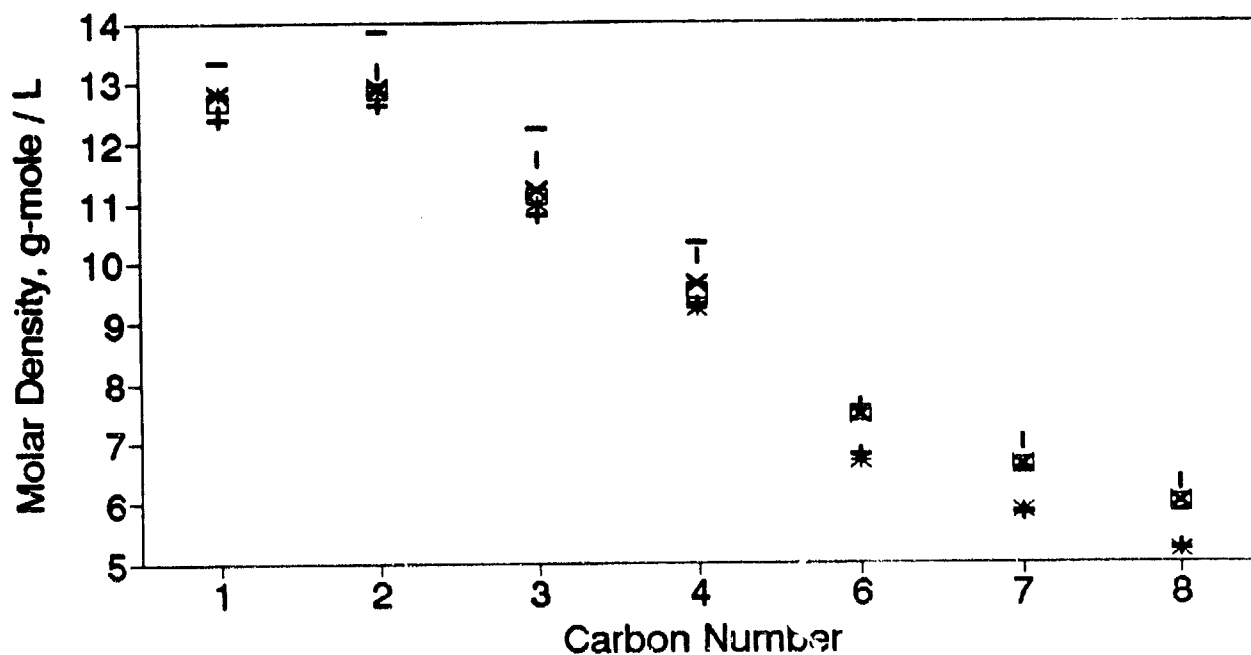


Fig. 2. Densities of Heavy n-Alkanes at 500 Bar & 373 K from Various Equations

