

ASPHALTENE PRECIPITATION
AND SOLVENT PROPERTIES OF CRUDE OILS

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ABSTRACT

Improved prediction of the onset of asphaltene precipitation may be achieved using refractive index (RI) to characterize crude oils and their mixtures with precipitants and solvents. Experimental measurements of RI for mixtures of several crude oils with the precipitant *n*-heptane, are reported at ambient conditions. Theoretical developments are described that will permit extension of these observations to reservoir conditions.

Measurements of RI at the onset of precipitation have shown that the onset occurs at a characteristic RI for each oil/precipitant combination, supporting the premise that precipitation is dominated by London dispersion interactions and thus, that RI can be used to predict the onset of precipitation. Reports in the literature showing that the onset of precipitation occurs at constant solvent-to-precipitant ratios provide additional confirmation.

The theory is developed on the assumption that London dispersion forces dominate aggregation and precipitation of asphaltenes. The interaction energy of asphaltene molecules or aggregates in a medium of oil can be expressed as a function of the difference between the RI of asphaltene and oil. The RI of live crude oil during pressure depletion can be calculated from the RI of the stock tank oil, the molar refraction of the separator gas, the formation volume factor, B_o , and the solution gas/oil ratio, R_s .

INTRODUCTION

There is significant commercial interest in understanding the conditions under which asphaltene precipitation occurs during pressure depletion, CO₂ flooding, or natural gas flooding of petroleum reservoirs. Simple and reliable methods are needed to characterize crude oils and to predict the conditions at which precipitation occurs.

Thermodynamic models for predicting asphaltene precipitation traditionally have used the Hildebrand solubility parameter (Hildebrand and Scott, 1964) to estimate the heat of solution (Hirschberg *et al.*, 1984; Leontaritis and Mansoori, 1987; Burke *et al.*, 1990; MacMillan *et al.*, 1995; Cimino *et al.*, 1995a, 1995b; Rassamdana *et al.*, 1996; Victorov and Firoozabadi, 1996; Pan and Firoozabadi, 1996). In these models, the heat of asphaltene-crude oil interaction, ΔH^M , is a function of the difference between the solubility parameter of the asphaltene (d_a) and that of the remaining components of the crude oil (d_s).

$$\Delta H^M \propto (d_a - d_s)^2 \quad (1)$$

where the subscript a denotes asphaltene and the subscript s denotes the remaining components of the oil or the "solvent."

The Flory-Huggins model describes the intermolecular interactions with a dimensionless interaction parameter, χ .

$$\chi = \frac{V_s}{RT} (d_a - d_s)^2 \quad (2)$$

This term represents the heat or excess energy of solute-solvent interactions. The models' predictions are limited by the accuracy of this term. The solubility parameter of the oil is estimated by approximating the cohesive energy density from the equation-of-state fit to live oil PVT data.

ASSUMPTION REGARDING LONDON DISPERSION INTERACTIONS

We assume that the dominant intermolecular interaction energy governing asphaltene precipitation is the London dispersion contribution to the van der Waals forces. London dispersion interactions occur between all molecules, including nonpolar ones; their occurrence is due to induced polarization. The London dispersion properties of a material can be characterized by the wavelength dependence of the refractive index (RI) or the "dispersion" of visible light. Polar interactions (dipole, ionic, charge transfer, hydrogen bonding, etc.), which are

commonly used to describe asphaltene-resin interactions, are assumed to be of secondary importance. In the work that follows, the resin fraction of the crude oil will not receive special treatment. Resins will be considered to be components of the "solvent" fraction and the asphaltenes will be treated as the "solute." Electronic polarizability, related to aromaticity, is an important resin property in this model.

In support of this assumption, we observe that nonpolar materials of similar molecular size and structure can be either solvents or precipitants for asphaltenes, depending on their degree of polarizability. Consider, for example, the 7-carbon compounds, *n*-heptane (RI=1.3878) and toluene (RI=1.4961). The former is a precipitant and the latter is a solvent for asphaltenes. Also consider liquid carbon dioxide, CO₂ (RI=1.195) and carbon disulfide, CS₂ (RI=1.6319). The former is a precipitant and the latter is a solvent for asphaltenes. Thus, the induced polarizability, as quantified by the RI, appears to be important in determining the ability of hydrocarbons to serve as a precipitant or as a solvent for asphaltenes.

Further support is provided by the solubility parameter mapping of Wiehe (1996) which shows that asphaltene insolubility is dominated by aromaticity and molecular weight, not by polar or hydrogen bonding interactions.

The assumption of dominance of London dispersion forces would certainly not be true if significant amounts of polar materials were added to the crude oil mixture. However, since polar components are relatively minor compared to the amount of hydrocarbon in crude oils, we will ignore the contribution of polar interactions in this analysis.

The interaction energy between asphaltene molecules in a solvent medium with only London dispersion interactions (assuming the adsorption frequency of the asphaltene and the solvent are the same) is as follows (Israelachvili, 1991, Eq. 6.35):

$$w(r) = -\frac{\sqrt{3}h\mathbf{n}_e}{4} \frac{(n_a^2 - n_s^2)^2}{(n_a^2 + 2n_s^2)^{3/2}} \frac{a_a^6}{r^6} \quad (3)$$

$$= -\frac{C}{r^6}, \quad r > 2a_a$$

$$C = \frac{\sqrt{3}h\mathbf{n}_e a_a^6}{4} \frac{(n_a^2 - n_s^2)^2}{(n_a^2 + 2n_s^2)^{3/2}} \quad (4)$$

where h is Planck's constant, \mathbf{n}_e is the absorption frequency in the ultraviolet, n_a and n_s are the refractive indices of asphaltene and the solvent (extrapolated to zero

frequency), a_a is the equivalent radius of the asphaltene molecule, r is distance between the centers of the molecules, and C is the coefficient of the distance dependence. The interaction energy is now expressed as a function of the differences between the squares of the refractive indices rather than the difference between the solubility parameters of asphaltene and solvent. Expressions for interaction energy for varying geometric arrangements of asphaltene are developed in Appendix I.

The relationship between the solubility parameter and refractive index, derived in Appendix II, is as follows:

$$d = \left(\frac{\sqrt{3}p h n_e}{384 s^3} \right)^{1/2} \frac{s^3}{V / N_o} \frac{n^2 - 1}{(n^2 + 2)^{3/4}} \quad (5)$$

The correlation between the solubility parameter and the RI at ambient conditions for a number of n -alkane and aromatic hydrocarbons (Weast, 1987; Barton, 1991) is illustrated in **Fig. 1**. The exponent of $3/4$ in Eq. 5 has been approximated by an exponent of unity. The comparison shown here is between a function of RI

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

and the corresponding solubility parameters for paraffinic and aromatic hydrocarbons. Ethane and methane deviate from an otherwise linear trend because they are near or above their critical temperatures at ambient conditions.

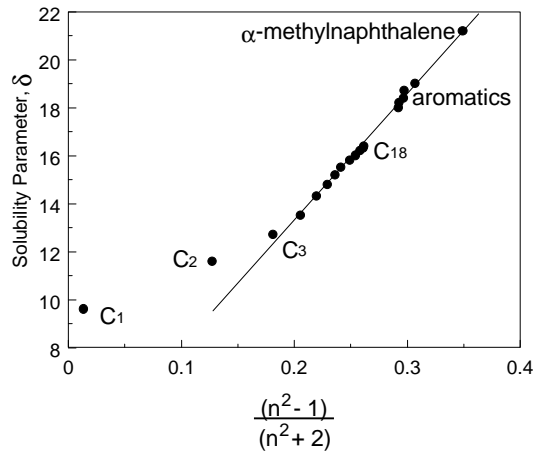


FIG. 1. Comparison of solubility parameter and F_{RI} .

COMPOSITION AND DENSITY DEPENDENCE OF RI

The refractive index is expressed as a function of composition and density through the Clausius-Mossotti or Lorenz-Lorentz equation (Feynman, *et al.*, 1989; Vedam and Limsuwan, 1978).

$$\frac{3}{4\pi} \left(\frac{n^2 - 1}{n^2 + 2} \right) = \sum_i \frac{C_i \mathbf{a}_i N_o}{4\pi \epsilon_o} \quad (7)$$

where C_i is the molar concentration of species i , \mathbf{a}_i is the electronic polarizability of species i , ϵ_o is the permittivity of free space, and N_o is Avogadro's number. This can be expressed in terms of the RI at some reference condition.

$$\left(\frac{n^2 - 1}{n^2 + 2} \right) = \sum_i \frac{C_i}{C_i^o} \left(\frac{n^2 - 1}{n^2 + 2} \right)_i \quad (8)$$

This expression describes the composition and density dependence of the RI. The coefficients of the C_i term are molar refractions. At ambient conditions and with ideal volume of mixing, the ratio, C_i / C_i^o is equal to the volume fraction of component i in the mixture. The molar refraction of a mixture can be expressed as a function of the mole fractions and molar refractions of its components by dividing Eq. 8 by the total molar concentration, C_Σ .

$$\begin{aligned} \frac{1}{C_\Sigma} \left(\frac{n^2 - 1}{n^2 + 2} \right) &= \sum_i \frac{X_i}{C_i^o} \left(\frac{n^2 - 1}{n^2 + 2} \right)_i \\ C_\Sigma &= \sum_i C_i \\ X_i &= \frac{C_i}{C_\Sigma} \end{aligned} \quad (9)$$

The validity of the Lorenz-Lorentz equation to describe the density dependence of RI was investigated by Vedam and Limsuwan (1978). For example, **Fig. 2** compares the calculated and measured change in RI of *n*-octane with pressure. The observation that the calculated RI is greater than the measured RI implies that the electronic polarizability and molar refraction are not strictly independent of density.

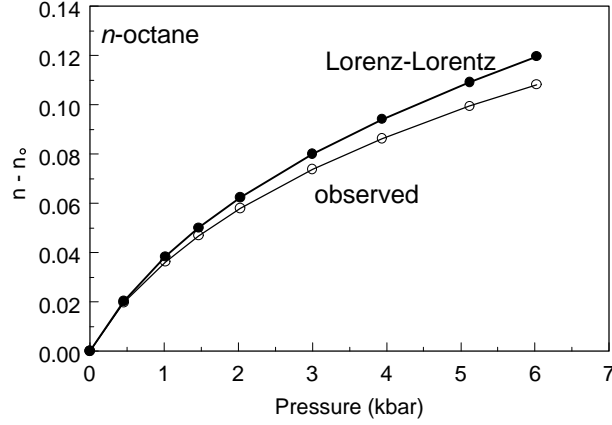


FIG. 2. Comparison of calculated and measured RI values for *n*-octane.

Live crude oil can be treated as a mixture of stock tank oil and separator gas. The RI of the live oil can be calculated from the formation volume factor, $B_o(P)$, (RB/STB), the solution gas/oil ratio, $R_s(P)$, (scf/STB), the RI of the stock tank oil, and the molar refraction of the separator gas.

$$\left(\frac{n^2 - 1}{n^2 + 2}\right)(P) = \frac{1}{B_o} \left(\frac{n^2 - 1}{n^2 + 2}\right)_{STO} + 7.52 \times 10^{-6} \frac{R_s}{B_o C_{gas}^o} \left(\frac{n^2 - 1}{n^2 + 2}\right)_{gas}^o \quad (10)$$

The factor of 7.52×10^{-6} in the second term on the right-hand-side of Eq. 10 converts R_s from scf/bbl to moles/cm³.

The molar refraction of the components of the separator gas can be calculated from group contributions (Weast, 1987).

$$\frac{1}{C_{gas}^o} \left(\frac{n^2 - 1}{n^2 + 2}\right)_{gas}^o = R_{gas} = \sum_i X_i R_i \quad (11)$$

where X_i is the mole fraction and R_i is the molar refraction of component i .

Refractive indices calculated from molar refractions and values reported from measurements (Weast, 1987) are compared for a number of *n*-alkanes and aromatic hydrocarbons in **Fig. 3**. The agreement is very good for all except styrene.

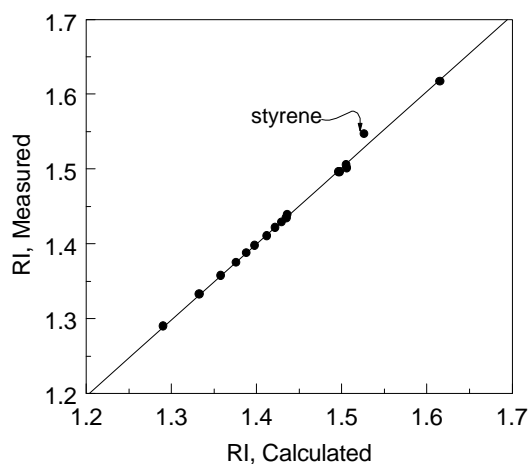


FIG. 3. Comparison of calculated and measured RI.

FREQUENCY DEPENDENCE OF RI

The expression for the intermolecular interactions in Eq. 3 has the RI, extrapolated to zero frequency, as a parameter. Often, the RI is available only at the frequency of the sodium-D line. **Fig. 4** is a Cauchy plot (Hough and White, 1980) of selected hydrocarbons. The slope is used to determine the absorption frequency, and the intercept gives the RI extrapolated to zero frequency. The value of RI at the sodium-D line is indicated. The curves are nearly parallel. Thus, since it is the difference between RI values that is related to the interaction energy, the values of RI measured at the frequency of the sodium-D line can be used to approximate the RI extrapolated to zero frequency.

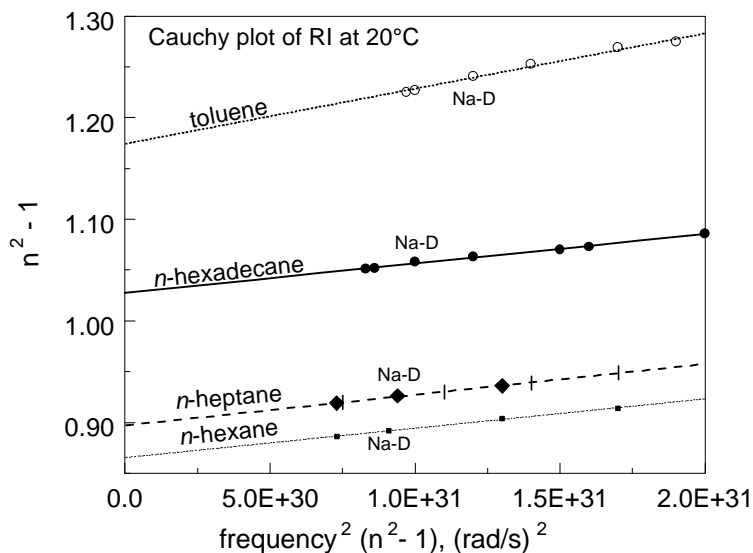


FIG. 4. Dielectric polarizability is determined from RI as a function of frequency.

The frequency dependence of RI for asphaltenes probably does not parallel those for the transparent hydrocarbon shown in Fig. 4. Asphaltenes are black indicating that they absorb in the range of visible wavelengths. Since they absorb at a lower frequency than the transparent hydrocarbons, they should have a larger Cauchy plot slope, contradicting the assumption implicit in Eq. 3 that asphaltene and solvent absorption frequencies are the same and that the Cauchy plots are parallel.

PRECIPITATION OF MODEL SYSTEMS

We have hypothesized that London dispersion interactions dominate asphaltene precipitation. Therefore, we have selected coronene as a model compound. Coronene is hexabenzobenzene, a flat molecule with six benzene rings surrounding a central benzene ring. It is a polycyclic aromatic hydrocarbon with no polar functionality. We expect that coronene has an RI greater than 1.6, based on data for similar materials (see Appendix III).

Approximately 3 mg/ml of coronene were dissolved in toluene (RI=1.496); *n*-heptane (RI=1.3878) was added as the precipitant. Precipitation occurred when the volume fraction of *n*-heptane was 0.61 and the mixture RI decreased below 1.4275. This value of RI at the onset of precipitation is very similar to experimental observations with crude oils, shown in the next section. Unlike crude oils, however, the precipitation is sudden and crystalline material precipitates. Nevertheless, this experiment demonstrates that decreasing RI is sufficient to

precipitate a polycyclic, aromatic hydrocarbon in a system with no polar interactions.

REFRACTIVE INDEX OF CRUDE OILS

Measurements

The RI of crude oil samples was measured at 20°C using an Abbe refractometer with a sodium lamp. Two problems were encountered. Volatile oils may lose light components during the measurement, and heavier oils may be too opaque to be measured.

For volatile oils, several measurements were made with each sample, as recommended in ASTM D1218-92. Initial measurements provided a first estimate of the RI. The refractometer was then set at this initial value and the final measurement was made very quickly to minimize the extent of evaporation.

For opaque oils, RI was estimated by extrapolating F_{RI} (defined in Eq. 6) of oil/hydrocarbon mixtures, as shown in **Fig. 5**. The fit to a straight line for F_{RI} as a function of volume fraction of crude oil in the crude oil-plus-*n*-heptane mixture is excellent.

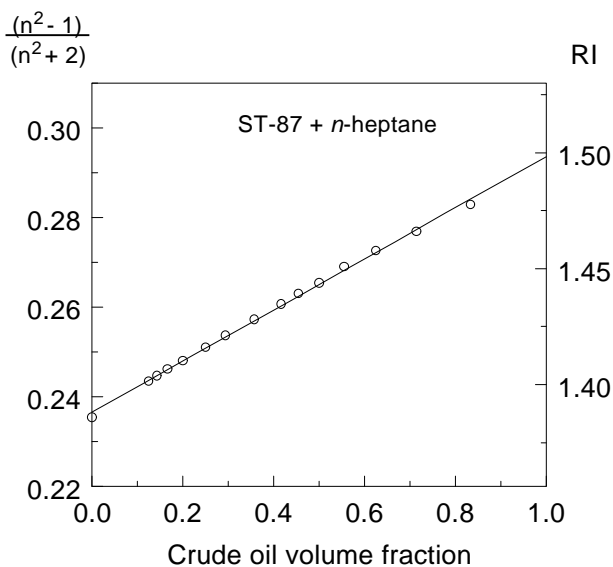


FIG. 5. F_{RI} and RI of mixtures of ST-87 crude oil with *n*-heptane. No asphaltenes precipitated from any of these mixtures.

Fig. 6 shows measured values of F_{RI} and RI for Lagrave crude oil mixtures with *n*-heptane. In this case, the oil is light enough to permit direct measurement

of its RI so the measured and extrapolated values can be compared. Each mixture is examined microscopically for the presence of asphaltene precipitate; open circles indicate mixtures with no asphaltenes. For the asphaltene-free mixtures, F_{RI} is a linear function of the volume fraction of crude oil. The straight line shown is a least-squares fit to the F_{RI} data for the Lagrave oil sample, pure n -heptane, and asphaltene-free mixtures of the two. Measured and extrapolated values of RI for this oil (1.470) are indistinguishable.

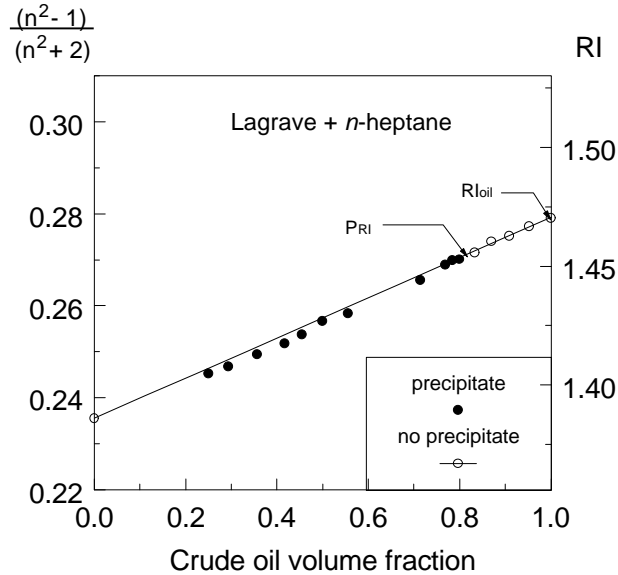


FIG. 6. F_{RI} and RI of mixtures of Lagrave crude oil with n -heptane. Mixtures with $RI < 1.453$ contain precipitated asphaltene.

RI of Mixtures Containing Precipitate

Mixtures with $RI < P_{RI}$ (RI at onset of precipitation) contain varying amounts of precipitate. **Fig. 7** shows refractive index measurements for two crude oils and n -heptane; mixtures containing precipitate are indicated by solid symbols and those with no precipitate are shown with open symbols. Straight lines are least-squares fits to the open symbol data points only. In the case of A-93, mixtures containing precipitate do not deviate appreciably from the linear relationship between RI and volume fraction of crude oil in the oil-heptane mixture. The oil from California is quite different, with a large deviation for mixtures containing precipitate. Lagrave crude oil (Fig. 5) is an intermediate example.

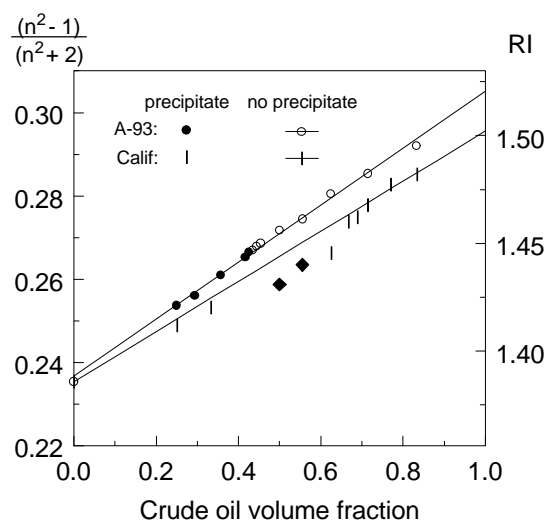


FIG. 7. F_{RI} and RI of mixtures of A-93 and California crude oils with *n*-heptane. Mixtures containing precipitate may deviate from linear relationship between F_{RI} and volume fraction of crude oil in the mixture.

Refractive Index at the Onset of Precipitation, P_{RI}

Microscopic examination established that mixtures of Lagrave crude oil and heptane with RI less than 1.453 contained asphaltene precipitate. Thus the RI at the onset of precipitation (P_{RI}) is 1.453 for Lagrave mixed with *n*-heptane. **Table I** summarizes the results of RI measurements and microscopic examination for 11 crude oils.

TABLE I
RI and P_{RI} Data for Mixtures of Crude Oils with *n*-Heptane.

Crude Oil	API gravity (°)	n-C ₅ asphaltenes %	RI	$f_{v,oil}$ at pptn	P_{RI}	$\Delta_{RI} = (RI - P_{RI})$
A-93	25.5	10.9	1.522	0.43	1.446	0.076
A-95	25.2	5.0	1.518	0.43	1.445	0.074
California	28.5		1.503	0.70	1.465	0.038
EMSU	32.0	1.2	1.484	0.43	1.429	0.055
Lagrave	41.3	3.8	1.470	0.82	1.454	0.016
Moutray	35.2	1.8	1.484	0.45	1.432	0.052
Oklahoma	26.0		1.568	0.23	1.427	0.141
Schuricht	24.6	9.9	1.514	0.47	1.448	0.066
Heavy CA	19.0	6.8	1.565	0.24	1.431	0.135
SQ-95	37.2	2.9	1.476	0.16	1.402	0.074
Tensleep	31.2	3.4	1.486	>1.00	1.490	-0.004

A fairly wide range of oils are represented in Table I. API gravity ranges from 19° to more than 41°. RI varies from a low of 1.47 to a high of almost 1.57. RI and API gravity are roughly correlated, with some exceptions, as shown in **Fig. 8**.

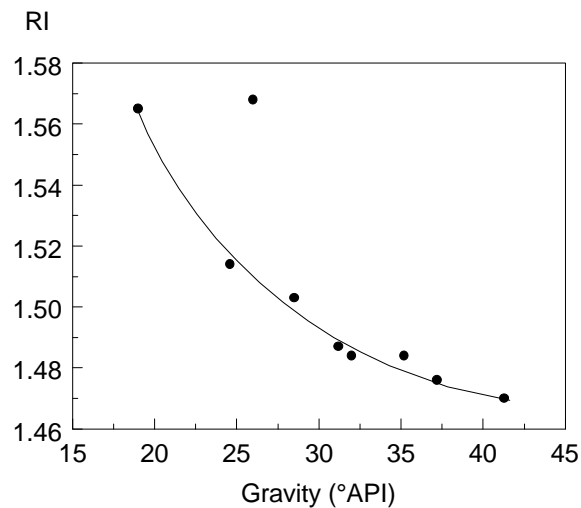


FIG. 8. As API gravity increases, RI of crude oils decreases.

Although the oils have a wide range of RI, P_{RI} varies over a narrower range, as shown in **Fig. 9** for 10 crude oils. The standard deviation of P_{RI} for this set of crude oils is only about half that for the oil RI values; average P_{RI} is ~ 1.44 . The range of asphaltene content in these samples is very broad, from a low of 1.2 to a high of 10.9 wt%. There is no correlation evident between asphaltene content and either RI or P_{RI} .

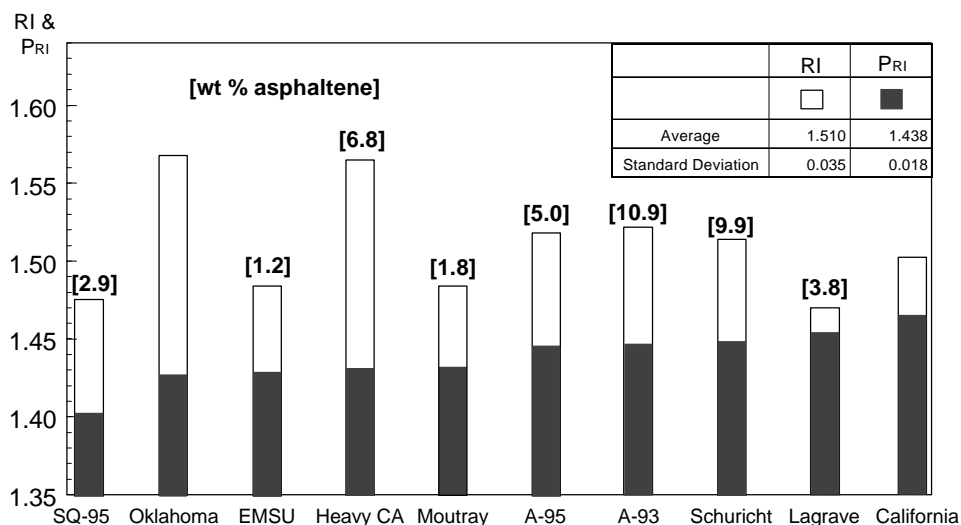


FIG. 9. Comparison of RI and P_{RI} .

P_{RI} —Calculation from Measurements at Infinite Dilution

The values of both RI and P_{RI} vary from one crude oil to another. For a given set of crude oil and precipitant, however, P_{RI} is approximately constant (Buckley, 1996). Addition of a hydrocarbon solvent, such as toluene, changes the volume fraction of precipitant required to initiate precipitation, but not the refractive index at which it occurs.

Destabilization at a constant ratio of solvent-to-precipitant has been reported by many observers (Heithaus, 1962; Bichard, 1969; Hotier and Robin, 1983; Reichert *et al.*, 1986; Dubey and Waxman, 1991; Cimino *et al.*, 1995b). Often, the volume of solvent greatly exceeds the amount of oil or bitumen in these tests. A constant solvent-to-precipitant ratio is observed since they are effectively working at infinite dilution. RI is determined by the ratio of solvent-to-precipitant. When the oil itself makes a significant contribution to mixture RI, the ratio can vary, but precipitation occurs at the same value of RI for a particular combination of oil and precipitant.

Assuming infinite dilution, the ratios reported in the literature can be used to calculate a value of RI at the onset of precipitation, which we will call P_{RI}^* . For a binary mixture of nonpolar molecules, RI can be calculated using Eq. 9 above.

Cimino *et al.* (1995b) precipitated asphaltenes with pentane from toluene and tetralin solutions. **Table II** shows the values used to calculate P_{RI}^* from their published onset of precipitation data. These values of P_{RI}^* are in the same range as observations of various crude oils with no added solvent and *n*-heptane as precipitant shown in Table I.

TABLE II
 P_{RI}^* Calculated from Onset of Precipitation at Infinite Dilution.
 (Cimino *et al.*, 1995)

	<i>n</i> -pentane	toluene	tetralin
M (g/mole)	72.15	92.14	132.21
ρ (g/cm ³)	0.6262	0.8669	.9702
RI	1.3579	1.4961	1.5413
precipitating mixture	201 g	296 g	
	240 g		258 g
P_{RI}^*		1.43	1.42

The results of similar calculations using the data of Hotier and Robin (1983) are shown in **Fig. 10** as P_{RI}^* as a function of number of carbon atoms in the precipitant. Many different solvents were used; the data for benzene, toluene, and xylene are shown here. P_{RI} is in the range of 1.42 - 1.43 for this oil (identified only as fuel oil K), when heptane is the precipitant.

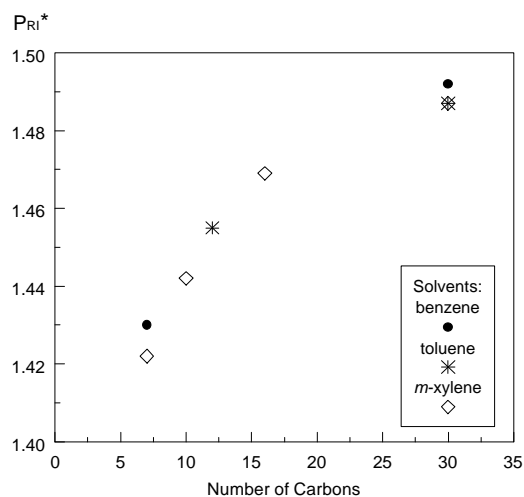


FIG. 10. P_{RI}^* as a function of precipitant chain length (from data of Hotier and Robin, 1983).

Addition of Aromatic Solvents

As reported previously (Buckley, 1996), addition of aromatic or other hydrocarbon solvents has minimal effect on P_{RI} . The fractions of various components in the mixture vary, concentration of the asphaltene fraction, and ratio of precipitant to solvent all vary, but the RI at the onset of precipitation is constant.

The effect of aromatic solvents, toluene and α -methylnaphthlene (AMN), on the volume fraction of oil at the onset of precipitation is illustrated in **Fig. 11**. Compared to toluene, AMN has a higher RI and thus permits a greater dilution with the precipitant before precipitation occurs. Thus AMN is an analog of a resin in its solvating power for the asphaltenes even though AMN has no polar functionality.

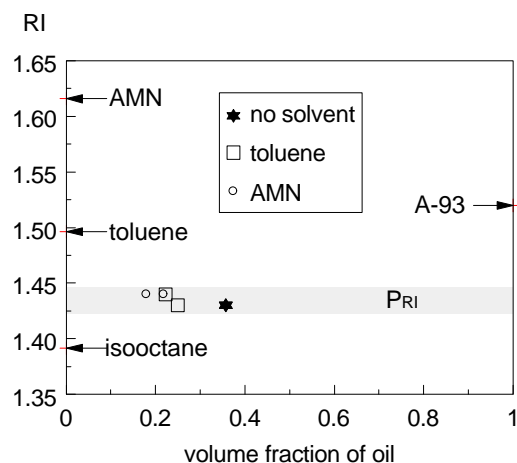


FIG. 11. Onset of precipitation of asphaltenes induced by isooctane from A-93 crude oil and its mixtures with toluene and α -methylnaphthalene. (data from Buckley, 1996)

Comparison of P_{RI} for Precipitants of Varying Molecular Size

P_{RI} varies with the size of added precipitant, as shown in **Fig. 12** for A-93 crude oil precipitated with *n*-alkanes from pentane to pentadecane. For the lighter compounds (pentane and hexane especially), volatility of the precipitant necessitates measurements in a closed system. RI was estimated in these cases by linear interpolation between RI of the pure precipitant and that of the crude oil using the volume fractions at the onset of precipitation.

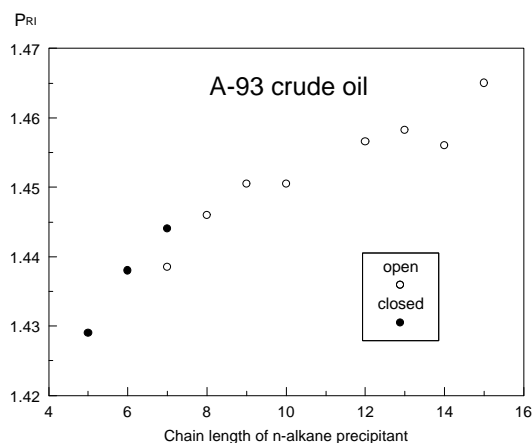


FIG. 12. P_{RI} as a function of precipitant size.

This variation of P_{RI} with the size of the precipitant can be interpreted with the help of the expression for the Flory-Huggins parameter χ in Eq. 2. This dimensionless parameter is a function of both the solvent solubility parameter and

the solvent molecular volume. The solvent in our case is the mixture of the crude oil and added precipitant. If the onset of precipitation occurs at a critical value of χ , then a solvent with a larger molecular volume must also have a larger solubility parameter at the onset of precipitation. Given the correlation demonstrated previously between solubility parameter and RI, precipitants with larger molecular volumes should initiate precipitation at higher RI, consistent with the results shown in Figs. 10 and 12.

RI of Asphaltene

An estimate of the RI of the asphaltene fraction has been made by extrapolation from RI measurements for mixtures of asphaltenes that were first precipitated from A-93 crude oil with *n*-hexane, then redissolved in toluene (**Fig. 13**). Volume fractions were calculated based on a measured asphaltene density of 1.2 g/ml. The extrapolated value of RI is about 1.72, assuming no volume change on mixing.

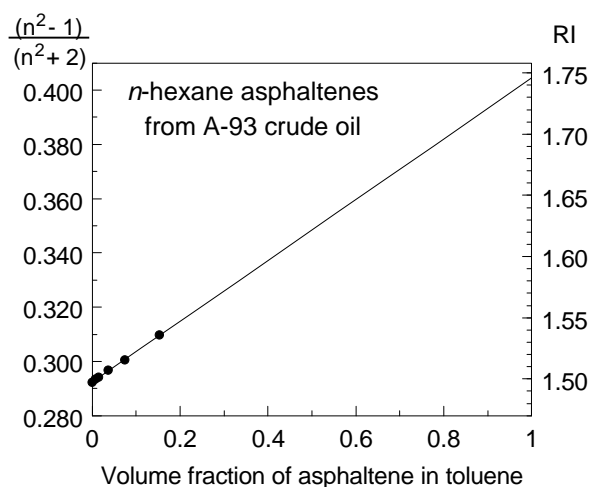


FIG. 13. F_{RI} and RI of asphaltenes precipitated from A-93 crude oil by *n*-hexane.

This estimate is somewhat higher than the RI of material adsorbed from a crude oil of 1.67 reported by Christenson and Israelachvili (1987). RI can only be measured for fairly dilute solutions because the mixtures become opaque with increasing asphaltene concentration. A long extrapolation is required, reducing the certainty of the calculated value. The density was measured by displacement of water with asphaltene; that value also is uncertain. Different measurement methods give a range of density results for asphaltenes (Parkash *et al.*, 1979). If the density were 1.0 g/ml, the estimate of asphaltene RI would be reduced to 1.7.

As discussed in the section on the frequency dependence of RI above, the RI at the sodium-D line may not be appropriate for asphaltenes because of the

slope of the Cauchy plot and because the adsorption frequency of asphaltenes may be substantially different from other components of the crude oil. An alternative to measurements is to estimate RI of asphaltenes from analogous polyaromatic compounds (see Appendix III).

Asphaltene/Maltene/Precipitant Model of Crude Oil

Thermodynamic models for the prediction of asphaltene precipitation will require the RI of the asphaltenes and of the remainder of the oil phase or solvent. This solvent pseudocomponent consists of (1) the deasphalted oil (resins, aromatics, and saturates), often known as maltenes, (2) precipitants such as methane, CO₂, or *n*-alkanes, and (3) added solvents such as toluene or AMN.

As an illustration, we can calculate the RI of the maltene fraction of a stock tank oil. The density and RI of asphaltene are assumed to be 1.26 g/cm³ and 1.61, respectively for this calculation. The step is to convert asphaltene content from weight % , w_a , to volume fraction, $f_{V(\text{asphaltene})}$.

$$f_{V(\text{asphaltene})} = \frac{w_a r_o}{100 r_a} \quad (12)$$

The maltene RI is determined by extrapolation to zero volume fraction of asphaltene as shown in **Fig. 14**; determinations for three crude oils are illustrated in **Table III**.

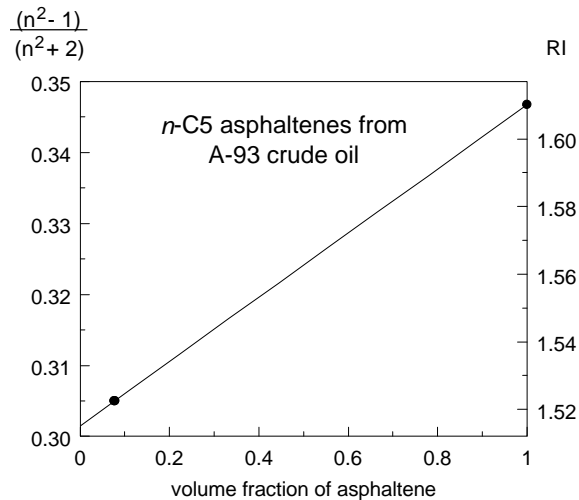


FIG. 14. RI of maltenes calculated by extrapolation for A-93 crude oil.

TABLE III
Estimation of Maltene RI.

Crude Oil	Asphaltene Fraction, wt %	Asphaltene Volume Fraction	RI of STO	RI of maltenes
Heavy CA	6.8%	0.050	1.550	1.547
Alaska-93	10.9%	0.077	1.522	1.515
Lagrange	3.8%	0.025	1.470	1.467

RI of Live Crude Oil upon Pressure Depletion

The RI of a 21.6°API gravity crude oil is modeled during pressure depletion as a binary mixture of stock tank oil (STO) and separator gas. Conventional “black oil” PVT data expresses the concentration of STO in the hydrocarbon liquid as the reciprocal of the formation volume factor, B_o (RB/STB). The dissolved gas is expressed as the solution gas/oil ratio, R_s (scf/STB). The concentration of separator gas in the hydrocarbon liquid is R_s/B_o . The PVT data is illustrated in **Fig. 15**.

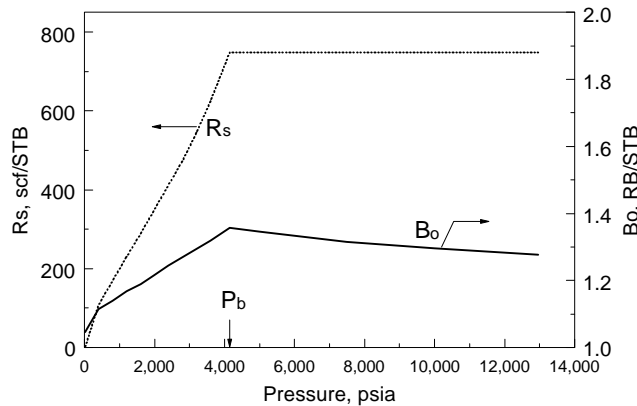


FIG. 15. Black oil PVT data.

No STO was available, so RI could not be measured; it was estimated to be 1.53 from the correlation with API gravity (Fig. 8). The separator gas was assumed to be methane with a molar refraction of $6.7 \text{ cm}^3/\text{mole}$. The calculated RI of the live oil at reservoir temperature during pressure depletion is shown in **Fig. 16**. For purpose of illustration, suppose that the precipitation RI, RI_{RI} , is equal to 1.44, shown by the dashed line. This illustrates that asphaltene precipitation will occur slightly above the bubble point pressure as a result of density reduction and will continue below the bubble point until the RI is increased to a value above the RI_{RI} as a result of loss of methane.

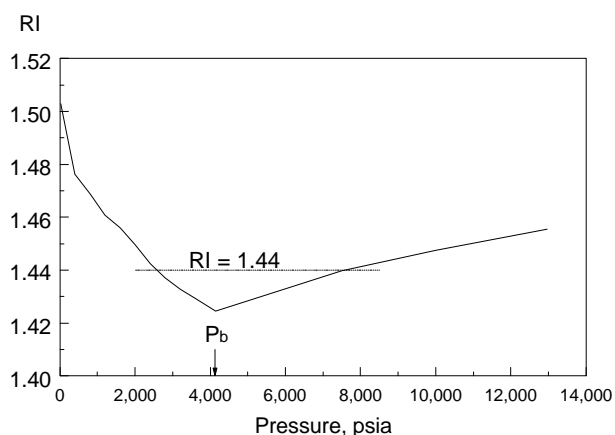


FIG. 16. Calculated RI of crude oil during pressure depletion.

REMAINING QUESTIONS

We have assumed—first in Eq. 3 and again in substituting RI at the sodium-D line for RI extrapolated to zero frequency—that the asphaltenes have the same absorption frequency as the maltenes. This assumption is not strictly valid. A better approximation may be gained by determining RI of the asphaltenes as a function of wavelength and using the exact Lifshitz theory to calculate interaction energies.

Asphaltenes have been treated as a single component. In reality, the asphaltenes have a distribution of polarizability or RI and of molecular sizes. More realistic thermodynamic models of asphaltene solvation and precipitation will require treatment of the asphaltenes and resins as distributions of components. The aggregates they form must also be described as having distributions of size and composition.

CONCLUSIONS

1. The solubility parameters of several hydrocarbons have the dependence on RI as predicted for London dispersion interactions.
2. The density dependence of the RI can be accurately estimated by the Clausius-Mossotti or Lorenz-Lorentz equations over the pressure range of interest in petroleum reservoirs.
3. The difference between the RIs of hydrocarbons, extrapolated to zero frequency, can be estimated from the differences between the RIs measured at the sodium-D line if the hydrocarbons have similar absorption frequencies. This may not be valid for asphaltenes since they absorb in the frequencies of visible light.
4. The F_{RI} of mixtures of a crude oil or its asphaltenes with hydrocarbon solvents and precipitants are a linear function of the volume fraction of the crude oil as predicted by the Clausius-Mossotti and Lorenz-Lorentz equations. This makes it possible to estimate the RI of the crude oil or asphaltene when it is too opaque to measure directly.
5. The RI of live crude oil during pressure depletion can be calculated from the RI of STO, molar refraction of the separator gas, the formation volume factor, B_o , and the solution gas/oil ratio, R_s .
6. For a number of crude oils with RI in the range, 1.51 ± 0.04 , precipitation with addition of *n*-heptane begins when the mixture RI is less than the average P_{RI} of 1.44 ± 0.02 . Note that the value of P_{RI} is more nearly constant than is the RI of the original oils.
7. In a model system with the pure hydrocarbons, hexabenzobenzene and toluene, addition of *n*-heptane initiates precipitation when the RI drops below 1.4275. This value of P_{RI} is within the range of values observed for crude oil systems. Thus precipitation phenomena analogous to asphaltene precipitation occurs in a system with no polar interactions. This is evidence that polar interactions are not necessary for asphaltene precipitation.
8. The addition of the aromatic solvent, α -methylnaphthalene, to crude oil allows more dilution with isooctane before precipitation occurs, but the values of P_{RI} is unchanged. Thus AMN is an analog of a resin in its solvating power for the asphaltenes even though AMN has no polar groups to contribute to solvation due to polar interactions. This is evidence that the aromatic character of the resins is responsible for the solvating properties of the resins.

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APPENDIX I

INTERMOLECULAR AND INTERPARTICLE INTERACTIONS

For a molecule of asphaltene interacting with the surface of a macroscopic body of asphaltene across a solvent medium, the energy is as follows (Israelachvili, 1991, Eq. 10.2):

$$w(D) = -\frac{\mathbf{p} C r_a}{6D^3} \quad (\text{molecule} - \text{surface}) \quad (\text{AI-1})$$

where D is the distance of the molecule from the surface and r_a is the number density of asphaltene molecules in the macroscopic body. If the interaction is between two spherical aggregates of asphaltene or between a spherical aggregate and the surface of a macroscopic body of asphaltene, then the energy of interaction is as follows (Israelachvili, 1991, Eq. 10.5):

$$W(D) = -\frac{\mathbf{p}^2 C r_a^2 R}{6D} \quad (\text{sphere} - \text{sphere or sphere} - \text{surface}) \quad (\text{AI-2})$$

where R is the radius of the spherical particle. If the interaction is between two parallel surfaces of macroscopic bodies of asphaltene, the interaction energy per unit area is as follows (Israelachvili, 1991, Eq. 10.8):

$$W(D) = -\frac{\mathbf{p} C r_a^2}{12D^2} \quad (\text{surface} - \text{surface, per unit area}) \quad (\text{AI-3})$$

Hirasaki (1993) used a generalization of these concepts to predict the contact angles of non-polar materials on Teflon and the spreading of non-polar materials at the gas/water interface.

APPENDIX II

RELATIONSHIP BETWEEN RI AND SOLUBILITY PARAMETER

The solubility parameter will be approximated by the van Laar-Lorenz approach using the van der Waals equation of state (EOS) cohesion parameter (Hildebrand and Scott, 1964).

$$d \approx \frac{a^{1/2}}{V} \quad (\text{AII-1})$$

where a is the van der Waals (vdW) EOS cohesion parameter and V is the molar volume. The vdW cohesion parameter can be expressed in terms of the parameters of the pair interaction energy (Israelachvili, 1991, Eq. 6.10):

$$a = \frac{2p N_o^2 C}{3s^3} \quad (\text{AII-2})$$

where s is the hard sphere diameter. The pair interaction model, Eq. (3) & (4), will be used for the parameters in this equation. Let the "solvent" be vacuum (i.e., RI=1.0) and "asphaltene" be the species for which the solubility parameter is to be determined. The resulting expression for the solubility parameter is as follows:

$$d = \left(\frac{\sqrt{3}p h n_e}{384 s^3} \right)^{1/2} \frac{s^3}{V / N_o} \frac{n^2 - 1}{(n^2 + 2)^{3/4}} \quad (\text{AII-3})$$

This equation expresses the solubility parameter in terms of the refractive index.

APPENDIX III

RI AND DENSITY OF POLYAROMATIC COMPOUNDS

Table AIII-1 lists the density and RI of some polyaromatic compounds that may be used to estimate the density and RI of asphaltenes and Table AIII-2 lists some solubility parameters.

Table AIII-1
Density and RI of Polyaromatic Compounds. (Weast, 1987)

Name	Formula	m.p., °C	Density	RI
naphthalene	C ₁₀ H ₈	80.5	0.962 ^{100/4} 1.0253	1.5898 ⁸⁵ 1.4003 ²⁴
α-methylnaphthalene	α-CH ₃ C ₁₀ H ₇	-22	1.0202 ^{20/4}	1.617 ²⁰
1,2,5 trimethylnaphthalene	1,2,5-(CH ₃) ₃ C ₁₀ H ₅	33.5	1.0103 ^{22/4}	1.6093 ²²
α-phenylnaphthalene	α-C ₆ H ₅ C ₁₀ H ₇	45	1.096 ^{20/4}	1.6664 ²⁰
phenanthrene	C ₁₄ H ₁₀	101	0.9800 ⁴	1.5943
anthracene	C ₁₄ H ₁₀	216	1.283 ^{25/4}	
1-methylanthracene	1-CH ₃ C ₁₄ H ₉	85-6	1.0471 ^{99/4}	1.680 ^{99/4}
fluorathene	C ₁₆ H ₁₀		1.252 ^{0/4}	
pyrene	C ₁₆ H ₁₀	156	1.271 ^{23/4}	
coronene	C ₂₄ H ₁₂	438-40	1.371	

Table AIII-2
Solubility Parameters. (Barton, 1991)

Name	Solubility Parameter MPa ^{1/2}	RI
naphthalene	20.3	1.5898 ⁸⁵
α-methylnaphthalene	21.2	1.617 ²⁰
phenanthrene	20.0	1.5943
anthracene	20.3	
average of above	20.4	1.60
carbon disulfide	20.5	1.6319 ²⁰

The solubility parameters of the model compounds above are close to the values of 19.5 and 20.5 MPa^{1/2} estimated for asphaltenes by Hirschberg *et al.* (1984) and Burke *et al.* (1990), respectively. If these compounds are analogues for asphaltenes, then the estimated RI for asphaltene is about 1.6.

SYMBOLS

a_a	molecular radius of asphaltene molecule
B_o	formation volume factor (RB/STB)
C	coefficient, defined in Eq. 3
C_i	molar concentration of component i
C_i^o	molar concentration at a reference condition where the RI is evaluated
C_S	sum of molar concentrations (Eq. 9)
D	distance from a molecule to a surface (Appendix I)
f_V	volume fraction
F_{RI}	function of n, $F_{RI} = (n^2 - 1)/(n^2 + 2)$
h	Plank's constant
DH^M	heat of interaction between asphaltene and remainder of crude oil
n	refractive index
N_o	Avogadro's number
P	pressure
P_b	bubble point pressure
P_{RI}	RI at the onset of asphaltene precipitation (see Fig. 6)
P_{RI}^*	P_{RI} calculated from solvent-to-precipitant ratio
r	distance between centers of two molecules (Eq. 3)
R	radius of spherical particle (Eq. AI-2)
R	gas constant
R_i	molar refraction of component i
R_s	dissolved gas content (scf/STB)
T	temperature
V	molar volume
w	interaction energy (molecules)
W	interaction energy (surfaces)
w_o	weight percent
X	mole fraction
a	electronic polarizability
c	Flory-Huggins interaction parameter
d	solubility parameter
e_o	permittivity of free space
r	number density (Appendix I)
r	density (g/ml)
s	hard sphere diameter
n_e	absorption frequency in the uv

Subscripts

a	asphaltene
i	component i
o	oil
s	solvent