

Property Scaling Relations for Nonpolar Hydrocarbons

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S Supporting Information

ABSTRACT: Petroleum fluids are complex mixtures primarily composed of nonpolar hydrocarbons. Thus, a good knowledge of the properties of nonpolar hydrocarbons is required in predicting the overall fluid behavior of petroleum systems. In this article, generalized correlations for molecular polarizability, dielectric constant, critical temperature, critical pressure, and surface tension of nonpolar hydrocarbons and their mixtures, in terms of molecular weight, mass density, and normal boiling point, are derived. The scaling expressions reduce the number of fitting parameters and the need for extensive experimental data. As an extension of this work, the potential calculation of some thermophysical properties of the heaviest fraction of crude oil called asphaltene are also explored.

1. INTRODUCTION

A petroleum fraction is a mixture of different hydrocarbons, mostly nonpolar in nature, belonging to different homologous groups. A good estimation of the properties of petroleum mixtures depends on the estimation of properties of the pure compounds existing in the mixture. Thus, accurate knowledge of volumetric, physical, and thermophysical properties of pure hydrocarbons is important in the optimum design and operation of equipment related to petroleum production, processing, transportation, and related industries. Because experimental measurements of these properties are technically difficult, time consuming, and expensive, methods for property estimation are becoming increasingly important.

Estimation methods for most of the thermophysical properties of petroleum fluids are empirical, and the parameters needed to estimate a property may not be readily available or easily measurable.¹ Thus, theoretically based equations are required for better property estimations. Based on the molecular theories like liquid hole theory,² one-third rule,³ and the Hildebrand solubility parameter of nonelectrolytes, generalized property correlations for nonpolar hydrocarbons can be derived.

The main objective of this work is to use readily available physical properties of hydrocarbons, such as the normal boiling temperature, density, and molecular weight, to estimate the less easily measurable properties such as molecular polarizability, dielectric constant, critical temperature, critical pressure, and surface tension of pure nonpolar hydrocarbons. The correlations are also applied for nonpolar hydrocarbon mixtures wherever applicable. All the data along with corresponding references are reported in the Supporting Information.

2. ONE-THIRD RULE

Refractometry is used extensively for crude oil characterization and petroleum product quality control. Refractive index (n) is defined as the ratio of the speed of light in space (vacuum) to its speed in a given substance. For practical purposes, the speed of light in air may be taken as equivalent to that in vacuum.

Refractive index for any given substance varies with the wavelength of light and the temperature. Specific refractivity (r) is a function of refractive index divided by density (ρ). Molar refractivity (mr) is specific refractivity multiplied by molecular weight (MW).

The specific and molar refraction of individual hydrocarbons and mixtures of hydrocarbons are independent of the temperature and pressure. However, when the values of these quantities are calculated, the refractive index and the density are used, and these are definitely dependent on the temperature, pressure, and state of aggregation of the substance. Moreover, the molar refraction of individual hydrocarbons is additive and equal to the sum of the atomic refractions, so that they can be used for calculations in analytical practice.⁴ Thus, various attempts were made to know the constant function of refractive index and density.

The earliest equation relating refractive index and density is that which Newton deduced from the general laws of force,⁵

$$\frac{n^2 - 1}{\rho} = \text{constant} \quad (1)$$

Laplace derived the same equation from the emission theory of light and added the concept that for any one compound the constant should be independent of external influence such as temperature and pressure.⁶ Laplace's interpretation of the Newton equation had a profound influence on the development of refraction theory, because it directed attention to the change of refractive index and density of any one compound with changes in temperature and pressure.

In the period 1805–1863, it was shown that the constant of the Newton specific refraction equation (eq 1) is not independent of temperature.^{7,8} Many attempts were made to modify the formula. One of the more interesting attempts is

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Table 1. Application of One-Third Rule for Nonpolar Hydrocarbons and Polymers

serial no.	component	MW (g/mol)	n_D	density (ρ , g/cm ³)	$[(n^2 - 1)/(n^2 + 2)](1/\rho)$	temperature (°C)
1	cyclopentane	70.13	1.407	0.746	0.330	20
2	diphenyl	154.21	1.588	1.010	0.333	75
3	triphenylmethane	244.34	1.584	1.014	0.330	100
4	<i>n</i> -dotriacontane	450.87	1.455	0.813	0.334	20
5	polystyrene		1.592	1.040	0.325	20
6	polypropylene		1.500	0.900	0.327	20

that of Schrauf,⁹ who proposed that n be replaced by the A of Cauchy's formula,¹⁰

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \text{etc.} \quad (2)$$

The A in this formula is the hypothetical refractive index for a line of infinite wavelength. No one succeeded in modifying the Newton formula to produce a constant that is independent of temperature, and the formula as such was discarded soon after the Gladstone–Dale paper published in 1863. Gladstone and Dale, in addition to confirming the dependence of the Newton equation on temperature, presented a simple empirical equation,⁸

$$\frac{n - 1}{\rho} = \text{constant} \quad (3)$$

and justified it on the grounds that, for 90 liquids, the constant in this equation decreased less rapidly with increasing temperature than did the constant of the Newton equation.

In 1880 the Lorentz–Lorenz specific refraction equation,

$$\left(\frac{n^2 - 1}{n^2 + 2}\right)\frac{1}{\rho} = \text{constant} \quad (4)$$

was simultaneously derived by Lorentz, who started with Maxwell's electromagnetic theory of light, and Lorenz, who started with the undulatory theory of light.^{11,12} The specific and molar refractions given by this equation increase slightly with increasing temperature. Therefore, in the period 1880–1895, there was intensive investigation of these and many other specific and molecular refraction formulas until Eykman presented his empirical equation, which represents the relationship between refractive index and density accurately for any one liquid at various temperature.¹³

$$\left(\frac{n^2 - 1}{n + 0.4}\right)\frac{1}{\rho} = \text{constant} \quad (5)$$

The Lorentz–Lorenz equation in particular has been widely accepted because of its theoretical derivation. Application of this equation to hydrocarbon mixtures opens the possibility of developing novel methods to predict a wide range of thermophysical properties of crude oils.¹⁴

Assuming the molecules of a substance are spherical perfect conductors, Maxwell's electromagnetic theory leads to the relation¹⁵

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

where n is the refractive index and j is the ratio of the volume actually occupied by the molecules to that apparently occupied by the molecules. Dealing with a unit volume of a substance of density ρ ,

$$\frac{n^2 - 1}{n^2 + 2} = \text{true volume of the molecules in unit volume} \quad (7)$$

and therefore,

$$\frac{\rho}{\left(\frac{n^2 - 1}{n^2 + 2}\right)} = \text{true density of the molecules} \quad (8)$$

that is, the mass of unit volume of molecules without intermolecular spaces. The reciprocal of equation 8,

$$\left(\frac{n^2 - 1}{n^2 + 2}\right)\frac{1}{\rho} = \text{true volume per unit mass of the molecules} \quad (9)$$

When the refractive index is measured at the sodium D line, the Lorentz–Lorenz constant for pure nonpolar hydrocarbons is approximately one-third and, even when extended to such complex mixtures as petroleum systems, shows good agreement.¹⁴ The one-third value does not differ significantly when measured at other wavelengths. For example, at 20 °C and 589.26 nm, the refractive index of *n*-butylcyclohexane yields a $[(n^2 - 1)/((n^2 + 2) \times \rho)]$ of 0.330, and at 435.83 nm, the value is 0.337.

The validation of the one-third rule is shown in Table 1. An exhaustive application to various nonpolar hydrocarbon systems including polymers can be found in the Supporting Information. Refractive index and density values for some of the polymers reported are from separate studies, even though the separate studies used the standard ASTM method. This may increase the error in the estimated properties.

For methane, ethane, and propane, the liquidlike property is estimated from the molar volume reported by Barton et al.¹⁶ The lightest compounds like methane and ethane deviate the most from the one-third rule because they are above or near their critical temperature at ambient conditions.

The one-third rule has a wide range of usefulness because it provides a constant characteristic of all hydrocarbons, a constant which is practically independent of boiling point or molecular weight. In practice, the one-third rule has proven very valuable in calling attention to

- errors in the transcription of data
- improper correction for temperature
- uncertainty concerning the purity of the hydrocarbon
- unsound data

The subsequent sections show the usefulness of the one-third rule in obtaining simplified expressions for thermophysical properties from the existing equations in the literature.

3. MOLECULAR POLARIZABILITY

The polarizability of an atom or molecule describes the response of the electron cloud to an external field. Technically

the polarizability is a tensor quantity, but for spherically symmetric charge distributions, it reduces to a single number. For most practices, an average polarizability is adequate in calculations. Molecular polarizabilities are very slightly temperature dependent because the size of a molecule depends on its rotational and vibrational states.

The knowledge of molecular polarizability is essential in determining the following: diamagnetic susceptibility, long range interaction energy, ion mobility in a gas, van der Waals interaction between two systems, dynamic polarizability, and Rayleigh scattering cross section. Experimentally, molecular polarizability is determined through studies of refractive indices and relative permittivities, through Rayleigh and Raman scattering, and through the quadratic Stark effect.¹⁷ A quantum mechanical calculation of molecular polarizability may be carried out by solving the coupled perturbed Hartree–Fock equations with electric field perturbations.¹⁸ Thus, a simpler way of determining the molecular polarizability from easily measurable properties provides a convenience in the use of the polarizability parameter. In this regard we start with Lorentz–Lorenz equation to develop a simple expression for polarizability.

$$\text{Lorentz–Lorenz equation: } \frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N\alpha \quad (10)$$

where n is the refractive index, N is the number of molecules per unit volume, and α is the mean polarizability. Both the refractive index and polarizability are independent of the amount of substance. Hence, the Lorentz–Lorenz equation can be rewritten as

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \frac{N_A}{\nu} \alpha \quad (11)$$

where N_A is the Avogadro number (6.022×10^{23}) and ν is the molar volume given by

$$\nu = \frac{MW}{\rho} \quad (12)$$

Rearranging the Lorentz–Lorenz equation for molecular polarizability,

$$\alpha = \frac{3MW}{4\pi N_A \rho} \left(\frac{n^2 - 1}{n^2 + 2} \right) \quad (13)$$

From the one-third rule discussed in the previous section we have

$$\left(\frac{n^2 - 1}{n^2 + 2} \right) \frac{1}{\rho} \cong \frac{1}{3} \quad (14)$$

Thus, the simple expression for obtaining mean molecular polarizability is

$$\alpha = \frac{MW}{4\pi N_A} \quad (15)$$

The above equation (eq 15) is independent of the state of the system, and the mean molecular polarizability can be computed with a single input and conveniently measurable quantity “molecular weight”. Table 2 shows the applicability of the mean molecular polarizability equation (eq 15) for a few nonpolar hydrocarbons. Figure 1 compares the predicted and experimentally observed polarizabilities for various nonpolar hydrocarbons belonging to different homologous series, the

Table 2. Mean Molecular Polarizability for Nonpolar Hydrocarbons

serial no.	component	MW (g/mol)	experiment mean polarizability ($\text{cm}^3 \times 10^{-24}$)	$\alpha = MW/4\pi N_A$ mean polarizability ($\text{cm}^3 \times 10^{-24}$)
1	cyclopropane	42.08	5.66	5.56
2	1,3-cyclopentadiene	66.10	8.64	8.74
3	benzene	78.11	10.32	10.33
4	1-heptyne	96.17	12.80	12.71
5	fluorene	166.22	21.68	21.98
6	<i>n</i> -dodecane	170.34	22.75	22.52

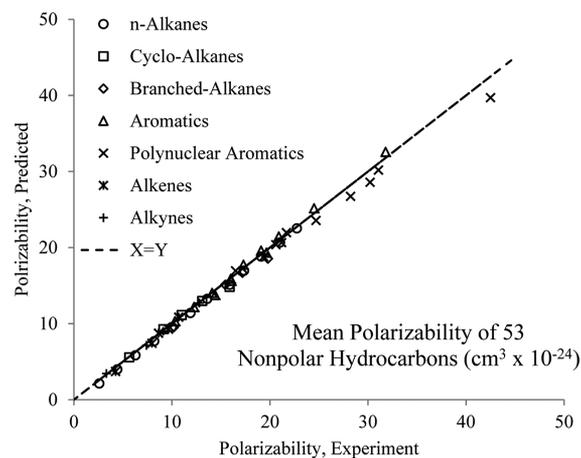


Figure 1. Comparison of the predicted and experimentally observed mean molecular polarizability for various nonpolar hydrocarbons. The average absolute deviation is 3.5% and is majorly contributed by C_1 – C_3 which deviate the most from the one-third rule.

data of which are presented in the Supporting Information. Crude oils are dominated by nonpolar interactions, and the knowledge of individual molecular polarizabilities can be helpful in predicting the overall phase behavior.

4. DIELECTRIC CONSTANT

The permittivity of a substance is the ratio of the electric displacement to the electric field strength when an external field is applied to the substance. The dielectric constant is the ratio of the permittivity of a substance to the permittivity of free space. It is an expression of the extent to which a material concentrates electric flux and is the electrical equivalent of relative magnetic permeability.

For hydrocarbons, the dielectric constant is an essential piece of information to understand the production of electrical conductance by the action of high energy radiation.^{19,20} Almost any type of electrical equipment employs dielectric materials in some form or another. Wires and cables that carry electrical current are always coated or wrapped with insulating (dielectric) material. Sophisticated electronic equipment such as rectifiers, semiconductors, transducers, and amplifiers contain or are fabricated from dielectric materials.²¹ When capacitors are characterized where a material might be expected to introduce capacitance into a circuit, dielectric materials are chosen such that they are resistant to ionization. This allows the capacitor to operate at higher voltages before the insulating dielectric ionizes and begins to allow undesirable current. Dielectric constant measurements are also essential for

understanding results obtained from remote-radar-sensing experiments.²² In pharmaceutical sciences, the dielectric constant of mixed solvents is required to predict the solubility and chemical stability of a drug.²³

The dielectric constant is experimentally measured using the coaxial line technique,²² capacity bridge method,²⁴ and free space method.²⁵ All the theories concerned with the dielectric constant, even though sound in derivation, cannot be applied for practical purposes because of the complexities in the expression.^{26–29} Additionally, the parameters are not easily obtainable. Thus, a simpler way of determining the dielectric constant that is valid across temperature and mixtures, from an easily measurable property such as bulk density, provides a convenience in the use of the dielectric constant parameter at the production facility. In this regard, we start with the electromagnetic theory relating refractive index and electrical permittivity.

$$n = \frac{c}{\nu} = \sqrt{\frac{E\mu}{E_0\mu_0}} \quad (16)$$

where E_0 is the permittivity of a vacuum and μ_0 is the magnetic permeability of a vacuum. In weakly magnetic materials, $\mu_0 = \mu$ and the above expression at a fixed frequency simplifies to

$$n = \sqrt{\frac{E}{E_0}} = \sqrt{k} \quad (17)$$

where k is the dielectric constant of a material. From the one-third rule for nonpolar hydrocarbons, it is known that the refractive index varies with the density of the material as

$$\left(\frac{n^2 - 1}{n^2 + 2}\right)\frac{1}{\rho} \cong \frac{1}{3} \quad (18)$$

In the case of low loss materials (e.g., nonpolar hydrocarbons), $\omega\tau < 1$ (at operating frequency ω and dielectric relaxation time τ), the frequency dependent dielectric constant $k(\omega)$ can be approximated by its static value $k(0)$.²² Thus, the dielectric constant can be substituted in the place of the refractive index in the one-third rule expression

$$\left(\frac{k - 1}{k + 2}\right)\frac{1}{\rho} \cong \frac{1}{3} \quad (19)$$

The expression for obtaining the dielectric constant with only the density as an input parameter is

$$k = \frac{2\rho + 3}{3 - \rho} \quad (20)$$

Figure 2 shows the accuracy of the above expression (eq 20) by comparing the calculated values with the experimental observations. The predictions differ the most for alkyne.

In the one-third rule, the one-third value represents specific refraction of hydrocarbon molecules and is nearly independent of temperature, pressure, and mixing, as discussed in the One-Third Rule section. Because the proposed dielectric constant expression (eq 20) is an extension of the one-third rule, it can inherently handle temperature and composition variations. The validity of the proposed dielectric constant expression (eq 20) at various temperatures is shown in Figure 3 where the dielectric constants of different complex nonpolar hydrocarbons at different temperatures are compared with their experimental values. Thus, the expression can be applied for a

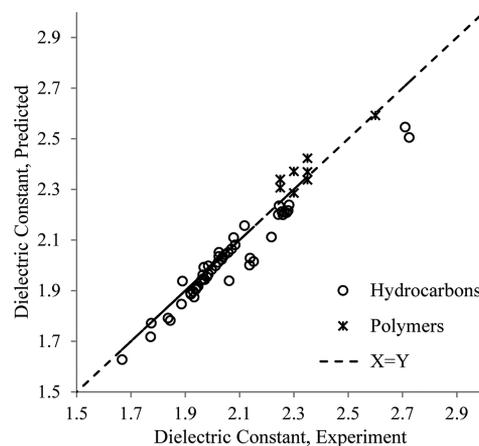


Figure 2. Dielectric constants for 50 nonpolar hydrocarbons and 8 nonpolar polymers at 20 °C. The average absolute deviation is 2.1%.

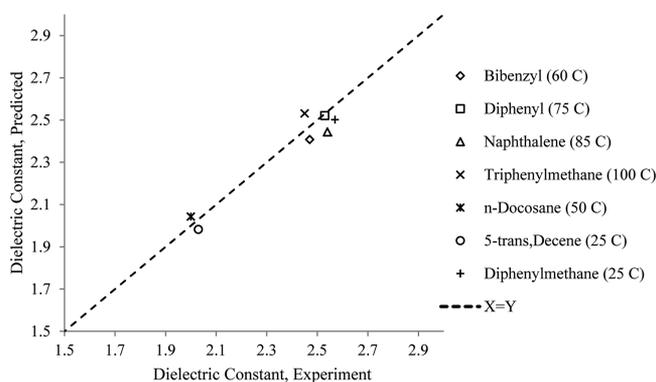


Figure 3. Dielectric constants for nonpolar hydrocarbons at different temperatures (°C). The average absolute deviation is 2.4%.

wide temperature range, as shown in Figure 4. For validation of the dielectric constant expression to handle compositional changes, Figure 5 is plotted for the dielectric constant of nonpolar hydrocarbon mixtures as a function of temperature. Table 3 shows a few hydrocarbons used for the analysis of the proposed dielectric constant expression (eq 20). All the data are reported in the Supporting Information.

5. CRITICAL PROPERTIES

Critical properties are important input parameters for cubic equation of state and to estimate thermodynamic and transport properties. In addition, the critical temperature and pressure are important information in high pressure phase equilibrium processes such as enhanced oil recovery and supercritical fluid extraction.

Most of the measured critical data in the literature are usually limited to low molecular weight compounds. Even with the advances in experimental methods for the measurement of critical properties of high molecular weight and thermally unstable fluids,^{30–32} the data remain scarce because of the difficulty associated with their measurement. When experimental data are not available, estimation methods are used to get an approximated value for these properties.

Available methods for the estimation of critical properties can be divided into two groups. The first group contains methods based on group contribution techniques. The first work in this regard is by Lydersen.³³ The group contribution methods represent two distinctive classes.

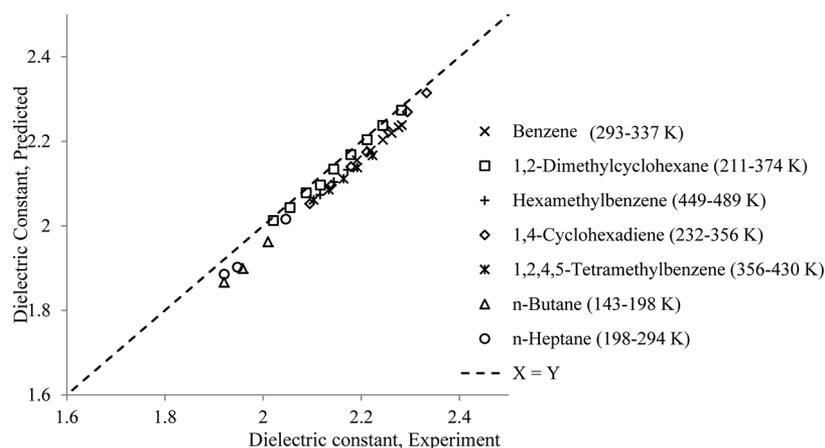


Figure 4. Dielectric constants of different nonpolar hydrocarbons as a function of temperature (K). The average absolute deviation is 1.8%.

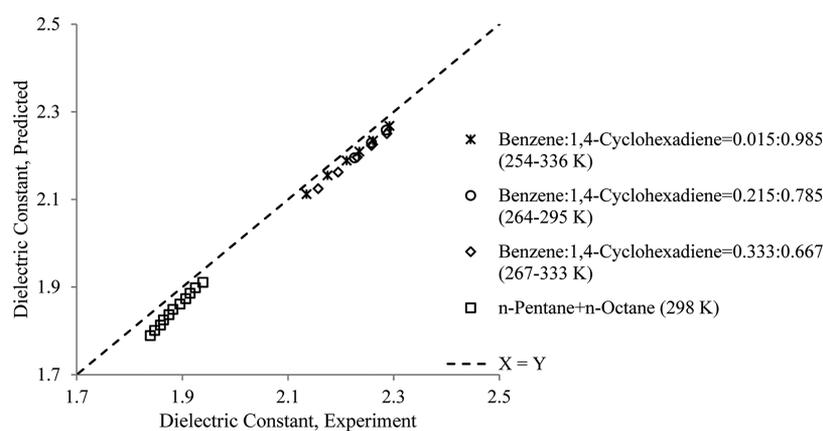


Figure 5. Dielectric constants as a function of composition and temperature (K). The average absolute deviation is 1.5%.

Table 3. Dielectric Constant of Nonpolar Hydrocarbons

serial no.	component	MW (g/mol)	density (ρ , g/cm ³)	refractive index, n_D	dielectric constant		temperature (°C)
					experiment	$k = (2\rho + 3)/(3 - \rho)$	
1	<i>n</i> -butane	58.12	0.579	1.333	1.77	1.72	20
2	naphthalene	128.17	0.975	1.590	2.54	2.44	85
3	5-decene (trans)	140.27	0.740	1.420	2.03	1.98	25
4	bibenzyl	182.27	0.958	1.548	2.47	2.41	60
5	<i>n</i> -docosane	310.61	0.774	1.440	2.00	2.04	50
6	polypropylene		0.900	1.500	2.30	2.29	20

- The first-order group techniques, which determine the molecule by means of simple group contribution, neglecting the next nearest neighbor's effects. The methods of Ambrose, Joback, Fedors, and Somayajulu belong to this class.^{34–37}
- The second-order group techniques, which additionally take into consideration the influence of first- and second-level neighbors of a considered group. The methods of Daubert and Constantinou belong to this class.^{38,39}

All the group contribution methods require the knowledge of the molecular structure of the compound. Such methods cannot be applied to mixtures of unknown composition or even for a single component without knowing its nature. The other predictive methods (second group) use some easily measurable properties, such as boiling point and specific gravity, and can be applied to undefined mixtures without the knowledge of component molecular structure. Examples of these methods are

Kesler–Lee, Riazi–Daubert, and Cavett.^{40–43} Unfortunately, none of the equations are theoretically based and these methods cannot be applied to all types of compounds as they are valid only for specific hydrocarbon systems.¹ In addition, the correlations do not cover compounds such as light hydrocarbons. Moreover, in some equations, estimating critical pressure requires critical temperature as an input parameter.⁴⁴ Therefore, any error associated with the predicted critical temperature will be propagated to much larger errors for the other critical properties.

5.1. Pure Compounds. In this section we develop a simple, reliable, and generalized method for estimating the critical properties of various nonpolar hydrocarbons using easily measurable properties and without the knowledge of chemical structure.

From fundamental thermodynamic relations:

$$P = -\left(\frac{\partial A}{\partial V}\right)_T = -\left(\frac{\partial E}{\partial V}\right)_T + T\left(\frac{\partial S}{\partial V}\right)_T \quad (21)$$

and by substituting the Maxwell relation,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad (22)$$

Equation 23 can be readily obtained

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \quad (23)$$

Hildebrand measured $(\partial P/\partial T)_V$ for a number of liquids and realized that for most liquids below their boiling points, P is negligible in comparison with $T(\partial P/\partial T)_V$.⁴⁵ Thus,

$$\left(\frac{\partial E}{\partial V}\right)_T \cong T\left(\frac{\partial P}{\partial T}\right)_V \quad (24)$$

During the same time, Westwater together with Hildebrand showed that^{46,47}

$$T\left(\frac{\partial P}{\partial T}\right)_V = \frac{a}{\nu^2} \quad (25)$$

where a is the molecular force term in the van der Waals equation of state. And hence,

$$\left(\frac{\partial E}{\partial V}\right)_T \cong \frac{a}{\nu^2} \quad (26)$$

For a van der Waals fluid (i.e., phase behavior is dominated by nonpolar interactions) over a small range of volumes,⁴⁸

$$\left(\frac{\partial E}{\partial V}\right)_T = \frac{\Delta E^V}{\nu} \quad (27)$$

thus,

$$\frac{\Delta E^V}{\nu} \cong \frac{a}{\nu^2} \quad (28)$$

For nonpolar liquids, one can use $T(\partial P/\partial T)_V$ as a measure of the Hildebrand solubility parameter,⁴⁹

$$\left(\frac{T C_\alpha}{C_\beta}\right)^{1/2} = \left[T\left(\frac{\partial P}{\partial T}\right)_V\right]^{1/2} \cong \delta \quad (29)$$

where C_α is the coefficient of thermal expansion and C_β is the isothermal compressibility coefficient. Reasonable values of the solubility parameter can be obtained from

$$\delta \cong \frac{a^{1/2}}{\nu} \quad (30)$$

Buckley et al. showed that for nonpolar compounds, the Hildebrand solubility parameter at ambient conditions varies as⁵⁰

$$\delta = 52.042\left(\frac{n^2 - 1}{n^2 + 2}\right) + 2.904 \quad (31)$$

where n is the refractive index determined at 20 °C. Combining eqs 30 and 31, one can estimate the a parameter of the van der Waals equation as

$$a^{1/2} = 52.042\left(\frac{n^2 - 1}{n^2 + 2}\right)\left(\frac{MW}{\rho_{20}}\right) + 2.904\left(\frac{MW}{\rho_{20}}\right) \quad (32)$$

Observed from the One-Third Rule section, the quantity of $[(n^2 - 1)/(n^2 + 2)](1/\rho)$ can be approximated as $1/3$ independent of temperature, pressure, and composition. Thus, the van der Waals a parameter, in terms of critical temperature and pressure, varies as a function of molecular weight and density. The equation is expected to be linear, but not with same terms as in eq 32, because the molecules are not perfectly spherical as in the case with van der Waals.

$$\frac{T_C}{P_C^{1/2}} = \text{function}(MW, \rho_{20}) \quad (33)$$

The correlation between $T_C/P_C^{1/2}$ and $MW + 0.1674(MW/\rho_{20})$ for a number of nonpolar hydrocarbons (alkanes, alkenes, alkynes, aromatics, polynuclear aromatics, and their corresponding isomers) is illustrated in Figure 6. The best fit straight

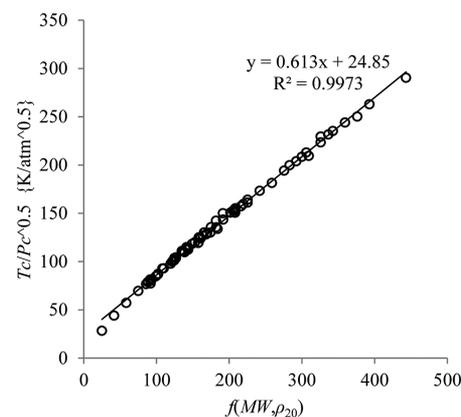


Figure 6. Correlation of critical temperature and pressure in terms of molecular weight and density.

line has a slope of 0.613 and an intercept 24.85. That means for any nonpolar hydrocarbon belonging to any homologous series, the following is valid:

$$\frac{T_C}{P_C^{1/2}} = 0.613f(MW, \rho_{20}) + 24.85 \quad (34)$$

where

$$f(MW, \rho_{20}) = MW + 0.1674\frac{MW}{\rho_{20}}$$

The critical temperature is a measure of intermolecular attractions, and a similar temperature parameter, which provides the measure of intermolecular attractions, is the boiling point. Thus, critical temperature in expression 33 can be partially or completely replaced by normal boiling temperature and the following should also hold true:

$$\left(\frac{T_C T_B}{P_C}\right)^{1/2} = \text{function}(MW, \rho_{20}) \quad (35)$$

The correlation between $(T_C T_B/P_C)^{1/2}$ and $f(MW, \rho_{20})$ for a number of nonpolar hydrocarbons (alkanes, alkenes, alkynes, aromatics, polynuclear aromatics, and their corresponding isomers) is illustrated in Figure 7. The best fit straight line has a slope of 0.577 and intercept 11.12. That means for any

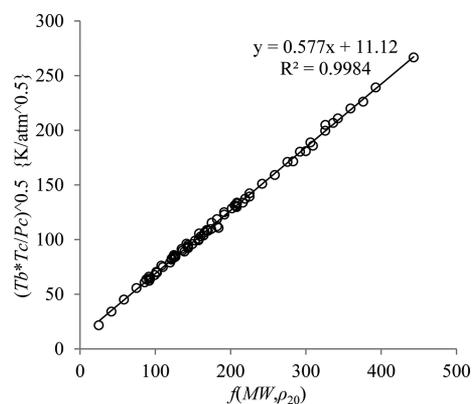


Figure 7. Correlation of critical temperature and pressure in terms of molecular weight, normal boiling point, and density.

nonpolar hydrocarbon belonging to any homologues series the following is valid:

$$\left(\frac{T_C T_B}{P_C}\right)^{1/2} = 0.577f(MW, \rho_{20}) + 11.12 \quad (36)$$

Solving for the unknowns T_C and P_C in eqs 34 and 36, the following correlations are obtained.

$$T_C = T_b \left[\frac{0.613f(MW, \rho_{20}) + 24.85}{0.577f(MW, \rho_{20}) + 11.12} \right]^2 \quad (37)$$

$$P_C = T_b^2 \frac{[0.613f(MW, \rho_{20}) + 24.85]^2}{[0.577f(MW, \rho_{20}) + 11.12]^4} \quad (38)$$

Figures 8 and 9 show the accuracy of predicted critical temperature and pressure using expressions 37 and 38 in

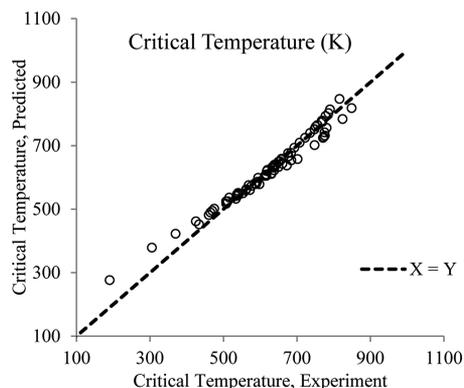


Figure 8. Comparison of predicted and experimentally observed critical temperatures for 75 nonpolar hydrocarbons belonging to various homologous series. The average absolute deviation is 2.2% excluding methane, ethane, and propane.

comparison with the experimental values, respectively, for 75 different nonpolar hydrocarbons. It is encouraging to see an increasing accuracy in the predicted critical temperature and critical pressure of high molecular weight compounds. Data are reported in the Supporting Information. The three most deviated points in Figures 8 and 9 correspond to methane, ethane, and propane. They deviate the most from one-third rule. Also, they are above their boiling points at room

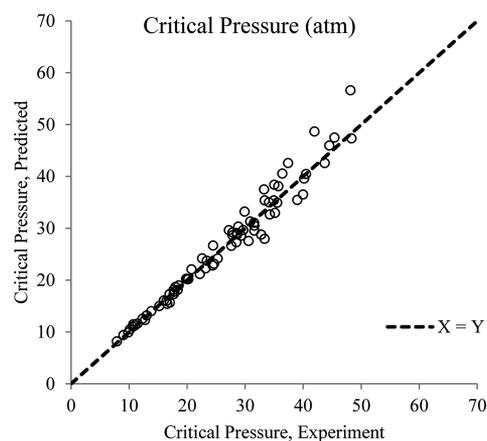


Figure 9. Comparison of predicted and experimentally observed critical pressures for 75 nonpolar hydrocarbons belonging to various homologous series. The average absolute deviation is 4.5% excluding methane, ethane, and propane.

temperature, and eq 23 cannot be approximated to eq 24 for gases

As a comparison with other methods, Tsonopoulos correlations based on the critical properties of aromatic compounds give average errors of 0.75% and 3.5% for the estimation of critical temperature and pressure of aromatic hydrocarbons.⁵¹ From the method of Riazi and Daubert, the average absolute deviation for critical temperature prediction is 0.7% and for critical pressure is 3.7%.⁴¹ A later work by Riazi et al. predicts the hydrocarbon's critical temperature with 0.6% and critical pressure with 2.5% error.⁴³ The nomogram-based equations of Sim and Daubert give average absolute deviations of 1% and 1.5% for critical temperature and pressure, respectively.¹

5.2. Mixtures. The assumptions made in deriving the expressions for critical properties are

- fluid is nonpolar
- refractive index is a direct measure of solubility parameters
- one-third rule

For mixtures, the solubility parameter varies as¹⁴

$$\delta_{\text{mix}}^2 = \sum_i \hat{\phi}_i \delta_i^2 \quad (39)$$

where

$$\hat{\phi}_i = \frac{x_i V_i}{V_{\text{mix}}} \quad (40)$$

Thus,

$$\frac{a}{V_{\text{mix}}^2} = \sum_i \left[\frac{x_i \hat{V}_i}{V_{\text{mix}}} \left(52.042 \left(\frac{n_i^2 - 1}{n_i^2 + 2} \right) + 2.904 \right)^2 \right] \quad (41)$$

With the help of the one-third rule, the above expression in "a" simplifies as

$$a = V_{\text{mix}} \sum_i \left[x_i \hat{V}_i \left(52.042 \left(\frac{\rho_{i,20}}{3} \right) + 2.904 \right)^2 \right] \quad (42)$$

or

Table 4. Critical Temperature and Pressure for the Binary Mixture of Toluene and Ethylbenzene

serial no.	components			density ^a (ρ_{20}) g/cm ³	T_B^a (K)	partial molar volume		experiment ^b			
	toluene (1)	ethylbenzene (2)	MW (g/mol)			V_1^a (cm ³ /mol)	V_2^a (cm ³ /mol)	T_C (K)	P_C (atm)	eq 47 T_C (K)	eq 48 P_C (atm)
1	0.1	0.9	104.77	0.8558	406.0	107.556	124.054	615.5	36.66	603.0	35.20
2	0.2	0.8	103.36	0.8559	402.8	107.549	124.055	613.3	37.19	600.1	35.58
3	0.3	0.7	101.96	0.8560	399.9	107.542	124.057	611.0	37.75	597.5	36.01
4	0.4	0.6	100.56	0.8561	397.1	107.537	124.060	608.7	38.32	595.2	36.48
5	0.5	0.5	99.16	0.8562	394.5	107.531	124.064	606.2	38.86	593.2	37.01
6	0.6	0.4	97.75	0.8563	392.0	107.527	124.070	603.7	39.37	591.5	37.58
7	0.7	0.3	96.35	0.8564	389.7	107.524	124.076	601.2	39.83	590.0	38.20
8	0.8	0.2	94.95	0.8566	387.5	107.521	124.083	598.7	40.26	588.7	38.87
9	0.9	0.1	93.54	0.8567	385.5	107.520	124.092	596.0	40.70	587.7	39.59

^aData generated by VLXE 4.0 using PC-SAFT equation of state. ^bData from Hicks and Young.⁵²

$$\frac{T_C}{P_C^{1/2}} = \text{function}(g) \quad (43)$$

and

$$\left(\frac{T_C T_B}{P_C}\right)^{1/2} = \text{function}(g) \quad (44)$$

where

$$g = \left(\frac{MW_{\text{mix}}}{\rho_{\text{mix},20}} \sum_i [x_i \hat{V}_i (\rho_{i,20} + 0.1674)^2]\right)^{1/2}$$

Here, the normal boiling point in eq 35 is replaced by bubble point temperature at normal atmospheric pressure when applied to mixtures. It is observable that for a single component system, eqs 43 and 44 are simplified to eqs 33 and 35. Hence, the corresponding equations for (34) and (36), which are valid for the mixtures of nonpolar compounds, are

$$\frac{T_C}{P_C^{1/2}} = 0.613g + 24.85 \quad (45)$$

and

$$\left(\frac{T_C T_B}{P_C}\right)^{1/2} = 0.577g + 11.12 \quad (46)$$

respectively. Solving for T_C and P_C from expressions 45 and 46, we get

$$T_C = T_B \left[\frac{0.613g + 24.85}{0.577g + 11.12} \right]^2 \quad (47)$$

and

$$P_C = T_B^2 \frac{[0.613g + 24.85]^2}{[0.577g + 11.12]^4} \quad (48)$$

Because of the validity of the above assumptions for nonpolar mixtures composed of similarly sized molecules, the derived critical property correlations hold only for mixtures without large size disparities. The predictions are poor for molecules with a carbon number difference of five or more even when present in the same homologous series. Table 4 shows the ability of eqs 47 and 48 to handle hydrocarbon mixtures of similarly sized molecules.

6. SURFACE TENSION

Surface tension is the molecular property of a substance and is a characteristic of the interface between vapor and liquid. Surface tension is an important thermophysical property for many industrial processes. In reservoir engineering, it is mainly used for the calculation of capillary pressure. In separation units such as distillation, adsorption, or stripping columns, surface tension is a useful parameter to determine foaming characteristics. Surface tension is also needed in the calculation of the rate of oil dispersion on a seawater surface polluted by an oil spill.⁵³ The determination of surface tension by experimental techniques is time consuming, expensive, and prone to experimental and human errors during the interpretation of data. Thus, reliable prediction methods are highly desired.

In the literature, several approaches are used to calculate surface tensions of pure components and mixtures ranging from empirical correlations such as the parachor method,⁵⁴ group contribution techniques,⁵⁵ and the corresponding states principle⁵⁶ to more advanced methods such as density functional theories^{57,58} and the gradient theory.^{59,60} This work focuses on the application of liquid hole theory for the calculation of surface tension of nonpolar hydrocarbons in contact with their saturated vapor.

Solving the Schrodinger wave equation for a hole in a liquid leads to an expression in the intrinsic pressure, which does not contain the temperature but only contains the surface tension and difference in density between liquid and vapor.⁶¹ For practical purposes, the density of the vapor can be neglected

$$P_o = 3.5\sigma \left[\frac{7\pi\sigma}{15E} \right]^{1/2} \quad (49)$$

where

$$E = 3.1 \frac{h^{4/7} \sigma^{5/7}}{\rho^{2/7}} \quad (50)$$

where h is the Planck constant and σ is the surface tension. For hydrocarbons dominated by nonpolar attractions, the van der Waals equation can be assumed to apply to the liquid. Thus we have

$$P_o = (a/\nu^2) \quad (51)$$

where ν is the molar volume and a is the molecular force term in the van der Waals equation

$$a = 9.322V^2 \left[\frac{\rho\sigma^8}{h^2} \right]^{1/7} \quad (52)$$

From eq 32, we have

$$\frac{a^{1/2}}{\nu} \cong 52.042 \left(\frac{n^2 - 1}{n^2 + 2} \right) + 2.904 \quad (53)$$

Thus,

$$\sqrt{9.322} \left(\frac{\rho\sigma^8}{h^2} \right)^{1/14} \cong 52.042 \left(\frac{n^2 - 1}{n^2 + 2} \right) + 2.904 \quad (54)$$

From the One-Third Rule section, the quantity of $((n^2 - 1)/(n^2 + 2))^{1/3}$ can be approximated as $1/3$, and eq 54 at ambient temperature can be rewritten as

$$\sigma = \text{function}(h(\rho)) \quad (55)$$

where

$$h(\rho) = \left[\frac{(\rho + 0.1674)^{14}}{\rho} \right]^{1/8}$$

A validation of eq 55 is made at an ambient temperature of 20 °C. At 20 °C, the best fit straight line for nonpolar hydrocarbons based on eq 55 has a slope 34.39 and intercept -7.509. Thus,

$$\sigma_{20} = 34.39h(\rho_{20}) - 7.509 \quad (56)$$

Figure 10 compares the correlated and experimentally measured surface tensions at 20 °C. Surface tension and

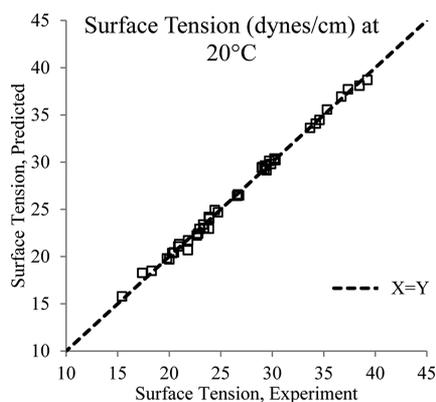


Figure 10. Comparison of predicted and experimentally observed surface tensions at 20 °C for 42 nonpolar hydrocarbons. The average absolute deviation is 1.1%.

density for other temperatures reported in Figure 11 show the validity of eq 55 for other temperatures.

In Figure 11, trend lines are plotted showing the equation of the straight line and the average deviation of the data points from the trend line. The practical application of eq 55 is improved further by incorporating the temperature variation of the surface tension.

$$\sigma \propto (T_C - T)h(\rho_T) \quad (57)$$

Using eq 56 for the reference temperature of 20 °C, surface tension at any other temperature can be calculated as

$$\sigma_T = [34.39h(\rho_{20}) - 7.509] \left[\frac{T_C - T}{T_C - 293} \right] \left(\frac{h(\rho_T)}{h(\rho_{20})} \right) \quad (58)$$

The parameter of critical temperature can be eliminated using the equation (eq 37) obtained in the Critical Properties section. Thus, the final expression for surface tension computed from just knowing the density, molecular weight, and normal boiling temperature of a compound is

$$\sigma_T = [34.39h(\rho_{20}) - 7.509] \left[\frac{T_b \left[\frac{0.613f(MW, \rho_{20}) + 24.85}{0.577f(MW, \rho_{20}) + 11.12} \right]^2 - T}{T_b \left[\frac{0.613f(MW, \rho_{20}) + 24.85}{0.577f(MW, \rho_{20}) + 11.12} \right]^2 - 293} \right] \left(\frac{h(\rho_T)}{h(\rho_{20})} \right) \quad (59)$$

Figure 12 compares the surface tension predicted using eq 59 and experimental results. All the data used in the Surface Tension section are reported in the Supporting Information. Accurate prediction of the critical temperature is required for computing the surface tension near the critical point region. This work on surface tension cannot be extended to mixtures because the liquid hole theory is valid only for single component systems.

As compared with other predictive methods, the general error in Brock and Bird's correlation is 5%.⁵⁶ A generalized correlation developed by Miqueu et al. has an average reported error of 3.5%.⁶² Another equation obtained by correlating the parachor of hydrocarbons by Tsonopoulos can predict the surface tension of pure hydrocarbons with an average deviation of about 1%.⁵¹ However, parachors are empirically fitted parameters and are not available for many hydrocarbons. Surface tension predictions by Escobedo and Mansoori have an average absolute deviation of 2.8%.⁶³ Almost all the methods need critical constants as input parameters when predicting the surface tension.

7. ASPHALTENE PROPERTIES

Asphaltenes can be considered nonpolar because their phase behavior is dominated by London dispersion interactions.⁶⁴ Neither the polarizability nor the dielectric constant of asphaltene can be obtained using the current experimental techniques. Also, no theoretical models exist in the literature for determining those properties of asphaltene. From the molecular polarizability expression proposed in this work

$$\alpha = \frac{MW}{4\pi N_A} \quad (15)$$

the polarizability of an asphaltene molecule of molecular weight 750 g/mol will be $99.16 \times 10^{-24} \text{ cm}^3$. For a polydisperse asphaltene system, individual fractions' polarizability can be computed and utilized in determining the order of aggregation.

From the simple dielectric constant expression

$$k = \frac{2\rho + 3}{3 - \rho} \quad (20)$$

an asphaltene polydisperse system with density ranging between 1.1 and 1.2 g/cm³ at ambient conditions will have a dielectric constant between 2.737 and 3. That eq 20 is fairly independent of temperature, pressure, and composition can be utilized to understand the insulating capabilities of asphaltene-containing systems. Such information on electrical conductivity

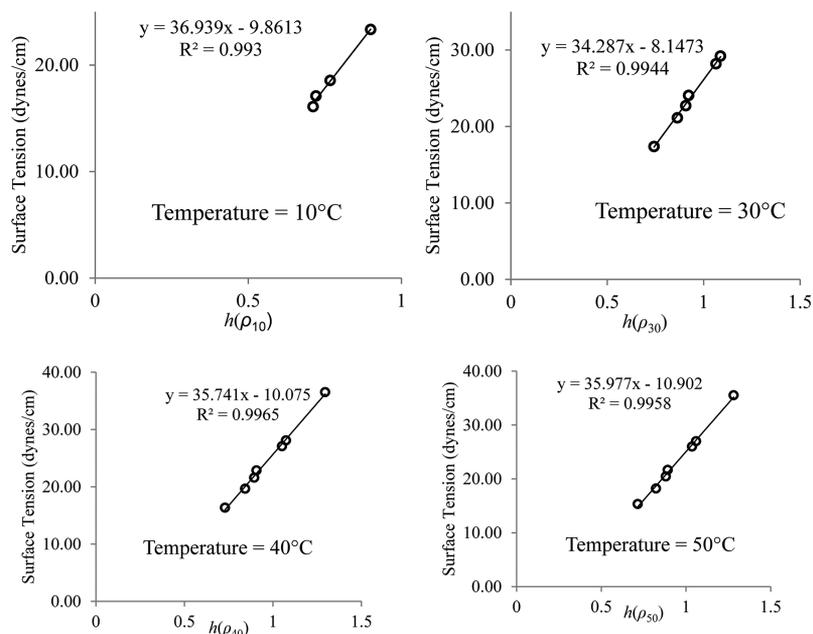


Figure 11. Correlation of surface tension and density at different temperatures.

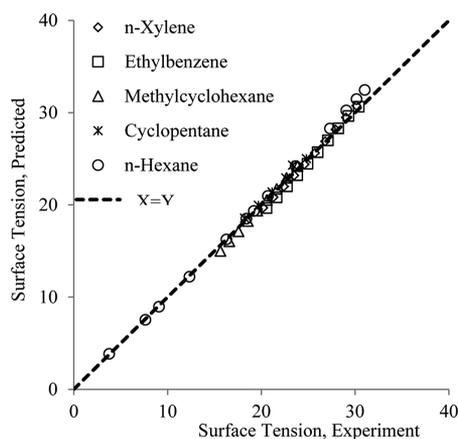


Figure 12. Comparison of predicted and experimentally observed surface tensions as a function of temperature for nonpolar hydrocarbons. The average absolute deviation is 1.8%.

is useful in determining the asphaltene adsorption on mineral surfaces in the reservoirs.⁶⁵

Applying the one-third rule in eq 31 of this paper, the solubility parameter at ambient conditions can be calculated from just the density as

$$\delta = 17.347\rho_{20} + 2.904 \quad (60)$$

Such an equation is helpful in calculating the solubility parameter of complex systems such as an asphaltene system from just the knowledge of bulk density. For example, the solubility parameter of an asphaltene-rich phase with density 1.1 g/cm^3 will be 21.99 MPa. The surface tension interpreted from eq 56 for the same asphaltene-rich phase with density 1.1 g/cm^3 will be 43.94 dyn/cm. Even though the asphaltene substance is opaque, its refractive index can be indirectly computed from the one-third rule as 1.732 when its density is 1.2 g/cm^3 . Finally, the van der Waals a parameter of asphaltene with a molecular weight of 750 g/mol and a density of 1.1 g/

cm^3 , which is useful for the cubic equation of state as calculated from eq 34, is $873.6 \text{ atm L}^2/\text{mol}^2$.

8. CONCLUSION

In this article, we have developed semitheoretically based simple expressions for determining the molecular polarizability, dielectric constant, critical temperature, critical pressure, and surface tension of nonolar hydrocarbons. For the dielectric constant and critical properties, the equations are also applicable for mixtures. It is unfortunate that the boiling point cannot be experimentally obtained for all the hydrocarbons because of some hydrocarbons' tendency to decompose before reaching the boiling temperature. However, the ratio of T_c and P_c as observed in Figure 6 will be helpful as a verification whenever such experiments are conducted. For surface tension and dielectric constant, the equations are generalized to work across different temperatures. Knowledge of the chemical structure of a hydrocarbon is not needed in these methods, and the only input parameters are normal boiling point, mass density, and molar mass. The proposed equation for the dielectric constant enables us to predict the dielectric constant for hydrocarbon mixtures without knowing the individual constituents of the mixture or the composition, and the only input parameter is the bulk density at the operational conditions. Such an equation can be used in predicting the in situ reservoir fluid density during dielectric logging. Finally, the work as discussed in the Asphaltene Properties section can be applied in predicting the properties of complex, unknown, and polydisperse hydrocarbon systems.

■ ASSOCIATED CONTENT

📄 Supporting Information

All the data used in the main manuscript. The references for each of the data are also reported. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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NOMENCLATURE

- n = refractive index
 ρ = density (g/cm³)
 N = number of molecules per unit volume
 α = mean polarizability (cm³)
 N_A = Avogadro number (6.022×10^{23} molecules/mol)
 ν = molar volume (cm³/mol)
 V = volume (cm³)
 MW = molecular weight (g/mol)
 E = permittivity (F/m)
 μ = magnetic permeability (N/A²)
 k = dielectric constant
 δ = solubility parameter (MPa^{1/2})
 a = van der Waals parameter which is a measure of the attraction between the particles (atm cm⁶/mol²)
 T_C = critical temperature (K)
 P_C = critical pressure (atm)
 T_B = normal boiling temperature (K)
 \hat{V} = partial molar volume (cm³/mol)
 x = mole fraction
 ϕ = volume fraction
 σ = surface tension (dyn/cm)
 T = temperature (K)

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